

# Carnegie Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY

## THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Doctor of Philosophy

TITLE Fate of Organic Compounds in High Salinity Waters and  
Supercritical CO<sub>2</sub> Associated with Carbon Storage Environments

PRESENTED BY Aniela S. Burant

ACCEPTED BY THE DEPARTMENTS OF

Civil and Environmental Engineering

Athanasios Karamalidis September 23, 2015  
CO-ADVISOR, MAJOR PROFESSOR DATE

Greg Lowry September 25, 2015  
CO-ADVISOR, MAJOR PROFESSOR DATE

David A. Dzombak September 25, 2015  
DEPARTMENT HEAD DATE

APPROVED BY THE COLLEGE COUNCIL

Vijayakumar Bhagavatula September 29, 2015  
DEAN DATE

**FATE OF ORGANIC COMPOUNDS IN HIGH SALINITY WATERS AND  
SUPERCRITICAL CO<sub>2</sub> ASSOCIATED WITH CARBON STORAGE ENVIRONMENTS**

Submitted in partial fulfillment of the requirements for

the degree of

Doctor of Philosophy

in

Civil and Environmental Engineering

Aniela S. Burant

B.S., Environmental Engineering, University of Florida  
M.S., Environmental Engineering, Carnegie Mellon University

Carnegie Mellon University  
Pittsburgh, PA

September, 2015

## Acknowledgements

This work was performed as part of the National Energy Technology Laboratory's former Regional University Alliance (NETL-RUA) under the RES contract DE-FE0004000. Additional support for tuition and research was provided by the Carnegie Mellon College of Engineering Dean's Fellowship (2011/2012), the Jared and Maureen Cohon Fellowship (2012), and the Bradford and Diane Smith Fellowship (2013).

I would like to thank my advisors Dr. Athanasios Karamalidis (committee chair) and Dr. Gregory Lowry. I've lost count of how many times I've knocked on Dr. Karamalidis' door and asked him for help, which he has always been more than willing to provide. There have been many roadblocks along the way, and Dr. Karamalidis has always found a way to help me get around them. He is an extremely good problem solver, and I am eternally grateful for his chats on anything ranging from running to the best fonts to use in a presentation. Dr. Lowry is the blunt and tough advisor. His frankness has made me a better researcher and scientist. Dr. Lowry has always encouraged me to ask the tough and relevant questions, see the big picture, and to always update my conceptual model. Due to Dr. Karamalidis and Dr. Lowry, I have grown and learned so much during my time at CMU, and will always be appreciative of their advising.

I would like to thank my committee member Dr. David Dzombak for his help, insightful ideas and comments, and encouragement for my thesis, the carbon storage and shale gas research group, and in his water chemistry class. His comments during my proposal exam inspired much of the modeling work in this thesis; work that I found extremely satisfying and important to the field. For that, I am grateful. I would like to thank my committee member Dr. Christopher Thompson of Pacific Northwest National Laboratory (PNNL) for all of his help. Dr. Thompson helped me set up my experiments and fix many of the problems I encountered at PNNL and the Environmental Molecular Sciences Laboratory (EMSL), which was not a trivial task. The

experiments were not easy at PNNL/EMSL, and I would not have been able to complete them without Dr. Thompson's help, support, and encouragement. I consider Dr. Thompson my PNNL/EMSL mentor, and am grateful he agreed to be on my dissertation committee. I would also like to thank Dr. Alexandra Hakala for her encouragement and support. Dr. Hakala has given me insightful comments and ideas for my work. She provided excellent feedback on my both qualifying and proposal committees. It was because of her that I decided to take a class to expand my knowledge on organic geochemistry, which I found surprisingly fun and interesting, as well as extremely useful for my PhD.

I would like to thank Ronald Ripper, the laboratory manager of the Hauck Environmental Engineering Laboratories in Civil and Environmental Engineering (CEE) at CMU. Ron was instrumental in helping me set-up experiments and ordering supplies. Ron also made the CMU CEE community a much greener place. Ron and I always commiserate about moving recycling and compostables into the correct receptacles; those chats have been a favorite part of time at CMU.

Some of this work was performed at EMSL, and there are several people there who helped me with my work, who I would like to thank, including Dr. John Loring and Dr. Zheming Wang. Without their help, I would never have gotten the FTIR set-up for measurements.

I would like to thank the entire CEE staff, especially Maxine Leffard, for making the CMU CEE department the best in the country. This is such an amazing community of students, staff, and faculty and it's all due to their support.

I am extremely grateful to my colleagues and friends at CMU, especially those in the 207C office. I have told my advisors that I have not wanted to graduate because I love the group in the office so much. We are a really supportive, encouraging, and fun group of students. I

would like to thank Dr. Jessica Wilson, Dr. Yuxin Wang, Dr. Arvind Muralimohan, Dr. Stacey Louie, Dr. Daniel Ross, Dr. Theresa Dankovich, Dr. Nicholas Azzolina, Dr. Rui Ma, Megan Leitch, Adam Cadwallader, Ke Gai, Bundhit (Kai) Chucherdwatanasak, Brian Vencalek, Hao Liu, Kaiqi Fang, John Stegemeier, Eleanor Spielman-Sun, Lauren Strahs, Meng-Chen Lee, and Alex Bertuccio, among others. Thank you to Unnati Rao for help with experimental work and Xingshi Zhou for help with Aspen. A special thanks to Eric McGivney for letting me take over part of his desk and to Joe Dallas Moore for setting up the 207C Journal Club, which has been one of my favorite things at CMU CEE. Finally, I would like to thank Dr. Djuna Gulliver, Dr. Hariprasad Parthasarathy, Nizette Consolazio, and Clinton W. Noack, my closest colleagues at CMU CEE. Dr. Gulliver is one of my best friends outside the department, and has always given me good advice on navigating my PhD. Nizette has been a great resource, as she is one of the only other students performing organic research. Finally Dr. Parthasarathy and Clint have been the best sounding boards, advice-givers, editors, and friends in the department. My time here would not have been the same without them.

I would like to thank all of my friends outside of CMU. They have been a constant support through good and bad times. They are great drinking, eating, running, and traveling buddies, and have truly made my time in Pittsburgh the best. I would not have been able to complete my PhD without them.

Finally, I would like to thank my family. My parents, Stephen and Roxane, and brother, Nick have been my biggest supporters. This thesis is dedicated to them.

## Abstract

Carbon capture, utilization, and storage (CCUS), including enhanced oil recovery (EOR), is one of the most promising mitigation strategies for climate change. CCUS involves the capture of CO<sub>2</sub> from point sources and the subsequent injection of that CO<sub>2</sub> into geologic storage formations. Depleted oil reservoirs will be the first targets of CCUS due to the economic benefits associated with EOR. EOR operations are expected to produce large volumes of wastewater brines with the crude oil. Brines, which can have high concentrations of salts and dissolved organic compounds; and CO<sub>2</sub>, which can have dissolved organic compounds, have potential to leak into shallower aquifers. Therefore, fundamental research is needed on the levels of organic compounds in both the reservoir brines and CO<sub>2</sub> in case of leakage.

This thesis was divided into two parts. Part I was concerned with the aqueous solubility of organic compounds in brines. The presence of dissolved salts typically results in a decrease in organic compound aqueous solubility, this is called the salting-out effect, and it is typically modeled by the Setschenow Equation. Setschenow constants, which are empirical salting-out parameters, are assumed to be additive, meaning that they are applicable in mixed electrolyte solutions. However, this has not been verified by extensive experimental work. For accurate risk assessment modeling, Setschenow constants are needed for NaCl and CaCl<sub>2</sub> for hundreds of organic compounds relevant to oil and gas reservoirs. However, there are only ~190 reported NaCl Setschenow constants and ~19 reported CaCl<sub>2</sub> Setschenow constants. For the majority of these compounds, the validity of the Setschenow Equation has only been proven up to 0.5 – 1 M NaCl/CaCl<sub>2</sub>; and has not been extended up to salt concentrations relevant to oil and gas reservoir brines.

The first objective of this study was to determine the validity of the Setschenow Equation for selected hydrophobic compounds in the range of 2 – 5 M NaCl, 1.5 – 2 M CaCl<sub>2</sub>, and in

mixed electrolyte brines. The salting-out effect was measured in NaCl, CaCl<sub>2</sub>, and mixed Na-Ca brines for naphthalene, fluorene, phenanthrene, thiophene, benzothiophene, and dibenzothiophene. In this study, the Setschenow Equation was proven to be valid up to 2 – 5 M NaCl and 1.5 – 2 M CaCl<sub>2</sub> for the organic compounds studied here. Setschenow constants were additive for fluorene and thiophene from moderate to high ionic strengths. Results demonstrated that previously determined Setschenow constants measured at low salt concentrations do not need to be re-measured at high salt concentrations.

Objective 2 was to determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines. The Setschenow Equation was proven to be valid in predicting the salting-out effect up to those high salt concentrations for three phenol, p-cresol, hydroquinone, 9-hydroxyfluorene, pyrrole, and hexanoic acid. Setschenow constants were additive for p-cresol and 9-hydroxyfluorene up to high ionic strengths. In addition to demonstrating the validity of the Setschenow Equation for these selected organic compounds, both Objective 1 and 2 added to a sparse database of NaCl and CaCl<sub>2</sub> Setschenow constants.

In Objective 3 models were evaluated, updated, and developed for prediction of Setschenow constants. Two models, a poly-parameter linear free energy relationship (pp-LFER) and a single parameter (sp) LFER, for prediction of NaCl Setschenow constants were evaluated and updated with new NaCl Setschenow constant data from both this study and the literature. The pp-LFER uses the Abraham solvation parameters of the organic compound of interest as inputs and the sp-LFER uses the octanol-water partitioning coefficient of the organic compound to predict NaCl Setschenow constants. Both models produced predictions of Setschenow constants that had good agreement with the experimental NaCl Setschenow constants in this

study. The update of these models increased the breadth of organic compounds, and therefore confidence, in these models. In addition, four new models were developed to predict Setschenow constants of four other salts, which include  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{LiCl}$ , and  $\text{NaBr}$ . Extensions of this study include determining whether the Setschenow Equation is valid in predicting the salting-out effect for additional organic organics, different salts, and in additional mixed electrolyte systems.

Finally, Part II of this study explored the data gaps related to the partitioning of organic compounds from water to  $\text{sc-CO}_2$ . Objective four was to develop new linear partitioning models based on experimental water- $\text{sc-CO}_2$  data of selected nitrogen, sulfur, and oxygen containing organic compounds and literature data. There are only ~37 organic compounds that have reported water- $\text{sc-CO}_2$  partitioning coefficients; however thousands of partitioning coefficients are needed over a range of temperature and pressure conditions. Therefore, models are needed to accurately predict these partitioning coefficients. Partitioning coefficients over a range of temperatures and pressures were measured for thiophene, pyrrole, and anisole. Those measured partitioning coefficients followed trends based on vapor pressure and aqueous solubility. These partitioning coefficients, along with literature values were used to update a pp-LFER. Five new models based on inputs of vapor pressure, aqueous solubility, and  $\text{CO}_2$  density were developed to predict water- $\text{sc-CO}_2$  partitioning coefficients. Those models were developed using data from this study and literature data. Four of those models are specific to organic compound classes, which include monopolar substituted benzenes, polar substituted benzenes, chlorinated phenols, and nitrogen containing compounds, and the other model is available to any organic compound that has vapor pressure, aqueous solubility, and  $\text{CO}_2$  density inputs that fall within the specified training range.

Possible extensions of this study include further research testing of different groups of organic compounds in water-sc-CO<sub>2</sub> systems, co-solvency effects, determining the effects of the salting-out effect in water-sc-CO<sub>2</sub> partitioning, and using sc-CO<sub>2</sub> for water treatment.

## Table of Contents

Acknowledgements.....	ii
Abstract.....	v
List of Tables .....	xiii
List of Figures.....	xvi
Chapter 1: Introduction, Problem Identification, and Research Objectives.....	1
1.1 Introduction.....	2
1.2 Problem Identification .....	3
1.3 Research Objectives.....	4
<i>Part I. Measurement and Modeling of Setschenow Constants for Hydrophobic and Hydrophilic Compounds in NaCl, CaCl<sub>2</sub>, and Mixed Electrolyte Brines .....</i>	<i>5</i>
<i>Objective 1 (Chapter 3).....</i>	<i>5</i>
<i>Objective 2 (Chapter 4).....</i>	<i>6</i>
<i>Objective 3 (Chapter 5).....</i>	<i>7</i>
<i>Part II. New Linear Partitioning Models based on Experimental Water-Supercritical CO<sub>2</sub> Partitioning Data of Selected Organic Compounds.....</i>	<i>7</i>
<i>Objective 4 (Chapter 6).....</i>	<i>7</i>
1.4 Thesis Organization .....	8
1.5 References.....	9
Chapter 2: Review of the Partitioning Behavior of Organic Compounds in Brines and Supercritical CO <sub>2</sub>	11
Nomenclature.....	12
2.1 Carbon Capture, Utilization, and Storage .....	14
2.2 Enhanced Oil Recovery .....	15
2.3 Oilfield Brines and Produced Waters.....	17
2.4 The Salting-Out Effect and the Setschenow Equation.....	20
2.4.1 The Additivity of Setschenow Constants.....	21
2.4.2 The Effect of pH on the Salting-Out Effect .....	23
2.5 Modeling of the Setschenow Equation .....	23
2.6 Measured Solubility of Organic Compounds in Supercritical CO <sub>2</sub> .....	26
2.6.1 Trends in Solubility of Organic Compounds in Supercritical CO <sub>2</sub> .....	26
2.6.2 Effects of Temperature and Pressure on Solubility of Organic Compounds in Supercritical Carbon Dioxide.....	31
2.6.3 Trends in Partitioning of Organic Compounds from Water to Supercritical CO <sub>2</sub> .....	32
2.7 Thermodynamic Principles and Modeling of Organic Compound Partitioning into Supercritical CO <sub>2</sub>	35

2.7.1 Equations of State .....	36
2.7.2 Poly-parameter Linear Free Energy Relationships .....	41
2.8 Reactive Transport Models used in Geologic Carbon Storage .....	42
2.9 References .....	43
Chapter 3: Measure Setschenow Constants for selected hydrophobic compounds in the range of 2 - 5 M NaCl, 1.5 - 2 M CaCl <sub>2</sub> , and mixed electrolyte brines. ....	52
Abstract .....	53
Nomenclature .....	54
3.1 Introduction .....	55
3.2 Experimental .....	59
3.2.1 Materials .....	60
3.2.2 Methods .....	61
3.3 Results and Discussion .....	62
3.3.1 NaCl Setschenow Constants .....	62
3.3.2 CaCl <sub>2</sub> Setschenow Constants .....	66
3.3.3 Mixed Electrolytes .....	68
3.3.4 Implications .....	69
3.4 Supplementary Information .....	70
3.5 References .....	71
Chapter 4: Determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl <sub>2</sub> , and in mixed electrolyte brines. ....	74
Nomenclature .....	76
4.1 Introduction .....	77
4.2 Experimental .....	80
4.2.1 Materials .....	81
4.2.2 Methods .....	82
4.3 Results and Discussion .....	84
4.3.1 NaCl Setschenow constants .....	85
4.3.2 CaCl <sub>2</sub> Setschenow constants .....	87
4.3.3 Mixed Electrolytes .....	90
4.3.4 Implications .....	91
4.5 Supplementary Information .....	93
4.6 References .....	93
Chapter 5: Evaluate, update, and create new models for the prediction of Setschenow constants. ....	96

Abstract.....	97
Nomenclature.....	98
5.1 Introduction.....	100
5.2 Modeling Methods.....	103
5.3 Comparison to Available Models.....	104
5.4 Updates of the log $K_{ow}$ LFER and the pp-LFER.....	107
5.5 New Single Parameter Linear Free Energy Relationships.....	110
5.6 Implications.....	114
5.7 Supplementary Information.....	114
5.8 References.....	115
Part II.....	117
Development of New Linear Partitioning Models based on Experimental Water-Supercritical CO <sub>2</sub> Partitioning Data of Selected Organic Compounds.....	117
Chapter 6: Development of New Linear Partitioning Models based on Experimental Water – Supercritical CO <sub>2</sub> Partitioning Data of Selected Organic Compounds.....	118
Abstract.....	119
6.1 Introduction.....	122
6.2 Experimental.....	126
6.2.1 Materials.....	126
6.2.2 Methods.....	126
6.3 Modeling Methods.....	130
6.4 Results and Discussion.....	131
6.4.1 Experimental.....	131
6.5 Modeling.....	134
6.5.1 Poly-parameter linear free energy relationship predictions.....	134
6.5.2 Update and Development of Models.....	134
6.5.2.1 ASP-LFER.....	134
6.5.2.2 New LFERs.....	135
6.5.3 Comparison of LFERs.....	138
6.6 Supplementary Information.....	141
6.7 References.....	141
Chapter 7: Summary, Major Contributions, and Limitations of this Thesis, Broader Impacts, and Future Work.....	144
7.1 Summary of this Thesis.....	145

<i>Objective 4 (Chapter 6)</i> .....	147
7.2 Major Contributions of this Thesis .....	147
7.3 Limitations of this Thesis.....	151
7.3.1 Validity of the Setschenow Equation.....	151
7.3.2 Modeling of Setschenow Constants.....	152
7.3.3 Modeling of Water – Supercritical Carbon Dioxide Partitioning Coefficients.....	152
7.4 Significance and Broader Impacts .....	153
7.4.1 Carbon capture, utilization, and storage.....	153
7.4.2 Produced Water Management.....	153
7.4.3 Water Treatment Industries.....	154
7.4.4 Organic Aerosols .....	155
7.5 Future Research Related to Part I .....	156
7.5.1 The Validity of the Setschenow Equation For Additional Organic Compounds .....	156
7.5.2 The Validity of the Setschenow Equation for other Salts .....	157
7.5.3 The Additivity of the Setschenow Equation in Mixed Electrolyte Systems .....	158
7.5.4 Molecular Modeling of Salting-Out Effect Mechanisms.....	159
7.6 Future Research Related to Part II.....	159
7.6.1 Additional Partitioning Coefficients for Solid Organic Compounds .....	160
7.6.2. Co-Solvency Effect.....	160
7.7 Future Work on Brine to sc-CO <sub>2</sub> Partitioning.....	161
7.8 Future Work on Modeling of Organic Compounds in CCUS Systems .....	162
7.9 References.....	163
Appendix A.....	166
A.1 Solid Phase Microextraction .....	167
A.2. Removal of Data Points: Depletion and Aqueous Solubility Tables .....	169
A.3 Abraham Solvation Parameters.....	179
A.4 Aqueous solubility, octanol-water partitioning coefficients, and experimentally determined NaCl and CaCl <sub>2</sub> Setschenow Constants and Associated Measurement Error.....	180
A.5 References.....	180
Appendix B.....	182
B.1. Solid Phase Microextraction .....	183
B.2. Depletion and Aqueous Solubility Tables.....	184
B.3. Abraham Solvation Parameters and log K <sub>ow</sub> of Organic Compounds .....	189

B.4. Change in pKa with salt concentration.....	189
B.5 List of oil and gas reservoirs with calculations for percent of organic acid in the neutral form. ....	190
B.6 References .....	190
Appendix C .....	192
C.1. Outlier and Influential Point Tests and Removal .....	193
C.2 Published NaCl Setschenow Constants along with New Model Predictions .....	198
C.3 Plots and Breakdown of Residuals .....	208
C.4 Data for the CaCl <sub>2</sub> , KCl, LiCl and NaBr sp-LFERs.....	210
C.4 References .....	214
Appendix D.....	218
Chapter 6:.....	218
D.1 Time to Equilibrium Curves for Organic Compound Partitioning.....	219
D.2 Equation of State Modeling and Binary Interaction Parameters .....	219
D.3 Iterations of the ASP-LFERs. ....	224
D.4. Lists of organic compounds partitioning coefficients from this study and the literature.....	225
D.5. Ranges of Vapor Pressure, Aqueous Solubility, CO <sub>2</sub> Density, and log K for LFERs .....	235
D.6 Table of Root Mean Square Errors .....	236
D.7 References .....	236

## List of Tables

<b>Table 2.1.</b> Maximum Reported Levels of Petroleum Hydrocarbons in Selected Produced Waters .....	17
<b>Table 2.2.</b> Reported Brine Concentrations for various oil reservoirs or CCUS demonstration sites. ....	19
<b>Table 2.3.</b> Measured Solubility of Selected Pure Phase Organic Compounds in sc-CO <sub>2</sub> .....	29
<b>Table 2.4.</b> Partitioning coefficients ( $K_{i,c/w}$ ) of Selected Organic Compounds in a Pure Phase-Water-sc-CO <sub>2</sub> System.....	34
<b>Table 3.1.</b> Summary of previously reported experimentally determined Setschenow constants for NaCl and data produced in this study for NaCl and CaCl <sub>2</sub> .....	65
<b>Table 4.1.</b> Previously reported, model predicted, and experimentally determined NaCl and CaCl <sub>2</sub> Setschenow Constants.....	84
<b>Table 5.1.</b> Abraham Solvation Parameters, log K <sub>ow</sub> , LFER predicted $K_s^{i,NaCl}$ , and Experimental $K_s^{i,NaCl}$ .....	105
<b>Table 6.1.</b> Properties and Ranges of Concentrations for Organic Compounds in the Partitioning Experiments .....	128
<b>Table 6.2.</b> Experimental partitioning coefficients of organic compounds of interest in this study over a range of temperatures and pressure, along with predictions from pp-LFER.....	133
<b>Table A.1.1</b> Fibers, time to equilibrium, and concentrations associated with the organic compounds in this study.....	167
<b>Table A.2.1.</b> Volumes of fibers used in this study.....	171
<b>Table A.2.2</b> Fiber-Water Partitioning Coefficients and Aqueous Solubility Sources for Each Compound.....	172
<b>Table A.2.3.</b> Depletion and Aqueous Solubility of Thiophene in Salt Solutions .....	173
<b>Table A.2.4.</b> Depletion and Aqueous Solubility of Naphthalene in Salt Solutions .....	174
<b>Table A.2.5.</b> Depletion and Aqueous Solubility of Benzothiophene in Salt Solutions.....	175
<b>Table A.2.6.</b> Depletion and Aqueous Solubility of Fluorene in Salt Solutions .....	176
<b>Table A.2.7.</b> Depletion and Aqueous Solubility of Phenanthrene in Salt Solutions.....	177
<b>Table A.2.8.</b> Depletion and Aqueous Solubility of Dibenzothiophene in Salt Solutions .....	178
<b>Table A.3.1.</b> Abraham Solvation Parameters of Organic Compounds in this Study.....	179
<b>Table A.4.1.</b> Partitioning information of organic compounds used in this study. ....	180
<b>Table B.1.1</b> Fibers, time to equilibrium, and concentrations associated with the organic compounds in this study.....	183
<b>Table B.2.1</b> Depletion and Aqueous Solubility of Pyrrole in Salt Solutions.....	184
<b>Table B.2.2.</b> Depletion and Aqueous Solubility of Phenol in Salt Solutions.....	185
<b>Table B.2.3.</b> Depletion and Aqueous Solubility of p-Cresol in Salt Solutions .....	186
<b>Table B.2.4.</b> Depletion and Aqueous Solubility of Hydroquinone in Salt Solutions.....	187
<b>Table B.2.5.</b> Depletion and Aqueous Solubility of Hexanoic Acid in Salt Solutions.....	187
<b>Table B.2.6.</b> Depletion and Aqueous Solubility of 9-Hydroxyfluorene in Salt Solutions.....	188
<b>Table B.3.1.</b> Abraham Solvation Parameters and log K <sub>ow</sub> of Organic Compounds in this Study .....	189
<b>Table B.4.1.</b> Change in pKa with NaCl Concentration.....	189
<b>Table B.5.1.</b> Reservoir fluid baseline and post-injection pH, total dissolved solids, and percent of an organic compound in the neutral form. ....	190

<b>Table C.1.1</b> Organic compounds which exceeded the threshold for Cook's Distance in the pp-LFER.....	197
<b>Table C.1.2</b> Organic compounds which exceeded the threshold for Cook's Distance in the log $K_{ow}$ .....	197
<b>Table C.2.1</b> Abraham Solvation Parameters (ASP), log $K_{ow}$ , published NaCl $K_s$ , and new model predictions.....	198
<b>Table C.2.2.</b> Range of Regressions for the NaCl Setschenow constant LFERs .....	208
<b>Table C.4.1.</b> Range of Regressions for the $CaCl_2$ , KCl, LiCl, and NaBr constant LFERs .....	210
<b>Table C.4.2</b> Organic compounds used in $CaCl_2$ LFER.....	210
<b>Table C.4.3.</b> Organic compounds used in KCl LFER.....	211
<b>Table C.4.4.</b> NaCl and LiCl Setschenow constants used in sp-LiCl-LFER.....	213
<b>Table C.4.5</b> NaCl and NaBr Setschenow constants used in sp-NaBr-LFER.....	214
<b>Table D.4.1.</b> Lists of Monopolar Substituted Benzenes.....	225
<b>Table D.4.2.</b> Lists of Polar Substituted Benzenes .....	227
<b>Table D.4.3.</b> Lists of Chlorinated Phenols .....	230
<b>Table D.4.4.</b> Lists of Nitrogen Containing Compounds .....	231
<b>Table D.4.5.</b> Lists of Other Organic Compounds .....	232
<b>Table D.5.1.</b> Range in Parameters for ASP-LFER.....	235
<b>Table D.5.2.</b> Range in Parameters for VP-AS-LFER .....	235
<b>Table D.5.3.</b> Range in Parameters for Monopolar Substituted Benzene-LFER .....	235
<b>Table D.5.4.</b> Range in Parameters for Polar Substituted Benzene-LFER.....	235
<b>Table D.5.5.</b> Range in Parameters for Chlorinated Phenols LFER.....	235
<b>Table D.5.6.</b> Range in Parameters for Nitrogen Containing-LFER.....	235
<b>Table D.6.1.</b> Root Mean Square Errors.....	236

## List of Figures

<b>Figure 1.1.</b> The organization of the thesis and research objectives. ....	5
<b>Figure 2.1.</b> The crossover pressure of naphthalene.....	31
<b>Figure 2.2</b> Isothermal pressure increase of n-decane at 377.6 K.82 .....	32
<b>Figure 3.1</b> The effect of salt addition (i.e. $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of selected organic compounds onto the SPME fiber as for A) thiophene, B) naphthalene, C) benzothiophene, D) fluorene, E) dibenzothiophene, and F) phenanthrene. ....	64
<b>Figure 3.2</b> The salting-out effect (i.e. $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of individual organic compounds onto the SPME fiber as a function of $\text{CaCl}_2$ concentration (M) for A) Thiophene, B) Benzothiophene, C) Fluorene, D) Dibenzothiophene, and E) Phenanthrene. ....	67
<b>Figure 3.3</b> The salting-out effect (i.e. $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of individual organic compounds onto the SPME fiber as a function of ionic strength (M) for A) Thiophene, and B) Fluorene.....	69
<b>Figure 4.1</b> The effect of salt addition (i.e. $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of selected organic compounds onto the SPME fiber as for A) phenol, B) pyrrole, C) p-cresol, D) hydroquinone, E) hexanoic acid, and F) 9-hydroxyfluorene.....	86
<b>Figure 4.2</b> The effect of salt addition (i.e. $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of selected organic compounds onto the SPME fiber as for A) phenol, B) pyrrole, C) p-cresol, D) hydroquinone, E) hexanoic acid, and F) 9-hydroxyfluorene.....	89
<b>Figure 4.3</b> The salting-out effect (i.e. $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of individual organic compounds onto the SPME fiber as a function of ionic strength (M) for A) p-Cresol, and B) 9-Hydroxyfluorene. ....	91
<b>Figure 5.1.</b> Plots of comparisons between the pp-LFER predicted and experimental NaCl Setschenow constant values and the $\log K_{\text{ow}}$ predicted and experimental NaCl Setschenow constant values. ....	106
<b>Figure 5.2.</b> Plots of comparisons between the A) pp-LFER predicted and experimental NaCl Setschenow constant values, B) $\log K_{\text{ow}}$ predicted and experimental NaCl Setschenow constant values. ....	108
<b>Figure 5.3.</b> Correlations between the measured A) $\text{CaCl}_2$ and NaCl Setschenow constants, B) KCl and NaCl Setschenow constants, C) LiCl and NaCl Setschenow constants, and D) NaBr and NaCl Setschenow constants. ....	113
<b>Figure 6.1.</b> Schematic of the experimental apparatus used to measure partitioning coefficients. ....	127
<b>Figure 6.2.</b> The partitioning of the three organic compounds of interest in this study versus $\text{CO}_2$ density, which is dependent on both temperature and pressure. ....	133
<b>Figure 6.3.</b> Predicted $\log$ partitioning coefficients of organic compounds coefficients versus $\log$ experimental partitioning coefficients of organic compounds from both this study and literature values for the pp-LFERs in this study: A) Abraham solvation parameter LFER, B) Vapor pressure and aqueous solubility LFER, C) Monopolar substituted benzene LFER, D) Polar substituted benzene LFER, E) Chlorinated phenol LFER, and F) Nitrogen containing compound LFER.....	140
<b>Figure A.1.1</b> Time to equilibrium uptake curves for the compounds of interest in this study... ..	168
<b>Figure A.2.1</b> The change in “salting-out” for thiophene in A) NaCl, B) $\text{CaCl}_2$ , and C) Mixed electrolyte solutions. ....	174
<b>Figure A.2.2.</b> The change in “salting-out” for naphthalene in NaCl.....	175
<b>Figure A.2.3.</b> The change in “salting-out” for benzothiophene in A) NaCl and B) $\text{CaCl}_2$ . ....	176
<b>Figure A.2.4.</b> The change in “salting-out” for fluorene in A) NaCl, B) $\text{CaCl}_2$ , and C) Mixed electrolyte solutions. ....	177

<b>Figure A.2.5.</b> The change in “salting-out” for phenanthrene in A) NaCl and B) CaCl <sub>2</sub> . .....	178
<b>Figure A.2.6.</b> The change in “salting-out” for dibenzothiophene in A) NaCl and B) CaCl <sub>2</sub> . ...	179
<b>Figure B.1.1</b> Time to equilibrium uptake curves for the compounds of interest in this study...	184
<b>Figure C.1.1.</b> Plots of comparisons between the A) pp-LFER predicted and experimental NaCl Setschenow constant values, B) log K <sub>ow</sub> predicted and experimental NaCl Setschenow constant values. ....	196
<b>Figure C.3.1.</b> Plots of absolute values of residuals between the A) pp-LFER predicted and experimental NaCl Setschenow constant values, B) log K <sub>ow</sub> predicted and experimental NaCl Setschenow constant values. ....	209
<b>Figure D.1.1.</b> Partitioning coefficients of organic compounds versus time to equilibrium for A) Thiophene, B) Pyrrole, and C) Anisole. ....	219

## **Chapter 1: Introduction, Problem Identification, and Research Objectives**

## 1.1 Introduction

The widespread implementation of carbon capture, utilization, and storage (CCUS), including enhanced oil recovery (EOR), is likely to become part of a multi-faceted plan to reduce emissions from stationary sources of CO<sub>2</sub>, which is one of the major contributors to climate change. CCUS involves the capture, compression, and injection of CO<sub>2</sub> into geologic storage formations, such as deep saline aquifers, depleted oil and gas reservoirs, un-mineable coal seams, organic rich shales, and basalt formations (NETL, 2012). At temperatures ( $T > 304.2$  K) and pressures ( $P > 73.8$  bar) of these storage formations, CO<sub>2</sub> compresses in its supercritical phase. Supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) has properties of both liquids and gases and is a known solvent for organic compounds.

The first adopters of CCUS technologies will be depleted oil reservoirs, due to the economic benefit associated with EOR (NETL, 2012). Enhanced oil recovery is considered a tertiary recovery method after primary production, and water-flooding (secondary recovery). Enhanced oil recovery involves the injection of CO<sub>2</sub> into the oil reservoir to reduce the viscosity of oil, resulting in more produced oil. Primary and secondary recovery typically extract 30 – 40 % of the original oil in place (OOIP); and CO<sub>2</sub>-EOR typically can remove up to another 15 % of the OOIP (Blunt et al. 1993; Gozalpour et al. 2005; Thomas, 2008). After EOR operations cease, large volumes of CO<sub>2</sub> [up to 60 vol% in pore spaces] are expected to be sequestered in these formations (Gozalpour et al., 2005), therefore the residual petroleum hydrocarbons have the potential to partition into the CO<sub>2</sub> phase.

Extraction of oil and gas also involves the production of large volumes of reservoir water, called produced water or flowback water. Produced water is the largest waste stream in the oil and gas industry (Neff et al. 2011) and often contains high concentrations of total dissolved

solids, metals, radionuclides, and dissolved organic compounds (Neff et al. 2011; Benko & Drewes 2008; Utvik 1999; Gregory et al. 2011).

## **1.2 Problem Identification**

The storage of CO<sub>2</sub> into these formations will cause geologic changes that may result in the leakage of brines and/or CO<sub>2</sub> into shallower aquifers. Leakage of these fluids may occur through poorly sealed wells (Lewicki et al. 2007), failure of the caprock (Shukla et al. 2010), well blow-out (Duncan et al. 2009), and seismic activity (Tsang et al. 2002). In addition to production of the crude oil, EOR and other unconventional oil and gas operations will result in the production of high volumes of saline water, which will need to be disposed of and treated safely. These oil and gas reservoir brines, among other inorganic and organic constituents, contain dissolved organic compounds that can partition to sc-CO<sub>2</sub> and are potentially toxic and carcinogenic. Due to leakage and produced water safety and treatment issues, a comprehensive understanding of the risks of these organic compounds associated with leaking brines, CO<sub>2</sub>, and produced waters is necessary.

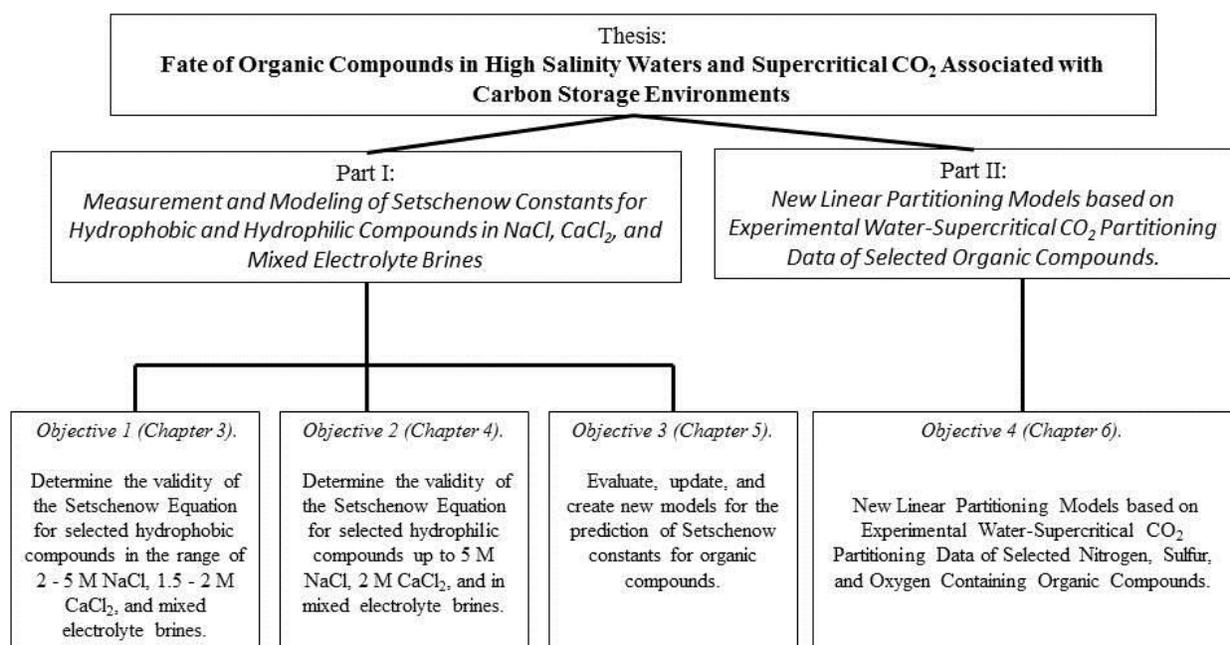
This thesis is specifically focused on the partitioning behavior of dissolved organic compounds (which are often toxic and carcinogenic) present in the oilfield brines and produced waters. The classes of organic compounds often found in these brines include, alkylated benzenes, including benzene, toluene, ethylbenzene, and the xylene isomers (BTEX), polycyclic aromatic hydrocarbons (PAHs), phenols, aliphatic and aromatic carboxylic acids, and nitrogen-, sulfur-, and oxygen- (NSO) containing compounds (Neff et al. 2011; Benko & Drewes 2008; Utvik 1999; Kharaka & Hanor 2003).

Brines associated with EOR and oil depleted sites typically have high concentrations of salts, such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$  (Kharaka & Hanor 2003), which have the potential to significantly decrease the aqueous solubility of organic compounds; this is called the “salting-out effect.” There is currently a lack of data on the salting-out effect for organic compounds of interest in high salinity brines. In our attempt to have more realistic risk assessment modeling results, aqueous solubility data of organic compounds at relevant salt concentrations are needed.

In addition, the introduction of  $\text{sc-CO}_2$  will result in the dissolution of organic compounds into  $\text{sc-CO}_2$ . Supercritical  $\text{CO}_2$  is an excellent solvent for small, volatile organic compounds (Burant et al. 2013), however there is a considerable lack of partitioning coefficient data between water and  $\text{sc-CO}_2$  over a range of temperatures and pressures for organic compounds of interest, such as PAHs and NSO-containing compounds. The lack of partitioning coefficient data for the above mentioned systems is motivation for the development and validation of models for the predictions of water- $\text{sc-CO}_2$  partitioning coefficients.

### **1.3 Research Objectives**

The overarching goal of this thesis is to be able to predict the partitioning behavior of selected organic compounds in brines and  $\text{sc-CO}_2$ . This dissertation is divided into two parts. The first part is concerned with the aqueous solubility of organic compounds in saline waters of various compositions. The second part is focused on the partitioning of organic compounds from water to  $\text{sc-CO}_2$ . Both parts have experimental and modeling tasks and are described in these four research objectives below. The objective organization is given in Figure 1.1, below.



**Figure 1.1.** The organization of the thesis and research objectives.

*Part I. Measurement and Modeling of Setschenow Constants for Hydrophobic and Hydrophilic Compounds in NaCl, CaCl<sub>2</sub>, and Mixed Electrolyte Brines*

*Objective 1 (Chapter 3).* Determine the validity of the Setschenow Equation for selected hydrophobic compounds in the range of 2 - 5 M NaCl, 1.5 - 2 M CaCl<sub>2</sub>, and mixed electrolyte brines.

The increase in aqueous activity coefficient (or decrease in aqueous solubility) of organic compounds in salt water is typically modeled by the Setschenow Equation (Sechenov 1889). The equation predicts a log-linear increase in aqueous activity coefficient with increasing salt concentration, related by an empirical salting-out parameter called the Setschenow constant. The applicability of the Setschenow Equation has only been confirmed up to high salinities for a few compounds. Most Setschenow constant data are collected up to 0.5 - 1 M, and primarily in NaCl. Therefore, it is unknown whether Setschenow constant data measured at low salt concentration

can be extrapolated up to high salt concentrations. This objective has three tasks. The first task is concerned with whether the reported NaCl Setschenow constants measured at those lower salt concentrations are applicable up to high salt concentrations (2 – 5 M NaCl) typical of oil and gas reservoirs. In addition, there is a considerable lack of data CaCl<sub>2</sub> Setschenow data (only ~19 available CaCl<sub>2</sub> Setschenow constants before this study). The second task aims to add to a sparse database of those CaCl<sub>2</sub> Setschenow constants and to determine if salting-out behavior in CaCl<sub>2</sub> solutions is log-linear up to 1.5 – 2 M. Finally, the third task is to determine if Setschenow constants measured in single electrolyte brines are applicable to mixed electrolyte brines, which are typical of oil and gas reservoirs.

*Objective 2 (Chapter 4).* Determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines.

The salting-out effect of the selected hydrophilic organic compounds in NaCl, CaCl<sub>2</sub>, and mixed electrolytes was investigated in this objective. Hydrophilic and hydrophobic compounds were divided into two objectives (Chapter 3 and Chapter 4, with the hydrophobic compound objective described above) because it was hypothesized their ability to undergo hydrogen bonding interactions would lead to differences in salting-out behavior. This objective was accomplished in three tasks. The first task involves determining new NaCl Setschenow constants and evaluating whether the salting-out effect is log-linear up to 5 M NaCl. The second task involves determining new CaCl<sub>2</sub> Setschenow constants and evaluating if log-linear salting-out behavior occurred up to 2 M CaCl<sub>2</sub>. There is considerably less data for hydrophilic compounds of interest to oil and gas reservoirs, so these two tasks add to a sparse database of hydrophilic NaCl and CaCl<sub>2</sub> Setschenow constants. Finally, in the third task, it was investigated whether

those Setschenow constants were applicable in predicting the salting-out effect for mixed electrolyte brines at moderate and high ionic strengths.

*Objective 3 (Chapter 5).* Evaluate, update, and create new models for the prediction of Setschenow constants for organic compounds.

The evaluation, update, and creation of new models for prediction of Setschenow constants will be accomplished in three parts. There are two available models (with widely available parameters) to predict NaCl Setschenow constants, a single parameter linear free energy relationship (sp-LFER) which predicts NaCl Setschenow constants from octanol – water partitioning coefficients ( $\log K_{ow}$ ), and a poly-parameter linear free energy relationships (pp-LFER), which uses the Abraham solvation parameters (ASP) to predict NaCl Setschenow constants. These were evaluated and updated both with literature data and with data from Objectives 1 and 2. These models cover a range of organic compound classes. There are no available models to predict Setschenow constants of other salts. Finally, new models were developed for the prediction of other salts, including  $\text{CaCl}_2$ , KCl, LiCl, and NaBr from NaCl Setschenow constants, and compared to reported values for those salts through cross-validation procedures.

*Part II. New Linear Partitioning Models based on Experimental Water-Supercritical  $\text{CO}_2$  Partitioning Data of Selected Organic Compounds.*

*Objective 4 (Chapter 6).* New Linear Partitioning Models based on Experimental Water-Supercritical  $\text{CO}_2$  Partitioning Data of Selected Nitrogen, Sulfur, and Oxygen Containing Organic Compounds.

Partitioning of organic compounds from water to sc-CO<sub>2</sub> is a function of the organic compounds inherent solubility in each phase. Since organic compound solubility in sc-CO<sub>2</sub> follows trends in vapor pressure, this means that organic compounds with relatively high volatility and low aqueous solubility should have higher partitioning to sc-CO<sub>2</sub>. However, there is a dearth of available partitioning coefficients of organic compounds (~37) between water and sc-CO<sub>2</sub>, which are highly dependent on temperature and pressure. There is another pp-LFER that also uses the ASPs to predict water-sc-CO<sub>2</sub> partitioning coefficients. This leads to two tasks that were accomplished in this objective. The first task involves the measurement of partitioning coefficients over a range of temperatures and pressures for three organic compounds. In the second task, models were improved and developed for more accurate water – sc-CO<sub>2</sub> partitioning coefficients predictions. The organic compounds were chosen, because they have no previously reported water – sc-CO<sub>2</sub> partitioning coefficients and to cover a range of volatility and aqueous solubility to further assess trends in water – sc-CO<sub>2</sub> partitioning.

#### **1.4 Thesis Organization**

The dissertation comprises of seven Chapters. Chapter 1: describes the problem identification, and research objectives. Chapter 2: is the background on the composition of oil and gas brines, the salting-out effect and the Setschenow Equation, modeling of Setschenow constants, trends in CO<sub>2</sub> solubility and partitioning, and modeling of partitioning to sc-CO<sub>2</sub>. Chapters 3, 4, and 5: A presentation of the materials and methods, results, discussion, and key conclusions from each objective for Part I. Chapter 6: Describes the materials and methods, results, discussion, and key conclusions from objective 4 for Part II. Chapter 7: Summarizes the

key conclusions and broader impacts from each objective, and includes suggestions for future work arising from the findings.

## 1.5 References

- Benko, K.L. & Drewes, J.E., 2008. Produced Water in the Western United States: Geographical Distribution, Occurrence, and Composition. *Environmental Engineering Science*, 25(2), pp.239–246. Available at: <http://dx.doi.org/10.1089/ees.2007.0026>.
- Blunt, M., Fayers, F.J. & Orr, F.M., 1993. Carbon dioxide in enhanced oil recovery. *Energ. Convers. Manage*, 34(9), pp.1197–1204.
- Burant, A., Lowry, G.V. & Karamalidis, A.K., 2013. Partitioning behavior of organic contaminants in carbon storage environments: a critical review. *Environmental science & technology*, 47(1), pp.37–54. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/23211055>.
- Duncan, I.J., Nicot, J.-P. & Choi, J.-W., 2009. Risk Assessment for future CO<sub>2</sub> Sequestration Projects Based CO<sub>2</sub> Enhanced Oil Recovery in the U.S. *Energy Procedia*, 1(1), pp.2037–2042. Available at: <http://www.sciencedirect.com/science/article/pii/S1876610209002665>.
- Gozalpour, F., Ren, S. R. & Tohidi, B., 2005. Récupération assistée du pétrole (EOR) et stockage du CO<sub>2</sub> dans des réservoirs pétroliers. *Oil & Gas Science and Technology - Rev. IFP*, 60(3), pp.537–546. Available at: <http://dx.doi.org/10.2516/ogst:2005036>.
- Gregory, K.B., Vidic, R.D. & Dzombak, D.A., 2011. Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements*, 7 (3), pp.181–186. Available at: <http://elements.geoscienceworld.org/content/7/3/181.abstract>.
- Kharaka, Y.K. & Hanor, J.S., 2003. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In E.-C. H. D. Holland & K. K. Turekian, eds. *Treatise on Geochemistry*. Oxford: Pergamon, pp. 1–48. Available at: <http://www.sciencedirect.com/science/article/pii/B0080437516050854>.
- Lewicki, J., Birkholzer, J. & Tsang, C.-F., 2007. Natural and industrial analogues for leakage of CO<sub>2</sub> from storage reservoirs: identification of features, events, and processes and lessons learned. *Environmental Geology*, 52(3), pp.457–467. Available at: <http://dx.doi.org/10.1007/s00254-006-0479-7>.
- Neff, J., Lee, K. & Deblois, E.M., 2011. Produced Water : Overview of Composition , Fates , and Effects. *Produced Water*, pp.3–54.
- NETL, 2012. *Carbon Utilization and Storage Atlas of the United States and Canada, 4th ed.*, Morgantown, WV.
- Sechenov, M., 1889. Über die Konstitution der Salzlösungen auf Grund ihres Verhaltens zu Kohlensäure. *Z. Phys. Chem.*, 4, p.117.
- Shukla, R. et al., 2010. A review of studies on CO<sub>2</sub> sequestration and caprock integrity. *Fuel*, 89(10), pp.2651–2664. Available at: <http://www.sciencedirect.com/science/article/pii/S0016236110002218>.
- Thomas, S., 2008. Enhanced Oil Recovery – An Overview. *Science And Technology*, 63, pp.9–19.

- Tsang, C.-F. et al., 2002. Scientific considerations related to regulation development for CO<sub>2</sub> sequestration in brine formations. *Environmental Geology*, 42(2), pp.275–281. Available at: <http://dx.doi.org/10.1007/s00254-001-0497-4>.
- Utvik, T.I.R., 1999. Chemical characterisation of produced water from four offshore oil production platforms in the North Sea. *Chemosphere*, 39(15), pp.2593–2606. Available at: <http://www.sciencedirect.com/science/article/pii/S004565359900171X>.

## Chapter 2: Review of the Partitioning Behavior of Organic Compounds in Brines and Supercritical CO<sub>2</sub>

The background on the partitioning behavior of organic compounds in supercritical carbon dioxide (sc-CO<sub>2</sub>) includes information adapted from Burant, A.; Lowry G.V.; Karamalidis, A.K. Partitioning Behavior of Organic Contaminants in Carbon Storage Environments: A Critical Review. *Environmental Science and Technology*, **2013**, *47*, 37-54.

## Nomenclature

$\alpha_2$ : Hydrogen bonding acidity of the organic compound  
 $\beta_0$ : Compressibility of water  
 $\beta_2$ : Hydrogen bonding basicity of the organic compound  
 $\gamma_w^{DI}$ : Aqueous activity coefficient of the organic compound in deionized water  
 $\gamma_w^{salt}$ : Aqueous activity coefficient of the organic compound in salt water  
 $\phi_i^L$ : Fugacity coefficient of the liquid phase  
 $\phi_i^V$ : Fugacity coefficient of the vapor phase  
 $\pi_1$ : Polarizability of the carbon dioxide  
 $\pi_2$ : Polarizability of the organic compound  
 $\rho_c$ : Critical density  
 $\rho_{H_2O}$ : Density of the aqueous phase  
 $\rho_{CO_2}$ : Density of the carbon dioxide phase  
 $\rho_r$ : Reduced density  
 $\omega$ : Acentric factor  
**a**: parameter used to account for ideality in the Peng-Robinson equation of state  
**API**: American Petroleum Institute  
**ASP**: Abraham solvation parameters  
**b**: parameter used to account for ideality in the Peng-Robinson equation of state  
**BIP**: Binary interaction parameters  
**BTEX**: Benzene, toluene, ethylbenzene, and xylene isomers  
 $C_{CO_2,i}$ : Concentration of organic compound in the carbon dioxide phase  
 $C_{H_2O,i}$ : Concentration of organic compound in the aqueous phase  
**CCUS**: Carbon capture, utilization, and storage  
**CO<sub>2</sub>**: Carbon dioxide  
**EOR**: Enhanced oil recovery  
**EOS**: Equation of state  
 $f_i^L$ : Fugacity of the liquid phase  
 $f_i^V$ : Fugacity of the vapor phase  
**K<sub>aw</sub>**: Air-water partitioning coefficient  
 $K_{i,c/w}$ : Water to supercritical CO<sub>2</sub> partitioning coefficient  
**K<sub>ow</sub>**: Octanol-water partitioning coefficient  
 $K_s^{i,k}$ : Setschenow constant in single electrolyte system  
 $K_s^{mixed}$ : Setschenow constant in mixed electrolyte system  
**L**: Liquid fraction  
**LFER**: Linear free energy relationship  
**MW**: Molecular weight  
**n**: number of observances  
**NSO**: Nitrogen, sulfur, and oxygen

**OOIP**: Original oil in place  
**P**: Pressure  
**P<sub>c</sub>**: Critical pressure  
**PAH**: Polycyclic aromatic hydrocarbons  
**pK<sub>a</sub>**: Acid dissociation constant  
**pp-LFER**: Poly-parameter linear free energy relationship  
**R**: Universal gas constant  
**R<sub>2</sub>**: Index of refraction of the organic compound  
**sc-CO<sub>2</sub>**: Supercritical carbon dioxide  
**STOMP**: Subsurface transport over multiple phases  
**T**: Temperature  
**T<sub>c</sub>**: Critical temperature  
**TDS**: Total dissolved solids  
**TOUGH**: Transport of unsaturated groundwater and heat  
**U.S. DOE**: United States Department of Energy  
**U.S. EIA**: United States Energy Information Administration  
**V**: Vapor fraction  
**V<sub>2</sub>**: Molar volume of the organic compound  
**V<sub>s</sub>**: Molar volume of the pure (liquid) electrolyte  
 $\overline{V}_s^0$ : Partial molar volume of the electrolyte at infinite dilution  
**x<sub>i</sub>**: mole fraction in the aqueous phase  
**y<sub>i</sub>**: mole fraction in the sc-CO<sub>2</sub> phase  
**z<sub>i</sub>**: Total number of moles inputted into the system for each compound  
**Z<sup>L</sup>**: Liquid phase compressibility  
**Z<sup>V</sup>**: Vapor phase compressibility

## 2.1 Carbon Capture, Utilization, and Storage

Carbon, capture, utilization, and storage (CCUS) is one of the most promising mitigation strategies for global climate change. CCUS involves the capture of CO<sub>2</sub> from point sources of CO<sub>2</sub>, and the injection of that CO<sub>2</sub> into geologic storage formations. The United States Department of Energy (U.S. DOE) has defined potential storage sites as having depths greater than 800 m and total dissolved solids (TDS) concentrations greater than 10 g/L (NETL 2012). Deep saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, organic rich shales, and basalt formations are all under consideration for CCUS (NETL 2012), however depleted oil reservoirs are expected to be the first adopters due to the economic benefit associated with enhanced oil recovery (EOR), so the focus of this dissertation is on carbon storage in depleted oil and gas reservoirs.

At the temperatures ( $T > 304.2$  K) and pressures ( $P > 73.8$  Bar) of those storage formations, CO<sub>2</sub> will be in the supercritical phase. Maximum reported temperatures and pressures of these storage formations are 423 K and 500 Bar, respectively (Kharaka & Hanor 2003). In this temperature and pressure range, supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) is a unique fluid as it has densities ( $\sim 100$ - $1000$  kg/m<sup>3</sup>) similar to liquids, and viscosities ( $\sim 20 - 115$   $\mu$ Pa·s) similar to gases.

There are five different trapping mechanisms for the injected CO<sub>2</sub>, all occurring on different time scales. The type of trapping that dominates will be different from site to site. These include: Structural trapping, a physical trapping mechanism, where CO<sub>2</sub> is sequestered in the formation by the caprock; hydrodynamic trapping, where the CO<sub>2</sub> is trapped in pore spaces due to differences in viscosity between the CO<sub>2</sub> plume and the reservoir waters; capillary trapping, which sequesters the CO<sub>2</sub> due to capillary forces; solubility trapping, which involves the dissolution of CO<sub>2</sub> into the formation waters and residual oil, and mineral trapping, which

occurs over hundreds of years where CO<sub>2</sub> is converted to carbonate rock (Harvey et al. 2013). These trapping mechanisms highlight the fact that CCUS involves the injection of another fluid into these formations, which will cause geologic changes that may have serious geochemical implications.

Despite the rigorous site selection that is expected to occur before full scale implementation of CCUS, leakage of CO<sub>2</sub> and/or formation brines can occur. The main leakage scenarios to occur through poorly sealed wells (Lewicki et al. 2007), failure of the caprock (Shukla et al. 2010), well-blow-out (Duncan et al. 2009), and seismic activity (Tsang et al. 2002). This has the potential to transport brines and/or CO<sub>2</sub>, along with toxic and/or carcinogenic metals, petroleum hydrocarbons, and radionuclides to shallower aquifers. Therefore, this calls for a thorough geochemical risk assessment before the widespread implementation of CCUS.

## **2.2 Enhanced Oil Recovery**

CCUS in depleted oil reservoirs will be initially accomplished through enhanced oil recovery (EOR). The U.S. Energy Information Administration (EIA) predicts that CO<sub>2</sub>-driven EOR will increase as the discovery of and production from conventional wells decrease, and the cost of anthropogenic CO<sub>2</sub> decreases (DOE/EIA 2014). They predict the use of CO<sub>2</sub>-EOR will increase after 2017 (DOE/EIA 2014).

There are many types of EOR; however CCUS will be accomplished through CO<sub>2</sub> flooding, which is used on light and medium API gravity oils. CO<sub>2</sub>-EOR involves the injection of CO<sub>2</sub>, which decreases the viscosity of the crude oil, resulting in increased production. EOR is considered a tertiary recovery method, after primary and secondary oil recovery. In primary production, crude oil is produced due to the inherent pressure of the formation. Secondary oil production, or water-flooding, is done to increase the pressure of the formation to allow for more production of oil. Primary and secondary oil production usually results in the 30 – 40% of the

original oil in place (OOIP). Typically, CO<sub>2</sub>-EOR can produce up to 15% of the OOIP (Blunt et al. 1993; Gozalpour, F. et al. 2005; Thomas 2008).

The way that EOR is currently practiced does not constitute CCUS, due to the fact that most sites still use natural sources of CO<sub>2</sub> (de Coninck & Benson 2014). Some newer sites, such as the Weyburn formation in Canada use anthropogenic sources of CO<sub>2</sub> (Emberley et al. 2004). However, despite the source of CO<sub>2</sub>, understanding the geochemical implications of the injected CO<sub>2</sub> will be essential as the technology becomes more widespread.

In EOR, CO<sub>2</sub> is recovered post-production for re-injection in the formation. However, large volumes of CO<sub>2</sub> are expected to remain sequestered in the formation. The amount of CO<sub>2</sub> stored will vary from site to site. Some researchers have estimated that up to 60 vol% of CO<sub>2</sub> will remain sequestered in the formations (Gozalpour, F. et al. 2005).

The sequestration of CO<sub>2</sub> in these depleted oil reservoirs is expected to have geochemical implications that need to be identified and quantified as part of a large scale risk assessment. The dissolved CO<sub>2</sub> is expected to change the pH of the formation waters, which will allow for the dissolution of heavy metals, such as arsenic, iron, and lead. In addition, sc-CO<sub>2</sub> is a known excellent solvent for organic compounds, therefore it will change the partitioning behavior of these organic compounds in these waters.

Once CO<sub>2</sub> is injected, it is expected that there will be up to four relevant phases present; CO<sub>2</sub>-saturated brines, with dissolved organic compounds present, a CO<sub>2</sub>-rich phase with dissolved hydrocarbons, an oil-rich phase with dissolved CO<sub>2</sub>, and the formation solids. These will all play a role in the partitioning of organic compounds present; however the focus of this dissertation is on partitioning of organic compounds in CO<sub>2</sub>-saturated brines and the CO<sub>2</sub>-rich phase.

### 2.3 Oilfield Brines and Produced Waters

Petroleum reservoirs have a considerable amount of associated water. These oilfield waters often contain high levels of dissolved electrolytes, and are classified as brines (greater than 35,000 mg/L TDS) (Kharaka & Hanor 2003). These brines are co-produced with crude oil, and are classified as produced water. Produced water is the largest waste stream in the oil and gas industry. In addition to salts, produced water contains dissolved organic compounds, oil-in-water emulsions, radionuclides, and metals. The most common organic compounds in produced waters are organic acids, phenols, monopolar alkylated benzenes, which include benzene, toluene, ethylbenzene, and the xylene isomers (BTEX), polycyclic aromatic hydrocarbons (PAHs), and other nitrogen- sulfur- and oxygen- (NSO) containing compounds, which include thiophenes (Kharaka & Hanor 2003; Neff et al. 2011; Utvik 1999). The highest reported concentrations of organic compounds found in selected produced waters are listed in **Table 2.1**. Alkanes and cycloalkanes, which are typically the largest constituents of oil, have very low aqueous solubility, and are typically not major constituents of produced waters, so are not included in **Table 2.1**.

**Table 2.1.** Maximum Reported Levels of Petroleum Hydrocarbons in Selected Produced Waters

Name	BTEX (ppm)	PAHs (ppm)	Thiophenes (ppm)	Phenols (ppm)	Organic Acids (ppm)
Kharaka & Hanor 2003	60	10	N/A	20	10,000
Utvik 1999	9	1.4	0.04	11	1135
Neff et al. 2011	578	3	(Included in PAHs)	23	7160

These produced waters and oilfield brines also have a wide range of salinities. Reservoirs that are targets for CCUS are defined as having TDS concentrations greater than 10 g/L (NETL 2012), and reported TDS of oilfield brines have been as high as 400 g/L (DOE/NETL-2003/119 2003; Long & Wilson 1993). Median reported TDS concentrations have ranged from 32 – 157

g/L (Benko & Drewes 2008; Haluszczak et al. 2013). **Table 2.2** highlights the fact that there is a range in reported TDS concentrations in oil and gas reservoirs.

Sodium ( $\text{Na}^+$ ) and calcium ( $\text{Ca}^{2+}$ ) are typically the most common cations in oilfield brines, however  $\text{Na}^+$  is typically more prevalent. Chloride ( $\text{Cl}^-$ ) is typically the most common anion (Kharaka & Hanor 2003). These oil reservoirs, therefore, are categorized by the type of dominant salt. A “Na – Cl” type brine has the high levels of  $\text{Na}^+$  and  $\text{Cl}^-$ , while a “Na – Ca – Cl” type brine, has higher levels of  $\text{Na}^+$  than  $\text{Ca}^{2+}$ . Examples are found in **Table 2.2**, which highlights the need for organic compound solubility information at these high salt concentrations.

**Table 2.2.** Reported Brine Concentrations for various oil reservoirs or CCUS demonstration sites.

Site	Location	Type of Storage Site	Brine Type	TDS (g/L)	Na (g/L)	Ca (g/L)	Cl (g/L)	pH~
Weyburn* (Emberley et al. 2004)	Williston Basin, Saskatchewan, Canada	Depleted Oil Reservoir/ Enhanced Oil Recovery	Na-Cl	70.2	25.2	1.4	38.4	6
Rangely^ (Kent A. Bowker 1991)	Pennsylvania-Permian Weber Sandstone, Colorado	Depleted Oil Reservoir/ Enhanced Oil Recovery	Na-Cl	35.0	11.7	1.0	20.1	7.5
In Salah* (Trémosa et al. 2014)	Krechba Formation, Algeria	Oil field	Na-Ca-Cl	175.4	35.5	22.4	110.3	5.2
Snohvit Field* (Trémosa et al. 2014)	Hammerfest Basin, Barents Sea, Norway	Natural gas field	Na-Cl	159.4	56.4	4.6	96.4	6.2
Ketzin* (Trémosa et al. 2014)	Northeast German Basin, Germany	Deep Saline	Na-Cl	236.4	90.4	2.1	139	6.4
Sleipner* (Portier & Rochelle 2005)	Utsira Formation, North Sea, Norway	Gas Field	Na-Cl	31.3	9.9	0.4	18.9	7.65
Tigre Lagoon (Kharaka & Hanor 2003)	Lafayette, LA	Oil field	Na-Cl	112.2	40.0	1.9	67.9	6.3
North Slope (Kharaka & Hanor 2003)	Prudhoe Bay, Alaska	Oil field	Na-Cl	21.9	7.6	0.18	10.6^	6.5
Reedy Creek (Kharaka & Hanor 2003)	Mississippi	Oil Field	Na-Ca-Cl	320	61.7	46.6	198	5.08
Silurian Strata, Well No. 2092 (Long & Wilson 1993)	Michigan Basin	Deep Saline	Ca-Na-Cl	343.7	38.0	72.9	218	5.1

\*CCUS Demonstration Site

^Post-CO<sub>2</sub> injection concentrations

~Baseline pH

## 2.4 The Salting-Out Effect and the Setschenow Equation

The Setschenow Equation is typically used to predict the decrease in aqueous solubility of organic compounds in seawater (~0.58 M, ~80% NaCl), and has been shown to be valid up to 1 M NaCl for most classes of organic compounds. The Setschenow Equation predicts a log-linear increase in aqueous activity coefficient (or decrease in aqueous solubility) with increasing salt concentration, which is related by a parameter called the Setschenow constant ( $K_s^{i,k}$ ), which is salt specific for each organic compound (Eqn. 2.1):

$$\log\left(\frac{\gamma_w^{salt}}{\gamma_w^{DI}}\right) = K_s^{i,k} [salt] \quad \text{Eqn. 2.1.}$$

In this equation,  $\gamma_w^{DI}$  is the activity coefficient of an organic compound in deionized water (DI water),  $\gamma_w^{salt}$  is the activity coefficient of the organic compound in water at the salt concentration of interest,  $K_s^{i,k}$  is the empirical Setschenow constant ( $M^{-1}$ ), and  $[salt]$  is the concentration of salt (M). The equation denotes that a positive Setschenow constant means the organic compound exhibits salting-out; the presence of salt causes an increase in the activity coefficient of the organic compound in the saline solution. The Setschenow constant can also be negative, and this occurs when the solubility of the compound exhibits a salting-in, meaning the salt acts as a co-solvent; it decreases the activity of the organic compound in solution. The electrolytes (i.e. NaCl,  $CaCl_2$ ) found in these energy related processes generally produce a salting-out effect. The Setschenow Equation can also predict an increase in partitioning to other phases, including air, solids, or sc- $CO_2$ .

Setschenow constants are typically measured in salt concentrations ranging from seawater to 1 M NaCl. The Setschenow Equation has not been validated for NaCl concentrations greater than

seawater for most classes of organic compounds; therefore it is unknown whether the Setschenow constants measured at low salt concentrations can be extrapolated up to high salt concentrations typical of oil and gas reservoirs. However, there are a few studies that have examined the solubility of several organic compounds in concentrated NaCl solutions. Keeley et al. (1988; 1991) found that the Setschenow Equation was valid up to 5 M NaCl for BTEX, while Jochmann et al. (2006) reported deviations from the Setschenow Equation for several polar organic compounds after 3 M NaCl. The maximum reported concentration for estimating CaCl<sub>2</sub> Setschenow constants is 1 M CaCl<sub>2</sub>, and has not been validated up to higher CaCl<sub>2</sub> concentrations expected of some oil and gas brines (Gordon & Thorne 1967). The validity of Setschenow constants measured at low salt concentrations has not been studied for a variety of other compound classes relevant to CCUS (PAHs, thiophenes, phenols, and organic acids).

Setschenow constants are most often reported for NaCl, and since CaCl<sub>2</sub> is the other major salt of oilfield brines, CaCl<sub>2</sub> Setschenow constants for petroleum hydrocarbons of interest will be needed to accurately predict the aqueous solubility of organic compounds in oilfield brines and produced waters. However there are only 19 reported Setschenow constants for organic compounds in CaCl<sub>2</sub> solutions. Since CaCl<sub>2</sub> is a major component of many oil and gas reservoir brines, more CaCl<sub>2</sub> Setschenow constants are needed.

#### **2.4.1 The Additivity of Setschenow Constants**

Oilfield brines and produced waters are often mixes of electrolytes. The Setschenow Equation is typically assumed to be additive (Eqn. 2.2) for mixed electrolyte systems such as seawater, meaning that it is assumed that the Setschenow constants measured for the single salt systems can be used to determine the Setschenow constant of a mixed salt system.

$$K_s^{mixed} \cong \sum_k K_s^{i,salt,k} \circ x_k \quad \text{Eqn. 2.2}$$

In this equation,  $K_s^{mixed}$  is the Setschenow constant of the mixed electrolyte system,  $K_s^{i,salt,k}$  is the Setschenow constant of a single salt system, and  $x_k$  is the mole fraction of the solid salt. This new Setschenow constant can then be applied to the Setschenow Equation in Eqn. 2.1 to predict changes in aqueous solubility due to the presence of multiple salts.

Setschenow constants have only been shown to be additive for a variety of different electrolyte systems only for benzene and naphthalene (McDevit & Long 1952; Gordon & Thorne 1967). Those studies, measured at low to moderate ionic strengths, show that Eqn. 2.2 is valid for predicting additivity of inorganic salts. However, the additivity of Setschenow constants failed for naphthalene in concentrated organic salt solutions. The authors of that study attributed the salting-in of naphthalene due to micelle formations of naphthalene with organic salts, which caused an increase in naphthalene's aqueous solubility.

Several studies on the salting-out effect of toluene in various salt solutions showed that the Setschenow Equation may not be additive (Poulson et al. 1999; Sada et al. 1975). The authors examined the Setschenow constants of toluene measured in individual salt solutions. They hypothesized that if individual ion effects are additive, then those ion effects will also be conservative. For example, the difference between Setschenow constants with common anions or cations should be the same. This was not applicable to the Setschenow constants for toluene, but it was for naphthalene and benzene. The authors hypothesized that this was due to the dipole moment of toluene ( $\mu = 0.375 \pm 0.010$  Debye) (Lide 2013), which is causing additional ion-dipole interactions that is resulting in deviations from the Setschenow Equation.

However, this hypothesis has not been tested experimentally for toluene or other types of organic compounds. Since the additivity of Setschenow constants has only been tested for two organic compounds, this calls for the need to examine it for more organic compounds of interest, including monopolar organic compounds with dipole moments, and polar petroleum hydrocarbons, such as phenols and organic acids.

#### **2.4.2 The Effect of pH on the Salting-Out Effect**

The salting-out of organic acids and phenols is dependent on the pH of the solution, as neutral and de-protonated organic compounds will have different partitioning behavior (Schwarzenbach et al. 2003). The ionized organic compounds are not expected to salt-out of aqueous solutions. However, the protonated forms of organic acids are expected to have lowered aqueous solubility due to the presence of NaCl and CaCl<sub>2</sub>. Therefore, it will be important to study the salting-out behavior of these organic acids in saline solutions.

The activity of dissolved species is dependent on the ionic strength of the solution; therefore the pK<sub>a</sub> of organic acids is expected to change with different salt concentrations (Barriada et al. 2000). This is expected to have important implications for the partitioning behavior of organic acids, since the salt concentration can possibly be both changing the speciation of the organic acids and reducing solubility of the neutral forms of organic acids. However, this effect will be site specific, as the pH of these formation waters is also dependent on the buffering capacity of those CCUS sites.

### **2.5 Modeling of the Setschenow Equation**

There are only ~190 reported NaCl Setschenow constants and ~19 reported CaCl<sub>2</sub> Setschenow constants. Many of those reported Setschenow constants are not for compounds

typically found in oil and gas reservoirs. Therefore, accurate models for prediction of Setschenow constants are needed.

One of the first attempts to predict Setschenow constants was from McDevit and Long, who developed the internal pressure theory of salting-out (McDevit & Long 1952). This theory says that the salt changes the internal pressure of the solvent (i.e. water), therefore the salt changes the energy required to create a cavity to solvate the non-electrolyte molecule. This theory is given by Eqn. 2.3:

$$K_s^{i,k} = \frac{\bar{V}_i^0 (V_s - \bar{V}_s^0)}{2.3\beta_0 RT} \quad \text{Eqn. 2.3.}$$

Here  $\bar{V}_i^0$  is the partial molar volume of the solute an infinite dilution,  $V_s$  is the molar volume of the pure (liquid) electrolyte, or the volume that the salt occupies as a liquid,  $\bar{V}_s^0$  is the partial molar volume of the electrolyte at infinite dilution,  $\beta_0$  is the compressibility of water,  $R$  is the universal gas constant, and  $T$  is the temperature.  $V_s$  cannot be measured directly, and therefore, cannot be known with certainty. One can measure the change in effective pressure of the saline solution with change in salt concentration to approximate  $V_s$ , however there is still considerable uncertainty associated with this method. In addition, there is still error with predicting Setschenow constants using Eqn. 2.3. For example, the McDevit Long Equation predicts a NaCl Setschenow constant of  $0.601 \text{ M}^{-1}$  for ethylbenzene, however its experimental value is  $0.28 \text{ M}^{-1}$  (Sanemasa et al. 1984).

There have been several other attempts used to predict Setschenow constants using available parameters. The first attempt involves correlating Setschenow constants with molar volume (Long & McDevit 1952; Xie et al. 1997; Endo et al. 2012). Molar volume has a low to moderate correlation with Setschenow constants ( $R^2 = 0.513$ ); the correlation is stronger when

separating polar and apolar organic compounds, however this is not applicable to every class of organic compound. For example, Jonker & Muijs (2010) found no correlation of the Setschenow constants of PAHs with molar volume ( $R^2=0.04$ ). However, in general, there are separate trends in predicting salting-out based on polarity of the organic compound, based on an analysis of experimental data (Xie et al. 1997).

Octanol-water partitioning coefficients also have been used to predict Setschenow constants. Ni & Yalkowsky (2003) found a fairly good correlation ( $n=101$ ,  $R^2=0.772$ , standard error = 0.041) of NaCl Setschenow constants with  $\log K_{ow}$  (Eqn. 2.4). This follows the observation that larger and more hydrophobic organic compounds have higher Setschenow constants. However, this was not replicated with the data set used by Endo, et al. ( $n=43$ ,  $R^2=0.50$ ,  $SD = 0.051$ ) (Endo et al. 2012).

$$K_s^{i,NaCl} = 0.040 \log K_{ow} + 0.114 \quad \text{Eqn. 2.4.}$$

Since Setschenow constants typically follow trends based on both size and polarity of the organic compound; a predictive model would need to be able to account for both those types of interactions. Endo et al. (2012) developed a poly-parameter linear free energy relationship (pp-LFER) to predict NaCl Setschenow constants. This has proven to be fairly successful ( $n=43$ ,  $R^2 = 0.83$ , standard deviation = 0.031), and tries to account for the multiple properties of the compound that may account for the magnitude of the Setschenow Constant:

$$K_s^{i,NaCl} = 0.112 - 0.020R_2 - 0.042\pi_2 - 0.047\alpha_2 - 0.060\beta_2 + 0.171V_2 \quad \text{Eqn. 2.5}$$

Here, the  $R_2$  is the index of refraction of the organic compound, the  $\pi_2$  is the polarizability of the organic compound,  $\alpha_2$  is the hydrogen bonding acidity of the organic compound,  $\beta_2$  is the

hydrogen bonding basicity of the organic compound, and  $V_2$  is the molar volume of the compound. These parameters are called the Abraham solvation parameters (ASPs). However, not all organic compounds have reported ASPs. Of the 192 reported NaCl Setschenow constants, only 160 of them have reported ASPs. These ASPs cannot be predicted, therefore the pp-LFER cannot be used to predict NaCl Setschenow constants if an organic compound has no reported ASPs. However, many organic compounds have reported  $\log K_{ow}$ , which also has several available predictive models. Therefore, the  $\log K_{ow}$  LFER can be used for any organic compound of interest. The NaCl Setschenow constant predictions from both the  $\log K_{ow}$  LFER and the pp-LFER are evaluated in this study.

There are no models, with readily available parameters to predict other Setschenow constants, including  $\text{CaCl}_2$  Setschenow constants, or other Setschenow constants of important salts such as KCl, LiCl, or NaBr. Models to predict these Setschenow constants are needed to determine the aqueous solubility of organic compounds in oil and gas brines.

## **2.6 Measured Solubility of Organic Compounds in Supercritical $\text{CO}_2$**

### **2.6.1 Trends in Solubility of Organic Compounds in Supercritical $\text{CO}_2$**

Supercritical  $\text{CO}_2$  has been used for decades in the food (Peker et al. 1992; Machmudah et al. 2011) and pharmaceutical industry (Ting et al. 1993), in treatment technologies (e.g. soil remediation) (Smyth et al. 1999; Hawthorne et al. 1992), and energy production (e.g. oil and gas extraction) (Goodarznia & Esmaeilzadeh 2002), among other areas, to extract organic compounds into the sc- $\text{CO}_2$  phase. The solubility of many types of organics in the binary system of pure solute and sc- $\text{CO}_2$  has been measured. This data set, albeit dispersed in the literature can be used to predict the types of compounds that are expected to be mobilized by sc- $\text{CO}_2$ , even if the mechanisms driving the solubility of these organic compounds are unknown.

The trends of solubility of several organic compound classes of importance in dry sc-CO<sub>2</sub> (i.e. in absence of dissolved water in the sc-CO<sub>2</sub> phase) follow the respective thermodynamic rules, e.g. apolar and polar organic compounds with high vapor pressure have higher solubility in sc-CO<sub>2</sub>, and trends expected based on their structures and functional groups (**Table 2.3**). Small apolar and weakly monopolar compounds, such as hexane and benzene, have relatively high solubility in sc-CO<sub>2</sub> (Ohgaki & Katayama 1976; Li et al. 1981; Gupta et al. 1982; Kim et al. 1986). Small polar compounds, such as acetic acid and phenol, have lower inherent volatility and lower solubility in sc-CO<sub>2</sub> compared to small apolar and weakly monopolar compounds (Dandge et al. 1985; Van Leer & Paulaitis 1980; García-González et al. 2001). As temperature increases, the vapor pressure and the solubility of both apolar and polar compounds in sc-CO<sub>2</sub> increase. Larger compounds, typically with a molecular weight greater than 200 g/mol, have lower solubility in sc-CO<sub>2</sub> due to their lower inherent volatility whether, apolar, monopolar, or polar. These larger compounds include longer-chained alkanes, larger aromatic acids, long-chained aliphatic acids, large PAHs, and other larger organic compounds. As the length of a carbon chain or number of rings increase in an organic compound, solubility in sc-CO<sub>2</sub> tends to decrease.

The position of functional groups appears to affect the solubility of aromatic organic acids, where aromatics with functional groups on the ortho- position have greater solubility in sc-CO<sub>2</sub> than their meta- and para- counterparts (Dandge et al. 1985; Pfohl et al. 1997; Coutsikos et al. 1995; Gurdial & Foster 1991; Yamini et al. 1998; Krukoniš & Kurnik 1985; Gurdial et al. 1993; Lucien & Foster 1996; Lucien & Foster 1998; García-González et al. 2002). Pfohl et al. (1997) explained the increase in solubility by steric hindrance; the group on the ortho- position acted as a shield to the hydroxyl group, decreasing the compound's ability to form strong

intermolecular bonds. This was found to be true especially for the cresol, dihydroxybenzene, and hydroxybenzoic acid isomers.

**Table 2.3.** Measured Solubility of Selected Pure Phase Organic Compounds in sc-CO<sub>2</sub>

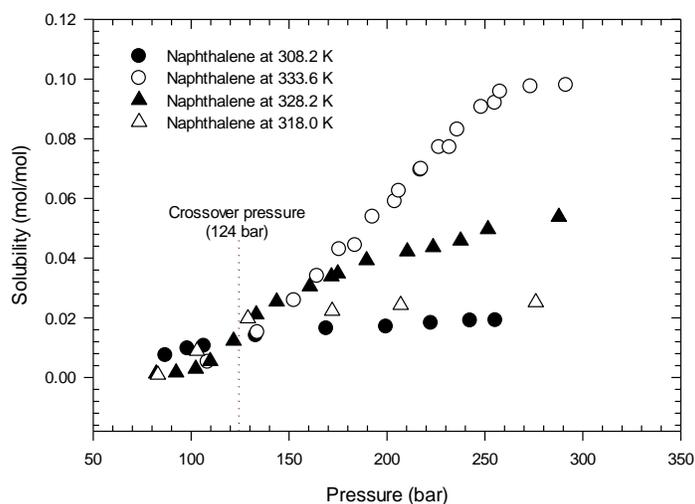
Organic Compound	Temperature (K)	Vapor Pressure at 298 K (bar)	Pressure (bar)	Solubility (mol/mol)
<b>Alkanes</b>				
n-Hexane (Li et al. 1981)	353	6.8E-01 (Schwarzenbach et al. 2003)	75	5.10E-02
			92	7.00E-02
			107	1.14E-01
n-Decane (Eustaquio-Rincón & Trejo 2001)	344	1.7E-03 (Schwarzenbach et al. 2003)	90	3.2E-03
			105	6.0E-03
			126	3.4E-02
n-Hexadecane (Eustaquio-Rincón & Trejo 2001)	308	1.9E-06 (Schwarzenbach et al. 2003)	83	2.6E-03
			96	7.8E-03
			113	8.7E-03
n-Octadecane (Eustaquio-Rincón & Trejo 2001)	310	1.7E-07 (Schwarzenbach et al. 2003)	100	1.10E-03
			140	3.90E-03
			180	5.80E-03
<b>BTEX</b>				
Benzene (Kim et al. 1986)	373	1.3E-01 (Schwarzenbach et al. 2003)	40	5.5E-02
			52	4.4E-02
			59	4.4E-02
Toluene (Kim et al. 1986)	373	3.7E-02 (Schwarzenbach et al. 2003)	38	3.8E-02
			46	3.3E-02
			55	3.1E-02
Ethylbenzene (Bamberger et al. 1994)	393	1.2E-02 (Schwarzenbach et al. 2003)	81	2.7E-02
			121	3.4E-02
			161	7.7E-02
o-Xylene (Knez et al. 2008)	353	8.9E-03 (Schwarzenbach et al. 2003)	88	3.8E-02
			136	6.5E-02
			148	1.4E-01
m-Xylene (Ng et al. 1982)	394	1.1E-02 (Schwarzenbach et al. 2003)	102	2.8E-02
			125	3.7E-02
			161	7.1E-02
p-Xylene (Kim et al. 1986)	373	1.2E-02 (Schwarzenbach et al. 2003)	40	2.2E-02
			49	2.2E-02
			59	2.2E-02
<b>Aromatic Acids</b>				
o-Cresol (Pfohl et al. 1997)	373	4.0E-04 (Schwarzenbach et al. 2003)	104	4.5E-03
			201	3.2E-02
			252	9.4E-02
m-Cresol (Pfohl et al. 1997)	373	2.0E-04 (Schwarzenbach et al. 2003)	102	3.1E-03
			199	1.9E-02
			250	4.0E-02
p-Cresol (Pfohl et al. 1997)	373	1.6E-04 (Schwarzenbach et al. 2003)	103	3.2E-03
			202	2.0E-02
			302	3.9E-02
o-Dihydroxybenzene (Coutsikos et al. 1995)	318	2.2E-06 (Schwarzenbach et al. 2003)	109	7.9E-06
			130	1.1E-05
			141	1.2E-05
o-Hydroxybenzoic Acid (Gurdial & Foster 1991)	328	2.0E-07 (Schwarzenbach et al. 2003)	122	1.3E-04
			162	4.0E-04
			203	6.2E-04
Benzoic Acid(Lee et al. 2001)	328	1.1E-06(Schwarzenbach et al. 2003)	120	4.5E-04
			220	4.0E-03

			270	4.6E-03
Aliphatic Acids				
Acetic Acid (Briones et al. 1987)	323	2.1E-02 (Schwarzenbach et al. 2003)	70	1.1E-02
			77	1.3E-02
			84	1.6E-02
PAHs				
Acenaphthene (Yamini & Bahramifar 2000)	308	3.1E-06 (Schwarzenbach et al. 2003)	122	2.0E-03
			152	2.1E-03
			182	2.4E-03
Phenanthrene (Goodarznia & Esmailzadeh 2002)	308	2.2E-07 (Schwarzenbach et al. 2003)	101	5.6E-04
			141	9.4E-04
			181	1.2E-04
Anthracene (Goodarznia & Esmailzadeh 2002)	308	9.8E-09 (Schwarzenbach et al. 2003)	102	1.3E-06
			141	5.4E-06
			181	8.4E-06
Other Groups (NSO Compounds)				
Thiophene (Elizalde-Solis & Galicia-Luna 2005)	334	5.3E-02 (Schwarzenbach et al. 2003)	80	2.3E-02
			90	3.0E-02
			96	4.1E-02
p-Nitrophenol (Shamsipur et al. 2002)	328	5.5E-08 (Schwarzenbach et al. 2003)	122	1.6E-04
			162	3.1E-04
			203	4.6E-04

The sc-CO<sub>2</sub> is a nonpolar solvent with low polarizability and low dielectric constant, which theoretically makes it a good solvent for hydrocarbons. However, the analysis above suggests that sc-CO<sub>2</sub> is not a good solvent for larger molecules (e.g. MW >200 g/mol) such as large PAHs (Miller et al. 1996). Carbon dioxide is net apolar, but the polar C-O bonds allow it to act as a Lewis acid and Lewis base (Raveendran et al. 2005). In a sc-CO<sub>2</sub>-water system in a depleted oil reservoir, this allows for sc-CO<sub>2</sub> to solvate small polar molecules, but not as strongly as H<sub>2</sub>O since the dipole moments between C-O bonds are not as strong as for H-O bonds in water. For the dissolution of large apolar molecules in water there is a diminishing effect of favorable entropy of dissolution, which accounts for lower aqueous solubility (Schwarzenbach et al. 2003). Similar arguments can be applied to sc-CO<sub>2</sub> as a solvent. Since both water and CO<sub>2</sub> are more greatly displaced by large molecules, dissolution of larger molecular weight compounds is not a favorable process.

## 2.6.2 Effects of Temperature and Pressure on Solubility of Organic Compounds in Supercritical Carbon Dioxide

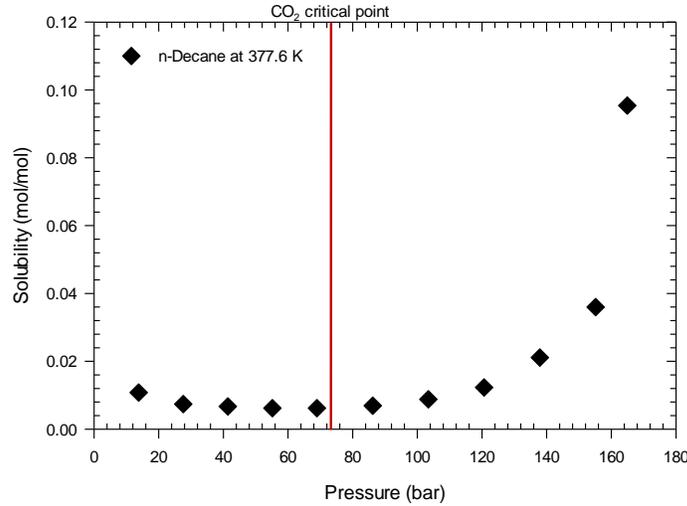
The effect of temperature and pressure on the vapor pressure of an organic compound and therefore on its solubility in sc-CO<sub>2</sub> has been well documented in the literature. An isobaric temperature increase results in a decrease in solubility of organic compounds in sc-CO<sub>2</sub>, until a “crossover pressure”, where their solubility in sc-CO<sub>2</sub> increases with increased temperature at the same pressure (*Figure 2.1*) (Foster et al. 1991). The crossover pressure, however, is characteristic of each solute. This phenomenon has been well documented by Foster et al. (1991) who modeled the crossover pressure in fluid phase equilibrium. They emphasized that the crossover pressure is a function of the organic compound-sc-CO<sub>2</sub> system, and the location of this point was in the vicinity of the critical density of the system (Foster et al. 1991):



**Figure 2.1.** The crossover pressure of naphthalene (McHugh & Paulaitis 1980; Chang & Morrell 1985).

Isothermal pressure increase results in a decrease in solubility up to the critical point, but then solubility increases steadily after reaching the critical point (*Figure 2.2*) (Reamer & Sage 1963; Li et al. 1981). While solubility data for low pressures is not typically applicable to

depleted oil reservoirs, it is interesting to note that the minimum solubility occurs at around the critical pressure of CO<sub>2</sub>; therefore the solubility of organic compounds in sc-CO<sub>2</sub> should increase with increasing pressure given that reservoir pressures and temperatures are above the critical point for CO<sub>2</sub>.



**Figure 2.2** Isothermal pressure increase of n-decane at 377.6 K.82

### 2.6.3 Trends in Partitioning of Organic Compounds from Water to Supercritical CO<sub>2</sub>

Partitioning coefficients ( $K_{i,c/w}$ ) of organic compounds between water (or brine) and sc-CO<sub>2</sub> are necessary for contaminant transport models to determine the levels of organic compounds that will mobilize with the sc-CO<sub>2</sub> (Zheng et al. 2011). The partitioning coefficient is a ratio of the solubility of the organic compound in the supercritical phase to the solubility of the organic in the aqueous phase:

$$K_{i,c/w} = \frac{C_{CO_2,i}}{C_{H_2O,i}} \frac{\rho_{H_2O}}{\rho_{CO_2}} \frac{MW_{CO_2}}{MW_{H_2O}} = \frac{y_{CO_2,i}}{x_{H_2O,i}} \quad \text{Eqn. 2.6}$$

$K_{i,c/w}$  is the mole fraction partitioning coefficient of the organic compound between water and supercritical CO<sub>2</sub>.  $C_{CO_2,i}$  is the concentration of the organic compound in sc-CO<sub>2</sub>.  $C_{H_2O,i}$  is the concentration of the organic compound in water.  $\rho_{H_2O}$  is the density of water at the temperature and pressure of interest.  $\rho_{CO_2}$  is the density of CO<sub>2</sub> at the temperature and pressure of interest.  $MW_{CO_2}$  is the molecular weight of CO<sub>2</sub> and  $MW_{H_2O}$  is the molecular weight of H<sub>2</sub>O.  $y_{CO_2,i}$  is the mole fraction of organic compound in the CO<sub>2</sub> phase.  $x_{H_2O,i}$  is the mole fraction of the organic compound in the aqueous phase.

$K_{i,c/w}$  for some organic compounds (~37 organic compounds) between sc-CO<sub>2</sub> and water have been reported (**Table 2.4**). These partitioning coefficients will depend on temperature and pressure for water-sc-CO<sub>2</sub> partitioning, especially near the critical point of CO<sub>2</sub> where the density of the gas increases most with changes in pressure. Models of sc-CO<sub>2</sub> partitioning will need to be able to capture this dynamic behavior of  $K_{i,c/w}$  over the temperature and pressure space relevant to carbon storage. Further away from the critical point, the partitioning behavior does not change as drastically with temperature and pressure. Despite this, reported  $K_{i,c/w}$  (determined experimentally) for partitioning of organics between water and sc-CO<sub>2</sub> indicate trends that are consistent with thermodynamic expectations (**Table 2.4**).

**Table 2.4.** Partitioning coefficients ( $K_{i,c/w}$ ) of Selected Organic Compounds in a Pure Phase-Water-sc-CO<sub>2</sub> System

Organic Compound	Temperature (K)	Pressure (bar)	$K_{i,c/w}$ (mol CO <sub>2</sub> per mol H <sub>2</sub> O)	$K_{aw}$ at 298 K
Alkanes				
Hexane (Timko et al. 2004)	300	80	9.0E+03	5.5E+01 (Schwarzenbach et al. 2003)
Cyclohexane(Timko et al. 2004)	300	80	4.9E+03	7.8E+00 (Schwarzenbach et al. 2003)
BTEX				
Benzene (Yeo & Akgerman 1990)	318	80	8.6E+02	4.5E+00 (Schwarzenbach et al. 2003)
		90	1.6E+03	
		101	2.8E+03	
Aromatic Acids				
Phenol (Brudi et al. 1996)	313	81	5.6E-01	2.6E-05 (Schwarzenbach et al. 2003)
		158	9.9E-01	
		255	1.0E+00	
m-Cresol (Ghonasgi et al. 1991)	313	97	6.0E-01	3.8E-05 (Schwarzenbach et al. 2003)
		124	2.2E+00	
		165	3.9E+00	
Benzoic Acid (Brudi et al. 1996)	313	79	6.1E-01	1.6E-06 (Schwarzenbach et al. 2003)
		150	1.4E+00	
		251	2.0E+00	
Aliphatic Acids				
Acetic Acid (Dooley et al. 1997)	313	146	4.3E-02	1.1E-05 (Schwarzenbach et al. 2003)
PAHs				
Naphthalene (Yeo & Akgerman 1990)	318	81	1.3E+02	1.8E-02 (Schwarzenbach et al. 2003)
		90	2.1E+02	
		100	3.5E+02	
Other Groups				
2-Nitrophenol (Karásek et al. 2002)	333	200	7.2E+01	7.9E-04 (Schwarzenbach et al. 2003)
4-Nitrophenol (Karásek et al. 2002)	333	200	1.8E-01	2.2E-08 (Schwarzenbach et al. 2003)

Trends in the partitioning data follow those expected based on the relative solubility of the compounds in each phase (water and sc-CO<sub>2</sub>), similar to the air-water partitioning coefficient ( $K_{aw}$ ). Small apolar compounds, such as benzene and hexane (Timko et al. 2004; Yeo & Akgerman 1990; Ghonasgi et al. 1991), have relatively higher partitioning coefficients to sc-CO<sub>2</sub>, due to their high solubility in sc-CO<sub>2</sub> and relatively low solubility in water. Small polar

compounds, such as phenol and acetic acid, which have only moderate solubility in sc-CO<sub>2</sub>, but high aqueous solubility, have low partitioning coefficients (Brudi et al. 1996; Ghonasgi et al. 1991; Dooley et al. 1997; Karásek et al. 2002; Panagiotopoulos et al. 1988). Conversely, naphthalene has moderate solubility in sc-CO<sub>2</sub>, but low aqueous solubility, and thus exhibits a high partitioning coefficient to sc-CO<sub>2</sub> (Yeo & Akgerman 1990). Phenol, which exhibits similar behavior in pure phase solubility to sc-CO<sub>2</sub> as naphthalene, has a much lower partitioning coefficient from water to sc-CO<sub>2</sub> than naphthalene because of its ability to form hydrogen bonds with water (Brudi et al. 1996; Ghonasgi et al. 1991; Karásek et al. 2002). Analysis of the masses of the organic compounds in the CO<sub>2</sub> and aqueous phase usually involve the depressurization of those respective phases. These reported partitioning coefficients, therefore, may have some error with measurements due to the fact there may be volatile losses when depressurization occurred.

There are few studies on the effect of electrolytes in the aqueous phase on the partitioning behavior of organic compounds to sc-CO<sub>2</sub>. Curren & Burk (2000) measured the partitioning of pentachlorophenol (not found in depleted oil reservoirs) between water and sc-CO<sub>2</sub>. With the addition of NaCl they found that the activity of pentachlorophenol in water, and therefore its partitioning into sc-CO<sub>2</sub> from the NaCl solution, increased with increasing ionic strength. Their findings are consistent with expectations based on the salting-out effect. Partitioning experiments of phenol between saline solutions and sc-CO<sub>2</sub> at 313 K and various pressures suggests that the Setschenow Equation may be applicable in predicting the salting-out effect of phenol to sc-CO<sub>2</sub> up to NaCl concentration of 2.7 mol/kg (Wagner et al. 2003).

## **2.7 Thermodynamic Principles and Modeling of Organic Compound Partitioning into Supercritical CO<sub>2</sub>**

Partitioning coefficients for organic compounds of environmental significance are needed over a range of temperature, pressure, and salinity conditions typical of oil and gas reservoirs.

Since there is a dearth of reported partitioning coefficients of organic compounds between water and sc-CO<sub>2</sub> (~37 organic compounds), accurate models are needed to be able to predict organic compound partitioning coefficients *a priori*. There are two types of models used to predict partitioning coefficients, which can be estimated using established thermodynamic methods including equations of state (EOS) and poly-parameter linear free energy relationships (pp-LFER). Each of these is briefly described here along with an indication of the data required to develop and calibrate these approaches relevant to CO<sub>2</sub> storage conditions.

### **2.7.1 Equations of State**

Several EOS, all of which are empirical, including Redlich & Kwong (1949), Soave modification of Redlich-Kwong equations (Soave 1972), Peng & Robinson (1976), Stryjek-Vera modifications of Peng-Robinson (Stryjek & Vera 1986a; Stryjek & Vera 1986b), Patel & Teja (1982) and Adachi & Lu (1984) among others can potentially be used, with varying levels of accuracy, to model the partitioning behavior of organics in the depleted oil reservoirs. These EOS require an application of mixing rules to calculate the solubility of organic compounds in sc-CO<sub>2</sub>; binary interaction parameters (BIPs) need to be incorporated into EOS to account for the repulsive and attractive terms between the various organic compounds and sc-CO<sub>2</sub>. Typical mixing rules include the van der Waals mixing rules, Panagiotopoulos & Reid (1986) and Wong & Sandler (1992), among others. Valderrama (2003) in his review on EOS, stated Gibbs free energy models and nonquadratic mixing rules with interaction parameters in the volume constraints give the best results for mixtures containing a supercritical component.

The Peng-Robinson EOS, along with van der Waals mixing rules are used in this dissertation, and are presented to demonstrate how to calculate the solubility of an organic compound in equilibrium with a sc-CO<sub>2</sub> phase. This general process applies to any cubic EOS and can be applied to determining both the partitioning of an organic compound from crude oil into sc-CO<sub>2</sub>

or brine into sc-CO<sub>2</sub>. In both scenarios, an isothermal flash calculation (Sandler 2006) is performed. This process determines the mutual solubility of the brine and the sc-CO<sub>2</sub>. This can be used to determine the partitioning coefficients, as well. This type of calculation starts with the Peng-Robinson EOS, which is given by Eqn. 2.7:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (\text{Eqn. 2.7})$$

Where  $v$  is the molar volume of the compound of interest,  $a$  and  $b$  are parameters used to account for the deviations from ideality of the compounds of interest, i.e. they account for all attractive and repulsive forces of all of the species in the system.

The  $a$  and  $b$  parameters from the Peng-Robinson EOS are given in Eqns. 2.8-2.9.

$$a = \frac{0.457(RT_c)^2}{P_c} \quad (\text{Eqn. 2.8})$$

$$b = \frac{0.078 \cdot RT_c}{P_c} \quad (\text{Eqn. 2.9})$$

The  $a$  (Eqn. 2.8) and  $b$  (Eqn. 2.9) constants in the Peng-Robinson EOS are calculated for the compound using the critical temperature,  $T_c$ , and critical pressure,  $P_c$ . The value of  $\kappa$  (Eqn. 2.10) and  $\alpha(T)$  (Eqn. 2.11) are also calculated for a given temperature,  $T$ . The  $\kappa$  (Eqn. 2.10) contains a property called the acentric factor ( $\omega$ ), which is a measure of the non-sphericity of a compound and can be found in tables or calculated. Values for the  $A$  (Eqn. 2.12) and  $B$  (Eqn. 2.13) parameters can then be calculated. These  $A$  and  $B$  values are needed to calculate the compressibilities of the liquid and vapor phases ( $Z^L$  and  $Z^V$ ).

$$\kappa = 0.375 + 1.54\omega - 0.269\omega^2 \quad (\text{Eqn. 2.10})$$

$$\alpha(T) = \left(1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2 \quad (\text{Eqn. 2.11})$$

$$A = \frac{a \cdot \alpha(T) \cdot P}{(RT)^2} \quad (\text{Eqn. 2.12})$$

$$B = \frac{b \cdot P}{R \cdot T} \quad (\text{Eqn. 2.13})$$

For multicomponent mixtures these parameters are adjusted using mixing rules. The most basic mixing rules, as given by van der Waals are given by Eqns. 2.14 and 2.15:

$$a_{mix} = \sum_{i=1}^c \sum_{j=1}^c y_i y_j a_{ij} \quad (\text{Eqn. 2.14})$$

$$b_{mix} = \sum_{i=1}^c y_i b_i \quad (\text{Eqn. 2.15})$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (\text{Eqn. 2.16})$$

Where  $a_{mix}$  is the  $a$  parameter of the mixture,  $y_i$  and  $y_j$  are the mole fractions of each component in the systems, and  $b_{mix}$  is the  $b$  parameter of the mixture. Equation 2.8 is then solved using  $a_{ij}$  (Eqn. 2.10), which is the new  $a$  parameter of all the combinations of the system and  $k_{ij}$  is the BIP between components  $i$  and  $j$  in the system.

The Peng-Robinson EOS (Eqn. 2.7) is then used to solve for a compressibility factor ( $Z$ ) of both the liquid and vapor phases (Eqn. 2.17). The smallest real root is the liquid phase compressibility and the largest real root is the vapor phase compressibility:

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad (\text{Eqn. 2.17})$$

The fugacity coefficients ( $\phi_i^L$  and  $\phi_i^V$ ) are then calculated for the liquid and vapor phases of a mixture, respectively using Eqns. 2.18 and 2.19 and an initial guess for the values of  $x_i$  and  $y_i$ .

$$\begin{aligned} \ln \phi_i^L &= \frac{b_i}{b_{mix}} (Z^L - 1) - \ln \left( Z^L - \frac{b_{mix}P}{RT} \right) \\ &- \frac{a_{mix}}{2\sqrt{2}b_{mix}RT} \left[ \frac{2\sum x_i a_{ij}}{n} - \frac{b_i}{b_{mix}} \right] \ln \left[ \frac{Z^L + (1 + \sqrt{2}) \frac{b_{mix}P}{RT}}{Z^L + (1 - \sqrt{2}) \frac{b_{mix}P}{RT}} \right] \end{aligned} \quad (\text{Eqn. 2.18})$$

$$\begin{aligned} \ln \phi_i^V &= \frac{b_i}{b_{mix}} (Z^V - 1) - \ln \left( Z^V - \frac{b_{mix}P}{RT} \right) \\ &- \frac{a_{mix}}{2\sqrt{2}b_{mix}RT} \left[ \frac{2\sum y_i a_{ij}}{n} - \frac{b_i}{b_{mix}} \right] \ln \left[ \frac{Z^V + (1 + \sqrt{2}) \frac{b_{mix}P}{RT}}{Z^V + (1 - \sqrt{2}) \frac{b_{mix}P}{RT}} \right] \end{aligned} \quad (\text{Eqn. 2.19})$$

The  $x_i$  is the mole fraction of the compound of interest in the liquid phase, and  $y_i$  is the mole fraction of the compound of interest in the vapor (or supercritical) phase. Note that the calculation of the fugacity coefficients contain the  $a_{ij}$ ,  $a_{mix}$ , and  $b_{mix}$  parameters. The fugacity of each phase, liquid  $f_i^L$  (Eqn. 2.20) and vapor (or supercritical)  $f_i^V$  (Eqn. 2.21), is then calculated:

$$\ln f_i^L = \ln \phi_i^L x_i P \quad (\text{Eqn. 2.20})$$

$$\ln f_i^V = \ln \phi_i^L y_i P \quad (\text{Eqn. 2.21})$$

Because the liquid phase fugacity and the vapor phase fugacity of a compound are equal when the compound is at equilibrium in each phase of interest, the solution is found iteratively. Guesses for the mole fraction are updated based on the prior result until the fugacity of a compound in each phase of interest are equal. There is an additional constraint in an isothermal flash calculation, namely, that a mass balance for each phase is satisfied. This is also determined iteratively using Eqn. 2.22.

$$x_i L + y_i V = z_i \quad (\text{Eqn. 2.22})$$

Where  $L$  is the liquid fraction,  $V$  is the vapor fraction, and  $z_i$  is the total number of moles inputted into the system for each compound. The methodology described above can be used to calculate the solubility of each compound into sc-CO<sub>2</sub>, and brine-sc-CO<sub>2</sub> partitioning coefficients when phase equilibrium is satisfied.

However, the use of EOS to model systems with a supercritical component is still lacking; some organic compound solubility in sc-CO<sub>2</sub> cannot be accurately modeled by these systems (Valderrama 2003). BIPs, which are just arbitrary factors with no theoretical basis, are required for accurate modeling of these partitioning coefficients. Valderrama, in his review on EOS, stated that these models may be best for interpolating between experimental data points (Valderrama 2003). In addition, these BIPs cannot be predicted, so therefore, it must be determined if these EOS can be used without BIPs to predict partitioning coefficients of organic compounds between water and sc-CO<sub>2</sub> *a priori*.

### 2.7.2 Poly-parameter Linear Free Energy Relationships

An alternative to EOS is the development of pp-LFERs. Poly-parameter LFERs have been used to estimate the partitioning of organic compounds from water to sc-CO<sub>2</sub> (Lagalante & Bruno 1998; Timko et al. 2004). This empirical pp-LFER was developed to predict the partitioning of organics between water and sc-CO<sub>2</sub>, and has a CO<sub>2</sub> density term incorporated, which allows for the prediction of the partitioning coefficients over a range of temperatures and pressures. This pp-LFER (Eqn. 2.23) requires the input of the polarizability of CO<sub>2</sub> at the temperature and pressure of interest.

$$\log K_{i,c/w} = 3.810 - 1.230\pi_2 - 3.110\alpha_2 - 2.010\beta_2 + 0.110V_2 + 2.450\pi_1 \quad \text{Eqn. 2.23}$$

This uses the ASPs described in Chapter 2.5. Here the  $\pi_1$  is the polarizability of the CO<sub>2</sub> at a specific temperature and pressure. This requires an additional calculation, based on the reduced density ( $\rho_r$ ) of CO<sub>2</sub> (Eqn. 2.24), which is a function of the density at the temperature and pressure of interest ( $\rho_{T,P}$ ) and the critical density of CO<sub>2</sub> ( $\rho_c=467.6 \text{ kg/m}^3$ ). This relationship for predicting the polarizability of CO<sub>2</sub> is based on the work of Smith et al. (1987).

$$\rho_r = \rho_{T,P} / \rho_c \quad \text{Eqn. 2.24.}$$

$$\pi_1 = 1.15\rho_r - 0.98 \quad (\rho_r < 0.7) \quad \text{Eqn. 2.25.}$$

$$\pi_1 = 0.173\rho_r - 0.37 \quad (\rho_r > 0.7) \quad \text{Eqn. 2.26.}$$

This pp-LFER was based on partitioning coefficients of 33 compounds and 332 data points, with an  $R^2 = 0.88$  and an average absolute deviation of the log partitioning coefficients was 0.29. Although there is error in predicting the partitioning coefficients of these organic compounds, it is unknown if the errors are larger due to inaccuracies of experimental partitioning coefficients after depressurization of these systems used to measure the partitioning coefficients.

This suggests that a LFER could be developed for a range of values in the temperature and pressure space; however, they still need to be adjusted to account for salinity, which would change the partitioning behavior. This could be accounted for with the application of the Setschenow Equation.

## **2.8 Reactive Transport Models used in Geologic Carbon Storage**

Data and knowledge on the solubility of organic compounds in brines and sc-CO<sub>2</sub> obtained from this work will feed contaminant reactive transport models for CO<sub>2</sub> storage. The modeling of geologic storage contains four major geochemical aspects: Thermal and hydrologic, geomechanical, chemical, and biological. These will follow the laws of conservation of mass, momentum and energy. There are many existing models used for carbon storage, however there are two types models have been used in the literature specifically to model the fate and transport of organic compounds.

The Subsurface Transport Over Multiple Phases, or STOMP model, developed by Pacific Northwest National Laboratory, can incorporate multiple phases to model subsurface flow (Ward et al. 2005). This model was originally used to model remediation efforts at sites contaminated by volatile organic compounds (VOCs) and/or radioactive material; however it has been adapted to be used in a carbon storage scenario. Zhong, et al., used STOMP to model the transport of organics in sc-CO<sub>2</sub> through sandstone, which used partitioning coefficients and solubility information of BTEX and naphthalene to determine if those compounds would absorb onto the sandstone from sc-CO<sub>2</sub> (Zhong et al. 2014). Another existing model is called TOUGHREACT, which is used for multiphase reactive non-isothermal flow in porous and fractured media (Xu et al. 2006). This is built on the multiphase fluid and heat simulator, Transport of Unsaturated Groundwater and Heat, or TOUGH, which was developed at Lawrence Berkeley National Laboratory (LBNL). TOUGHREACT builds on TOUGH by adding reactive chemistry into the

model. TOUGHREACT can be linked with TMVOC (this linked model is called TMVOC\_REACT), which can model flow of water, gas, and VOCs in a multidimensional porous media. Zheng, et al., used TMVOC\_REACT to model the partitioning of benzene from water into sc-CO<sub>2</sub> and the subsequent transport of benzene into a shallower formation over three years (Zheng et al. 2013). None of these transport models have incorporated salting-out effects for organic compounds.

This dissertation aims to fill in some of the knowledge gaps that are needed for these reactive transport models, including adding Setschenow constant data to estimate the salting-out effect and partitioning coefficients from water to sc-CO<sub>2</sub>, as well as models needed to predict both Setschenow constants and water-sc-CO<sub>2</sub> partitioning coefficients.

## 2.9 References

- Adachi, Y. & Lu, B.C.-Y., 1984. Simplest equation of state for vapor-liquid equilibrium calculation: A modification of the van der waals equation. *AIChE Journal*, 30(6), pp.991–993. Available at: <http://dx.doi.org/10.1002/aic.690300619>.
- Bamberger, A. et al., 1994. High-pressure vapour-liquid equilibria in binary mixtures of carbon dioxide and benzene compounds: experimental data for mixtures with ethylbenzene, isopropylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, ethenylbenzene and isopropenylbenzene, a. *Fluid Phase Equilibria*, 97(0), pp.167–189. Available at: <http://www.sciencedirect.com/science/article/pii/0378381294850143>.
- Barriada, J.L., Brandariz, I. & de Vicente, M.E., 2000. Acid–Base Equilibria of Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations. *Journal of Chemical & Engineering Data*, 45(6), pp.1173–1178. Available at: <http://dx.doi.org/10.1021/je000150p>.
- Benko, K.L. & Drewes, J.E., 2008. Produced Water in the Western United States: Geographical Distribution, Occurrence, and Composition. *Environmental Engineering Science*, 25(2), pp.239–246. Available at: <http://dx.doi.org/10.1089/ees.2007.0026>.
- Blunt, M., Fayers, F.J. & Orr, F.M., 1993. Carbon dioxide in enhanced oil recovery. *Energ. Convers. Manage*, 34(9), pp.1197–1204.
- Briones, J.A. et al., 1987. Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide. *Fluid Phase Equilibria*, 36(0), pp.235–246. Available at: <http://www.sciencedirect.com/science/article/pii/0378381287850264>.
- Brudi, K., Dahmen, N. & Schmieder, H., 1996. Partition coefficients of organic substances in two-phase mixtures of water and carbon dioxide at pressures of 8 to 30 MPa and temperatures of 313 to 333 K. *The Journal of Supercritical Fluids*, 9(3), pp.146–151. Available at: <http://www.sciencedirect.com/science/article/pii/S089684469690025X>.

- Chang, H. & Morrell, D.G., 1985. Solubilities of methoxy-1-tetralone and methyl nitrobenzoate isomers and their mixtures in supercritical carbon dioxide. *Journal of Chemical & Engineering Data*, 30(1), pp.74–78. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00039a025>.
- Coutsikos, P., Magoulas, K. & Tassios, D., 1995. Solubilities of Phenols in Supercritical Carbon Dioxide. *Journal of Chemical & Engineering Data*, 40(4), pp.953–958. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00020a049>.
- Curren, M.S.S. & Burk, R.C., 2000. Partitioning of Acidic Solutes between Water and Supercritical Carbon Dioxide. Effect of pH and Ionic Strength. *Journal of Chemical & Engineering Data*, 45(5), pp.746–750. Available at: <http://pubs.acs.org/doi/abs/10.1021/je000008o>.
- Dandge, D.K., Heller, J.P. & Wilson, K.V., 1985. Structure solubility correlations: organic compounds and dense carbon dioxide binary systems. *Industrial & Engineering Chemistry Product Research and Development*, 24(1), pp.162–166. Available at: <http://pubs.acs.org/doi/abs/10.1021/i300017a030>.
- de Coninck, H. & Benson, S.M., 2014. Carbon Dioxide Capture and Storage: Issues and Prospects. *Annual Review of Environment and Resources*, 39(1), pp.243–270. Available at: <http://dx.doi.org/10.1146/annurev-environ-032112-095222>.
- DOE/EIA, 2014. *Annual Energy Outlook 2014 with projections to 2040*, DOE/NETL-2003/119, 2003. *U.S. Brine Wells Database*,
- Dooley, K.M., Cain, A.W. & Knopf, F.C., 1997. Supercritical fluid extraction of acetic acid, alcohols and other amphiphiles from acid-water mixtures. *The Journal of Supercritical Fluids*, 11(1–2), pp.81–89. Available at: <http://www.sciencedirect.com/science/article/pii/S0896844697000260>.
- Duncan, I.J., Nicot, J.-P. & Choi, J.-W., 2009. Risk Assessment for future CO<sub>2</sub> Sequestration Projects Based CO<sub>2</sub> Enhanced Oil Recovery in the U.S. *Energy Procedia*, 1(1), pp.2037–2042. Available at: <http://www.sciencedirect.com/science/article/pii/S1876610209002665>.
- Elizalde-Solis, O. & Galicia-Luna, L.A., 2005. Solubility of thiophene in carbon dioxide and carbon dioxide-1-propanol mixtures at temperatures from 313 to 363 K. *Fluid Phase Equilibria*, 230(1–2), pp.51–57. Available at: <http://www.sciencedirect.com/science/article/pii/S0378381204005382>.
- Emberley, S. et al., 2004. Geochemical monitoring of fluid-rock interaction and CO<sub>2</sub> storage at the Weyburn CO<sub>2</sub>-injection enhanced oil recovery site, Saskatchewan, Canada. *Energy*, 29(9-10), pp.1393–1401. Available at: <http://www.sciencedirect.com/science/article/pii/S0360544204001562> [Accessed February 21, 2014].
- Endo, S., Pfennigsdorff, A. & Goss, K.-U., 2012. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. *Environmental science & technology*, 46(3), pp.1496–503. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22191628>.
- Eustaquio-Rincón, R. & Trejo, A., 2001. Solubility of n-octadecane in supercritical carbon dioxide at 310, 313, 333, and 353 K, in the range 10–20 MPa. *Fluid Phase Equilibria*, 185(1–2), pp.231–239. Available at: <http://www.sciencedirect.com/science/article/pii/S0378381201004733>.
- Foster, N.R. et al., 1991. Significance of the crossover pressure in solid-supercritical fluid phase equilibria. *Industrial & Engineering Chemistry Research*, 30(8), pp.1955–1964. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie00056a044>.

- García-González, J. et al., 2001. Solubilities of Phenol and Pyrocatechol in Supercritical Carbon Dioxide. *Journal of Chemical & Engineering Data*, 46(4), pp.918–921. Available at: <http://pubs.acs.org/doi/abs/10.1021/je0003795>.
- García-González, J. et al., 2002. Solubilities of hydroquinone and p-quinone in supercritical carbon dioxide. *Fluid Phase Equilibria*, 200(1), pp.31–39. Available at: <http://www.sciencedirect.com/science/article/pii/S0378381202000109>.
- Ghonasgi, D. et al., 1991. Supercritical CO<sub>2</sub> extraction of organic contaminants from aqueous streams. *AIChE Journal*, 37(6), pp.944–950. Available at: <http://dx.doi.org/10.1002/aic.690370617>.
- Goodarznia, I. & Esmaeilzadeh, F., 2002. Solubility of an Anthracene, Phenanthrene, and Carbazole Mixture in Supercritical Carbon Dioxide. *Journal of Chemical & Engineering Data*, 47(2), pp.333–338. Available at: <http://pubs.acs.org/doi/abs/10.1021/je010093f>.
- Gordon, J.E. & Thorne, R.L., 1967. Salt effects on non-electrolyte activity coefficients in mixed aqueous electrolyte solutions—II. Artificial and natural sea waters. *Geochimica et Cosmochimica Acta*, 31(12), pp.2433–2443. Available at: <http://www.sciencedirect.com/science/article/pii/0016703767900130>.
- Gozalpour, F., Ren, S. R. & Tohidi, B., 2005. Récupération assistée du pétrole (EOR) et stockage du CO<sub>2</sub> dans des réservoirs pétroliers. *Oil & Gas Science and Technology - Rev. IFP*, 60(3), pp.537–546. Available at: <http://dx.doi.org/10.2516/ogst:2005036>.
- Gupta, M.K. et al., 1982. Phase equilibrium for carbon dioxide-benzene at 313.2, 353.2, and 393.2 K. *Journal of Chemical & Engineering Data*, 27(1), pp.55–57. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00027a017>.
- Gurdial, G.S. et al., 1993. Influence of chemical modifiers on the solubility of o- and m-hydroxybenzoic acid in supercritical carbon dioxide. *Industrial & Engineering Chemistry Research*, 32(7), pp.1488–1497. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie00019a022>.
- Gurdial, G.S. & Foster, N.R., 1991. Solubility of o-hydroxybenzoic acid in supercritical carbon dioxide. *Industrial & Engineering Chemistry Research*, 30(3), pp.575–580. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie00051a020>.
- Haluszczak, L.O., Rose, A.W. & Kump, L.R., 2013. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry*, 28, pp.55–61. Available at: <http://www.sciencedirect.com/science/article/pii/S0883292712002752> [Accessed December 1, 2014].
- Harvey, O.R. et al., 2013. Geochemical Implications of Gas Leakage associated with Geologic CO<sub>2</sub> Storage—A Qualitative Review. *Environmental Science & Technology*, 47(1), pp.23–36. Available at: <http://dx.doi.org/10.1021/es3029457>.
- Hawthorne, S.B. et al., 1992. Comparison of supercritical CHCl<sub>3</sub>, N<sub>2</sub>O, and CO<sub>2</sub> for the extraction of polychlorinated biphenyls and polycyclic aromatic hydrocarbons. *Analytical chemistry*, 64(14), pp.1614–1622. Available at: <http://cat.inist.fr/?aModele=afficheN&cpsidt=5475440> [Accessed June 6, 2012].
- Jochmann, M.A., Kmiecik, M.P. & Schmidt, T.C., 2006. Solid-phase dynamic extraction for the enrichment of polar volatile organic compounds from water. *Journal of chromatography. A*, 1115(1-2), pp.208–16. Available at: <http://www.sciencedirect.com/science/article/pii/S0021967306004535> [Accessed April 18, 2014].

- Jonker, M.T.O. & Muijs, B., 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere*, 80, pp.223–227.
- Karásek, P. et al., 2002. Partition Coefficients of Environmentally Important Phenols in a Supercritical Carbon Dioxide–Water System from Cocurrent Extraction without Analysis of the Compressible Phase. *Analytical Chemistry*, 74(16), pp.4294–4299. Available at: <http://pubs.acs.org/doi/abs/10.1021/ac025599v>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1988. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: benzene and toluene. *Journal of Chemical & Engineering Data*, 33(2), pp.87–89. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00052a006>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1991. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: C<sub>2</sub>-Substituted benzenes. *Journal of Chemical & Engineering Data*, 36(4), pp.456–459. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00004a032>.
- Kent A. Bowker, P.J.S., 1991. Carbon Dioxide Injection and Resultant Alteration of Weber Sandstone (Pennsylvanian-Permian), Rangely Field, Colorado: ABSTRACT. *AAPG Bulletin*, 75(9), pp.1489 – 1499.
- Kharaka, Y.K. & Hanor, J.S., 2003. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In E.-C. H. D. Holland & K. K. Turekian, eds. *Treatise on Geochemistry*. Oxford: Pergamon, pp. 1–48. Available at: <http://www.sciencedirect.com/science/article/pii/B0080437516050854>.
- Kim, C.-H., Vimalchand, P. & Donohue, M.D., 1986. Vapor-liquid equilibria for binary mixtures of carbon dioxide with benzene, toluene and p-xylene. *Fluid Phase Equilibria*, 31(3), pp.299–311. Available at: <http://www.sciencedirect.com/science/article/pii/0378381286870145>.
- Knez, Ž. et al., 2008. Vapor–liquid equilibrium of binary CO<sub>2</sub>–organic solvent systems (ethanol, tetrahydrofuran, ortho-xylene, meta-xylene, para-xylene). *The Journal of Supercritical Fluids*, 43(3), pp.383–389. Available at: <http://www.sciencedirect.com/science/article/pii/S0896844607002823>.
- Krukoniš, V.J. & Kurnik, R.T., 1985. Solubility of solid aromatic isomers in carbon dioxide. *Journal of Chemical & Engineering Data*, 30(3), pp.247–249. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00041a002>.
- Lagalante, A.F. & Bruno, T.J., 1998. Modeling the Water–Supercritical CO<sub>2</sub> Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship†. *The Journal of Physical Chemistry B*, 102(6), pp.907–909. Available at: <http://dx.doi.org/10.1021/jp973047o>.
- Lee, L., Huang, J. & Zhu, O., 2001. Solubilities of Solid Benzoic Acid, Phenanthrene, and 2,3-Dimethylhexane in Supercritical Carbon Dioxide. *Journal of Chemical & Engineering Data*, 46(5), pp.1156–1159. Available at: <http://pubs.acs.org/doi/abs/10.1021/je0100140>.
- Lewicki, J., Birkholzer, J. & Tsang, C.-F., 2007. Natural and industrial analogues for leakage of CO<sub>2</sub> from storage reservoirs: identification of features, events, and processes and lessons learned. *Environmental Geology*, 52(3), pp.457–467. Available at: <http://dx.doi.org/10.1007/s00254-006-0479-7>.
- Li, Y.-H., Dillard, K.H. & Robinson, R.L., 1981. Vapor-liquid phase equilibrium for carbon dioxide-n-hexane at 40, 80, and 120 .degree.C. *Journal of Chemical & Engineering Data*, 26(1), pp.53–55. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00023a018>.

- Lide, D.R., 2013. *CRC Handbook of Chemistry and Physics, 94th Edition, 2013-2014*,
- Long, D.T. & Wilson, T.P., 1993. Geochemistry and isotope chemistry of CaNaCl brines in Silurian strata, Michigan Basin, U.S.A. *Applied Geochemistry*, 8, pp.507–524.
- Long, F.A. & McDevit, W.F., 1952. Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions. *Chemical Reviews*, 51(1), pp.119–169. Available at: <http://pubs.acs.org/doi/abs/10.1021/cr60158a004>.
- Lucien, F.P. & Foster, N.R., 1996. Influence of Matrix Composition on the Solubility of Hydroxybenzoic Acid Isomers in Supercritical Carbon Dioxide. *Industrial & Engineering Chemistry Research*, 35(12), pp.4686–4699. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie950649q>.
- Lucien, F.P. & Foster, N.R., 1998. Solubilities of Mixed Hydroxybenzoic Acid Isomers in Supercritical Carbon Dioxide. *Journal of Chemical & Engineering Data*, 43(5), pp.726–731. Available at: <http://pubs.acs.org/doi/abs/10.1021/je980026u>.
- Machmudah, S. et al., 2011. Simultaneous Extraction and Separation Process for Coffee Beans with Supercritical CO<sub>2</sub> and Water. *Industrial & Engineering Chemistry Research*, 50(4), pp.2227–2235. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie101252w>.
- McDevit, W.F. & Long, F.A., 1952. The Activity Coefficient of Benzene in Aqueous Salt Solutions. *Journal of the American Chemical Society*, 74(7), pp.1773–1777. Available at: <http://pubs.acs.org/doi/abs/10.1021/ja01127a048>.
- McHugh, M. & Paulaitis, M.E., 1980. Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide. *Journal of Chemical & Engineering Data*, 25(4), pp.326–329. Available at: <http://pubs.acs.org/doi/abs/10.1021/je60087a018>.
- Miller, D.J. et al., 1996. Solubility of Polycyclic Aromatic Hydrocarbons in Supercritical Carbon Dioxide from 313 K to 523 K and Pressures from 100 bar to 450 bar. *Journal of Chemical & Engineering Data*, 41(4), pp.779–786. Available at: <http://pubs.acs.org/doi/abs/10.1021/je960022u>.
- Neff, J., Lee, K. & Deblois, E.M., 2011. Produced Water : Overview of Composition , Fates , and Effects. *Produced Water*, pp.3–54.
- NETL, 2012. *Carbon Utilization and Storage Atlas of the United States and Canada, 4th ed.*, Morgantown, WV.
- Ng, H.J., Huang, S.S.S. & Robinson, D.B., 1982. Equilibrium phase properties of selected m-xylene binary systems. m-Xylene-methane and m-xylene carbon dioxide. *Journal of Chemical & Engineering Data*, 27(2), pp.119–122. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00028a004>.
- Ni, N. & Yalkowsky, S.H., 2003. Prediction of Setschenow constants. *International journal of pharmaceuticals*, 254, pp.167–172.
- Ohgaki, K. & Katayama, T., 1976. Isothermal vapor-liquid equilibrium data for binary systems containing carbon dioxide at high pressures: methanol-carbon dioxide, n-hexane-carbon dioxide, and benzene-carbon dioxide systems. *Journal of Chemical & Engineering Data*, 21(1), pp.53–55. Available at: <http://pubs.acs.org/doi/abs/10.1021/je60068a015>.
- Panagiotopoulos, A.Z. & Reid, R.C., 1986. New Mixing Rule for Cubic Equations of State for Highly Polar, Asymmetric Systems. In *Equations of State*. pp. 571–582. Available at: <http://pubs.acs.org/doi/abs/10.1021/bk-1986-0300.ch028>.
- Panagiotopoulos, A.Z., Willson, R.C. & Reid, R.C., 1988. Phase equilibria in ternary systems with carbon dioxide, water and carboxylic acids at elevated pressures. *Journal of Chemical*

- & *Engineering Data*, 33(3), pp.321–327. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/je00053a028>.
- Patel, N.C. & Teja, A.S., 1982. A new cubic equation of state for fluids and fluid mixtures. *Chemical Engineering Science*, 37(3), pp.463–473. Available at:  
<http://www.sciencedirect.com/science/article/pii/0009250982800997>.
- Peker, H. et al., 1992. Caffeine extraction rates from coffee beans with supercritical carbon dioxide. *AIChE Journal*, 38(5), pp.761–770. Available at:  
<http://dx.doi.org/10.1002/aic.690380513>.
- Peng, D.-Y. & Robinson, D.B., 1976. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1), pp.59–64. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/i160057a011>.
- Pfohl, O., Avramova, P. & Brunner, G., 1997. Two- and three-phase equilibria in systems containing benzene derivatives, carbon dioxide, and water at 373.15 K and 10–30 MPa. *Fluid Phase Equilibria*, 141(1–2), pp.179–206. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0378381297002100>.
- Portier, S. & Rochelle, C., 2005. Modelling CO<sub>2</sub> solubility in pure water and NaCl-type waters from 0 to 300 °C and from 1 to 300 bar. *Chemical Geology*, 217(3-4), pp.187–199. Available at: <http://www.sciencedirect.com/science/article/pii/S0009254104004929> [Accessed February 22, 2014].
- Poulson, S., Harrington, R. & Drever, J., 1999. The solubility of toluene in aqueous salt solutions. *Talanta*, 48, pp.633–641.
- Raveendran, P., Ikushima, Y. & Wallen, S.L., 2005. Polar Attributes of Supercritical Carbon Dioxide. *Accounts of Chemical Research*, 38(6), pp.478–485. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/ar040082m>.
- Reamer, H.H. & Sage, B.H., 1963. Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the n-Decane-CO<sub>2</sub> System. *Journal of Chemical & Engineering Data*, 8(4), pp.508–513. Available at: <http://pubs.acs.org/doi/abs/10.1021/je60019a010>.
- Redlich, O. & Kwong, J.N.S., 1949. On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chemical Reviews*, 44(1), pp.233–244. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/cr60137a013>.
- Sada, E., Kito, S. & Ito, Y., 1975. Solubility of toluene in aqueous salt solutions. *Journal of Chemical & Engineering Data*, 20(4), pp.373–375. Available at:  
<http://dx.doi.org/10.1021/je60067a030>.
- Sandler, S.I., 2006. *Chemical, Biochemical, and Engineering Thermodynamics* 4th ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Sanemasa, I. et al., 1984. The Effects of Salts on the Solubilities of Benzene, Toluene, Ethylbenzene, and Propylbenzene in Water. *Bulletin of the Chemical Society of Japan*, 57(6), pp.1539–1544.
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Shamsipur, M. et al., 2002. Solubility determination of nitrophenol derivatives in supercritical carbon dioxide. *The Journal of Supercritical Fluids*, 23(3), pp.225–231. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0896844601001437>.
- Shukla, R. et al., 2010. A review of studies on CO<sub>2</sub> sequestration and caprock integrity. *Fuel*, 89(10), pp.2651–2664. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0016236110002218>.

- Smith, R.D. et al., 1987. Solvent properties of supercritical xenon and sulfur hexafluoride. *The Journal of Physical Chemistry*, 91(11), pp.3059–3062. Available at: <http://pubs.acs.org/doi/abs/10.1021/j100295a083>.
- Smyth, T.J., Zytner, R.G. & Stiver, W.H., 1999. Influence of water on the supercritical fluid extraction of naphthalene from soil. *Journal of Hazardous Materials*, 67(2), pp.183–196. Available at: <http://www.sciencedirect.com/science/article/pii/S0304389499000436>.
- Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, 27(6), pp.1197–1203. Available at: <http://www.sciencedirect.com/science/article/pii/0009250972800964>.
- Stryjek, R. & Vera, J.H., 1986a. PRSV — An improved peng-Robinson equation of state with new mixing rules for strongly nonideal mixtures. *The Canadian Journal of Chemical Engineering*, 64(2), pp.334–340. Available at: <http://dx.doi.org/10.1002/cjce.5450640225>.
- Stryjek, R. & Vera, J.H., 1986b. PRSV: An improved peng—Robinson equation of state for pure compounds and mixtures. *The Canadian Journal of Chemical Engineering*, 64(2), pp.323–333. Available at: <http://dx.doi.org/10.1002/cjce.5450640224>.
- Thomas, S., 2008. Enhanced Oil Recovery – An Overview. *Science And Technology*, 63, pp.9–19.
- Timko, M.T. et al., 2004. Partition Coefficients of Organic Solutes between Supercritical Carbon Dioxide and Water: Experimental Measurements and Empirical Correlations. *Journal of Chemical & Engineering Data*, 49(4), pp.768–778. Available at: <http://pubs.acs.org/doi/abs/10.1021/jc030197l>.
- Ting, S.S.T. et al., 1993. Solubility of naproxen in supercritical carbon dioxide with and without cosolvents. *Industrial & Engineering Chemistry Research*, 32(7), pp.1471–1481. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie00019a022>.
- Trémosa, J. et al., 2014. Long-term assessment of geochemical reactivity of CO<sub>2</sub> storage in highly saline aquifers: Application to Ketzin, In Salah and Snøhvit storage sites. *International Journal of Greenhouse Gas Control*, 20, pp.2–26. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1750583613003757> [Accessed May 1, 2014].
- Tsang, C.-F. et al., 2002. Scientific considerations related to regulation development for CO<sub>2</sub> sequestration in brine formations. *Environmental Geology*, 42(2), pp.275–281. Available at: <http://dx.doi.org/10.1007/s00254-001-0497-4>.
- Utvik, T.I.R., 1999. Chemical characterisation of produced water from four offshore oil production platforms in the North Sea. *Chemosphere*, 39(15), pp.2593–2606. Available at: <http://www.sciencedirect.com/science/article/pii/S004565359900171X>.
- Valderrama, J.O., 2003. The State of the Cubic Equations of State. *Industrial & Engineering Chemistry Research*, 42(8), pp.1603–1618. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie020447b>.
- Van Leer, R.A. & Paulaitis, M.E., 1980. Solubilities of phenol and chlorinated phenols in supercritical carbon dioxide. *Journal of Chemical & Engineering Data*, 25(3), pp.257–259. Available at: <http://pubs.acs.org/doi/abs/10.1021/jc60086a020>.
- Wagner, K.-D., Dahmen, N. & PiaGriesheimer, 2003. Salt effects on the partition coefficients of phenol in two-phase mixtures of water and carbon dioxide at pressures from 8 to 30 MPa at a temperature of 313 K. *The Journal of Chemical Thermodynamics*, 35(4), pp.677–687. Available at: <http://www.sciencedirect.com/science/article/pii/S0021961402002392>.
- Ward, A.L. et al., 2005. *STOMP: Subsurface Transport Over Multiple Phases. Version 1.0: Addendum: Sparse Vegetation, Evapotranspiration Model for the Water-Air-Energy*

- Operational Mode. (PNNL-15465)*, Available at:  
[http://www.pnl.gov/main/publications/external/technical\\_reports/PNNL-15465.pdf](http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15465.pdf).
- Wong, D.S.H. & Sandler, S.I., 1992. A theoretically correct mixing rule for cubic equations of state. *AIChE Journal*, 38(5), pp.671–680. Available at:  
<http://dx.doi.org/10.1002/aic.690380505>.
- Xie, W.-H., Shiu, W.-Y. & Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research*, 44(4), pp.429–444. Available at: <http://www.sciencedirect.com/science/article/pii/S0141113697000172>.
- Xu, T. et al., 2006. TOUGHREACT—A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration. *Computers & Geosciences*, 32(2), pp.145–165. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0098300405001500> [Accessed April 17, 2015].
- Yamini, Y. et al., 1998. Solubility of dihydroxybenzene isomers in supercritical carbon dioxide. *Fluid Phase Equilibria*, 152(2), pp.299–305. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0378381298003859>.
- Yamini, Y. & Bahramifar, N., 2000. Solubility of Polycyclic Aromatic Hydrocarbons in Supercritical Carbon Dioxide. *Journal of Chemical & Engineering Data*, 45(1), pp.53–56. Available at: <http://pubs.acs.org/doi/abs/10.1021/je990129s>.
- Yeo, S.-D. & Akgerman, A., 1990. Supercritical extraction of organic mixtures from aqueous solutions. *AIChE Journal*, 36(11), pp.1743–1747. Available at:  
<http://dx.doi.org/10.1002/aic.690361116>.
- Zheng, L. et al., 2011. *Modeling Studies on the Transport of Benzene and H<sub>2</sub>S in CO<sub>2</sub>-Water Systems*, Berkeley, California. Available at: <http://escholarship.org/uc/item/121205mq>.
- Zheng, L. et al., 2013. On modeling the potential impacts of CO<sub>2</sub> sequestration on shallow groundwater: Transport of organics and co-injected H<sub>2</sub>S by supercritical CO<sub>2</sub> to shallow aquifers. *International Journal of Greenhouse Gas Control*, 14, pp.113–127. Available at:  
<http://www.sciencedirect.com/science/article/pii/S1750583613000303> [Accessed May 21, 2014].
- Zhong, L. et al., 2014. Transport of organic contaminants mobilized from coal through sandstone overlying a geological carbon sequestration reservoir. *International Journal of Greenhouse Gas Control*, 21, pp.158–164. Available at:  
<http://www.sciencedirect.com/science/article/pii/S1750583613004386> [Accessed May 2, 2014].

**PART I**

**Measurement and Modeling of Setschenow Constants for Hydrophobic and Hydrophilic Compounds in NaCl, CaCl<sub>2</sub>, and Mixed Electrolyte Brines**

**Chapter 3: Measure Setschenow Constants for selected hydrophobic compounds in the range of 2 - 5 M NaCl, 1.5 - 2 M CaCl<sub>2</sub>, and mixed electrolyte brines.**

The information presented in this chapter is part of a manuscript that has been submitted: Burant, A.; Lowry, G.V.; Karamalidis, A.K. Measuring and Modeling of the Setschenow Equation for Hydrophobic Compounds in Simulated Oil and Gas Binary Brines, (2015).

## Abstract

Treatment and reuse of brines, produced from energy extraction activities, requires aqueous solubility data for organic compounds in saline solutions. The presence of salts decreases the aqueous solubility of organic compounds (i.e. salting-out effect) and can be modeled using the Setschenow Equation, the validity of which has not been assessed in high salt concentrations. In this study, we used solid-phase microextraction, with gas chromatography coupled with a flame ionization detector to determine Setschenow constants for selected hydrophobic organic compounds (naphthalene, fluorene, phenanthrene, thiophene, benzothiophene, and dibenzothiophene) in aqueous solutions up to 2 - 5 M NaCl, 1.5 - 2 M CaCl<sub>2</sub>, and in Na-Ca binary electrolyte solutions to assess additivity of the constants. These compounds exhibited log-linear behavior up to these high NaCl concentrations. Log-linear decreases in solubility with increasing salt concentration were observed up to 1.5 - 2 M CaCl<sub>2</sub> for all compounds, and added to a sparse database of CaCl<sub>2</sub> Setschenow constants. Setschenow constants were additive in binary electrolyte mixtures. Overall, these data shows that the Setschenow Equation is valid for hydrophobic compounds over a wide range of salinity conditions typically found in energy-related technologies.

## Nomenclature

$\gamma_w^{DI}$ : Activity coefficient of an organic compound in deionized water

$\gamma_w^{salt}$ : Activity coefficient of an organic compound in salt water

$A_{salt}$ : Area count from the GC chromatogram after salt exposure

$A_{DI}$ : Area count from the GC chromatogram in deionized water

**BTEX**: Benzene, toluene, ethylbenzene, and the xylene isomers

**CCUS**: Carbon capture, utilization, and storage

**CO<sub>2</sub>**: Carbon dioxide

**EOR**: Enhanced oil recovery

**GC-FID**: Gas chromatography with a flame ionization detector

**I**: Ionic strength

$K_s^{i,k}$ : Setschenow constant in a single electrolyte system

$K_s^{mixed}$ : Setschenow constant in a mixed electrolyte system

**OLS**: Ordinary least squares

**PA**: Polyacrylate

**PAH**: Polycyclic aromatic hydrocarbon

**PDMS**: Polydimethylsiloxane

**PTFE**: Polytetrafluoroethylene

**SE**: Standard error

**SPME**: Solid phase microextraction

### 3.1 Introduction

Many energy-related technologies, such as carbon capture, utilization, and storage (CCUS); enhanced oil recovery (EOR); and unconventional oil and gas extraction; and desalination technologies (e.g. reverse osmosis) produce highly saline waters containing dissolved organic compounds (e.g. petroleum and synthetic hydrocarbons). The solubility of organic compounds in water usually decreases with increasing salinity. Therefore, assessing the risks of mobilization of organics from brine and/or CO<sub>2</sub> leakage from geologic storage formations (e.g. leakage from Sleipner gas field in the North Sea) (Monastersky 2013) or migration of produced waters from unconventional oil and gas reservoirs into freshwater aquifers require reliable ways of predicting the solubility of a number of different apolar and semi-polar organic compounds in brines. The composition of the brines mentioned above is typically dominated by dissolved alkaline and alkali metal chlorides (e.g. NaCl, CaCl<sub>2</sub>) which sometimes can reach total dissolved solids concentration of 400,000 mg/L (DOE/NETL-2003/119 2003; Shaffer et al. 2013). The effect of dissolved salts on the aqueous solubility of organic compounds, called the “salting-out” effect, is typically modeled by the empirical Setschenow Equation (Eqn. 3.1) (Sechenov 1889; Burant et al. 2013). The model is empirical, with Setschenow constants ( $K_s^{i,k}$  Eqn. 3.1) determined experimentally for each organic compound as well as each salt of interest.

$$\log\left(\frac{\gamma_w^{salt}}{\gamma_w^{DI}}\right) = K_s^{i,k} [salt] \quad \text{Eqn. 3.1.}$$

In this equation,  $\gamma_w^{DI}$  is the activity coefficient of an organic compound in deionized water (DI water),  $\gamma_w^{salt}$  is the activity coefficient of the organic compound in water at the salt

concentration of interest,  $K_s^{i,k}$  is the Setschenow constant of the organic compound ( $i$ ) for the specific salt ( $k$ ) ( $M^{-1}$ ), and  $[salt]$  is the concentration of salt (M). The presence of salt causes an increase in the activity coefficient of the organic compound in the saline solution relative to the DI water. In mixed salt solutions the Setschenow constant is determined based on the mole fractions of the salts present:

$$K_s^{mixed} \cong \sum_k K_s^{i,salt,k} \cdot x_k \quad \text{Eqn. 3.2.}$$

where  $K_s^{mixed}$  is the Setschenow constant of the mixed electrolyte system,  $K_s^{i,salt,k}$  is the Setschenow constant of organic compound ( $i$ ) in a single electrolyte solution ( $k$ ), and  $x_k$  is the mole fraction of each species in the mixture. The  $K_s^{mixed}$  can then be applied to Eqn. 3.1, replacing  $K_s^{i,k}$ , to predict the aqueous activity coefficient or solubility of a compound in the mixed electrolyte solution.

The ability of the Setschenow Equation to predict the solubility for many organic compounds has been confirmed only for aqueous solutions with salt concentrations up to 1 M NaCl (Xie et al. 1997). Data for the solubility of organic compounds for high salinity NaCl and CaCl<sub>2</sub> solutions is scarce. In addition, there are only 19 reported CaCl<sub>2</sub> Setschenow constants, despite the fact that CaCl<sub>2</sub> is a major component of oil and gas reservoir brines (Kharaka & Hanor 2003). The additive nature of the salting-out effect (Eqn 3.2) has only been demonstrated for benzene and naphthalene at moderate ionic strengths (McDevit & Long 1952; John E Gordon & Thorne 1967).

Reported aqueous solubility data are available for benzene, toluene, ethylbenzene, and the xylene isomers (BTEX) up to 5 M NaCl (Keeley et al. 1988; Keeley et al. 1991). However, these compounds are relatively small and monopolar, and more data on representative compounds from different classes of organic compounds are needed to assess the validity of the Setschenow Equation over a broader range of salt concentration, and to determine if Setschenow constants determined at low salt concentration are extensible to brines ( $\geq 1$  M). The Setschenow Equation may not be valid for larger and monopolar/apolar or polar organic compounds (Jochmann et al. 2006; Eisen & Joffe 1966; Janado et al. 1983; Meranda & Furter 1974; Lee 1997). For example, Janado et al. (1983) found that the Setschenow Equation did not predict the salting-out effect for naphthalene and biphenyl in aqueous NaSCN and KSCN solutions, which exhibited both salting-out and then salting-in effects, while benzene only exhibited salting-out behavior. Although deviations from the Setschenow Equation are not common for solutions of moderate salt concentration (i.e. up to 1 M), Whitehouse (1985) observed deviations from the Setschenow Equation for 1,2-benzanthracene, a PAH, in concentrations of NaCl up to seawater. Whitehouse (1985) Since there are ~190 reported NaCl Setschenow constants (Endo et al. 2012; Ni & Yalkowsky 2003), the extension of the previously measured Setschenow constants up to high salt concentrations would be ideal, since that data would not have to be re-measured. However, due to lack of high salinity data, it is uncertain if the Setschenow Equation can be used to accurately predict the aqueous solubility of a variety of organic compounds at high salt concentrations expected in brines (Endo et al. 2012).

The additivity of Setschenow constants for mixed electrolytes (Eqn 3.2) has not been confirmed with extensive data collection, and never for high salinity fluids. The additivity of the Setschenow constants was confirmed for benzene and naphthalene, over a range of different salt

compositions with different anions and cations, and for a several hydrophobic organic compounds up to seawater salinity (Sutton & Calder 1975; Eganhouse & Calder 1976; Rossi & Thomas 1981). A study on the salting-out effect for toluene in different salts suggested that the salting-out effect for organic compounds with a dipole moment may result in deviations from the Setschenow Equation (Poulson et al. 1999). This has not been tested on organic compounds with a dipole moment.

Objectives 1 and 2 are to determine the validity of the Setschenow Equation for selected hydrophobic (Objective 1) and hydrophilic (Objective 2) organic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines. The hydrophobic and hydrophilic compounds were divided into two different objectives because it was hypothesized that hydrophobic and hydrophilic organic compounds would have different salting-out behavior. This division was based on whether the organic compound had the ability to undergo both hydrogen bond accepting and donating intermolecular reactions.

Objective 1 is to determine the validity of the Setschenow Equation for selected hydrophobic compounds in the range of 2 – 5 M NaCl, 1.5 – 2 M CaCl<sub>2</sub>, and mixed electrolyte brines. This objective was accomplished in three parts. The first part is concerned with whether reported NaCl Setschenow constants measured at those lower salt concentrations are applicable up to high salt concentrations (2 – 5 M NaCl) typical of oil and gas reservoirs. The second part aims to add to a sparse database of those CaCl<sub>2</sub> Setschenow constants and to determine if salting-out behavior in CaCl<sub>2</sub> solutions is log-linear up to 1.5 – 2 M CaCl<sub>2</sub>. Part three is to determine if Setschenow constants measured in single electrolyte brines are applicable up mixed electrolyte brines, which are typical of oil and gas reservoirs.

The salting-out effect was measured for three PAHs, naphthalene, fluorene, phenanthrene, and three sulfur heterocyclics, thiophene, benzothiophene, and dibenzothiophene in NaCl and CaCl<sub>2</sub> brines. Naphthalene was not measured in CaCl<sub>2</sub> solutions, because naphthalene already has a reported CaCl<sub>2</sub> Setschenow constant. The salting-out effect of thiophene and fluorene were measured in mixed electrolyte brines. Those three PAHs were chosen because they represent the smaller, more water-soluble version of the PAHs, and already had reported NaCl Setschenow constants. This allowed us to determine if Setschenow constants measured at low NaCl concentrations could extend to high NaCl concentrations. The thiophenes were chosen because they had no previously reported Setschenow constants, and few organosulfur compounds have reported Setschenow constants, contributing to a more diverse database of Setschenow constants.

### 3.2 Experimental

The estimation of Setschenow constants was completed using solid phase microextraction (SPME), followed with analysis of the adsorbed organic compounds using gas-chromatography coupled with a flame ionization detector (GC-FID). SPME, has been used in previous studies to measure Setschenow constants and has proven to produce consistent and accurate results (Jonker & Muijs 2010; Endo et al. 2012). The Setschenow constants were estimated by linear regression of Eqn. 3.3, where differences in area count output from the GC-FID was used to represent the change in aqueous activity coefficient (Eqn 3.3).

$$\log\left(\frac{A_{salt}}{A_{DI}}\right) = K_s^{i,k} [salt] \quad \text{Eqn. 3.3}$$

In this equation,  $A_{salt}$  is the area count from the SPME fiber after salt exposure, and  $A_{DI}$  is the area count from the SPME fiber before salt exposure (in deionized water). In this method the salt does not change the activity of the SPME fiber (Endo et al. 2012).

One measurement was made per vial after salt addition and all replicate measurements were done in separate samples. For accurate measurements of Setschenow constants, two criteria have to be met. First, the aqueous solubility of the organic compound in solution cannot be exceeded, as this would cause an introduction of a third phase (which would cause a decrease in organic compound partitioning to the fiber). Second, depletion of the organic compound in solution due to sorption of the organic compound on the fiber must be minimized. A rigorous explanation for each data point is given in Appendix A.2. Therefore, the experimental data shown here are of high accuracy (non-depleting and below saturation solubility).

### **3.2.1 Materials**

Thiophene ( $\geq 99.5\%$ ), benzothiophene (98%), dibenzothiophene (98%), fluorene (98%), and phenanthrene (98%) were obtained from Sigma Aldrich. Naphthalene (99%) was obtained from Acros Organics. Sodium chloride (ACS Grade,  $\geq 99\%$ ) and anhydrous calcium chloride (ACS Grade,  $>96\%$ ) were obtained from Fisher Scientific. The organic compounds were dissolved in pesticide grade acetone. Glassware was silanized overnight with 90 vol% toluene (ACS Grade,  $\geq 99.5\%$ , Fisher Scientific) and 10 vol% dichlorodimethylsilane (99+%, Acros Organics). The vials used for analysis were cleaned with acetone and methanol (ACS grade  $\geq 99.8\%$ ), and a detergent rinse (Sparkleen, Fisher Scientific). After cleaning, they were dried at  $105\text{ }^{\circ}\text{C}$  for  $>1$  hour. Three different types of SPME fibers (Sigma Aldrich) were used to measure PAHs; 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) for naphthalene, fluorene, and dibenzothiophene;

7  $\mu\text{m}$  and 100  $\mu\text{m}$  PDMS fiber for phenanthrene; and 85  $\mu\text{m}$  polyacrylate (PA) for thiophene, and benzothiophene.

### 3.2.2 Methods

Between 35 – 39 mL of deionized water (Barnstead nanopure 18.2 M $\Omega$ -cm), depending on the target salt concentration, was added to a 40 mL silanized glass vial, capped with a PTFE-lined silicone septa, and wrapped in aluminum foil to prevent exposure to light. Target organic compounds were dissolved in pesticide grade acetone, and 20  $\mu\text{L}$  of the solution was added to the water. The small amount of acetone is expected to have negligible effect on the salting-out effect. Solution masses and dilutions were performed gravimetrically ( $\pm 0.001$  g). A PTFE stir bar was added to each vial to assist achieving faster equilibrium times by stirring. The SPME fiber was exposed directly to the water for a predetermined amount of time; larger compounds typically took longer to reach equilibrium with the SPME fiber (See Appendix A.1), which was determined by conducting an uptake curve. After the SPME fiber was desorbed by direct injection in the GC inlet, salt was added to the vial, and the fiber was exposed to the solution once again. The time required for each compound to reach equilibrium between the dissolved phase and the fiber increased with increasing salt concentration, so the time the fiber was exposed to the aqueous solution was increased accordingly to ensure equilibrium was obtained at each salt concentration (See Appendix A.1). After equilibration, the stainless steel part of the needle was rinsed with DI water, and wiped off to remove the salt from the surface of the stainless steel, to protect the GC-FID and prolong fiber's life. The fibers were finally desorbed in the GC inlet for quantification of the increased amount of organic compound on the fiber. All experiments were conducted at room temperature ( $23 \pm 2^\circ\text{C}$ ). The Setschenow constant is not responsive to small changes of room temperature (May et al. 1978).

The organic compound analysis was carried out with a GC-FID (Agilent 6890A) equipped with a split/splitless injector. Helium at 23 mL/min was used as the carrier gas. The inlet temperature was set at 250 °C for 100 μm PDMS, at 320 °C for the 7 μm PDMS, and at 280 °C for 85 μm PA fibers. The fiber was desorbed for two minutes in the inlet. The column used was 30m×320 μm×0.25 μm 5% phenyl-95% methyl (HP-5, J&W Scientific). The oven program varied across analytes. The FID was kept at a temperature of 320 °C.

The NaCl salt concentrations measured were 1 M, 2 M, 3 M, 4 M, and 5 M NaCl for thiophene and naphthalene; 1 – 4 M NaCl for benzothiophene, 1 – 3 M NaCl for phenanthrene and 1 – 2 M NaCl for dibenzothiophene and fluorene. The CaCl<sub>2</sub> salt concentrations measured were 0.25 M, 0.5 M, 0.75 M, 1 M, 1.5 M, and 2 M for thiophene, benzothiophene, and dibenzothiophene, 0.25 – 1.5 M for fluorene and phenanthrene. The mixed electrolytes systems were for thiophene and fluorene at ionic strengths of 1.5 M (0.75 M NaCl, 0.25 M CaCl<sub>2</sub>), 2.0 M (0.5 M NaCl, 0.5 M CaCl<sub>2</sub>), 2.5 M (0.25 M NaCl, 0.75 M CaCl<sub>2</sub>), and 5 M (2 M NaCl, 1 M CaCl<sub>2</sub>) (only for thiophene). These were chosen because they are the relevant concentrations of oil and gas reservoirs. Concentrations of 2 M NaCl represent typical median total dissolved solids concentrations for some oil and gas reservoirs (Benko & Drewes 2008; Gregory et al. 2011). The Setschenow constants reported here were estimated from ordinary least-squares (OLS) linear regressions of log change in area against salt concentration, as in Equation 3, performed in MATLAB using the Statistics Toolbox [Matlab R2013A].

### **3.3 Results and Discussion**

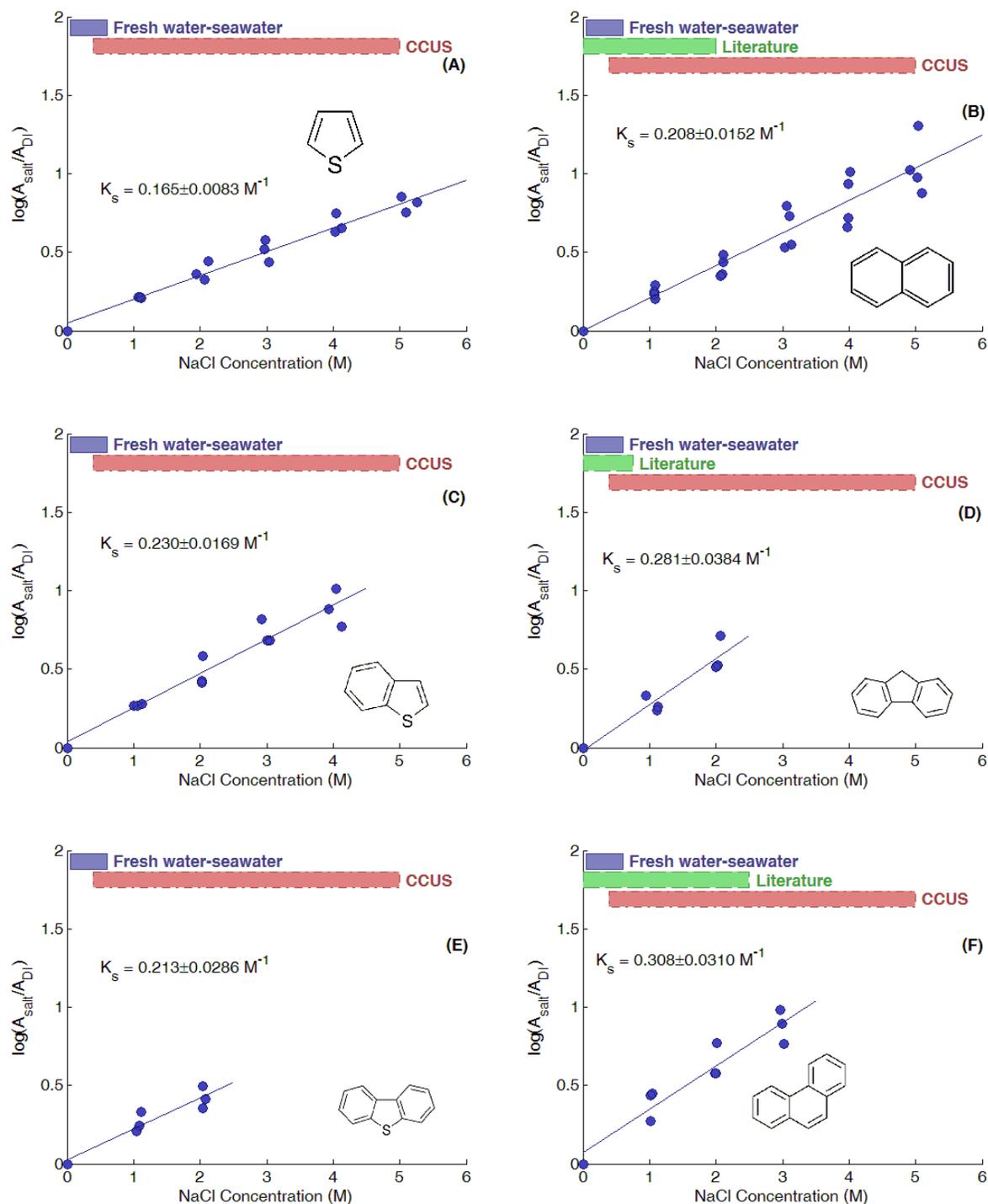
#### **3.3.1 NaCl Setschenow Constants**

Setschenow constants for selected compounds were determined using the SPME method (*Figure 3.1* and **Table 3.1**). Previously reported NaCl Setschenow constants for the PAHs are found in **Table 3.1**, while thiophenes have no reported NaCl Setschenow constants. The standard

error of those estimates for  $K_s^{i,NaCl}$  were low (0.008 – 0.043 M<sup>-1</sup>). Measurements made at higher salt concentrations required longer time to reach equilibrium, which led to higher standard errors, also consistent with previous observations using the SPME method (Jochmann et al. 2006).

Setschenow constants values from this study are comparable to previously reported measurements of Setschenow constants determined at lower salt concentration, especially for the PAHs (Jonker & Muijs 2010; Jochmann et al. 2006). The magnitude of the NaCl Setschenow constants for the PAHs followed expectations based on their molar volumes and their previously reported Setschenow constants, with phenanthrene having the largest salting-out parameters, followed by fluorene and naphthalene. This did not occur for the thiophenes, with benzothiophene ( $K_s^{i,NaCl} = 0.230$  M<sup>-1</sup>) having a larger in magnitude NaCl Setschenow constant than dibenzothiophene ( $K_s^{i,NaCl} = 0.213$  M<sup>-1</sup>). A review of NaCl Setschenow constant data shows that there is only a fair correlation of Setschenow constants with molar volume ( $R^2 = 0.513$ ). This also highlights that there is difficulty in predicting Setschenow constants and there are multiple mechanisms controlling the salting-out effect, which is discussed in detail in Chapter 5.

In addition, the NaCl Setschenow constants measured at low salt concentration for the thiophenes also extend up to higher salt concentrations. The Setschenow Equation for the hydrophobic compounds reported here are log-linear up to 2 – 5 M NaCl.



**Figure 3.1** The effect of salt addition (i.e.  $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of selected organic compounds onto the SPME fiber as for A) thiophene, B) naphthalene, C) benzothiophene, D) fluorene, E) dibenzothiophene, and F) phenanthrene. Colored bars represent ranges of salt concentrations for previously reported Setschenow constants (green); seawater (blue bars) and for CCUS conditions 0.6 M-5 M NaCl (this study, red bars). The valid range of  $K_s$  estimates are indicated by the black regression line. Reported constants ( $K_s$ ) are the regression mean  $\pm 2 \cdot \text{SE}$ .

**Table 3.1.** Summary of previously reported experimentally determined Setschenow constants for NaCl and data produced in this study for NaCl and CaCl<sub>2</sub>

Organic Compound	Reported NaCl K <sub>s</sub> (M <sup>-1</sup> )	Range of NaCl Concs. (M) (reported)	NaCl Setschenow Constants from this study (M <sup>-1</sup> )	CaCl <sub>2</sub> Setschenow Constants from this study (M <sup>-1</sup> )
Naphthalene	0.213 (May et al. 1978)	0 – 0.75	0.208 ±0.015	0.32* (John Edward Gordon & Thorne 1967)
	0.22 (John E Gordon & Thorne 1967)	0 – 2		
	0.23 (Hashimoto et al. 1984)	0 – 1		
	0.255 (John Edward Gordon & Thorne 1967)	0 – 2		
	0.26 (Paul 1952)	0 – 0.02		
	0.303 (Eganhouse & Calder 1976)	0 – 0.5		
	0.62 (Schwarz 1977)	0 – 0.5		
Fluorene	0.267(May et al. 1978)	0 – 0.75	0.281± 0.038 <sup>a</sup>	0.362 ±0.043 <sup>d</sup>
Phenanthrene	0.24 (Schwarz 1977)	0 – 0.5	0.308 ±0.029 <sup>b</sup>	0.373 ±0.03 <sup>d</sup>
	0.269 (Whitehouse 1984; Whitehouse 1985)	0 – 0.6		
	0.272 (Hashimoto et al. 1984)	0 – 1		
	0.275 (May et al. 1978)	0 – 0.75		
	0.287 (Aquan-Yuen et al. 1979)	0 – 2.5		
	0.38 (Jonker & Muijs 2010)	0 – 0.45		
	0.387 (Eganhouse & Calder 1976)	0 – 0.5		
Thiophene	N/A	N/A	0.165 ±0.008	0.295 ±0.017
Benzothiophene	N/A	N/A	0.230 ±0.015 <sup>c</sup>	0.289 ±0.018
Dibenzothiophene	N/A	N/A	0.213 ±0.03 <sup>a</sup>	0.217 ±0.025

<sup>a</sup>Determined using data up to 2 M NaCl

<sup>b</sup>Determined using data up to 3 M NaCl

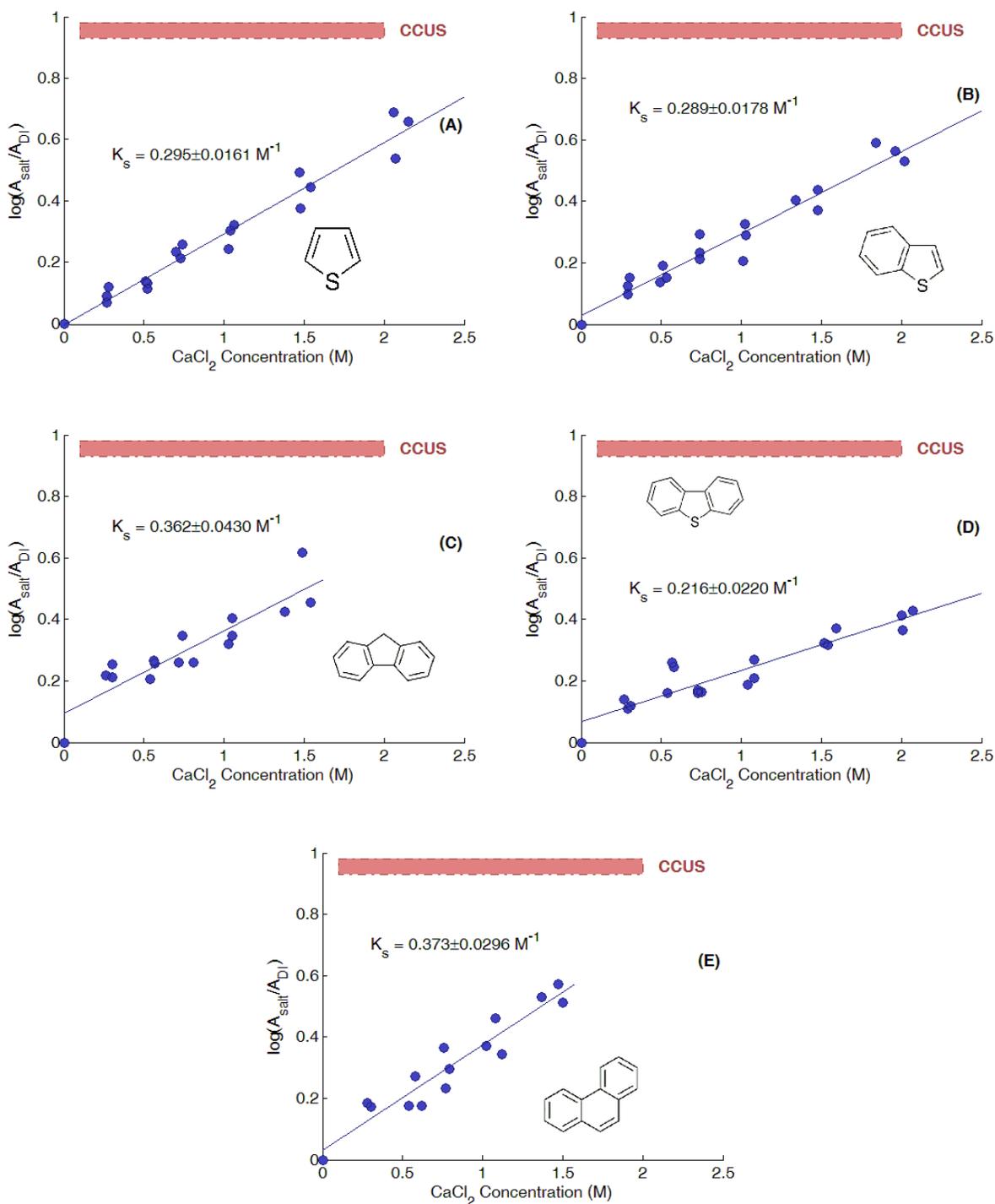
<sup>c</sup>Determined using data up to 4 M NaCl

<sup>d</sup>Determined using data up to 1.5 M CaCl<sub>2</sub>

\*Measured in a different study.

### 3.3.2 CaCl<sub>2</sub> Setschenow Constants

Calcium chloride Setschenow constants were measured for all of the compounds in this study, with the exception of naphthalene, which has a previously reported CaCl<sub>2</sub> Setschenow constant ( $K_s^{i, CaCl_2} = 0.322 \text{ M}^{-1}$ ) (John Edward Gordon & Thorne 1967) (**Table 3.1** and *Figure 3.2*). This has added to a sparse database of CaCl<sub>2</sub> Setschenow constants, and will contribute to the predictive modeling of CaCl<sub>2</sub> Setschenow constants in Chapter 5 of this dissertation. The CaCl<sub>2</sub> constants, due to the fact that Ca<sup>2+</sup> is a divalent cation, were higher than NaCl for all of the compounds of interest. This is consistent with expectation because salting-out effects of cations and anions follow a specific order, known as the Hofmeister series (Cacace et al. 1997), in magnitude of salting out (or in) for organic compounds, gases, and proteins (Jungwirth & Cremer 2014). In addition, all the exhibited salting-out effects for these compounds were log-linear up to 1.5 – 2 M CaCl<sub>2</sub>, showing that the previously reported CaCl<sub>2</sub> constants can be used with confidence up to CaCl<sub>2</sub> concentrations typical of oil and gas reservoirs.

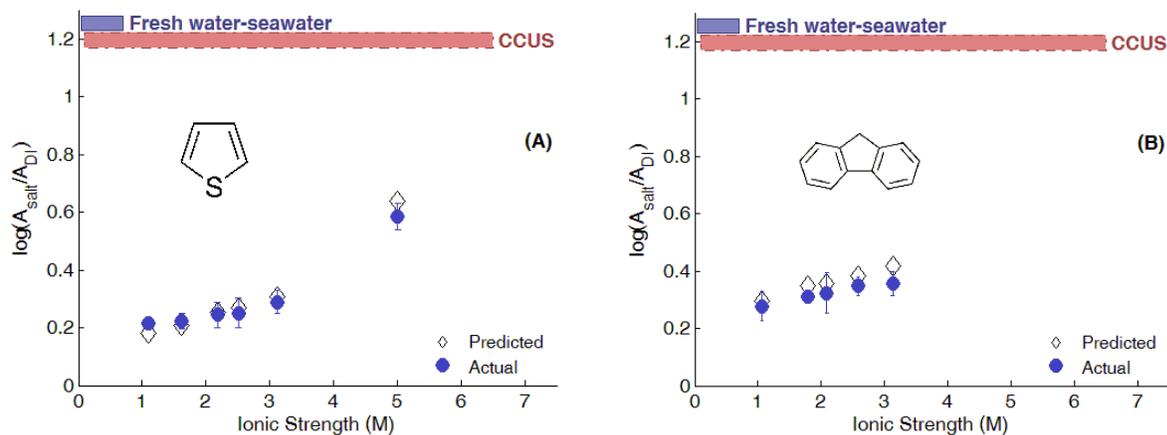


**Figure 3.2** The salting-out effect (i.e.  $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of individual organic compounds onto the SPME fiber as a function of  $\text{CaCl}_2$  concentration (M) for A) Thiophene, B) Benzothiophene, C) Fluorene, D) Dibenzothiophene, and E) Phenanthrene. Red bars represent salt concentrations for Setschenow constants reported for: CCUS 0.1M-5M  $\text{CaCl}_2$  (this study). Reported constants ( $K_s$ ) are the regression mean  $\pm 2 \cdot \text{SE}$ .

### 3.3.3 Mixed Electrolytes

Thiophene and fluorene were chosen to test the additivity of Setschenow constants in high salinity brines. Thiophene has a dipole moment ( $\mu=0.536$  Debye) contrary to fluorene which has a zero dipole moment. Poulson et al. (1999) hypothesized that organic compounds with a non-zero dipole moment will have additional interactions with salts in mixed electrolyte systems that could cause the Setschenow Equation to be non-additive. In addition, the salting-out effect was tested up to an ionic strength of  $\sim 5$  M (2 M NaCl and 1 M CaCl<sub>2</sub>) for thiophene to determine if the Setschenow Equation was additive under these conditions.

The results for both thiophene and fluorene at the lower ionic strengths, 1 M – 3 M (Na-Ca-Cl), where the Setschenow Equation is known to be valid in NaCl and CaCl<sub>2</sub> single electrolyte systems, indicates that the Setschenow constants for NaCl and CaCl<sub>2</sub> are additive (*Figure 3.3*). *Figure 3.3* has both the measured and predicted (from Eqns. 3.1 and 3.2) values of the salting-out at these ionic strengths. The predicted values fall within the standard error of the measurements. For thiophene, at  $I=5$ M, the predicted values for salting-out fall in line with the experimental values (*Figure 3.3A*), which was expected because it had log-linear salting-out behavior up to 5 M NaCl and additive Setschenow constants.



**Figure 3.3** The salting-out effect (i.e.  $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of individual organic compounds onto the SPME fiber as a function of ionic strength (M) for A) Thiophene, and B) Fluorene. Colored bars represent salt concentrations for Setschenow constants reported for: Blue bars in seawater; red bars in CCUS 0.1 – 7M I. The diamonds represent predicted values based on the respective single electrolyte Setschenow constants, and the blue circles (with standard deviations) represent the actual measured values in this study.

### 3.3.4 Implications

All of the data here exhibited log-linear behavior up to high NaCl and CaCl<sub>2</sub> concentrations. This study shows that the salting-out effect for naphthalene, fluorene, phenanthrene, thiophene, benzothiophene, and dibenzothiophene was log-linear up to high concentrations of NaCl and CaCl<sub>2</sub>, therefore previously reported NaCl and CaCl<sub>2</sub> Setschenow constants for those compounds at low ionic strength can be used with confidence in the range 2 - 5 M NaCl and 1.5 - 2 M CaCl<sub>2</sub> to predict aqueous activity coefficients and solubility. Importantly, the Setschenow Equation was found to be additive for thiophene and fluorene in mixed electrolyte brines, typical of oil and gas reservoirs. The previously reported Setschenow constants for naphthalene, fluorene, and phenanthrene all scaled up to NaCl concentrations up to 5 M, 2 M, and 3 M, respectively. This means that Setschenow constants estimated in low salt concentrations do not need to be re-measured. This work also added to a sparse database of NaCl and CaCl<sub>2</sub> Setschenow constants. This is especially important for the CaCl<sub>2</sub> Setschenow

constants, as there are only 19 reported  $\text{CaCl}_2$  Setschenow constants in the literature. This is especially important for a variety of CCUS and EOR sites (Burant et al. 2013), such as Sleipner gas field (Portier & Rochelle 2005), Weyburn EOR site (Emberley et al. 2004), Cranfield demonstration site (Lu et al. 2012), and Frio Formation (Kharaka et al. 2006); all of which can use the Setschenow Equation to predict the aqueous solubility of dissolved organic compounds. In addition, the Setschenow Equation should be capable of predicting the salting-out effect in brine concentrates from many unconventional oil and gas produced waters (e.g. Marcellus Shale), where the median total dissolved solid concentrations are reported around 150,000 mg/L (containing around 1.44 M NaCl, and a total of 4.18 eq/L ionic strength) (Gregory et al. 2011). The Setschenow Equation also can be used for risk assessment from desalination technologies, such as reverse osmosis brines, which have NaCl concentrations around 1.2 M (TDS of 70,000 mg/L).

While the Setschenow Equation was extended for selected organic compounds here, this does not comprise all organic compounds found in oil and gas reservoirs, and in desalination brines (see Chapter 7.3 for a full discussion on limitations). These organic compounds are representative of small to moderately sized organic compounds. This includes organic compounds with up to three aromatic rings, and includes the BTEX compounds, small PAHs and heterocycles. Future work should include determining the validity of the Setschenow Equation for larger hydrophobic compounds, such as PAHs and other larger compounds with four or more rings, and hydrophobic organic compounds with substituents, such as halogenated compounds.

### **3.4 Supplementary Information**

Appendix A contains experimental details about SPME, data defense and removal based on depletions at each salt concentration for each compound and predicted aqueous solubility for

each compound based on the Setschenow Equation, Abraham solvation parameters, and data on the organic compounds used in this study.

### 3.5 References

- Aquan-Yuen, M., Mackay, D. & Shiu, W.Y., 1979. Solubility of hexane, phenanthrene, chlorobenzene and p-dichlorobenzene in aqueous electrolyte solutions. *Journal of Chemical & Engineering Data*, 24(1), pp.30–34. Available at: <http://pubs.acs.org/doi/abs/10.1021/je60080a009>.
- Benko, K.L. & Drewes, J.E., 2008. Produced Water in the Western United States: Geographical Distribution, Occurrence, and Composition. *Environmental Engineering Science*, 25(2), pp.239–246. Available at: <http://dx.doi.org/10.1089/ees.2007.0026>.
- Burant, A., Lowry, G.V. & Karamalidis, A.K., 2013. Partitioning behavior of organic contaminants in carbon storage environments: a critical review. *Environmental science & technology*, 47(1), pp.37–54. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/23211055>.
- Cacace, M.G., Landau, E.M. & Ramsden, J.J., 1997. The Hofmeister series: salt and solvent effects on interfacial phenomena. *Quarterly reviews of biophysics*, 30, pp.241–277.
- DOE/NETL-2003/119, 2003. *U.S. Brine Wells Database*,
- Eganhouse, R.P. & Calder, J.A., 1976. The solubility of medium molecular weight aromatic hydrocarbons and the effects of hydrocarbon co-solutes and salinity. *Geochimica et Cosmochimica Acta*, 40(5), pp.555–561. Available at: <http://www.sciencedirect.com/science/article/pii/0016703776902234>.
- Eisen, E.O. & Joffe, J., 1966. Salt Effects in Liquid-Liquid Equilibria. *Journal of Chemical & Engineering Data*, 11(4), pp.480–484. Available at: <http://pubs.acs.org/doi/abs/10.1021/je60031a007>.
- Emberley, S. et al., 2004. Geochemical monitoring of fluid-rock interaction and CO<sub>2</sub> storage at the Weyburn CO<sub>2</sub>-injection enhanced oil recovery site, Saskatchewan, Canada. *Energy*, 29(9-10), pp.1393–1401. Available at: <http://www.sciencedirect.com/science/article/pii/S0360544204001562> [Accessed February 21, 2014].
- Endo, S., Pfennigsdorff, A. & Goss, K.-U., 2012. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. *Environmental science & technology*, 46(3), pp.1496–503. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22191628>.
- Gordon, J.E. & Thorne, R.L., 1967. Salt effects on non-electrolyte activity coefficients in mixed aqueous electrolyte solutions—II. Artificial and natural sea waters. *Geochimica et Cosmochimica Acta*, 31(12), pp.2433–2443. Available at: <http://www.sciencedirect.com/science/article/pii/0016703767900130>.
- Gordon, J.E. & Thorne, R.L., 1967. Salt effects on the activity coefficient of naphthalene in mixed aqueous electrolyte solutions. I. Mixtures of two salts. *The Journal of Physical Chemistry*, 71(13), pp.4390–4399. Available at: <http://pubs.acs.org/doi/abs/10.1021/j100872a035>.
- Gregory, K.B., Vidic, R.D. & Dzombak, D.A., 2011. Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements*, 7 (3), pp.181–186. Available at: <http://elements.geoscienceworld.org/content/7/3/181.abstract>.

- Hashimoto, Y. et al., 1984. Prediction of seawater solubility of aromatic compounds. *Chemosphere*, 13(8), pp.881–888. Available at: <http://www.sciencedirect.com/science/article/pii/0045653584901619>.
- Janado, M. et al., 1983. Peculiar effects of alkali thiocyanates on the activity coefficients of aromatic hydrocarbons in water. *Journal of Solution Chemistry*, 12(10), pp.741–754. Available at: <http://dx.doi.org/10.1007/BF00647385>.
- Jochmann, M.A., Kmiecik, M.P. & Schmidt, T.C., 2006. Solid-phase dynamic extraction for the enrichment of polar volatile organic compounds from water. *Journal of chromatography. A*, 1115(1-2), pp.208–16. Available at: <http://www.sciencedirect.com/science/article/pii/S0021967306004535> [Accessed April 18, 2014].
- Jonker, M.T.O. & Muijs, B., 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere*, 80, pp.223–227.
- Jungwirth, P. & Cremer, P.S., 2014. Beyond Hofmeister. *Nat Chem*, 6(4), pp.261–263. Available at: <http://dx.doi.org/10.1038/nchem.1899>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1988. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: benzene and toluene. *Journal of Chemical & Engineering Data*, 33(2), pp.87–89. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00052a006>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1991. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: C<sub>2</sub>-Substituted benzenes. *Journal of Chemical & Engineering Data*, 36(4), pp.456–459. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00004a032>.
- Kharaka, Y.K., Cole, D.R. & Hovorka, S.D., 2006. Gas-water-rock interactions in Frio Formation following CO<sub>2</sub> injection: Implications for the storage of greenhouse gases in sedimentary basins. ..., 34(7), p.577. Available at: <http://geology.gsapubs.org/cgi/doi/10.1130/G22357.1> [Accessed February 13, 2014].
- Kharaka, Y.K. & Hanor, J.S., 2003. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In E.-C. H. D. Holland & K. K. Turekian, eds. *Treatise on Geochemistry*. Oxford: Pergamon, pp. 1–48. Available at: <http://www.sciencedirect.com/science/article/pii/B0080437516050854>.
- Lee, L.L., 1997. A molecular theory of Setchenov's salting-out principle and applications in mixed-solvent electrolyte solutions. *Fluid Phase Equilibria*, 131(1-2), pp.67–82. Available at: <http://www.sciencedirect.com/science/article/pii/S0378381296031986> [Accessed April 18, 2014].
- Lu, J. et al., 2012. CO<sub>2</sub>-rock-brine interactions in Lower Tuscaloosa Formation at Cranfield CO<sub>2</sub> sequestration site, Mississippi, U.S.A. *Chemical Geology*, 291, pp.269–277. Available at: <http://www.sciencedirect.com/science/article/pii/S0009254111004293> [Accessed July 7, 2014].
- May, W.E., Wasik, S.P. & Freeman, D.H., 1978. Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. *Analytical Chemistry*, 50(7), pp.997–1000. Available at: <http://pubs.acs.org/doi/abs/10.1021/ac50029a042>.
- McDevit, W.F. & Long, F.A., 1952. The Activity Coefficient of Benzene in Aqueous Salt Solutions. *Journal of the American Chemical Society*, 74(7), pp.1773–1777. Available at: <http://pubs.acs.org/doi/abs/10.1021/ja01127a048>.

- Meranda, D. & Furter, W.F., 1974. Salt effects on vapor-liquid equilibrium: Some anomalies. *AIChE Journal*, 20(1), pp.103–108. Available at: <http://dx.doi.org/10.1002/aic.690200113>.
- Monastersky, R., 2013. Seabed scars raise questions over carbon-storage plan. *Nature*, 504, pp.1–2.
- Ni, N. & Yalkowsky, S.H., 2003. Prediction of Setschenow constants. *International journal of pharmaceutics*, 254, pp.167–172.
- Paul, M.A., 1952. The Solubilities of Naphthalene and Biphenyl in Aqueous Solutions of Electrolytes. *Journal of the American Chemical Society*, 74(21), pp.5274–5277. Available at: <http://pubs.acs.org/doi/abs/10.1021/ja01141a011>.
- Portier, S. & Rochelle, C., 2005. Modelling CO<sub>2</sub> solubility in pure water and NaCl-type waters from 0 to 300 °C and from 1 to 300 bar. *Chemical Geology*, 217(3-4), pp.187–199. Available at: <http://www.sciencedirect.com/science/article/pii/S0009254104004929> [Accessed February 22, 2014].
- Poulson, S., Harrington, R. & Drever, J., 1999. The solubility of toluene in aqueous salt solutions. *Talanta*, 48, pp.633–641.
- Rossi, S.S. & Thomas, W.H., 1981. Solubility behavior of three aromatic hydrocarbons in distilled water and natural seawater. *Environmental Science & Technology*, 15(6), pp.715–716. Available at: <http://dx.doi.org/10.1021/es00088a013>.
- Schwarz, F.P., 1977. Determination of temperature dependence of solubilities of polycyclic aromatic hydrocarbons in aqueous solutions by a fluorescence method. *Journal of Chemical & Engineering Data*, 22(3), pp.273–277. Available at: <http://pubs.acs.org/doi/abs/10.1021/je60074a010>.
- Sechenov, M., 1889. Über die Konstitution der Salzlösungen auf Grund ihres Verhaltens zu Kohlensäure. *Z. Phys. Chem.*, 4, p.117.
- Shaffer, D.L. et al., 2013. Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions. *Environmental Science & Technology*, 47(17), pp.9569–9583. Available at: <http://pubs.acs.org/doi/abs/10.1021/es401966e>.
- Sutton, C. & Calder, J.A., 1975. Solubility of alkylbenzenes in distilled water and sea water at 25.0 deg. *Journal of Chemical & Engineering Data*, 20(3), pp.320–322. Available at: <http://dx.doi.org/10.1021/je60066a018>.
- Whitehouse, B.G., 1985. Observation of abnormal solubility behavior of aromatic hydrocarbons in seawater. *Marine Chemistry*, 17(4), pp.277–284. Available at: <http://www.sciencedirect.com/science/article/pii/0304420385900015>.
- Whitehouse, B.G., 1984. The effects of temperature and salinity on the aqueous solubility of polynuclear aromatic hydrocarbons. *Marine Chemistry*, 14(4), pp.319–332. Available at: <http://www.sciencedirect.com/science/article/pii/0304420384900288>.
- Xie, W.-H., Shiu, W.-Y. & Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research*, 44(4), pp.429–444. Available at: <http://www.sciencedirect.com/science/article/pii/S0141113697000172>.

**Chapter 4: Determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines.**

The information presented in this chapter is part of a manuscript under preparation: Burant, A.; Lowry G.V.; Karamalidis, A.K. Validation and Modeling of the Setschenow Equation for Selected Hydrophilic Compounds in NaCl and CaCl<sub>2</sub> Simulated Brines, (2015).

## Abstract

The widespread implementation of fossil fuel related technologies will result in the production of large volumes of highly saline water containing dissolved petroleum hydrocarbons. Safe treatment, re-use, and disposal of these produced waters calls for the need to understand the fate and transport of the dissolved organic compounds, especially hydrophilic compounds, which are more difficult to remove from water. The aqueous solubility of organic compounds in saline waters is typically modeled by the Setschenow Equation, which predicts a log-linear increase in aqueous activity coefficient with increasing salt concentration related by an empirical parameter called the Setschenow constant. Setschenow constants for hydrophilic compounds in NaCl and CaCl<sub>2</sub> solutions are typically measured up to seawater concentrations of salts (about 0.5M NaCl equivalent). It is unknown whether the Setschenow Equation is valid for a variety of hydrophilic compounds, including phenols, carboxylic acids, and pyrroles in brines. Here, new Setschenow constants for phenol, p-cresol, hydroquinone, pyrrole, hexanoic acid, and 9-hydroxyfluorene were measured up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in Na-Ca brines. This work showed that those Setschenow constants measured at low salt concentration are applicable to high salt concentrations typical of oil and gas brines, meaning the salting-out effect exhibited log-linear behavior up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in those mixed electrolyte brines. In addition, this work added to a sparse database of NaCl and CaCl<sub>2</sub> Setschenow constants for hydrophilic compounds found in oil and gas reservoirs.

## Nomenclature

$\gamma_w^{DI}$ : Activity coefficient of an organic compound in deionized water

$\gamma_w^{salt}$ : Activity coefficient of an organic compound in salt water

$A_{salt}$ : Area count from the GC chromatogram after salt exposure

$A_{DI}$ : Area count from the GC chromatogram in deionized water

**BTEX**: Benzene, toluene, ethylbenzene, and the xylene isomers

**CCUS**: Carbon capture, utilization, and storage

**CO<sub>2</sub>**: Carbon dioxide

**EOR**: Enhanced oil recovery

**GC-FID**: Gas chromatography with a flame ionization detector

**I**: Ionic strength

$K_s^{i,k}$ : Setschenow constant in a single electrolyte system

$K_s^{mixed}$ : Setschenow constant in a mixed electrolyte system

**NSO**: Nitrogen, sulfur, and oxygen

**OLS**: Ordinary least squares

**PA**: Polyacrylate

**PAH**: Polycyclic aromatic hydrocarbon

**pKa**: Acid dissociation constant

**PTFE**: Polytetrafluoroethylene

**sc-CO<sub>2</sub>**: Supercritical carbon dioxide

**SE**: Standard error

**SPME**: Solid phase microextraction

**STOMP**: Subsurface transport over multiple phases

**TDS**: Total dissolved solids

## 4.1 Introduction

Fossil fuel extraction technologies, such as conventional and unconventional oil and gas extraction, and carbon capture, utilization, and storage (CCUS), including enhanced oil recovery (EOR) are also accompanied by usage and production of large volumes of saline water. With the implementation of desalination technologies expected to increase in the future, concentrated reject brines are expected to increase in volume as well. Both produced waters and reject brines potentially bear high concentrations of both hydrophobic and hydrophilic organic compounds. The treatment, re-use, and disposal of these waters calls for the need to understand the fate and transport of potential organic contaminants.

This study focuses on the fate of polar organic compounds, found in produced waters from oil and gas extraction activities, such as naturally occurring aliphatic and aromatic organic acids, phenolic compounds, and polar nitrogen compounds (Utvik 1999; Neff et al. 2011; Benko & Drewes 2008; Li et al. 1992), as well as fracking additives, such as ethylene glycol and methanol (Carter et al. 2013). Desalination reject brines may also contain similar compounds, such as polar endocrine disruptors (Radjenović et al. 2008; Al-Rifai et al. 2007), which are emerging compounds of concern. The fate of organic contaminants is dependent on the salt concentration in the produced brines.

The high concentrations of salts in oil and gas reservoirs will cause a decrease in aqueous solubility of organic compounds. The phenomenon is also known as “salting-out effect”. The total dissolved solids (TDS) content of some oil and gas formations have been reported to be as high as 400 g/L, with reported median TDS concentrations ranging from 32 g/L (Benko & Drewes 2008) to 157 g/L (Haluszczak et al. 2013). The observed high salt concentrations could potentially have a significant effect on the partitioning of both hydrophobic and hydrophilic compounds in oil and gas formations. Understanding the partitioning behavior of organic

compounds is essential for the modeling of the retardation of organic compounds along a leakage path, partitioning of organic compounds into supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>), and treatment and removal of polar organic compounds from water.

Typically, the solubility of organic compounds in salt water is modeled by Setschenow Equation (Eqn. 4.1), which predicts a log-linear increase in aqueous activity coefficient ( $\gamma_w^{DI}$  is the aqueous activity coefficient in deionized water and  $\gamma_w^{salt}$  is the activity coefficient in salt water) with increasing salt concentration ( $[salt]$ ), related by an empirical Setschenow constant ( $K_s^{i,k}$ ).

$$\log\left(\frac{\gamma_w^{salt}}{\gamma_w^{DI}}\right) = K_s^{i,k} [salt] \quad \text{Eqn. 4.1}$$

In mixed salt solutions, the Setschenow constant is considered to be additive, meaning it is a sum of the Setschenow constants based on the mole fraction of the solid salt in the system. This new Setschenow constant (Eqn. 4.2) can be applied to Eqn. 4.1 to predict aqueous solubility.

$$K_s^{i,mixed} \cong \sum_k K_s^{i,salt,k} \cdot x_k \quad \text{Eqn. 4.2}$$

Here  $K_s^{i,mixed}$  is the Setschenow constant of the mixed electrolyte system,  $K_s^{i,salt,k}$  is the Setschenow constant of organic compound ( $i$ ) in a single electrolyte solution ( $k$ ), and  $x_k$  is the mole fraction of each species in the mixture.

The Setschenow Equation has shown deviations in its ability to predict aqueous solubility of organic compounds up to high concentrations of some salts (Noubigh, Abderrabba, et al. 2007; Noubigh, Mgaidi, et al. 2007; Jochmann et al. 2006). However, these deviations are not consistent across organic compound class. Benzene, toluene, ethylbenzene, and the xylene

isomers (BTEX) have shown log-linear salting-out behavior up to 5 M NaCl (Keeley et al. 1988; Keeley et al. 1991). A few polar organic compounds, including, alcohols, aromatic acids and other aliphatic polar organic compounds have shown deviations from log-linear behavior (Noubigh, Mgaidi, et al. 2007; Noubigh, Abderrabba, et al. 2007; Jochmann et al. 2006; Baldwin 1996; Khoshkbarchi & Vera 1997). There is relatively little salting-out data on the phenolic compounds, carboxylic acids, and nitrogen containing compounds, which will be some of the most important compounds in oil and gas field brines. It will be necessary to determine whether the Setschenow constants measured at low salt concentrations for these organic compounds are valid up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and Na-Ca mixtures, typical of oil and gas field brines.

However, there are not many reported Setschenow constants for polar organic compounds of interest to oil and gas brines. To our knowledge, there are only 200 reported NaCl Setschenow constants. Of those, there are only 82 NaCl Setschenow constants for polar compounds (~ 41%). Most of these are alcohols, pharmaceuticals and personal care products, halogenated phenols, and amino acids (Xie et al. 1997; Endo et al. 2012; Ni & Yalkowsky 2003) – compounds not typically found in oil and gas brines. In addition, of the 24 reported CaCl<sub>2</sub> Setschenow constants, only three (13%) are polar organic compounds (acetic acid, 1-butanol, and 1-naphthol). This is a major data gap for polar organic compounds found in oil and gas brines.

Objective 2 was to determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines. This objective was accomplished in three parts. The first part involves determining new NaCl Setschenow constants and evaluating whether the salting-out effect is log-linear up to 5 M NaCl. The second component involves determining new CaCl<sub>2</sub> Setschenow constants and evaluating if

log-linear salting-out behavior occurred up to 2 M CaCl<sub>2</sub>. There is considerably less data for hydrophilic compounds of interest to oil and gas reservoirs, so these two tasks add to a sparse database of hydrophilic NaCl and CaCl<sub>2</sub> Setschenow constants. Finally, in the third part, it was investigated whether those Setschenow constants were applicable in predicting the salting-out effect for mixed electrolyte brines at moderate and high ionic strengths.

The salting-out effect was measured for phenol, p-cresol, hydroquinone, pyrrole, hexanoic acid, and 9-hydroxyfluorene in NaCl and CaCl<sub>2</sub> solutions. The salting-out effect was measured for p-cresol and 9-hydroxyfluorene in mixtures of NaCl and CaCl<sub>2</sub>. Phenol and hexanoic acid were chosen because it has previously reported NaCl Setschenow constants, so it could be determined if the salting-out effect at low salt concentrations could be extrapolated up to high salt concentrations. Phenolic compounds, a nitrogen-containing compound, and the carboxylic acid were studied because they represent key classes of organic compounds found in oilfield brines. The three phenolic compounds and 9-hydroxyfluorene were studied to determine mechanistic differences in the salting-out effect of those organic compounds due to the presence of polar groups.

## **4.2 Experimental**

The estimation of Setschenow constants was completed using solid phase microextraction (SPME), followed with analysis of the adsorbed organic compounds using gas-chromatography coupled with a flame ionization detector (GC-FID). This method has been used in previous studies to measure Setschenow constants (Endo et al. 2012; Jonker & Muijs 2010). The Setschenow constants were estimated by linear regression of Eqn. 4.3, where differences in area count output from the GC-FID was used to represent the change in aqueous activity coefficient (Eqn 4.3).

$$\log\left(\frac{A_{salt}}{A_{DI}}\right) = K_s^{i,k} [salt] \quad \text{Eqn. 4.3}$$

In this equation,  $A_{salt}$  is the area count from the SPME fiber after salt exposure, and  $A_{DI}$  is the area count from the SPME fiber before salt exposure (in deionized water). In this method the salt does not change the activity of the SPME fiber (Endo et al. 2012).

The SPME method implemented here is considered non-depleting. The maximum amount of organic compound removed from solution was for 9-hydroxyfluorene at 5 M NaCl, in which the depletion was 7%. All of the other depletions were less than 1% of the total moles of organic compound in the vial.

#### 4.2.1 Materials

Pyrrrole ( $\geq 98\%$ ), p-cresol (99%), hydroquinone ( $\geq 99\%$ ), hexanoic acid ( $\geq 99.5\%$ ), and 9-hydroxyfluorene (96%) were obtained from Sigma Aldrich. Phenol ( $\geq 99\%$ ) was obtained from Fisher Scientific. Sodium chloride (ACS Grade,  $\geq 99\%$ ) and calcium chloride dihydrate (ACS Grade, 99 - 105%) were obtained from Fisher Scientific. Hydrochloric acid (37%) was obtained from VWR. Sodium hydroxide solution (50% w/w/Certified) was obtained from Fisher Scientific.

The organic compounds were dissolved in ACS Grade acetone ( $\geq 99.5\%$ ) obtained from VWR. Glassware was silanized overnight with 90 vol% toluene (ACS Grade,  $\geq 99.5\%$ , Fisher Scientific) and 10 vol% dichlorodimethylsilane (99+%, Acros Organics). The vials used for analysis were cleaned with acetone and methanol (ACS grade  $\geq 99.8\%$ ), and a detergent rinse (Sparkleen, Fisher Scientific). After cleaning, they were dried at 105 °C for >1 hour. The SPME fiber used to make all of the measurements were 85  $\mu\text{m}$  polyacrylate (PA) fibers.

#### 4.2.2 Methods

Between 35 – 39 mL of deionized water (Barnstead nanopure 18.2 M $\Omega$ -cm), depending on the target salt concentration, was added to a 40 mL silanized glass vial, capped with a PTFE-lined silicone septa, and wrapped in aluminum foil to prevent exposure to light. Target organic compounds were dissolved in ACS grade acetone ( $\geq 99.5\%$ ). The amount of stock solution dissolved into the water was 200  $\mu$ L (0.5% of the solution). For 9-hydroxyfluorene, the least soluble compound, 50  $\mu$ L of the stock solution was dissolved in water. Solution masses and dilutions were performed gravimetrically ( $\pm 0.001$  g). A PTFE stir bar was added to each vial to assist achieving faster equilibrium times by stirring. The SPME fiber was exposed directly to the water for a predetermined amount of time; larger compounds typically took longer to reach equilibrium with the SPME fiber (See Appendix B.1), which was determined by conducting an uptake curve. After the SPME fiber was desorbed by direct injection in the GC inlet, salt was added to the vial, and the fiber was exposed to the solution once again. The time required for each compound to reach equilibrium between the dissolved phase and the fiber increased with increasing salt concentration, so the time the fiber was exposed to the aqueous solution was increased accordingly to ensure equilibrium was obtained at each salt concentration (See Appendix B.1). After equilibration, the stainless steel part of the needle was rinsed with DI water, and wiped off to remove the salt from the surface of the stainless steel, to protect the GC-FID and prolong fiber's life. The fibers were finally desorbed in the GC inlet for quantification of the increased amount of organic compound on the fiber. All experiments were conducted at room temperature ( $23 \pm 2^\circ\text{C}$ ). The Setschenow constant is not responsive to small changes of room temperature (May et al. 1978). The working concentrations of the organic compound in the water were below saturation in DI water, and were below saturation for all salt concentrations tested (See Appendix B.2).

The salting-out of hexanoic acid was measured in pH-adjusted solutions. This was done so the speciation of hexanoic acid would not play a role in the salting-out effect; this study was focused on the change in aqueous activity due to the presence of salt. The change in speciation of hexanoic acid due to the presence of salt has already been described elsewhere (Barriada et al. 2000). The pH of those experiments was set to 2.3 using 200  $\mu\text{L}$  of 1 M HCl. At that pH, the hexanoic acid is 99.7% protonated, so a decrease in pH, after salt addition would not have an effect on the speciation of the hexanoic acid. The SPME fiber was exposed to a hexanoic acid solution with a pH adjusted to 6. This corresponded to hexanoic acid being 7% protonated. There was no corresponding sorption to the SPME fiber (there was no corresponding peak on the GC chromatogram).

The organic compound analysis was carried out with a GC-FID (Agilent 6890A) equipped with a split/splitless injector. Helium at 23 mL/min was used as the carrier gas. The inlet temperature was set at 280  $^{\circ}\text{C}$  for 85  $\mu\text{m}$  PA fibers. The fiber was desorbed for two minutes in the inlet. The column used was a DB-FFAP, which is a nitroterephthalic acid modified polyethylene glycol column (30 m $\times$ 250  $\mu\text{m}\times$ 0.25  $\mu\text{m}$  Agilent J&W), which was used so no derivitization of the polar compounds was necessary. For 9-hydroxyfluorene, the column used was 30m $\times$ 320  $\mu\text{m}\times$ 0.25  $\mu\text{m}$  5% phenyl-95% methyl (HP-5, J&W Scientific). The oven program varied across analytes. The FID was kept at a temperature of 320  $^{\circ}\text{C}$ .

The NaCl salt concentrations measured were 1 M, 2 M, 3 M, 4 M, and 5 M NaCl. The CaCl<sub>2</sub> salt concentrations measured were 0.5 M, 1 M, 1.5 M, and 2 M (triplicates were also performed at 0.25 and 0.75 CaCl<sub>2</sub> for pyrrole). These were chosen because they are the relevant concentrations of oil and gas reservoirs. The mixed electrolytes systems were for p-cresol and 9-hydroxyfluorene at ionic strengths of 1.5 M (0.75 M NaCl, 0.25 M CaCl<sub>2</sub>), 2.0 M (0.5 M NaCl,

0.5 M CaCl<sub>2</sub>), 2.5 M (0.25 M NaCl, 0.75 M CaCl<sub>2</sub>), and 5 M (2 M NaCl, 1 M CaCl<sub>2</sub>). The Setschenow constants reported here were estimated from ordinary least-squares (OLS) linear regressions of log change in area against salt concentration, as in Eqn. 3, performed in MATLAB using the Statistics Toolbox [MATLAB R2013A].

### 4.3 Results and Discussion

Reported Setschenow constants for the organic compounds of interest in this study are given in **Table 4.1**. For all the compounds measured here, the salting-out effect was log-linear up to 5 M NaCl and 2 M CaCl<sub>2</sub>. The percent depleted from each sample vial was low (Appendix B.2) and all of the working concentrations of the organic compounds were well below the saturation aqueous solubility of these compounds (Appendix B.2). In addition, the standard errors (**Table 4.1**) were low for the compounds of this study.

Both phenol and hexanoic acid have had previously measured NaCl Setschenow constants. For phenol, NaCl Setschenow constant published here is within the range of previously published Setschenow constants (**Table 4.1**). For hexanoic acid, the Setschenow constant is 0.02 M<sup>-1</sup>, showing that this method produces NaCl Setschenow constants close to the literature values.

**Table 4.1.** Previously reported, model predicted, and experimentally determined NaCl and CaCl<sub>2</sub> Setschenow Constants.

Organic Compound	Previously reported NaCl K <sub>s</sub> (M <sup>-1</sup> )	NaCl K <sub>s</sub> (M <sup>-1</sup> )	R <sup>2</sup>	sp-CaCl <sub>2</sub> LFER predicted K <sub>s</sub> (M <sup>-1</sup> )	CaCl <sub>2</sub> K <sub>s</sub> (M <sup>-1</sup> )	R <sup>2</sup>
Phenol (Xie et al. 1997; Bergen & Long 1956; Morrison 1944)	0.111, 0.172, 0.183	0.139±0.012	0.903	0.205	0.313±0.031	0.892
Pyrrole	N/A	0.148±0.012	0.916	0.217	0.182±0.009	0.967
p-Cresol	N/A	0.194±0.011	0.952	0.279	0.300±0.027	0.907
Hydroquinone	N/A	0.078±0.004	0.963	0.124	0.112±0.007	0.953
Hexanoic Acid(Ni & Yalkowsky 2003)	0.22 <sup>^</sup>	0.240±0.019	0.921	0.341	0.359±0.021	0.955
9-Hydroxyfluorene	N/A	0.234±0.019	0.903	0.330	0.295±0.029	0.879

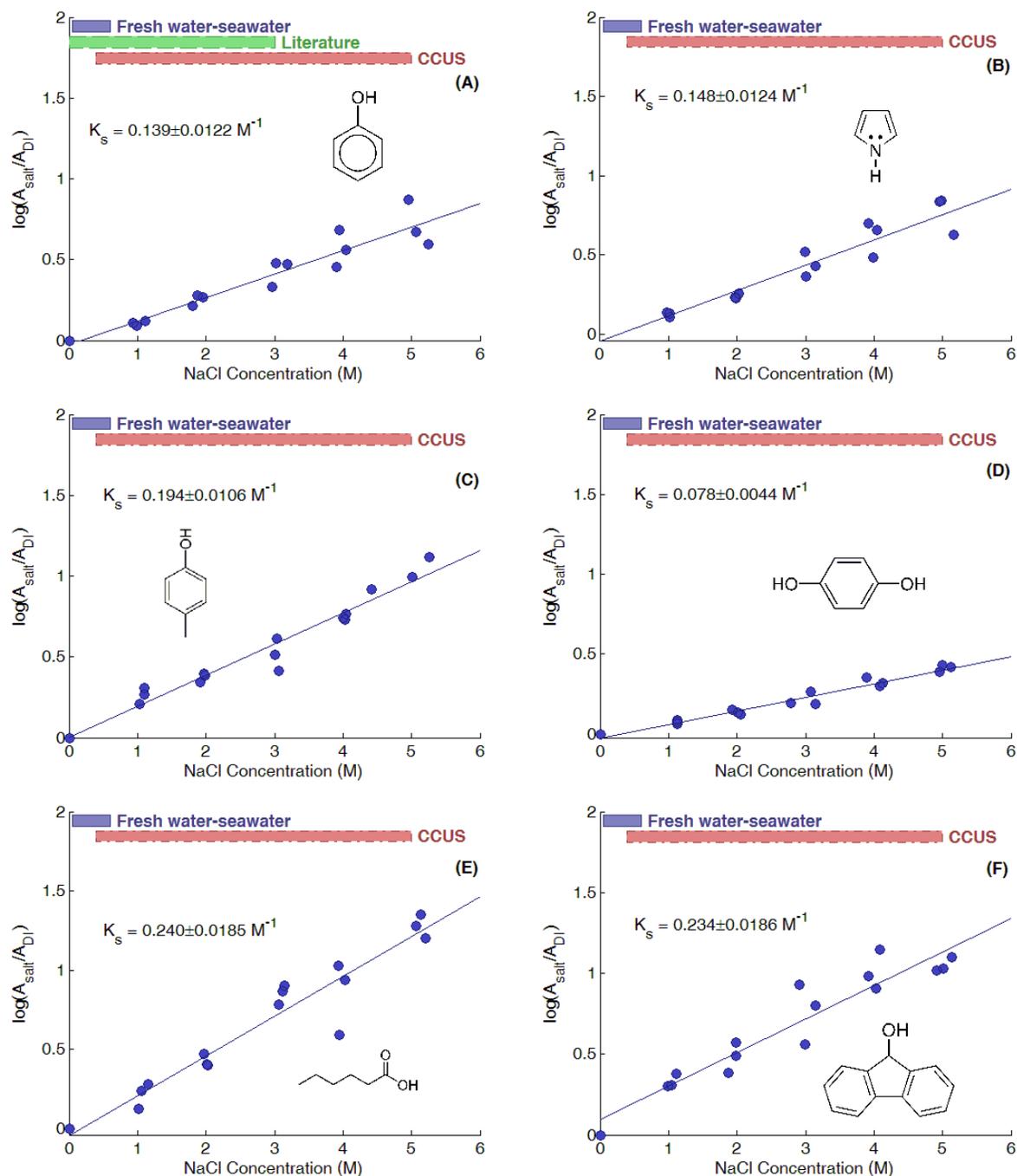
<sup>^</sup>Unknown salinity concentrations

\*log  $K_{ow}$  calculated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)

#### 4.3.1 NaCl Setschenow constants

The phenolic compounds were chosen to determine the trend in adding a methyl and hydroxyl group, i.e. decreasing and increasing the hydrophilicity of the compound, with respect to phenol. In addition, neither p-cresol nor hydroquinone has reported NaCl or CaCl<sub>2</sub> Setschenow constants. An addition of a methyl group (i.e. p-cresol) increases the NaCl Setschenow constant, where the presence of another hydroxyl group (i.e. hydroquinone) decreases it. The NaCl Setschenow constant for hydroquinone is one of the lowest reported NaCl Setschenow constants, showing that the addition of two hydroxyl groups significantly decreases the Setschenow constant, relative to the parent compound of benzene ( $K_s^{i,NaCl} = 0.19 \text{ M}^{-1}$ ).

This decrease in Setschenow constant due to the addition of a hydroxyl group also occurred for 9-hydroxyfluorene (in comparison to its parent compound, fluorene ( $K_s = 0.281 \pm 0.038 \text{ M}^{-1}$ )). The addition of the hydroxyl group on the hetero-bridge on the fluorene molecule, despite resulting in an increase in molar volume, decreased the NaCl Setschenow constant, in comparison to fluorene. This shows that there is a polar interaction occurring that is possibly leading to lower Setschenow constants.



**Figure 4.1** The effect of salt addition (i.e.  $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of selected organic compounds onto the SPME fiber as for A) phenol, B) pyrrole, C) p-cresol, D) hydroquinone, E) hexanoic acid, and F) 9-hydroxyfluorene. Colored bars represent ranges of salt concentrations for previously reported Setschenow constants (green); seawater (blue bars) and for CCUS conditions 0.6 M-5 M NaCl (this study, red bars). The valid range of  $K_s$  estimates are indicated by the black regression line. Reported constants ( $K_s$ ) are the regression mean  $\pm 2 \cdot \text{SE}$ .

The salting-out effect of hexanoic acid was measured at a fixed pH to control for salt effects. The effect of salt on the pKa of hexanoic acid has been studied elsewhere and is well-modeled by the Pitzer Equation (Barriada et al. 2000; Pitzer 1980). See Barriada et al. (2000) for the relevant equations. (Appendix B.4 reports the change in pKa of hexanoic acid with increasing NaCl concentration). The goal of this study was to determine if the NaCl Setschenow constant of the protonated version measured at low salinities could predict the salting-out effect at high salinities, which it did. The salting-out effect for hexanoic acid was log-linear up to 5 M NaCl, meaning the neutral acid has potential to partition to other phases due to increased salinity.

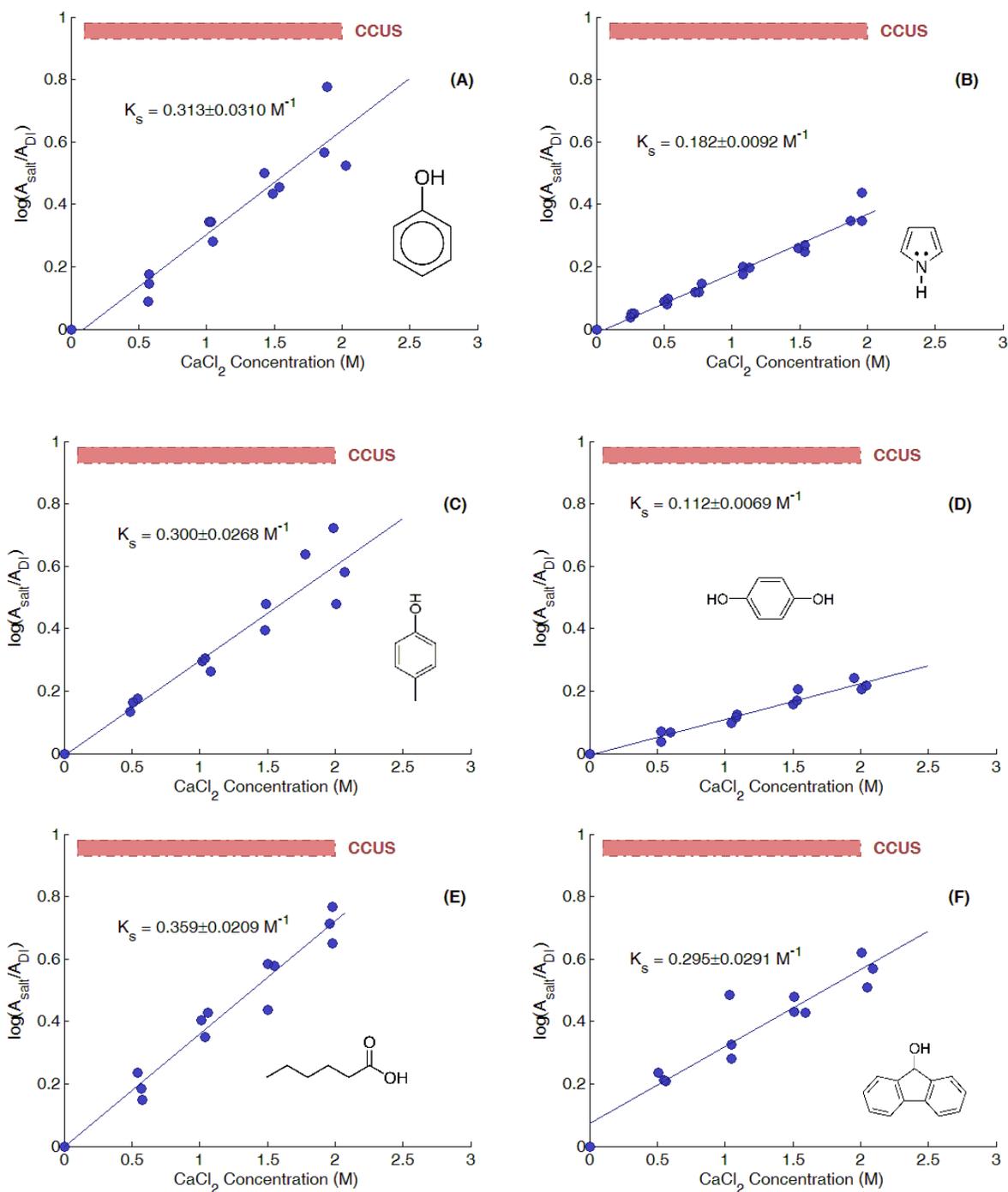
No deviations from log-linear salting-out for these organic compounds up to 5 M NaCl (*Figure 4.1*) were observed. Other studies have shown that several polar organic compounds exhibited deviations from log-linear salting-out behavior.(Noubigh, Mgaidi, et al. 2007; Noubigh, Abderrabba, et al. 2007; Jochmann et al. 2006) It is possible that there are additional intermolecular interactions occurring for those specific compounds that are not occurring for others, which are leading to these deviations.

#### **4.3.2 CaCl<sub>2</sub> Setschenow constants**

The newly calculated CaCl<sub>2</sub> Setschenow constants for phenol, p-cresol, hydroquinone, pyrrole, hexanoic acid, and 9-hydroxyfluorene, add to the sparse database of CaCl<sub>2</sub> Setschenow constants. The salting-out effect was log-linear for all of the target organic compounds up to 2 M CaCl<sub>2</sub> (*Figure 4.2*). All of the experimental CaCl<sub>2</sub> Setschenow constants reported here are greater than their respective NaCl Setschenow constants, as expected. Several compounds in this dataset have higher than expected CaCl<sub>2</sub> Setschenow constants. Phenol has an especially high CaCl<sub>2</sub> Setschenow constant. Other small organic compounds have exhibited similar behavior: Benzene has a reported CaCl<sub>2</sub> Setschenow constant at 0.33 M<sup>-1</sup>, higher than its NaCl Setschenow constant at 0.19 M<sup>-1</sup> (Boddu et al. 2001; Endo et al. 2012). Benzene has a higher CaCl<sub>2</sub> Setschenow

constant than toluene (however,  $K_s^{toluene,NaCl} > K_s^{benzene,NaCl}$ ) (Poulson et al. 1999). This also occurred for thiophene ( $K_s^{i,CaCl_2} = 0.295 \text{ M}^{-1}$  versus  $K_s^{i,NaCl} = 0.165 \text{ M}^{-1}$ ); in fact thiophene has a greater  $\text{CaCl}_2$  Setschenow constant than benzothiophene and dibenzothiophene, both of which have higher  $\text{NaCl}$  Setschenow constants than the  $\text{NaCl}$  Setschenow constant of thiophene.

All reported  $\text{CaCl}_2$  Setschenow constants are larger than their corresponding  $\text{NaCl}$  Setschenow constants; however this increase in magnitude of salting-out effect is not consistent for all organic compounds. This highlights that there are additional intermolecular interactions occurring in  $\text{CaCl}_2$  systems that are not applicable to  $\text{NaCl}$  systems.

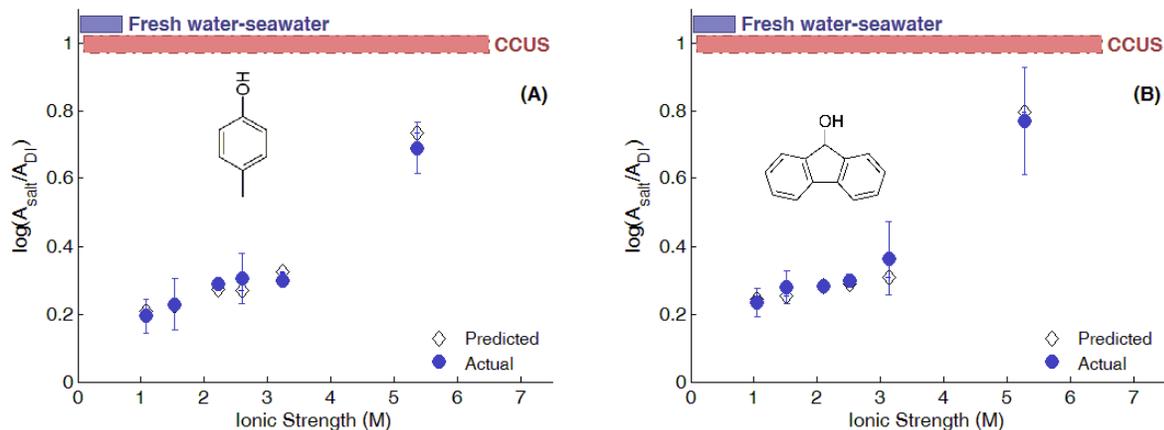


**Figure 4.2** The effect of salt addition (i.e.  $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of selected organic compounds onto the SPME fiber as for A) phenol, B) pyrrole, C) p-cresol, D) hydroquinone, E) hexanoic acid, and F) 9-hydroxyfluorene. Red bars represent ranges of salt concentrations for CCUS conditions 0.1 M-2 M  $\text{CaCl}_2$ . The valid range of  $K_s$  estimates are indicated by the black regression line. Reported constants ( $K_s$ ) are the regression mean  $\pm 2 \cdot \text{SE}$ .

### 4.3.3 Mixed Electrolytes

The additivity of the Setschenow Equation was investigated for p-cresol and 9-hydroxyfluorene. These organic compounds were chosen for two reasons. First, Poulson, et al., hypothesized that the Setschenow constant would not be additive for organic compounds with a dipole moment (Poulson et al. 1999). This was not the case in an investigation of the salting-out of thiophene, which has a dipole moment of  $\mu = 0.536$  Debye in mixed electrolyte brines. The NaCl and CaCl<sub>2</sub> Setschenow constants for thiophene were additive in those mixed electrolyte solutions. However, since p-cresol and 9-hydroxyfluorene are both polar organic compounds, with hydroxyl groups, it was hypothesized that this may contribute to deviations from expected behavior. Second, p-cresol and 9-hydroxyfluorene have differing sizes, and it was investigated whether size would play a role in deviations from salting-out behavior.

The Setschenow constants for both p-cresol and 9-hydroxyfluorene were additive in NaCl and CaCl<sub>2</sub> brines in moderate and high ionic strengths (*Figure 4.3*). The predicted mixed electrolyte Setschenow constants based on the Setschenow constants measured in single electrolyte solutions of NaCl and CaCl<sub>2</sub> are all within the standard deviations of the experimental triplicate measurements of the mixed electrolytes at moderate and high ionic strengths, representative of oil and gas brines. This means that Setschenow constants of inorganic salts are expected to be additive for similar types of compounds in this study.



**Figure 4.3** The salting-out effect (i.e.  $\log(A_{\text{salt}}/A_{\text{DI}})$ ) of individual organic compounds onto the SPME fiber as a function of ionic strength (M) for A) p-Cresol, and B) 9-Hydroxyfluorene. Colored bars represent salt concentrations for Setschenow constants reported for: Blue bars in seawater; red bars in CCUS 0.1 – 7M I. The diamonds represent predicted values based on the respective single electrolyte Setschenow constants, and the blue circles (with standard deviations) represent the actual measured values in this study.

#### 4.3.4 Implications

The Setschenow Equation is valid in predicting a log-linear decrease in aqueous solubility for all of the organic compounds in this study up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in Na-Ca-Cl mixtures. This salt range is applicable to many reservoir and desalination brines. The Setschenow constants for many polar organic compounds can be incorporated into models, such as STOMP and TOUGHREACT (Ward et al. 2005; Xu et al. 2006), to predict aqueous solubility and partitioning coefficients for organic compounds in CCUS sites. While the Setschenow Equation was proven to be valid in predicting the salting-out effect for the organic compounds in this study, these compounds are only representative of phenolic compounds with up to two polar groups, carboxylic acids up to C<sub>6</sub>, and aromatic and heterocyclic organic compounds with up to three rings. More data are necessary on aliphatic organics, such as the alcohols, larger polar organic compounds and organic compounds with multiple polar substituents.

Many polar compounds have relatively high aqueous solubility, meaning that at high salt concentrations these organic compounds could still possibly have high aqueous concentrations. These polar organic compounds, therefore, are more difficult to remove from water. The data presented in this study could be used to exploit removal of polar compounds from water in treatment technologies.

The injection of CO<sub>2</sub> into formations with dissolved organic acids could change the partitioning of those organic compounds, especially those sites with high salt concentrations. Hexanoic acid, with a  $K_s^{i,NaCl} = 0.24 \text{ M}^{-1}$  and a  $K_s^{i,CaCl_2} = 0.359 \text{ M}^{-1}$ , could possibly have increased partitioning to solids or supercritical CO<sub>2</sub>. However, this will be dependent on both the pH and salt concentration of the system. A survey of selected oil and gas reservoirs shows that the pH of these selected oil and gas reservoir brines is typically between 6 – 8 (Kharaka et al. 2006; Kharaka & Hanor 2003; Haluszczak et al. 2013). The injection of CO<sub>2</sub> will cause an initial decrease in pH, however due to the buffering capacity of many of the formations; the pH may not decrease noticeably (Kharaka et al. 2006; Emberley et al. 2004; Lu et al. 2012). These organic acids, such as hexanoic acid and other monocarboxylic acids, will still be in the ionized form and therefore will have limited salting-out. This phenomenon will vary from site to site. For some formations, such as the central Mississippi Salt Dome Basin, the pH of the Rodessa and Smackover production zones, are 5.08 and 5.48, respectively (Kharaka et al. 2006). The sites in the Mississippi Salt Dome Basin also have high TDS concentrations at 320 g/L and 275 g/L, respectively. The pKa of the organic acids are expected to increase.

#### 4.5 Supplementary Information

Appendix B contains experimental details about SPME, predicted depletion and aqueous solubility for each compound based on the Setschenow Equation, Abraham solvation parameters, the change in  $pK_a$  with salt concentration for hexanoic acid, and information about oil and gas reservoir brines, along with speciation of selected organic compounds.

#### 4.6 References

- Al-Rifai, J.H., Gabelish, C.L. & Schäfer, A.I., 2007. Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. *Chemosphere*, 69(5), pp.803–815. Available at: <http://www.sciencedirect.com/science/article/pii/S0045653507005966>.
- Baldwin, R.L., 1996. How Hofmeister ion interactions affect protein stability. *Biophysical Journal*, 71(4), pp.2056–2063. Available at: <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1233672/>.
- Barriada, J.L., Brandariz, I. & de Vicente, M.E., 2000. Acid–Base Equilibria of Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations. *Journal of Chemical & Engineering Data*, 45(6), pp.1173–1178. Available at: <http://dx.doi.org/10.1021/je000150p>.
- Benko, K.L. & Drewes, J.E., 2008. Produced Water in the Western United States: Geographical Distribution, Occurrence, and Composition. *Environmental Engineering Science*, 25(2), pp.239–246. Available at: <http://dx.doi.org/10.1089/ees.2007.0026>.
- Bergen, R.L. & Long, F.A., 1956. The Salting in of Substituted Benzenes by Large Ion Salts. *The Journal of Physical Chemistry*, 60(8), pp.1131–1135. Available at: <http://dx.doi.org/10.1021/j150542a024>.
- Boddu, V.M., Krishnaiah, A. & Viswanath, D.S., 2001. Liquid–Liquid Equilibria of the Benzene + Water + Acetic Acid Ternary System and Solubility of Benzene in Water: Effect of Calcium Chloride. *Journal of Chemical & Engineering Data*, 46(5), pp.1172–1175. Available at: <http://pubs.acs.org/doi/abs/10.1021/je000196i>.
- Carter, Kimberly E.; Hakala, J. Alexandra; Hammack, R.W., 2013. Hydraulic Fracturing and Organic Compounds - Uses, Disposal and Challenges. In *Society of Petroleum Engineers*. pp. 1–11.
- Emberley, S. et al., 2004. Geochemical monitoring of fluid-rock interaction and CO<sub>2</sub> storage at the Weyburn CO<sub>2</sub>-injection enhanced oil recovery site, Saskatchewan, Canada. *Energy*, 29(9-10), pp.1393–1401. Available at: <http://www.sciencedirect.com/science/article/pii/S0360544204001562> [Accessed February 21, 2014].
- Endo, S., Pfennigsdorff, A. & Goss, K.-U., 2012. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. *Environmental science & technology*, 46(3), pp.1496–503. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22191628>.
- Haluszczak, L.O., Rose, A.W. & Kump, L.R., 2013. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry*, 28, pp.55–61.

- Available at: <http://www.sciencedirect.com/science/article/pii/S0883292712002752> [Accessed December 1, 2014].
- Jochmann, M.A., Kmiecik, M.P. & Schmidt, T.C., 2006. Solid-phase dynamic extraction for the enrichment of polar volatile organic compounds from water. *Journal of chromatography. A*, 1115(1-2), pp.208–16. Available at: <http://www.sciencedirect.com/science/article/pii/S0021967306004535> [Accessed April 18, 2014].
- Jonker, M.T.O. & Muijs, B., 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere*, 80, pp.223–227.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1988. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: benzene and toluene. *Journal of Chemical & Engineering Data*, 33(2), pp.87–89. Available at: <http://pubs.acs.org/doi/abs/10.1021/jc00052a006>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1991. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: C<sub>2</sub>-Substituted benzenes. *Journal of Chemical & Engineering Data*, 36(4), pp.456–459. Available at: <http://pubs.acs.org/doi/abs/10.1021/jc00004a032>.
- Kharaka, Y.K., Cole, D.R. & Hovorka, S.D., 2006. Gas-water-rock interactions in Frio Formation following CO<sub>2</sub> injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology*, 34(7), p.577. Available at: <http://geology.gsapubs.org/cgi/doi/10.1130/G22357.1> [Accessed February 13, 2014].
- Kharaka, Y.K. & Hanor, J.S., 2003. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In E.-C. H. D. Holland & K. K. Turekian, eds. *Treatise on Geochemistry*. Oxford: Pergamon, pp. 1–48. Available at: <http://www.sciencedirect.com/science/article/pii/B0080437516050854>.
- Khoshkbarchi, M.K. & Vera, J.H., 1997. Effect of NaCl and KCl on the Solubility of Amino Acids in Aqueous Solutions at 298.2 K: Measurements and Modeling. *Industrial & Engineering Chemistry Research*, 36(6), pp.2445–2451. Available at: <http://dx.doi.org/10.1021/ie9606395>.
- Li, M. et al., 1992. Liquid chromatographic separation schemes for pyrrole and pyridine nitrogen aromatic heterocycle fractions from crude oils suitable for rapid characterization of geochemical samples. *Analytical Chemistry*, 64(13), pp.1337–1344. Available at: <http://dx.doi.org/10.1021/ac00037a007>.
- Lu, J. et al., 2012. CO<sub>2</sub>-rock-brine interactions in Lower Tuscaloosa Formation at Cranfield CO<sub>2</sub> sequestration site, Mississippi, U.S.A. *Chemical Geology*, 291, pp.269–277. Available at: <http://www.sciencedirect.com/science/article/pii/S0009254111004293> [Accessed July 7, 2014].
- May, W.E., Wasik, S.P. & Freeman, D.H., 1978. Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. *Analytical Chemistry*, 50(7), pp.997–1000. Available at: <http://pubs.acs.org/doi/abs/10.1021/ac50029a042>.
- Morrison, T.J., 1944. The salting-out effect. *Trans. Faraday Soc.*, 40(0), pp.43–48. Available at: <http://dx.doi.org/10.1039/TF94444000043>.
- Neff, J., Lee, K. & Deblois, E.M., 2011. Produced Water : Overview of Composition , Fates , and Effects. *Produced Water*, pp.3–54.
- Ni, N. & Yalkowsky, S.H., 2003. Prediction of Setschenow constants. *International journal of pharmaceutics*, 254, pp.167–172.

- Noubigh, A., Mgaidi, A., et al., 2007. Effect of salts on the solubility of phenolic compounds: experimental measurements and modelling. *Journal of the Science of Food and Agriculture*, 87(5), pp.783–788. Available at: <http://dx.doi.org/10.1002/jsfa.2762>.
- Noubigh, A., Abderrabba, M. & Provost, E., 2007. Temperature and salt addition effects on the solubility behaviour of some phenolic compounds in water. *The Journal of Chemical Thermodynamics*, 39(2), pp.297–303. Available at: <http://www.sciencedirect.com/science/article/pii/S0021961406001546> [Accessed December 11, 2014].
- Pitzer, K.S., 1980. Electrolytes. From dilute solutions to fused salts. *Journal of the American Chemical Society*, 102(9), pp.2902–2906. Available at: <http://pubs.acs.org/doi/abs/10.1021/ja00529a006>.
- Poulson, S., Harrington, R. & Drever, J., 1999. The solubility of toluene in aqueous salt solutions. *Talanta*, 48, pp.633–641.
- Radjenović, J. et al., 2008. Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. *Water research*, 42(14), pp.3601–10. Available at: <http://www.sciencedirect.com/science/article/pii/S0043135408002248> [Accessed May 8, 2015].
- Utvik, T.I.R., 1999. Chemical characterisation of produced water from four offshore oil production platforms in the North Sea. *Chemosphere*, 39(15), pp.2593–2606. Available at: <http://www.sciencedirect.com/science/article/pii/S004565359900171X>.
- Ward, A.L. et al., 2005. *STOMP: Subsurface Transport Over Multiple Phases. Version 1.0: Addendum: Sparse Vegetation, Evapotranspiration Model for the Water-Air-Energy Operational Mode. (PNNL-15465)*, Available at: [http://www.pnl.gov/main/publications/external/technical\\_reports/PNNL-15465.pdf](http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15465.pdf).
- Xie, W.-H., Shiu, W.-Y. & Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research*, 44(4), pp.429–444. Available at: <http://www.sciencedirect.com/science/article/pii/S0141113697000172>.
- Xu, T. et al., 2006. TOUGHREACT—A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration. *Computers & Geosciences*, 32(2), pp.145–165. Available at: <http://www.sciencedirect.com/science/article/pii/S0098300405001500> [Accessed April 17, 2015].

**Chapter 5: Evaluate, update, and create new models for the prediction of Setschenow constants.**

The information presented in this chapter is part of two manuscripts under preparation: Burant, A.; Lowry, G.V.; Karamalidis, A.K. Measuring and Modeling of the Setschenow Equation for Hydrophobic Compounds in Simulated Oil and Gas Binary Brines, (2015), *submitted*.

Burant, A.; Lowry G.V.; Karamalidis, A.K. Validation and Modeling of the Setschenow Equation for Selected Hydrophilic Compounds in NaCl and CaCl<sub>2</sub> Simulated Brines, (2015).

## Abstract

There are hundreds of organic compounds found in oil and gas reservoirs, including both petroleum and synthetic hydrocarbons. Risk assessment modeling may require aqueous solubility data of those organic compounds in saline solutions. Since there are ~200 NaCl Setschenow constants and only ~19 CaCl<sub>2</sub> Setschenow constants, this calls for the need for accurate models to predict these unknown Setschenow constants. Here, the two available models, or linear free energy relationships (LFERs), for predicting NaCl Setschenow constants are evaluated. The first LFER uses octanol-water partitioning coefficients ( $\log K_{ow}$ ). The other model, a poly-parameter (pp-) LFER uses Abraham solvation parameters (ASPs) to predict NaCl Setschenow constants. Both the  $\log K_{ow}$  LFER and the pp-LFER have good agreement with experimental NaCl Setschenow constants; however the  $\log K_{ow}$  LFER has a better balance of goodness of fit and simplicity than the pp-LFER. In addition, not all organic compounds have available ASPs, so the  $\log K_{ow}$  can be used to predict NaCl Setschenow constants for those organic compounds. Both of these models were then updated with all of the available literature data, which increased the confidence in both models, as each has a wider range of organic compound classes in each model. Classes of organic compounds in these models include monopolar substituted benzenes, chlorinated ethanes and ethenes, alcohols, polycyclic aromatic hydrocarbons, ketones, carboxylic acids, chlorinated benzenes, carboxylic acid esters, alkanes and cycloalkanes, substituted phenols, and polar nitrogens, among others. Finally, new single parameter (sp-) LFERs were developed to predict Setschenow constants for CaCl<sub>2</sub>, KCl, LiCl, and NaBr from NaCl Setschenow constants. These LFERs can be incorporated into reactive transport models for prediction of aqueous solubility.

## Nomenclature

$\alpha$  : P-value

$\alpha_2$  : Hydrogen bonding acidity of the organic compound

$\beta_0$  : Compressibility of water

$\beta_2$  : Hydrogen bonding basicity of the organic compound

$\pi_2$  : Polarizability of the organic compound

$\gamma_w^{DI}$  : Activity coefficient of an organic compound in deionized water

$\gamma_w^{salt}$  : Activity coefficient of an organic compound in salt water

**ASP**: Abraham solvation parameters

**BTEX**: Benzene, toluene, ethylbenzene, and the xylene isomers

**CCUS**: Carbon capture, utilization, and storage

**CO<sub>2</sub>**: Carbon dioxide

**CV**: Cross-validation

$D_i$  : Cook's Distance

$e_i$  : Calculation of the deleted residual

**EOR**: Enhanced oil recovery

**GC-FID**: Gas chromatography with a flame ionization detector

$h_{ii}$  : *ith* element on the main diagonal of the hat matrix between 0 and 1.

**I**: Ionic strength

$K_{ow}$ : Octanol water partitioning coefficient

$K_s^{i,k}$  : Setschenow constant in a single electrolyte system

$K_s^{mixed}$  : Setschenow constant in a mixed electrolyte system

**LFER**: Linear free energy relationship

*MSE* : Mean square error of the original model

**NSO**: Nitrogen, sulfur, and oxygen

**n**: Number of observations

**OLS**: Ordinary least squares

$p$  : Number of predictor variables

**PAH**: Polycyclic aromatic hydrocarbon

**pKa**: Acid dissociation constant

**pp-LFER**: Poly parameter linear free energy relationship

$R_2$  : Index of refraction of the organic compound

**RMSE**: Root mean square error

**sc-CO<sub>2</sub>**: Supercritical carbon dioxide

**SDR**: Studentized deleted residuals

**SE**: Standard error

**sp-LFER**: Single parameter linear free energy relationship

**SPME**: Solid phase microextraction

**STOMP**: Subsurface transport over multiple phases

$t_{n-p-1}$  :t-distribution

**TDS**: Total dissolved solids

$V_2$  : Molar volume of the organic compound

$V_s$  : Molar volume of the pure (liquid) electrolyte

$\overline{V}_s^0$  : Partial molar volume of the electrolyte at infinite dilution

**vdW**: van der Waals

$\hat{y}_j$  : Prediction from the full regression model for observation  $j$ ,

$\hat{y}_{j(i)}$  : Prediction for the observation  $j$  from a refitted regression model when it has been removed from the dataset

## 5.1 Introduction

There are hundreds of petroleum hydrocarbons found in oil and gas reservoirs, as well as many more synthetic hydrocarbons that are used in energy extraction activities (Carter, et al 2013; Reddy et al. 2012). Many additional organic compounds, such as pesticides, pharmaceuticals and personal care products (PPCPs) (Al-Rifai et al. 2007), are found in desalination brines. This suggests that Setschenow constants for many organic compounds relevant to oil and gas brines will be needed to predict aqueous solubility; however, there are currently only ~200 reported NaCl Setschenow constants and ~19 reported CaCl<sub>2</sub> Setschenow constants. In addition, there are few reported Setschenow constants for other salts. The salts with the most available data include KCl (~47 reported Setschenow constants), LiCl (~27 reported Setschenow constants), and NaBr (~22 reported Setschenow constants).

Avoiding experimental determination of new Setschenow constants is desirable, especially for CaCl<sub>2</sub>, KCl, LiCl, and NaBr as data are especially sparse. This will require the use of predictive models. One of the first equations used to predict a Setschenow constant for any salt, was the McDevit-Long Equation (Eqn. 5.1):

$$K_s^{i,k} = \frac{\bar{V}_i^0(V_s - \bar{V}_s^0)}{2.3\beta_0 RT} \quad \text{Eqn. 5.1.}$$

Here  $\bar{V}_i^0$  is the partial molar volume of the solute an infinite dilution,  $V_s$  is the molar volume of the pure (liquid) electrolyte, or the volume that the salt occupies as a liquid,  $\bar{V}_s^0$  is the partial molar volume of the electrolyte at infinite dilution,  $\beta_0$  is the compressibility of water,  $R$  is the universal gas constant, and  $T$  is the temperature. This requires experimental data on volume of the salt as a liquid ( $V_s$ ) that cannot be directly measured (McDevit & Long 1952). In addition, this model has considerable error even when all parameters are available (Sanemasa et al. 1984).

Models with readily available parameters are needed to avoid experimental determination of Setschenow constants.

This can potentially be achieved through linear free energy relationships (LFERs), which are often used to estimate environmentally relevant parameters, such as vapor pressure, aqueous solubility, octanol-water partitioning coefficient ( $\log K_{ow}$ ), and partitioning from water to sc-CO<sub>2</sub> (Schwarzenbach et al. 2003). Note that all the current modeling approaches using LFERs are for NaCl Setschenow constants. The first modeling approaches for LFERs to predict NaCl Setschenow constants have used molar volume, with only slight success (Long & McDevit 1952; Xie et al. 1997; Endo et al. 2012; McDevit & Long 1952; Jonker & Muijs 2010). Qualitatively, it has been observed that compounds with larger molar volumes tend to have higher Setschenow constants. However this relationship only has an  $R^2 = 0.513$ , and does not capture any of the trends in polarity with the salting-out effect.

Another single parameter (sp) LFER for prediction of NaCl Setschenow constants involves using octanol-water partitioning coefficients (Ni & Yalkowsky 2003).  $\log K_{ow}$  is a good qualitative proxy for Setschenow constants, because both follow trends in size and polarity. It has been observed that apolar and monopolar compounds with high  $\log K_{ow}$  tend to have larger Setschenow constants than polar compounds, with lower  $\log K_{ow}$ . In addition, larger compounds with larger  $\log K_{ow}$  tend to have larger Setschenow constants than small compounds. The first attempt to capture these trends in a model to predict NaCl Setschenow constants was by regressing  $\log K_{ow}$  with measured NaCl Setschenow constants (Eqn. 5.2) (Ni & Yalkowsky 2003). This study showed good agreement between the predicted and experimental NaCl Setschenow constants. However, Endo et al. (2012) could not reproduce this simple fit using different compounds ( $n=43$ ,  $R^2=0.50$ ). Rather, Endo et al. (2012) developed a poly-parameter

linear free energy relationship (pp-LFER), which incorporates Abraham solvation parameters (ASPs) to account for size and intermolecular interactions, such as van der Waals forces and hydrogen bonding interactions, (Eqn. 5.3) to predict NaCl Setschenow constants.

$$K_s^{i,NaCl} = 0.040 \log K_{ow} + 0.114 \quad \text{Eqn. 5.2}$$

( $R^2_{adj}=0.770$ , Root Mean Square Error (RMSE) = 0.041, n=101)

$$K_s^{i,NaCl} = 0.112 - 0.020R_2 - 0.042\pi_2 - 0.047\alpha_2 - 0.060\beta_2 + 0.171V_2 \quad \text{Eqn. 5.3}$$

( $R^2_{adj} = 0.807$ , RMSE = 0.029, n= 43)

The coefficients in Eqn. 5.3 are the ASPs. The  $R_2$  is the index of refraction of the organic compound,  $\pi_2$  is the organic compounds polarizability,  $\alpha_2$  is the hydrogen bonding acidity of the organic compound,  $\beta_2$  is the hydrogen bonding basicity of the organic compound, and  $V_2$  is the molar volume of the compound. Since there are more predictor variables in the pp-LFER, the RMSE is lower for the pp-LFER than the RMSE for the log  $K_{ow}$  LFER.

Useful models only exist for the prediction of NaCl Setschenow constants. No LFER models have been developed to predict Setschenow constants for  $\text{CaCl}_2$ , KCl, LiCl, and NaBr. However models for prediction of  $\text{CaCl}_2$  Setschenow constants are essential to predict solubility of organic compounds in saline waters associated with CCUS and EOR.

The objective of this study is to evaluate, update, and develop models for the prediction of Setschenow constants. This objective will be accomplished in three parts. The first part involves evaluating the log  $K_{ow}$  LFER and pp-LFER for prediction of NaCl Setschenow constants. This will involve analyzing and comparing the model predictions to the experimental data collected in Chapters 3 and 4. In the second part, the log  $K_{ow}$  LFER and pp-LFER will be

updated with the experimental data collected in those chapters, as well as other literature data. Finally, respective single parameter (sp) LFERs will be developed for the prediction of CaCl<sub>2</sub>, KCl, LiCl, and NaBr Setschenow constants from NaCl Setschenow constants (i.e. the development of four new sp-LFERs).

## 5.2 Modeling Methods

The pp-LFER, log K<sub>ow</sub> LFER, and single parameter linear free energy relationships (sp-LFERs) for predicting CaCl<sub>2</sub>, KCl, LiCl, and NaBr Setschenow constants from NaCl constants were developed from ordinary least squares (OLS) linear regression using data from literature and data measured in Chapters 3 and 4. The model was validated and parameter uncertainty was evaluated using repeated k-fold cross-validation (CV) (Kohavi 1995). In this method the data was randomly divided into k-blocks (i.e. a set of Setschenow constants) of nearly equivalent size. The linear model was fit (or “trained”) using k-1 blocks of data while one block of Setschenow constants was left out. The predictive accuracy (reported here as RMSE) of the model was then tested using these excluded data. For this study the data were split into k = 10 partitions. To account for the small sample size (which may lead to large variance or high bias), the 10-fold CV was repeated 30 times. These permutations yielded 300 sp-LFER parameter estimates, which were averaged and reported. This method allows for all data points to be used in both the training and test set. The CV was performed in MATLAB R2013A.

Model selection analysis was accomplished with Akaike information criteria (AIC, Eqn. 5.4) and Bayesian information criteria (BIC, Eqn. 5.5). These were implemented here to accurately compare models.

$$AIC = 2k - 2\ln(\hat{\sigma}_e^2) \quad \text{Eqn. 5.4}$$

$$BIC = n \cdot \ln(\hat{\sigma}_e^2) + k \ln(n) \quad \text{Eqn. 5.5}$$

Here  $k$  is the number of predictors in the model, including the intercept,  $\hat{\sigma}_e^2$  is the error variance of the model, and  $n$  is the number of observations in the model.

RMSE and  $R^2$  cannot be used to compare models with different parameters. The model that minimizes the AIC and BIC is considered the best model, because that model achieves the least amount of error with the least number of predictive variables, i.e. it penalizes complex models. BIC is considered a harsher penalty, because it also accounts for sample size. These were used to compare the updates of the pp-LFER and log  $K_{ow}$  LFER.

Outlier and influential point statistical analyses were performed on the datasets. Please see Appendix C.1 for complete details.

### 5.3 Comparison to Available Models

The experimental values of NaCl Setschenow constants determined in Chapters 3 and 4 were compared to predictions from the published LFERs for these NaCl Setschenow constants including the one based on log  $K_{ow}$  (Eqn. 5.2, **Table 5.1**), and the second based on a pp-LFER (Eqn. 5.3, **Table 5.1**). These LFERs were developed from solubility data typically taken at lower salt concentrations than used in Chapters 3 and 4, but as discussed, the predictions of those Setschenow constants should be applicable up to high salt concentrations for a variety of the organic compounds. It is noteworthy that naphthalene, fluorene, phenanthrene, phenol, and hexanoic acid were included in the model training set for the log  $K_{ow}$  LFER. None of the compounds used in this study were included in the training set for the pp-LFER. There is also no pp-LFER-predicted NaCl Setschenow constant for 9-hydroxyfluorene because 9-hydroxyfluorene has no reported ASPs. Unlike the log  $K_{ow}$  of a compound, the ASPs for organic compounds cannot be easily and accurately predicted (Abraham 1993; Platts 2000; Devereux et al. 2009).

**Table 5.1.** Abraham Solvation Parameters, log K<sub>ow</sub>, LFER predicted  $K_s^{i,NaCl}$ , and Experimental

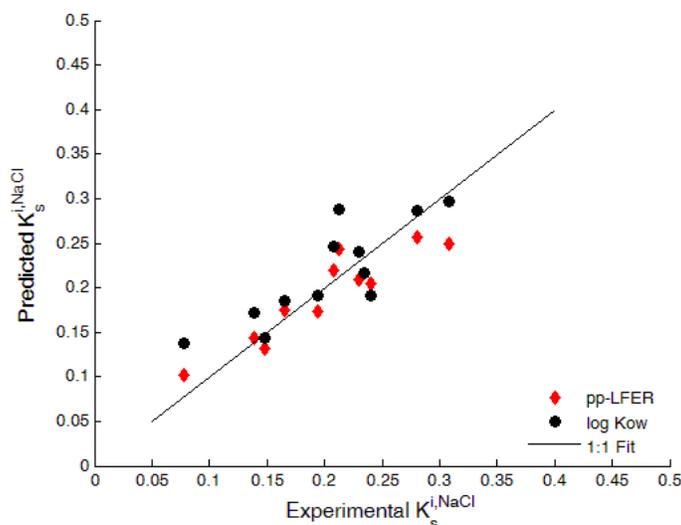
Organic Compound	$K_s^{i,NaCl}$					log K <sub>ow</sub> <sup>^^</sup>	pp-LFER pred. (M <sup>-1</sup> )	log Kow pred (M <sup>-1</sup> )	Actual NaCl K <sub>s</sub> (M <sup>-1</sup> )
	R <sub>2</sub>	π <sub>2</sub>	α <sub>2</sub>	β <sub>2</sub>	V <sub>2</sub>				
Naphthalene	1.34	0.92	0.00	0.20	1.09	3.33	0.220	0.247	0.208±0.015
Fluorene	1.59	1.05	0.00	0.20	1.36	4.32	0.256	0.287	0.281±0.038
Phenanthrene	2.06	1.29	0.00	0.26	1.45	4.57	0.250	0.297	0.308±0.029
Thiophene	0.69	0.56	0.00	0.15	0.64	1.81	0.175	0.186	0.165±0.008
Benzothiophene	1.32	0.88	0.00	0.20	1.01	3.17	0.209	0.241	0.23±0.015
Dibenzothiophene	1.96	1.31	0.00	0.18	1.38	4.36	0.243	0.288	0.213±0.03
Pyrrole	0.61	0.73	0.41	0.29	0.58	0.75	0.131	0.144	0.148±0.012
Phenol	0.81	0.89	0.60	0.31	0.78	1.44	0.144	0.172	0.139±0.012
p-Cresol	0.82	0.87	0.52	0.31	0.92	1.93	0.173	0.191	0.194±0.011
Hydroquinone	1.00	1.00	1.16	0.60	0.83	0.59	0.102	0.138	0.078±0.004
Hexanoic Acid	0.17	0.60	0.60	0.45	1.03	1.92	0.204	0.191	0.24±0.019
9-Hydroxyfluorene	N/A	N/A	N/A	N/A	N/A	2.56*	N/A	0.216	0.234±0.019

\* log K<sub>ow</sub> calculated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)

^^(Schwarzenbach et al. 2003; Johansen & Pawliszyn 1996; Andersson & Schröder 1999; Poole et al. 2000; Substance Identifier n.d.)

A plot of the predicted vs. experimental NaCl Setschenow constants for both models are given in *Figure 5.1*. Despite the fact that the pp-LFER has more predictor variables, the predictions from the log K<sub>ow</sub> model were closer to the experimental values for fluorene, phenanthrene, benzothiophene, pyrrole, and p-cresol than for the pp-LFER model (**Table 5.1**). For fluorene and phenanthrene, this is likely because these PAHs were part of the training set used to develop the log K<sub>ow</sub> LFER. The pp-LFER, however, under-predicted the NaCl Setschenow constants for fluorene and phenanthrene. The log K<sub>ow</sub> LFER is likely to have more accurate predictions for PAHs, due to its training with data from similar compounds. It is likely

that since there are few aromatic organic compounds similar to the PAHs in the training set of the pp-LFER, this perhaps led to less accurate predictions for fluorene and phenanthrene.



**Figure 5.1.** Plots of comparisons between the pp-LFER predicted and experimental NaCl Setschenow constant values and the log  $K_{ow}$  predicted and experimental NaCl Setschenow constant values. Lines represent model fit, so distance from the line is indicative of lack of goodness of fit.

Despite the use of naphthalene, phenol, and hexanoic acid in the training set of the log  $K_{ow}$  LFER, the pp-LFER had more accurate predictions for those organic compounds. In general, the prediction of both hydrophobic and hydrophilic compounds from both the log  $K_{ow}$  and pp-LFER had good agreement with experimental NaCl Setschenow constant values (**Table 5.1**). The log  $K_{ow}$  LFER exhibited larger errors in comparison with the pp-LFER. For example, the log  $K_{ow}$  LFER also over-predicted the NaCl Setschenow constant for hydroquinone (deviation of  $0.06 \text{ M}^{-1}$ ), compared only with a deviation of  $0.024 \text{ M}^{-1}$  for the pp-LFER.

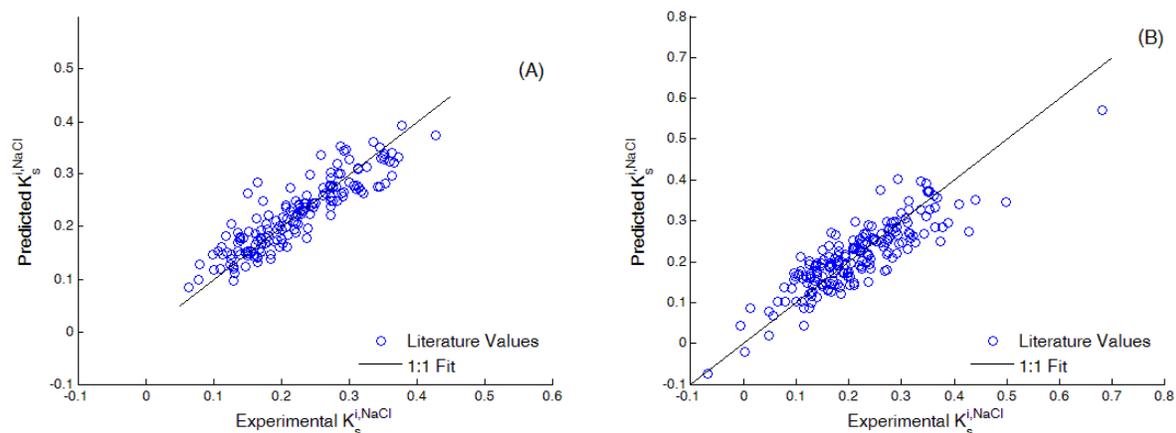
Despite the fact that both LFERs can provide reasonable predictions of NaCl Setschenow constants, this did not occur for dibenzothiophene. The measured NaCl Setschenow constant for dibenzothiophene,  $K_s^{i,NaCl} = 0.213 \pm 0.03 \text{ M}^{-1}$ , was lower than the log  $K_{ow}$  LFER predicted value

( $0.288 \text{ M}^{-1}$ ) or the pp-LFER predicted value ( $0.243 \text{ M}^{-1}$ ) (**Table 5.1**). The NaCl Setschenow constant for dibenzothiophene was also lower than expected given its high hydrophobicity, and relatively large molar volume (**Table 5.1**). For example, benzothiophene had a larger NaCl Setschenow constant than dibenzothiophene, contrary to expectations based on molar volume,  $\log K_{ow}$ , and ASPs (**Table 5.1**). Dibenzothiophene, which was not part of the training set for the  $\log K_{ow}$  model or pp-LFER, also has a lower hydrogen bonding basicity value than the similar thiophenes used in this study, which possibly led to differing intermolecular interactions that led to a lower NaCl Setschenow constant than predicted by the  $\log K_{ow}$  model or the pp-LFER. The presence of heterocyclic sulfur in between two aromatic rings possibly led to different interactions with the water and/or the ions in solution, leading to a lower than expected Setschenow constant.

There is no pp-LFER predicted value for 9-hydroxyfluorene, because it has no reported ASPs. Unlike the  $\log K_{ow}$  of a compound, the ASP for organic compounds cannot be easily and accurately predicted (Abraham 1993; Platts 2000; Devereux et al. 2009).

#### **5.4 Updates of the $\log K_{ow}$ LFER and the pp-LFER**

Since the publication of the pp-LFER and the  $\log K_{ow}$  LFER, new NaCl Setschenow constants have been reported; therefore these models have been updated with all of the available NaCl Setschenow constant data. All of the available NaCl Setschenow constants were compiled (Appendix C.2) including the NaCl Setschenow constant data collected in Chapters 3 and 4. This represents a database of almost all available NaCl Setschenow constants (Appendix C.2). Please note that not all of the organic compounds with reported NaCl Setschenow constants had available ASPs, so there are less data inputs in the pp-LFER. In addition, three outliers were removed from the pp-LFER, and six outliers were removed from the  $\log K_{ow}$  LFER (Appendix C.1).



**Figure 5.2.** Plots of comparisons between the A) pp-LFER predicted and experimental NaCl Setschenow constant values, B)  $\log K_{ow}$  predicted and experimental NaCl Setschenow constant values. Lines represent model fit, so distance from the line is indicative of error in the model.

The addition of NaCl Setschenow constant data increased confidence in both of these models, as the update of both these LFERs increased the breadth of classes of organic compounds relevant to these models. The training set of the original pp-LFER only had 43 organic compounds, and, now has been updated to contain 160 compounds in its training set. The  $\log K_{ow}$  LFER, which was trained with 101 organic compounds, now has 93 additional organic compounds (Appendix C.2).

In addition, the removal of the outliers improved the regression statistics of the pp-LFER and the  $\log K_{ow}$  LFER. The new and improved pp-LFER and  $\log K_{ow}$  LFERs are given by Eqn. 5.12 and 5.13.

$$K_s^{i,NaCl} = -0.009(\pm 0.006)R_2 - 0.037(\pm 0.01)\pi_2 - 0.044(\pm 0.01)\alpha_2 - 0.10(\pm 0.01)\beta_2 + 0.191(\pm 0.01)V_2 + 0.913(\pm 0.009) \quad \text{Eqn. 5.12}$$

$$n=160, R^2_{adj} = 0.80, \text{RMSE} = 0.035 \text{ M}^{-1}, \text{AIC} = -618, \text{BIC} = -596$$

$$K_s^{i,NaCl} = 0.042(\pm 0.006)\log K_{ow} + 0.113(\pm 0.002) \quad \text{Eqn. 5.13}$$

$$n= 194, R^2_{\text{adj}}=0.750, \text{RMSE} = 0.048 \text{ M}^{-1}, \text{AIC} = -626, \text{BIC} = -618$$

Both of these models display good agreement with experimental NaCl Setschenow constants (*Figure 5.2*). In fact, the majority of the residuals of the NaCl Setschenow constants in both these models are less than each of the respective, reported RMSEs for both predictive models. This is because RMSEs have harsher penalties for models with a few large residuals. A full breakdown of the residuals is given in Appendix C.3.

Since both models have relatively low error, model selection was focused on balancing goodness of fit, with simplicity. The AIC and BIC of both models were compared to determine the most ideal model. Both AIC and BIC penalize for number of predictors in the model. In addition, BIC takes into account sample size. The AIC and BIC for the log  $K_{ow}$  LFER are smaller than the pp-LFER, which means that the log  $K_{ow}$  LFER is considered a “better” model. This is because both have similar errors, yet the pp-LFER has more predictor variables, which typically leads to a better model fit. Another qualitative concern is the availability of ASPs, which is not considered in AIC or BIC. Not all organic compounds have available ASPs (i.e. there are 34 more organic compounds trained in the log  $K_{ow}$  LFER than in the pp-LFER), which makes the log  $K_{ow}$  LFER more ideal for predicting NaCl Setschenow constants.

Despite the improvements to these LFERs, the pp-LFER and log  $K_{ow}$  LFER still contain some inherent error. There is often experimental uncertainty associated with the measurement and calculation of Setschenow constants (Xie et al. 1997; Endo et al. 2012), which is contributing to error in this model. The organic compounds in this analysis were divided into their organic compound classes to determine if there was any particular group of organic compounds that was contributing to these errors. There is no apparent pattern in the errors of these organic compounds (Appendix C.3). However, some of the organic compounds with the

largest residuals are compounds that have relatively larger molar volumes. For example, larger PAHs tend to have larger residuals than smaller PAHs. This may be due to experimental artifact. For the three largest PAHs in the dataset, benzo(*ghi*)perylene ( $K_s = 0.292 \text{ M}^{-1}$ ), dibenzo(*ah*)anthracene ( $K_s = 0.336 \text{ M}^{-1}$ ), indeno(*123,cd*)pyrene ( $K_s = 0.346 \text{ M}^{-1}$ ), the standard deviations on the Setschenow constants are  $0.20 \text{ M}^{-1}$ ,  $0.26 \text{ M}^{-1}$ , and  $0.16 \text{ M}^{-1}$ , respectively (Jonker & Muijs 2010). This may be due to experimental uncertainty or deviations from predicted behavior for large organic compounds. Future work should focus on determining NaCl Setschenow constants for larger compounds, which could result in greater confidence in these predictive models.

### 5.5 New Single Parameter Linear Free Energy Relationships

This section involved the development of new single parameter LFERs for the prediction of  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{LiCl}$ , and  $\text{NaBr}$  Setschenow constants. This was motivated by the fact that  $\text{CaCl}_2$  is the second most abundant electrolyte after  $\text{NaCl}$  in most natural reservoir brines. The paucity of available Setschenow constants for  $\text{CaCl}_2$  motivated this study to develop a new model that predicts  $\text{CaCl}_2$  Setschenow constants from  $\text{NaCl}$  Setschenow constants. The developed model uses the experimentally determined  $\text{CaCl}_2$  Setschenow constants from this study as well as 18 literature reported Setschenow constants for  $\text{CaCl}_2$  (one was excluded for being an outlier, see Appendix C.5). The  $\text{CaCl}_2$  Setschenow constants estimated here for the hydrophobic and hydrophilic compounds adds to a more diverse training set for  $\text{CaCl}_2$  Setschenow constants for this model, especially for the hydrophilic compounds. Of the 19 compounds reported in the literature, only three are polar organic compounds.

The development of models for  $\text{KCl}$ ,  $\text{LiCl}$ , and  $\text{NaBr}$  were also included, because they all had enough data to train new models.  $\text{KCl}$  was included, because although  $\text{K}^+$  is less abundant in subsurface brines, it is the most studied salt after  $\text{NaCl}$  due to its presence in seawater and

physiological fluids. There was also considerable data for LiCl and NaBr, so those relationships were also included in this study.

The derived CaCl<sub>2</sub> Setschenow constants were systematically greater than the NaCl Setschenow constants measured in this study, and the NaCl Setschenow constants were greater than KCl, LiCl, and NaBr. This is consistent with expectation because salting-out effects of cations and anions follow a specific order, known as the Hofmeister series (Cacace et al. 1997), in magnitude of salting out (or in) for organic compounds, gases, and proteins (Jungwirth & Cremer 2014). This order shows that the salting-out due to Ca<sup>2+</sup> will be greater than the salting-out due to Na<sup>+</sup>, which will be greater than salting-out due to K<sup>+</sup> and Li<sup>+</sup>. Li<sup>+</sup>, being the smallest alkali metal, is expected to have greater salting-out behavior than Na<sup>+</sup> and K<sup>+</sup> due to Li<sup>+</sup>'s higher charge density, yet it does not. Both NaCl and KCl produce larger Setschenow constants than LiCl. This behavior has been explained by Thomas and Elcock (2007), who found in their MD simulations that Li<sup>+</sup> forms linear clusters with halide anions, therefore changing its salting-out behavior (Thomas & Elcock 2007). This is also applicable to anions, which is why salting-out due to Cl<sup>-</sup> is greater than salting-out due to Br<sup>-</sup>. These observations motivated the development of single parameter linear free energy relationships (sp-LFER) for predicting CaCl<sub>2</sub>, KCl, LiCl, and NaBr Setschenow constants from NaCl Setschenow constants. Cook's Distance and the SDR tests were done on each of these models. Only in one case was an organic compound removed from the dataset. This occurred for the sp-CaCl<sub>2</sub>-LFER, in which the Cook's Distance and SDR exceeded the thresholds for hexachlorobenzene, which was therefore removed from the sp-CaCl<sub>2</sub>-LFER. This led to an improvement in the accuracy of the model, (the R<sup>2</sup> improved from 0.799 to 0.863).

$$K_s^{i, CaCl_2} = 1.22(\pm 0.10)K_s^{i, NaCl} + 0.041(\pm 0.02) (M^{-1}) \quad \text{Eqn. 5.8}$$

$$(R^2_{\text{adj}}=0.858, \text{RMSE}=0.048, n= 29)$$

$$K_s^{i,\text{KCl}} = 0.907(\pm 0.02)K_s^{i,\text{NaCl}} - 0.011(\pm 0.004) (\text{M}^{-1}) \quad \text{Eqn. 5.9}$$

$$(R^2_{\text{adj}} = 0.927, \text{RMSE} = 0.024 \text{ M}^{-1}, n= 47)$$

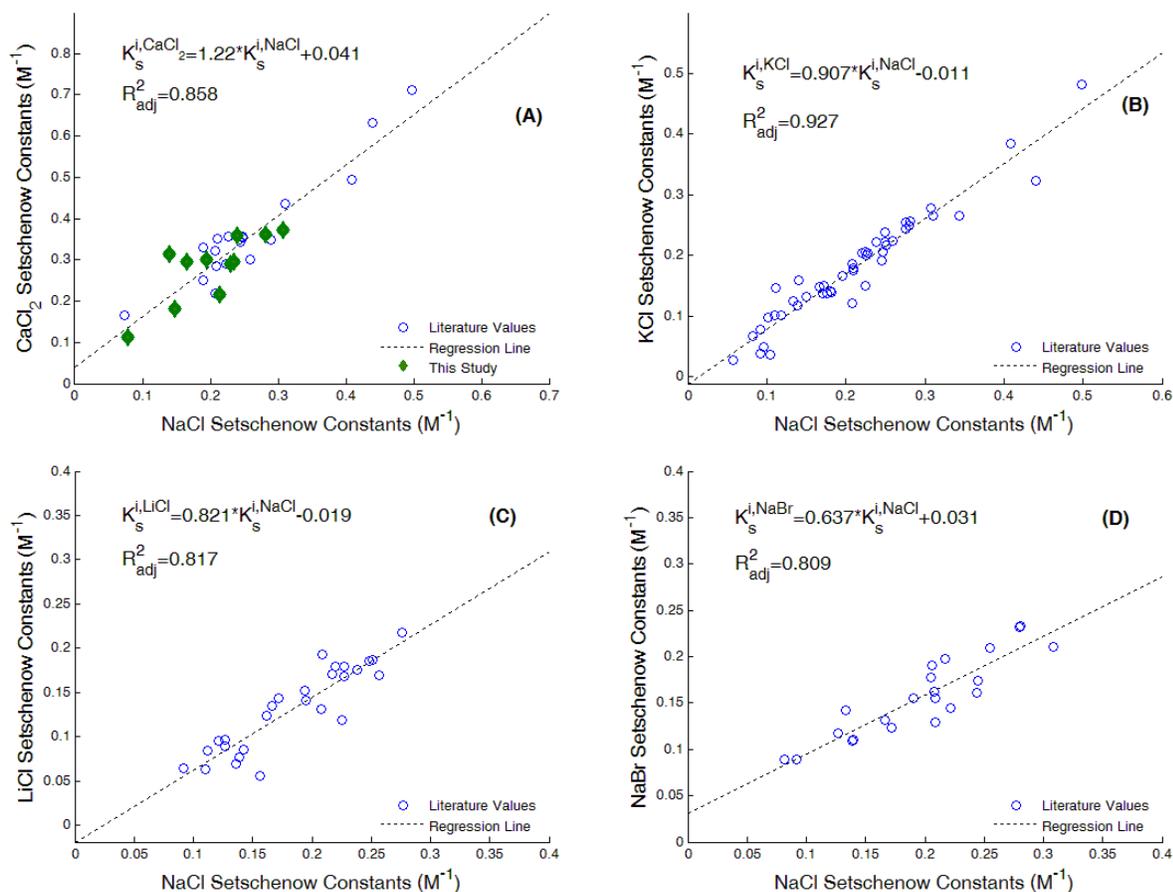
$$K_s^{i,\text{LiCl}} = 0.821(0.02)K_s^{i,\text{NaCl}} - 0.019(0.005) (\text{M}^{-1}) \quad \text{Eqn. 5.10}$$

$$(R^2_{\text{adj}} = 0.817, \text{RMSE} = 0.019, n = 27)$$

$$K_s^{i,\text{NaBr}} = 0.664(0.02)K_s^{i,\text{NaCl}} + 0.027(\pm 0.003) (\text{M}^{-1}) \quad \text{Eqn. 5.11}$$

$$(R^2_{\text{adj}} = 0.809, \text{RMSE} = 0.018, n = 22)$$

The RMSE for the sp-KCl-LFER (Eqn. 5.9) is lower than the any of the other sp-LFERs (Eqns. 5.8,5.10,5.11), presumably because both  $\text{Na}^+$  and  $\text{K}^+$  are monovalent ions and behave more similarly to each other than a monovalent and divalent cation does, and there is more KCl data than NaBr and LiCl data. However, the sp-LiCl-LFER and sp-NaBr-LFER are both fairly accurate due to the fact that they are monopolar and have a common ion with NaCl. As discussed in Chapter 4.2.2, there are several organic compounds that have higher than expected  $\text{CaCl}_2$  Setschenow constants, such as thiophene, which has a higher  $\text{CaCl}_2$  Setschenow constant than both benzothiophene and dibenzothiophene, both of which have higher NaCl Setschenow constants. This suggests that there may be multiple mechanisms controlling the salting-out effect for these organic compounds. These organic compounds with high  $\text{CaCl}_2$  Setschenow constants may contribute error in this model.



**Figure 5.3.** Correlations between the measured A)  $\text{CaCl}_2$  and NaCl Setschenow constants, B) KCl and NaCl Setschenow constants, C) LiCl and NaCl Setschenow constants, and D) NaBr and NaCl Setschenow constants. Open blue circles represent the literature values for Setschenow constants and green diamonds represent organic compounds measured in this study. Lines represent model fit, so distance from the line is indicative of error in the model.

Given the results for  $\text{CaCl}_2$ , KCl, LiCl, and NaBr we are cautiously optimistic of the extensibility of a sp-LFER approach to prediction of  $K_s^{i,k}$  of other salt systems. In addition, with the inclusion of the data from these studies, there is now a more diverse set of compounds in the sp- $\text{CaCl}_2$ -LFER that was not present before these measurements were completed. Lists of the organic compounds used to fit these linear models are presented in Appendix C.4, along with the range in Setschenow constants used to train these models.

## 5.6 Implications

The use of the LFERs to predict NaCl and CaCl<sub>2</sub> Setschenow constants has important implications for the prediction of solubility of organic compounds in brines. The use of the pp-LFER and/or the log K<sub>ow</sub> LFER and the sp-LFERs improved and developed in this study allows for the prediction of Setschenow constants for organic compounds in NaCl, CaCl<sub>2</sub>, and mixed electrolyte solutions (NaCl and CaCl<sub>2</sub>) typical of oil and gas reservoirs, and for KCl, LiCl, and NaBr solutions. Limitations to those predictions are given in Appendix C.2 and C.4. These are the ranges of log K<sub>ow</sub>, and Setschenow constants under which these LFERs were regressed.

All of these LFER models can confidently be incorporated into reactive transport models, such as Subsurface Transport Over Multiple Phases (STOMP) and TOUGHREACT (Ward et al. 2005; Xu et al. 2006), to predict aqueous solubility and partitioning coefficients of organic compounds from brines to solids and supercritical CO<sub>2</sub>, as well as in produced waters from unconventional oil and gas production, and in desalination brines, when the predominant ions in these brines are Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Br<sup>-</sup> and Cl<sup>-</sup>. In the presence of other dissolved species, such as Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and H<sub>2</sub>CO<sub>3</sub>(aq) and HCO<sub>3</sub><sup>-</sup>, which are usually present in EOR and CCUS sites at relatively higher concentrations, additional models need to be developed to accurately determine the change in aqueous solubility.

## 5.7 Supplementary Information

Appendix C contains a list of the published NaCl Setschenow constants, along with their ASPs, log K<sub>ow</sub>, and pp-LFER and log K<sub>ow</sub> LFER predictions, a list of organic compounds that exceeded the threshold for Cook's Distance, and a list of data for the CaCl<sub>2</sub>, KCl, LiCl, and NaBr sp-LFERs.

## 5.8 References

- Abraham, M.H., 1993. Scales of solute hydrogen-bonding: their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.*, 22(2), pp.73–83. Available at: <http://dx.doi.org/10.1039/CS9932200073>.
- Al-Rifai, J.H., Gabelish, C.L. & Schäfer, A.I., 2007. Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. *Chemosphere*, 69(5), pp.803–815. Available at: <http://www.sciencedirect.com/science/article/pii/S0045653507005966>.
- Andersson, J.T. & Schröder, W., 1999. A Method for Measuring 1-Octanol–Water Partition Coefficients. *Analytical Chemistry*, 71(16), pp.3610–3614. Available at: <http://dx.doi.org/10.1021/ac9902291>.
- Cacace, M.G., Landau, E.M. & Ramsden, J.J., 1997. The Hofmeister series: salt and solvent effects on interfacial phenomena. *Quarterly reviews of biophysics*, 30, pp.241–277.
- Carter, Kimberly E.; Hakala, J. Alexandra; Hammack, R.W., 2013. Hydraulic Fracturing and Organic Compounds - Uses, Disposal and Challenges. In *Society of Petroleum Engineers*. pp. 1–11.
- Devereux, M., Popelier, P.L.A. & McLay, I.M., 2009. A refined model for prediction of hydrogen bond acidity and basicity parameters from quantum chemical molecular descriptors. *Phys. Chem. Chem. Phys.*, 11(10), pp.1595–1603. Available at: <http://dx.doi.org/10.1039/B816321A>.
- Endo, S., Pfennigsdorff, A. & Goss, K.-U., 2012. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. *Environmental science & technology*, 46(3), pp.1496–503. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22191628>.
- Johansen, S. & Pawliszyn, J., 1996. Trace analysis of hetero aromatic compounds (NSO) in water and polluted groundwater by Solid phase micro- extraction (SPME). *Journal of High Resolution ...*, 19(November), pp.627–632. Available at: <http://onlinelibrary.wiley.com/doi/10.1002/jhrc.1240191107/full> [Accessed December 10, 2013].
- Jonker, M.T.O. & Muijs, B., 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere*, 80, pp.223–227.
- Jungwirth, P. & Cremer, P.S., 2014. Beyond Hofmeister. *Nat Chem*, 6(4), pp.261–263. Available at: <http://dx.doi.org/10.1038/nchem.1899>.
- Kohavi, R., 1995. A Study of Cross-Validation and Bootstrap for Accuracy Estimation and Model Selection. In *International Joint Conference on Artificial Intelligence*. pp. 1137–1143.
- Long, F.A. & McDevit, W.F., 1952. Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions. *Chemical Reviews*, 51(1), pp.119–169. Available at: <http://pubs.acs.org/doi/abs/10.1021/cr60158a004>.
- McDevit, W.F. & Long, F.A., 1952. The Activity Coefficient of Benzene in Aqueous Salt Solutions. *Journal of the American Chemical Society*, 74(7), pp.1773–1777. Available at: <http://pubs.acs.org/doi/abs/10.1021/ja01127a048>.
- Ni, N. & Yalkowsky, S.H., 2003. Prediction of Setschenow constants. *International journal of pharmaceuticals*, 254, pp.167–172.
- Platts, J.A., 2000. Theoretical prediction of hydrogen bond donor capacity. *Phys. Chem. Chem. Phys.*, 2(5), pp.973–980. Available at: <http://dx.doi.org/10.1039/A908853I>.

- Poole, S.K., Durham, D. & Kibbey, C., 2000. Rapid method for estimating the octanol–water partition coefficient (log Pow) by microemulsion electrokinetic chromatography. *Journal of Chromatography B: Biomedical Sciences and Applications*, 745(1), pp.117–126. Available at: <http://www.sciencedirect.com/science/article/pii/S0378434700000724> [Accessed June 10, 2015].
- Reddy, C.M. et al., 2012. Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. *Proceedings of the National Academy of Sciences*, 109 (50), pp.20229–20234. Available at: <http://www.pnas.org/content/109/50/20229.abstract>.
- Sanemasa, I. et al., 1984. The Effects of Salts on the Solubilities of Benzene, Toluene, Ethylbenzene, and Propylbenzene in Water. *Bulletin of the Chemical Society of Japan*, 57(6), pp.1539–1544.
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Substance Identifier, S.S., Advanced Chemistry Development (ACD/Labs) Software V11.02. Columbus, OH. Available at: <https://scifinder.cas.org>.
- Thomas, A.S. & Elcock, A.H., 2007. Molecular dynamics simulations of hydrophobic associations in aqueous salt solutions indicate a connection between water hydrogen bonding and the Hofmeister effect. *Journal of the American Chemical Society*, 129, pp.14887–14898. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/17994735>.
- Ward, A.L. et al., 2005. *STOMP: Subsurface Transport Over Multiple Phases. Version 1.0: Addendum: Sparse Vegetation, Evapotranspiration Model for the Water-Air-Energy Operational Mode. (PNNL-15465)*, Available at: [http://www.pnl.gov/main/publications/external/technical\\_reports/PNNL-15465.pdf](http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15465.pdf).
- Xie, W.-H., Shiu, W.-Y. & Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research*, 44(4), pp.429–444. Available at: <http://www.sciencedirect.com/science/article/pii/S0141113697000172>.
- Xu, T. et al., 2006. TOUGHREACT—A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration. *Computers & Geosciences*, 32(2), pp.145–165. Available at: <http://www.sciencedirect.com/science/article/pii/S0098300405001500> [Accessed April 17, 2015].

## **Part II**

**Development of New Linear Partitioning Models based on Experimental Water-Supercritical CO<sub>2</sub> Partitioning Data of Selected Organic Compounds.**

**Chapter 6: Development of New Linear Partitioning Models based on Experimental Water  
– Supercritical CO<sub>2</sub> Partitioning Data of Selected Organic Compounds**

The information presented in this chapter is part of a manuscript under preparation. The co-authors of this manuscript are Christopher Thompson, Gregory V. Lowry, and Athanasios K. Karamalidis

## Abstract

Partitioning coefficients of organic compounds between water and supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) can inform risk assessment models for CO<sub>2</sub> storage sites. There are only ~37 organic compounds that have reported water-sc-CO<sub>2</sub> partitioning coefficients; however risk assessment models will require more partitioning coefficients to predict the levels of organic compounds transporting with CO<sub>2</sub> in case of leakage. Here, the partitioning coefficients of three organic compounds were measured to add to this sparse database of partitioning coefficients. These partitioning coefficients were measured over a range of temperatures and pressures using a state-of-the-art *in-situ* pressurized batch reactor with dual spectroscopic detectors: A FT-NIR for measuring the organic analyte in the CO<sub>2</sub> phase, and a UV detector for measuring the analyte in the aqueous phase. The partitioning coefficients measured followed expected trends based on volatility and aqueous solubility. Those partitioning coefficients, along with literature data, were then used to update/re-train a model and develop new models for predicting water-sc-CO<sub>2</sub> partitioning coefficients. A published poly-parameter linear free energy relationship was re-trained with new data from both this study and the literature. However, this model requires Abraham solvation parameters which are not widely available. Therefore, five new models were developed, using both literature data and partitioning coefficients from this study. The new models use vapor pressure and aqueous solubility of the organic compound at 25 °C and CO<sub>2</sub> density to predict partitioning coefficients over a range of temperature and pressure conditions rather than the Abraham solvation parameters. These new models include four organic compound class specific models. The organic compound class specific models provide better estimates of partition behavior for compounds in that class than the model built for the entire dataset.

## Nomenclature

$\alpha_2$ : Hydrogen bonding acidity of organic compound  
 $\beta_2$ : Hydrogen bonding basicity of organic compound  
 $\rho_c$ : Critical density  
 $\rho_{CO_2}$ : Density of carbon dioxide  
 $\rho_{H_2O}$ : Density of water  
 $\rho_r$ : Reduced density  
 $\pi_1$ : Polarizability of carbon dioxide  
 $\pi_2$ : Polarizability of organic compound  
 $\omega$ : Acentric factor  
**v**: Molar volume in the Peng-Robinson equation of state  
**a**: parameter used to account for ideality in the Peng-Robinson equation of state  
**AAD**: Average absolute deviation  
**AS**: Aqueous solubility  
**ASP**: Abraham solvation parameters  
**ASP-LFER**: Abraham solvation parameter linear free energy relationship  
**b**: parameter used to account for ideality in the Peng-Robinson equation of state  
**BIP**: Binary Interaction Parameters  
**BTEX**: Benzene, toluene, ethylbenzene, and xylene isomers  
**CCUS**: Carbon capture, utilization, and storage  
**CO<sub>2</sub>**: Carbon dioxide  
 $C_{CO_2,i}$ : Concentration of the organic compound in CO<sub>2</sub>  
 $C_{H_2O,i}$ : Concentration of the organic compound in water  
**CV**: Cross-validation  
**EOR**: Enhanced oil recovery  
**EOS**: Equation of state  
**FTIR**: Fourier Transformation Infrared Spectrometry  
**HPLC**: High performance liquid chromatography  
**i**: Organic compound of interest  
 $K_{i,c/w}$ : Partitioning coefficient of an organic compound between water and CO<sub>2</sub>  
**mL**: Milliliter  
**MW**: Molecular weight  
**NIR**: Near infrared  
**NIST**: National Institutes of Standard and Technology  
**nm**: nanometer  
**P**: Pressure  
**P<sub>c</sub>**: Critical pressure  
**pp-LFER**: Poly-parameter linear free energy relationship  
**PAH**: Polycyclic aromatic hydrocarbons  
**PEEK**: Polyether ether ketone  
**PR**: Peng-Robinson  
**PR-EOS**: Peng-Robinson equation of state

**R**: Universal gas constant  
**R<sub>2</sub>**: Index of Refraction  
**RMSE**: Root mean square error  
**sc-CO<sub>2</sub>**: Supercritical carbon dioxide  
**SRK**: Soave-Redlich-Kwong  
**sp-LFER**: Single-parameter linear free energy relationship  
**STOMP**: Subsurface transport over multiple phases  
**T**: Temperature  
**T<sub>b</sub>**: Boiling point temperature  
**T<sub>c</sub>**: Critical temperature  
**UV**: Ultraviolet  
**V<sub>2</sub>**: Molar volume of the organic compound  
**vdW**: van der Waals  
**VP**: Vapor pressure  
**VP-AS-LFER**: Vapor pressure and aqueous solubility linear free energy relationship  
**x<sub>i</sub>**: mole fraction in the aqueous phase  
**y<sub>i</sub>**: mole fraction in the sc-CO<sub>2</sub> phase

## 6.1 Introduction

Carbon capture, utilization, and storage (CCUS) encompasses capturing CO<sub>2</sub> from point sources of emission, utilizing the CO<sub>2</sub> in a process such as enhanced oil recovery, and safely depositing the CO<sub>2</sub> in underground formations for long term storage. CCUS is considered a viable and economical technology due to the use of CO<sub>2</sub> for EOR. As the discovery of and production from conventional oil wells decreases (Murray & King 2012) and the cost of anthropogenic CO<sub>2</sub> decreases, CO<sub>2</sub>-driven EOR will likely increase (DOE/EIA 2014).

CO<sub>2</sub>-EOR involves the injection of CO<sub>2</sub> into oil formations to increase the amount of crude oil recovered. CO<sub>2</sub>-flooding, as it is typically called, is used for light to medium crude oils. CO<sub>2</sub> dissolves in the oil, making the oil less viscous and therefore more extractable. In addition, low molecular weight petroleum hydrocarbons are soluble in CO<sub>2</sub>, increasing the extractability of crude oil.

CO<sub>2</sub> injected into the aforementioned formations will exist as a supercritical fluid due to the increased temperatures (>304 K) and pressures (>75 bar) encountered at typical reservoir depths (> 800 m). Under those conditions, supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) is an excellent solvent for organic compounds with high volatility and low aqueous solubility (Burant et al. 2013). However, there is a dearth of partitioning coefficients for organic compounds of interest, especially benzene, toluene, ethylbenzene and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAH), phenols, carboxylic acids, and other polar organics, i.e., organic compounds typically found in oilfield brines (Neff et al. 2011). Partitioning coefficients are needed as inputs to reactive transport models, such as STOMP and TOUGHREACT (Ward et al. 2005; Xu et al. 2006), which can be used to predict what compounds may transport with CO<sub>2</sub> if leakage occurs.

The ability to measure or predict partitioning coefficients for petroleum-related compounds over a range of temperature, pressure, and salinity conditions typical of oil and gas reservoirs is needed for modeling because reservoir conditions are site-specific and can vary vastly; with measured temperatures up to 423 K, pressures up to 500 bar, and total dissolved solids concentrations up to 350 g/L (Kharaka & Hanor 2003). The partitioning coefficients of organic compounds between water and sc-CO<sub>2</sub> are dependent on pressure, temperature, and the presence of salts. These partitioning coefficients are difficult to measure accurately, especially for volatile organic compounds, due to the high pressures and temperatures required and the corresponding potential for artifacts in the measurements (e.g. losses during depressurization). Consequently, the available partitioning data are sparse (partitioning coefficients have been reported for only ~37 organic compounds) (Burant et al. 2013), and typically are not available over the entire range of temperature and pressures of interest. Particularly, partitioning coefficients of organic compounds with NSO-containing moieties are necessary to increase the breadth of compound classes in the available predictive models, which will allow for more accurate predictions.

For organic compounds that have no reported partitioning coefficients, models that are able to predict these values *a priori* are necessary for providing input parameters into reactive transport models for risk assessment purposes.

Equations of state, such as Soave-Redlich-Kwong (Redlich & Kwong 1949; Soave 1972) and Peng & Robinson (1976), are typically used for the interpolation of partitioning coefficients between data points; however, they are not used for their predictive capabilities of new partitioning coefficients. They require binary interaction parameters to correct model data to experimental data. Without binary interaction parameters, the predictions for partitioning

coefficients for these compounds are inaccurate, and cannot be used. In addition, these BIPs cannot be predicted from models, meaning that PR-EOS cannot be used accurately in any form for predictions.

Another type of model used for partitioning coefficients of organic compounds from water to sc-CO<sub>2</sub> is a poly-parameter linear free energy relationship (pp-LFER). Timko et al. (2004) building on Lagalante & Bruno's (1998) work, developed this pp-LFER (Eqn. 6.1) that incorporates a CO<sub>2</sub> density term, which allows the pp-LFER to be used over a range of temperatures and pressures for prediction of partitioning coefficients of organic compounds:

$$\log K_{i,c/w} = 3.810 - 1.230\pi_2 - 3.110\alpha_2 - 2.010\beta_2 + 0.110V_2 + 2.450\pi_1 \quad \text{Eqn. 6.1.}$$

This model requires inputs of Abraham solvation parameters, which include,  $R_2$ , the index of refraction of the organic compound;  $\pi_2$ , the polarizability of the organic compound;  $\alpha_2$  the hydrogen bonding acidity value of the organic compound;  $\beta_2$ , the hydrogen bonding basicity value of the organic compound; and  $V_2$ , the McGowan's molar volume of the organic compound (Timko et al. 2004; Abraham et al. 1994). This pp-LFER includes a CO<sub>2</sub> polarizability term ( $\pi_1$ ), calculated from the CO<sub>2</sub> density, that allows the partitioning coefficients to be predicted over a large temperature and pressure range. The calculation of  $\pi_1$  requires an additional calculation, based on the reduced density ( $\rho_r$ ) of CO<sub>2</sub> (Eqn. 6.2), which is a function of the density at the temperature and pressure of interest ( $\rho_{T,P}$ ) and the critical density of CO<sub>2</sub> ( $\rho_c$ ) (Smith et al. 1987).

$$\rho_r = \rho_{T,P} / \rho_c \quad \text{Eqn. 6.2.}$$

$$\pi_1 = 1.15\rho_r - 0.98 \quad (\rho_r < 0.7) \quad \text{Eqn. 6.3.}$$

$$\pi_1 = 0.173\rho_r - 0.37 \quad (\rho_r > 0.7) \quad \text{Eqn. 6.4.}$$

This pp-LFER (Eqn. 6.1) was based on partitioning coefficients of 33 compounds (providing 332 data points), with  $R^2_{\text{adj}} = 0.88$  and an average absolute deviation of the log values of the partitioning coefficients of 0.29. A root mean square error (RMSE) was not reported. The organic compounds of interest must have available Abraham solvation parameter values, or else it cannot be used for predictions.

Objective 4 was to develop new linear partitioning models based on experimental water-supercritical CO<sub>2</sub> partitioning data of selected nitrogen, sulfur, and oxygen containing organic compounds. Objective 4 has two tasks: 1) measure partitioning coefficients over a range of temperatures and pressures for three NSO-containing compounds, thiophene, pyrrole and anisole; and 2) improve and develop LFERs for more accurate water – sc-CO<sub>2</sub> partitioning coefficients predictions. These compounds were chosen because they have no previously reported water–sc-CO<sub>2</sub> partitioning coefficients, contain NSO moieties, and the compounds span a range of volatilities and aqueous solubilities to further assess trends in water – sc-CO<sub>2</sub> partitioning. This work adds to a sparse database of available water-sc-CO<sub>2</sub> partitioning coefficients. For the second task of this study, the pp-LFER model described above was updated with new data from this study, along with literature data that has been reported since the publication of the original pp-LFER. New pp-LFERs, based on inputs of vapor pressure, aqueous solubility, and CO<sub>2</sub> density, were developed using literature values and data from this study, meaning the data produced in task one (along with hundreds of literature values) was used to train models in task two.

## 6.2 Experimental

### 6.2.1 Materials

Carbon dioxide was supercritical fluid chromatography grade (99.999%) from Matheson Tri-Gas. Thiophene ( $\geq 99\%$ ) was obtained from Sigma Aldrich. Pyrrole (99%) and anisole (99%, extra dry) were obtained from Fisher Scientific. Water used in this study was treated with a Thermo Scientific Barnstead water purification system and had a resistivity of 18.2 M $\Omega$ -cm.

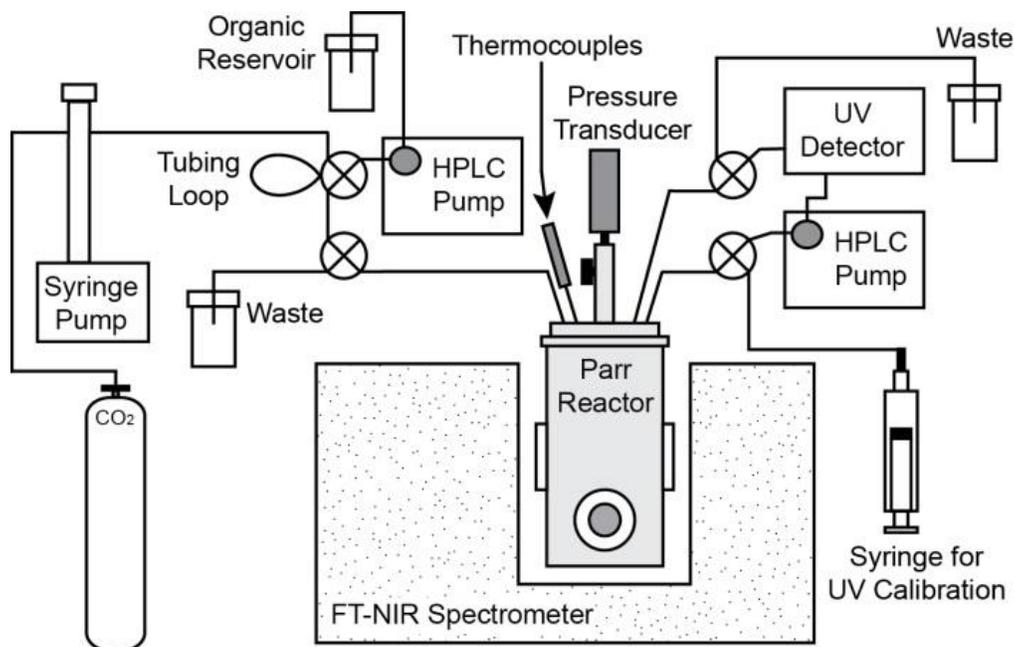
### 6.2.2 Methods

Partitioning coefficients here are given as a ratio of the mole fraction of organic compound of interest ( $i$ ) in the sc-CO<sub>2</sub> phase ( $y$ ) and aqueous phase ( $x$ ) (Eqn 6.5). They are calculated as functions of the mass concentration of the organic compound in both the CO<sub>2</sub> and H<sub>2</sub>O phases, respectively ( $C_{CO_2}$  and  $C_{H_2O}$ ), as well as the densities ( $\rho_{CO_2}$  and  $\rho_{H_2O}$ ) and molecular weights (MW) of the pure fluids.

$$K_{i,c/w} = \frac{y_i}{x_i} = \frac{C_{CO_2}}{C_{H_2O}} \cdot \frac{\rho_{H_2O}}{\rho_{CO_2}} \cdot \frac{MW_{CO_2}}{MW_{H_2O}} \quad \text{Eqn. 6.5}$$

Partitioning coefficients were measured *in-situ* using a unique batch reactor system equipped with dual spectroscopic detectors (*Figure 6.1*). The apparatus is described in detail elsewhere by Bryce et al. (in review). In brief, the system is comprised of a titanium Parr reactor, near-infrared and UV spectroscopic detectors, high-pressure pumps, and tubing and switching valves that enable quantitative injection of organics into the pressurized reactor. The reactor has an internal volume of approximately 104 mL and is fitted with quartz windows on opposite sides for optical measurements. Organic concentrations in the CO<sub>2</sub>-rich phase are measured by a Bruker IFS 66/S FT-IR spectrometer equipped with a tungsten source and a silicon diode detector for near infrared (NIR) measurements. Concentrations in the aqueous-rich phase are measured by circulating fluid from the bottom of the reactor past a Gilson model 151 UV

detector fitted with a high-pressure flow cell. An organic reagent can be injected into the reactor by filling a small loop of PEEK tubing with the reagent, switching a valve to place the loop in-line with the reactor, and using CO<sub>2</sub> supplied by the syringe pump to force the organic into the reactor.



**Figure 6.1.** Schematic of the experimental apparatus used to measure partitioning coefficients.

Protocols for calibrating the detectors and measuring partitioning coefficients are described in Bryce et al.; only limited details are provided here. A measured volume (21-22 mL) of water was added to the reactor, and the system was pressurized with CO<sub>2</sub> using the syringe pump. After the pressure and temperature have stabilized, the organic compound of interest was titrated into the reactor. NIR spectra were then collected every 5 minutes until both the NIR spectra and UV signal had stabilized, indicating that equilibrium had been reached. Spectra were recorded over the range 12,000 – 5,000 cm<sup>-1</sup>, and 128 scans were co-added for each spectrum. A linear baseline correction was applied to all NIR spectra by subtracting the average absorbances between 6255-6282 cm<sup>-1</sup> and 5736-5752 cm<sup>-1</sup>. Temperature, pressure, and UV

absorbance data were continuously collected during the entire partitioning experiment. Equilibrium was typically achieved in two hours (Appendix D.1).

The two spectroscopic detectors were calibrated independently with each organic compound of interest before partitioning coefficients were measured. NIR-spectral calibrations for the organic compound in sc-CO<sub>2</sub> were performed at each temperature and pressure of interest (i.e., six calibration curves per organic compound). This was done by adding a small amount of water (~0.2 mL; enough to fully saturate the CO<sub>2</sub> with water according to the Spycher et al. (2003) model for predicting aqueous solubility in sc-CO<sub>2</sub>) to the reactor, repeatedly injecting organic into the reactor, and measuring the NIR absorbance after each injection. The UV detector was calibrated by using a glass syringe to flow aqueous standards through the UV detector's flow cell at the temperatures of interest. Wavelengths used for the UV measurements were 225 nm for thiophene, 205 nm for pyrrole, and 269 nm for anisole. All calibration curves contained 4-5 points and were linear over the entire concentration range of interest.

Masses of pure organic compound injected into the reactor were chosen to avoid creation of a third, neat organic phase. To do this, organic compound concentrations need to be at a maximum of 30% of the saturation aqueous solubility. The calibration ranges for each of the organic compounds, along with their aqueous solubilities are given in **Table 6.1**.

**Table 6.1.** Properties and Ranges of Concentrations for Organic Compounds in the Partitioning Experiments

Organic Compound	MW (g/mol)	log VP at 25 °C (Pa)	Aqueous Solubility (g/L)	Range for Calibration Curve (g/L)
Thiophene	84.1	4.02 (Dearden 2003)	3 (Valvani et al. 1981)	0 – 0.37
Pyrrole	67.1	3.04 (Dearden 2003)	47.5 (Yaffe et al. 2001)	0 – 1.5
Anisole	108.1	2.31 (Schwarzenbach et al. 2003)	1.7 (Schwarzenbach et al. 2003)	0 – 0.18

Mole concentrations of organic compounds in the partitioning experiments were calculated using the equilibrium absorbance measurements and the appropriate calibration curves for each phase. These concentrations were then used to calculate mole fraction partitioning coefficients. The densities of CO<sub>2</sub> were calculated using the Span & Wagner (1996) EOS. The calculator <http://webbook.nist.gov/chemistry/fluid/>) used in this study is endorsed by the United States' National Institutes of Standards and Technology (NIST) and can calculate data for CO<sub>2</sub> density over a range of temperatures and pressures (National Institutes of Standards and Technology 2011).

Duplicate partitioning experiments were conducted for every temperature and pressure point, and the data show a high degree of reproducibility. The pressure variability was relatively low, with a mean standard deviation between duplicates of  $\pm 1.3$  bar, ranging from  $\pm 0.5 - 3.5$  bar. Temperature measurements were within  $\pm 1$  °C. Standard deviations of the measured partitioning coefficients were therefore relatively low as indicated by the small error bars in *Figure 6.2*, which portrays the partitioning coefficients determined in this study.

The *in-situ* dual spectroscopic detector/batch reactor system is ideal for measuring water-sc-CO<sub>2</sub> partitioning coefficients. It is advantageous to be able to measure the organic compounds *in-situ* and simultaneously in both phases. In addition, in other experimental systems, it is difficult to make measurements of the partitioning coefficient of highly volatile organic compounds. Organic compounds with high air-water partitioning coefficients will exhibit volatility losses from both phases after depressurization. No depressurization was needed during our experiments, eliminating this problem. Therefore, an *in situ* detection capability is especially advantageous for compounds that are prone to volatility losses, such as thiophene. In addition, the fact that the organic compound of interest is not captured in a cooled organic solvent, which

may result in an increase in uncertainty due to the dissolution of the solute into an organic solvent, is another advantage of this reactor.

### 6.3 Modeling Methods

Multi-parameter LFERs in this paper were all developed using ordinary least squares regression techniques using data from the literature and this study. The models were validated using parameter uncertainty using repeated k-fold cross-validation (CV) (Kohavi 1995). The data are randomly divided into k-blocks (these are the partitioning coefficients and inputs) of nearly equivalent size. One block is randomly withheld from each linear regression – this block becomes the test set, and the models are then trained on the remaining, k-1, blocks. There were 10 k-blocks used in this model. The predictive accuracy (root mean square error, RMSE) of the model is reported here using the test set (i.e. excluded data). This is then repeated 30 more times to account for the relatively small sample size, and those are averaged to determine the final parameters of the model, as well as the RMSE and  $R^2$  that are reported in **Table 6.3**. This leads to 300 parameter estimates, which are averaged and reported. CV calculations were performed using MATLAB R2013A.

Akaike information criteria (AIC, Eqn. 6.6) and Bayesian information criteria (BIC, Eqn. 6.7) were implemented here to accurately compare models.

$$AIC = 2k - 2 \ln(\hat{\sigma}_e^2) \quad \text{Eqn. 6.6}$$

$$BIC = n \cdot \ln(\hat{\sigma}_e^2) + k \ln(n) \quad \text{Eqn. 6.7}$$

Here  $k$  is the number of predictors in the model, including the intercept,  $\hat{\sigma}_e^2$  is the error variance of the model, and  $n$  is the number of observations in the model.

RMSE and  $R^2$  cannot be used to compare models with different parameters. The model that minimizes the AIC and BIC is considered the best model, because that model achieves the

least amount of error with the least number of predictive variables, i.e. it penalizes complex models. BIC is considered a harsher penalty than the AIC, because it also accounts for sample size.

## 6.4 Results and Discussion

### 6.4.1 Experimental

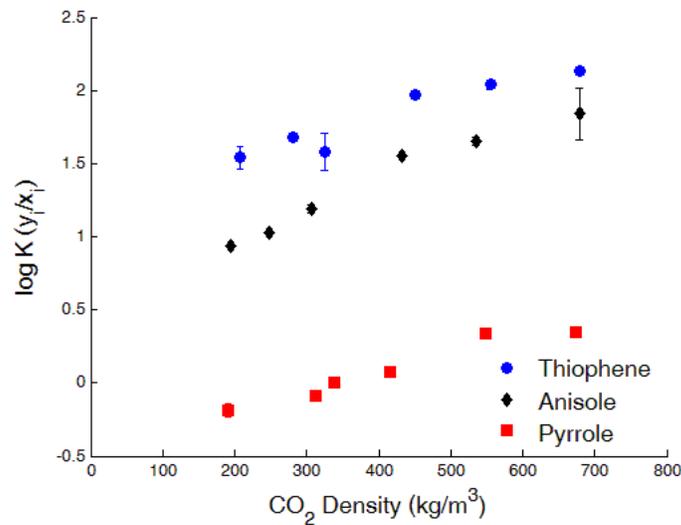
Results of the partitioning experiments of the organic compounds from water to sc-CO<sub>2</sub> are shown in **Table 6.2**, along with the temperatures, pressures, and CO<sub>2</sub> densities in which these partitioning coefficients were measured. The pp-LFER predictions for the partitioning coefficients are also listed and are discussed below.

The organic compounds of interest in this study, thiophene, pyrrole, and anisole, were chosen to span a range of vapor pressure and aqueous solubility. Vapor pressure can serve as a proxy for CO<sub>2</sub> solubility, and can be used to qualitatively estimate trends in CO<sub>2</sub> solubility (Burant et al. 2013). Thiophene is highly volatile, and therefore has higher CO<sub>2</sub> solubility, and is slightly soluble in water (**Table 6.1**). Pyrrole, which has about an order of magnitude lower vapor pressure than thiophene at 25 °C, and therefore lower CO<sub>2</sub> solubility, (**Table 6.1**), has the highest aqueous solubility of the three compounds in this study. By contrast, anisole, has the lowest CO<sub>2</sub> solubility and the lowest aqueous solubility (**Table 6.1**) at 25 °C. It was expected that thiophene would have the highest partitioning coefficients of the three, while pyrrole would have the lowest.

The results show that the partitioning behavior followed expected trends based on volatility and aqueous solubility. Thiophene had the highest partitioning coefficients for the range of temperatures and pressures measured; while pyrrole had the lowest due to its high aqueous solubility. Thiophene had comparable experimental water-sc-CO<sub>2</sub> partitioning coefficients to benzene, which is similar to thiophene in terms of magnitude of vapor pressure

and aqueous solubility. Using the same in-situ batch reactor, Bryce, et al. (in review), found that the water-sc-CO<sub>2</sub> partitioning coefficients were lower than previously reported water-sc-CO<sub>2</sub> partitioning coefficients (Ghonasgi et al. 1991; Yeo & Akgerman 1990). This is likely due to the fact that benzene had volatile losses from both phases in those partitioning experiments. Anisole and pyrrole, which have lower vapor pressures, had comparable experimental partitioning coefficients to similar compounds in terms of properties, (i.e. benzaldehyde and aniline) (Wagner et al. 1999) measured at similar temperatures and pressures.

An isothermal increase in pressure led to an increase in partitioning from water to sc-CO<sub>2</sub> for each compound. An isobaric increase in temperature led to decrease in partitioning from water to sc-CO<sub>2</sub> for each compound; this is because an isobaric increase in temperature leads to a decrease in CO<sub>2</sub> density. In fact, temperature and pressure effects can be attributed to changes in the CO<sub>2</sub> density. Partitioning from water to sc-CO<sub>2</sub> increased with increasing CO<sub>2</sub> density. The increase in partitioning was log-linear over the CO<sub>2</sub> density range (~190 – 680 kg/m<sup>3</sup>) studied here (*Figure 6.2*). The linear coefficient of determination values ( $R^2$ ) for each compound's  $\log K_{i,c/w}$  value versus CO<sub>2</sub> density was 0.879, 0.967, and 0.949 for thiophene, anisole, and pyrrole, respectively.



**Figure 6.2.** The partitioning of the three organic compounds of interest in this study versus CO<sub>2</sub> density, which is dependent on both temperature and pressure.

**Table 6.2.** Experimental partitioning coefficients of organic compounds of interest in this study over a range of temperatures and pressure, along with predictions from pp-LFER.

Organic Compound	T (°C)	P (bar)	CO <sub>2</sub> Density (kg/m <sup>3</sup> )	K (y <sub>i</sub> /x <sub>i</sub> )	log K	log K pp-LFER
Thiophene	43	83±2.1	281±21	47.11±0.5	1.68±0.01	2.17
	44	102±0.3	555.3±4	109.8±7.6	2.04±0.03	2.47
	44	122±0.9	679.1±3	133.6±7.4	2.13±0.02	2.58
	60	84±0.3	208.2±0.6	34.4±6.0	1.54±0.08	1.73
	61	107±1.8	325.4±11.7	38.6±12.1	1.58±0.13	2.26
	62	125±1.2	449.9±7.8	94.1±2.7	1.97±0.01	2.38
<b>RMSE =</b>						<b>0.504</b>
Pyrrole	43	86±0.7	312.7±17.7	0.83±0.04	-0.09±0.02	0.58
	44	102±0.5	547.9±6.5	2.20±0.02	0.34±0.005	0.69
	44	121±1.6	673.8±6	2.24±0.06	0.35±0.01	0.80
	61	81±3.5	191.2±12.1	0.64±0.07	-0.19±0.05	-0.15
	62	110±0.6	338.2±3.9	1.01±0.00	0.00±0.001	0.50
	62	121±3.4	415.6±2.6	1.19±0.07	0.08±0.02	0.57
<b>RMSE =</b>						<b>0.478</b>
Anisole	43	79±1.2	247.2±9.6	10.8±0.05	1.03±0.002	1.47
	44	101±0.2	535.3±2.6	44.3±2.8	1.65±0.03	1.96
	44	122±2	679.5±7.2	72.5±28.3	1.84±0.17	2.09
	61	81±2.1	194.2±7.1	8.8±0.11	0.94±0.006	1.15
	61	104±1.5	306.6±9.3	15.6±0.8	1.19±0.02	1.76
	62	123±0.1	433±0.4	35.8±0.2	1.55±0.002	1.87
<b>RMSE =</b>						<b>0.412</b>
<b>Average RMSE =</b>						<b>0.466</b>

## 6.5 Modeling

### 6.5.1 Poly-parameter linear free energy relationship predictions

The pp-LFER model, introduced by Timko et al. (2004), was reasonably accurate at predicting the partitioning coefficients of the organic compounds of interest in this study. The RMSE for the organic compounds of interest in this study was 0.466 log units for the pp-LFER. The pp-LFER for these 18 data points, consistently over-predicted the water-sc-CO<sub>2</sub> partitioning coefficients.

The pp-LFER also requires Abraham solvation parameters, which are available for a variety of organic compounds (Abraham et al. 1994) but not all compounds of interest. While some of the Abraham solvation parameters are easily predicted, such as molar volume, others require experimental measurement. For example, the hydrogen bonding acidity and basicity values require measurements of the organic compound with a reference base or acid (for acidity and basicity, respectively) in an apolar solvent, typically tetrachloromethane (Abraham 1993; Platts 2000; Devereux et al. 2009).

### 6.5.2 Update and Development of Models

The pp-LFER is capable of predicting partitioning coefficients; however, there is still associated error with those model predictions (**Table 6.2**), and it requires Abraham solvation parameters that may not be available for other organic compounds of interest. To solve these problems, the pp-LFER was re-trained to reduce error in the model (**Chapter 6.5.2.1**) and new LFERs were developed for organic compounds with no reported Abraham solvation parameters (**Chapter 6.5.2.2**).

#### 6.5.2.1 ASP-LFER

To reduce error in the pp-LFER, the model was re-trained to include new data from the literature and this study. In addition, three compounds, a total of 36 data points from a previous

study, were rejected, because very high injection concentrations of the organic were used, which contributed to abnormal partitioning behavior, because of possible formation of a separate neat phase. There are now 360 partitioning coefficients in the training set of the model, there were originally 332 data points in the study, (this includes the removal of 36 data points). The new LFER is termed ASP-LFER (Abraham Solvation Parameters-Linear Free Energy Relationship, **Table 6.3**, Eqn. 6.8) to differentiate it from the previously produced pp-LFER. The new model led to an increase in the adjusted  $R^2$  and a lower average absolute deviation (~0.23 log units) for the ASP-LFER. The total RMSE from the ASP-LFER fell to 0.413 log units for the organic compounds in this study.

Repeated k-fold cross validation, described in **Chapter 6.3**, allows for every organic compound to be in both the training and test set. The RMSE reported in **Table 6.3** is average of all the reported errors of the test set (there were 300 iterations of the model, resulting in an average of the RMSEs reported in **Table 6.3**). The RMSE is therefore the predictive accuracy of all the test sets. This is the magnitude of error that can be expected for a new organic compound that has not been a part of the training set.

#### **6.5.2.2 New LFERs**

A new type of LFER was developed for organic compounds with no reported Abraham solvation parameters. All of the available partitioning coefficients, including data in this study were used to train a new model with inputs of vapor pressure, aqueous solubility, and CO<sub>2</sub> density. This new model is called the VP-AS-LFER (Eqn. 6.9) and there are 369 data points in the VP-AS-LFER training set. The range of conditions used to satisfy VP-AS-LFER is presented in Appendix D. These are the range of values for which the LFERs have been established. This range of conditions includes the range of values for vapor pressure and aqueous

solubility of compounds in the training set, and the range of CO<sub>2</sub> density, and log  $K_{i,c/w}$  in partitioning measurements used to train the models. For the VP-AS-LFER (Eqn. 6.9), the vapor pressures range over eight orders of magnitude and the aqueous solubilities range over five orders of magnitude. This should allow for prediction of partitioning coefficients for organic compounds with a wide range of properties, including differing polarities and sizes.

This new VP-AS-LFER (Eqn. 6.9) works because partitioning coefficients indicate the organic compounds' relative solubilities in both the CO<sub>2</sub> and H<sub>2</sub>O phases and the inherent volatility of the organic compound. Partitioning coefficients are a function of CO<sub>2</sub> solubility, H<sub>2</sub>O solubility, and temperature and pressure, explained below:

- A. The solubility of a compound in sc-CO<sub>2</sub> is highly dependent on temperature and pressure and is therefore hard to predict (i.e., EOS modeling is needed); however, organic compound solubility in sc-CO<sub>2</sub> trends with vapor pressure.
- B. The same intermolecular forces that result in higher CO<sub>2</sub> solubility also govern the magnitude of vapor pressure (Burant et al. 2013).
- C. Vapor pressure data is also widely available and is more easily predicted than organic compound solubility in sc-CO<sub>2</sub>. This is also true for aqueous solubility, which is also easier to predict.

The CO<sub>2</sub> density term is calculated using the Span & Wagner (1996) EOS for predicting CO<sub>2</sub> phase behavior; described above. This model is also applicable for organic compounds with no literature value for vapor pressure or aqueous solubility. For compounds with no reported vapor pressure or aqueous solubility, these values can be predicted using one of many different estimation methods (Substance Identifier n.d.; Schwarzenbach et al. 2003; Boethling & Mackay 2000). The vapor pressure and/or aqueous solubility for compounds that have no reported

experimental values were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (Substance Identifier n.d.). Nine compounds had at least one estimate of vapor pressure and/or aqueous solubility from SciFinder; these are listed in Appendix D. The fits can be seen in *Figure 6.3*.

This study also includes four other models that are organic compound class specific LFERs (Eqns. 6.10 – 6.13). These were developed because prediction of partitioning coefficients from LFERs typically has better agreement with experimental values if predicted from an organic compound class specific LFER (Schwarzenbach et al. 2003). This led to the development of four individual compound group models, for substituted monopolar benzenes, polar-substituted benzenes, chlorinated phenols, and nitrogen-containing compounds (i.e., aromatic/heterocyclic nitrogen compounds) (Eqns. 6.10 – 6.13, **Table 6.3**). There was not enough data for the development of LFERs for other compound classes. There are also specific ranges of vapor pressure, aqueous solubility, and CO<sub>2</sub> density for these LFERs, and are found in Appendix D.

Similarly to the ASP-LFER, repeated k-fold cross validation allows for every organic compound to be in both the training and test set, so the RMSEs reported in **Table 6.3** represent the magnitude of error that can be expected for a new organic compound that has not been a part of the training set. The compound class specific LFERs have low relatively lower RMSE, discussed in the **Chapter 6.5.3**.

**Table 6.3.** Linear Free Energy Relationships for Predicting Water – Supercritical CO<sub>2</sub> Partitioning Coefficients.

Name	Formula	n	R <sup>2</sup> <sub>adi</sub>	RMSE	AIC	BIC	
ASP-LFER	$\log K_{i,c/w} = 1.29(\pm 0.10) - 0.83(\pm 0.08)R_2 - 3.01(\pm 0.07)\alpha_2 - 3.98(\pm 0.09)\beta_2 + 3.20(\pm 0.13)V_2 + 1.86(\pm 0.13)\pi_1$	360	0.919	0.303	169	195	Eqn. 6.8.
VP-AS-LFER	$\log K_{i,c/w} = -4.42(\pm 0.29) + 0.43(\pm 0.01) \log VP_{25^\circ C} - 0.83(\pm 0.02) \log AS_{25^\circ C} + 1.34(\pm 0.1) \log \rho_{CO_2}$	369	0.872	0.377	332	352	Eqn. 6.9.
Monopolar Substituted Benzenes	$\log K_{i,c/w} = -4.82(\pm 0.46) + 0.43(\pm 0.04) \log VP_{25^\circ C} - 1.47(\pm 0.11) \log AS_{25^\circ C} + 1.10(\pm 0.12) \log \rho_{CO_2}$	73	0.782	0.263	17	28	Eqn. 6.10.
Polar Substituted Benzenes	$\log K_{i,c/w} = -5.36(\pm 0.32) + 0.68(\pm 0.05) \log VP_{25^\circ C} - 1.29(\pm 0.12) \log AS_{25^\circ C} + 1.46(\pm 0.11) \log \rho_{CO_2}$	146	0.753	0.189	-64	-49	Eqn. 6.11.
Chlorinated Phenols	$\log K_{i,c/w} = -12.62(\pm 1.78) + 0.77(\pm 0.11) \log VP_{25^\circ C} - 1.12(\pm 0.11) \log AS_{25^\circ C} + 3.99(\pm 0.63) \log \rho_{CO_2}$	32	0.912	0.245	3	10	Eqn. 6.12.
Nitrogen-Containing Compounds	$\log K_{i,c/w} = -5.11(\pm 0.42) + 0.37(\pm 0.02) \log VP_{25^\circ C} - 1.19(\pm 0.05) \log AS_{25^\circ C} + 1.46(\pm 0.15) \log \rho_{CO_2}$	35	0.954	0.158	-26	-18	Eqn. 6.13.

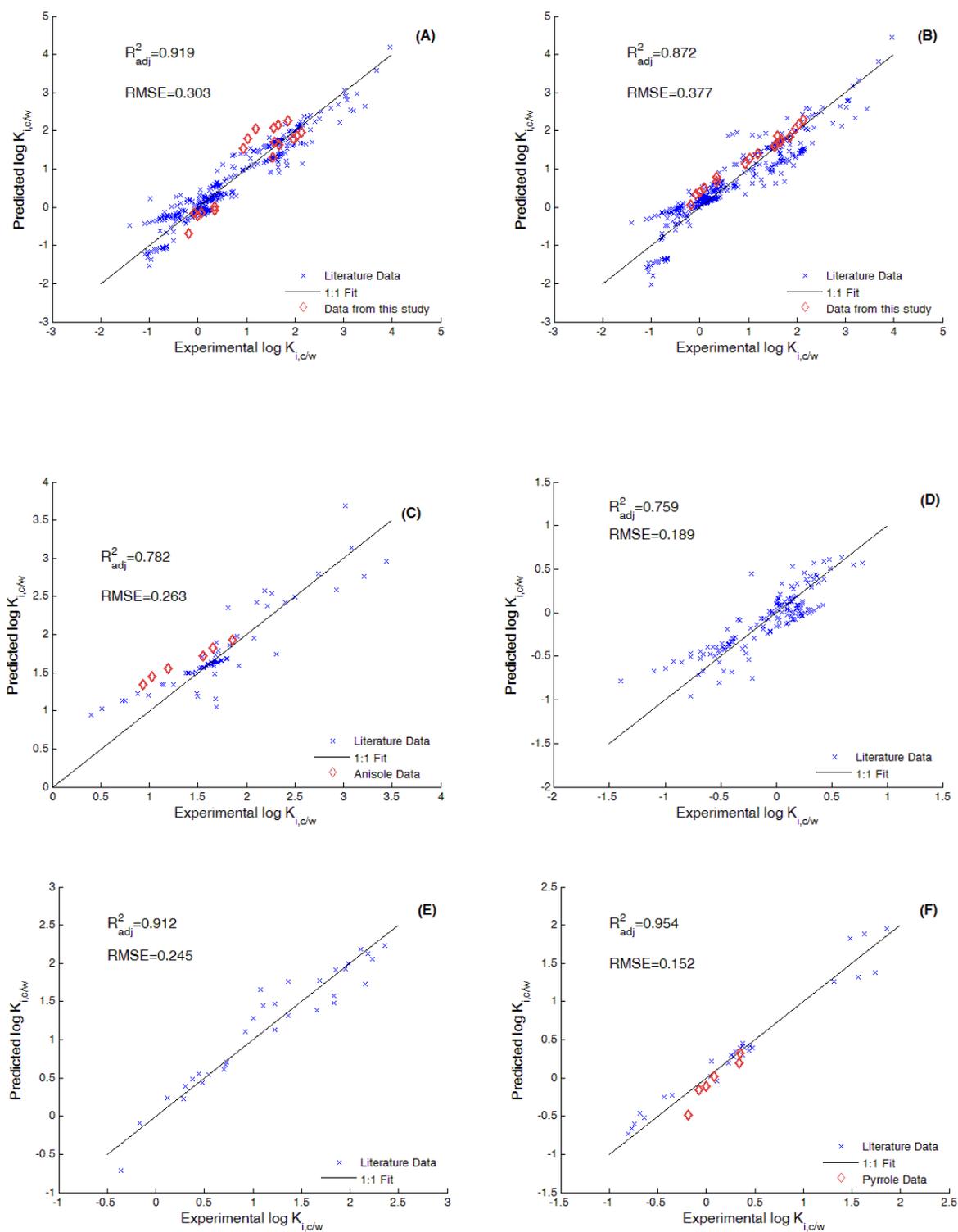
### 6.5.3 Comparison of LFERs

Any of the LFERs in **Table 6.3** can be used depending on the organic compound of interest and availability of the ASPs. The compound group-specific LFERs may be more appropriate than the ASP-LFER or the VP-AS-LFER—the overall AICs and BICs are lower for the specialized group LFERs. AIC and BIC both account for error and model complexity, and BIC also accounts for number of observations in the training set, and models that minimize both values are considered more accurate models.

It is therefore recommended that these individual LFERs be used to predict partitioning coefficients for organic compounds in those classes rather than either of the LFERs created from the total data set. However, this is only applicable to organic compounds in one of those specific groups. Compounds not in any of the compound classes may be estimated from either of the full

LFERs. It is recommended, since the AIC and BIC are lower for the ASP-LFER than the VP-AS-LFER, that the ASP-LFER should be used *if* the ASPs are available.

Either the ASP-LFER or VP-AS-LFER can be used depending on the available parameters for other compounds that do not belong in any of those classes of compounds. This is important for modeling purposes for CCUS, EOR, and other processes involving sc-CO<sub>2</sub> extraction. The available water-sc-CO<sub>2</sub> partitioning coefficients or the LFER predicted values can be incorporated into reactive transport models for risk assessment associated with CO<sub>2</sub> storage. This work has added to the database of existing water-sc-CO<sub>2</sub> partitioning coefficients with the measurement of thiophene, pyrrole, and anisole, respectively in water-sc-CO<sub>2</sub> systems, which has helped inform and train new LFERs that can predict partitioning coefficients *a priori* without the use of EOS and BIPs.



**Figure 6.3.** Predicted log partitioning coefficients of organic compounds versus log experimental partitioning coefficients of organic compounds from both this study and literature values for the pp-LFERs in this study: A) Abraham solvation parameter LFER, B) Vapor pressure and aqueous solubility LFER, C) Monopolar substituted benzene LFER, D) Polar

substituted benzene LFER, E) Chlorinated phenol LFER, and F) Nitrogen containing compound LFER. The lines indicate the 1:1 fit, blue crosses are literature data points, and red diamonds indicate data measured in this study.

## 6.6 Supplementary Information

Appendix D contains examples of time to equilibrium curves, information on the Peng-Robinson EOS and calculated binary interaction parameters, iterations of the ASP-LFERs, tables of the reported vapor pressures, aqueous solubilities, CO<sub>2</sub> densities, ASPs, experimental partitioning coefficients, and the new model predicted partitioning coefficients for all compounds with reported water-sc-CO<sub>2</sub> partitioning coefficients, RMSEs for thiophene, pyrrole, and anisole, for each model, and the range in parameters and partitioning coefficients for the new models.

## 6.7 References

- Abraham, M.H. et al., 1994. Hydrogen bonding. 32. An analysis of water-octanol and water-alkane partitioning and the  $\Delta \log p$  parameter of seiler. *Journal of Pharmaceutical Sciences*, 83(8), pp.1085–1100. Available at: <http://dx.doi.org/10.1002/jps.2600830806>.
- Abraham, M.H., 1993. Scales of solute hydrogen-bonding: their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.*, 22(2), pp.73–83. Available at: <http://dx.doi.org/10.1039/CS9932200073>.
- Boethling, R.S. & Mackay, D., 2000. *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*, CRC Press.
- Burant, A., Lowry, G.V. & Karamalidis, A.K., 2013. Partitioning behavior of organic contaminants in carbon storage environments: a critical review. *Environmental science & technology*, 47(1), pp.37–54. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/23211055>.
- Dearden, J.C., 2003. Quantitative structure-property relationships for prediction of boiling point, vapor pressure, and melting point. *Environmental Toxicology and Chemistry*, 22(8), pp.1696–1709. Available at: <http://dx.doi.org/10.1897/01-363>.
- Devereux, M., Popelier, P.L.A. & McLay, I.M., 2009. A refined model for prediction of hydrogen bond acidity and basicity parameters from quantum chemical molecular descriptors. *Phys. Chem. Chem. Phys.*, 11(10), pp.1595–1603. Available at: <http://dx.doi.org/10.1039/B816321A>.
- DOE/EIA, 2014. *Annual Energy Outlook 2014 with projections to 2040*,
- Ghonasgi, D. et al., 1991. Supercritical CO<sub>2</sub> extraction of organic contaminants from aqueous streams. *AIChE Journal*, 37(6), pp.944–950. Available at: <http://dx.doi.org/10.1002/aic.690370617>.
- Kharaka, Y.K. & Hanor, J.S., 2003. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In E.-C. H. D. Holland & K. K. Turekian, eds. *Treatise on Geochemistry*. Oxford:

- Pergamon, pp. 1–48. Available at:  
<http://www.sciencedirect.com/science/article/pii/B0080437516050854>.
- Kohavi, R., 1995. A Study of Cross-Validation and Bootstrap for Accuracy Estimation and Model Selection. In *International Joint Conference on Artificial Intelligence*. pp. 1137–1143.
- Lagalante, A.F. & Bruno, T.J., 1998. Modeling the Water–Supercritical CO<sub>2</sub> Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship†. *The Journal of Physical Chemistry B*, 102(6), pp.907–909. Available at:  
<http://dx.doi.org/10.1021/jp973047o>.
- Murray, J. & King, D., 2012. Climate policy: Oil’s tipping point has passed. *Nature*, 481(7382), pp.433–435. Available at: <http://dx.doi.org/10.1038/481433a>.
- National Institutes of Standards and Technology, 2011. Thermophysical Properties of Fluid Systems. Available at: <http://webbook.nist.gov/chemistry/fluid/>.
- Neff, J., Lee, K. & Deblois, E.M., 2011. Produced Water : Overview of Composition , Fates , and Effects. *Produced Water*, pp.3–54.
- Peng, D.-Y. & Robinson, D.B., 1976. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1), pp.59–64. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/i160057a011>.
- Platts, J.A., 2000. Theoretical prediction of hydrogen bond donor capacity. *Phys. Chem. Chem. Phys.*, 2(5), pp.973–980. Available at: <http://dx.doi.org/10.1039/A908853I>.
- Redlich, O. & Kwong, J.N.S., 1949. On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chemical Reviews*, 44(1), pp.233–244. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/cr60137a013>.
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Smith, R.D. et al., 1987. Solvent properties of supercritical xenon and sulfur hexafluoride. *The Journal of Physical Chemistry*, 91(11), pp.3059–3062. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/j100295a083>.
- Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, 27(6), pp.1197–1203. Available at:  
<http://www.sciencedirect.com/science/article/pii/0009250972800964>.
- Span, R. & Wagner, W., 1996. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa. *Journal of Physical and Chemical Reference Data*, 25(6).
- Spycher, N., Pruess, K. & Ennis-King, J., 2003. CO<sub>2</sub>-H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. *Geochimica et Cosmochimica Acta*, 67(16), pp.3015–3031. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0016703703002734> [Accessed December 17, 2014].
- Substance Identifier, S.S., Advanced Chemistry Development (ACD/Labs) Software V11.02. Columbus, OH. Available at: <https://scifinder.cas.org>.
- Timko, M.T. et al., 2004. Partition Coefficients of Organic Solutes between Supercritical Carbon Dioxide and Water: Experimental Measurements and Empirical Correlations. *Journal of Chemical & Engineering Data*, 49(4), pp.768–778. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/jc030197l>.

- Valvani, S.C., Yalkowsky, S.H. & Roseman, T.J., 1981. Solubility and partitioning IV: Aqueous solubility and octanol-water partition coefficients of liquid nonelectrolytes. *Journal of Pharmaceutical Sciences*, 70(5), pp.502–507. Available at: <http://dx.doi.org/10.1002/jps.2600700510>.
- Wagner, K.-D. et al., 1999. Partition coefficients of aromatic organic substances in two-phase mixtures of water and carbon dioxide at pressures from 8 to 30 MPa and at temperatures of 313 to 333 K. Part II. *The Journal of Supercritical Fluids*, 15(2), pp.109–116. Available at: <http://www.sciencedirect.com/science/article/pii/S0896844699000042> [Accessed January 15, 2015].
- Ward, A.L. et al., 2005. *STOMP: Subsurface Transport Over Multiple Phases. Version 1.0: Addendum: Sparse Vegetation, Evapotranspiration Model for the Water-Air-Energy Operational Mode. (PNNL-15465)*, Available at: [http://www.pnl.gov/main/publications/external/technical\\_reports/PNNL-15465.pdf](http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15465.pdf).
- Xu, T. et al., 2006. TOUGHREACT—A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration. *Computers & Geosciences*, 32(2), pp.145–165. Available at: <http://www.sciencedirect.com/science/article/pii/S0098300405001500> [Accessed April 17, 2015].
- Yaffe, D. et al., 2001. A Fuzzy ARTMAP Based on Quantitative Structure–Property Relationships (QSPRs) for Predicting Aqueous Solubility of Organic Compounds. *Journal of Chemical Information and Computer Sciences*, 41(5), pp.1177–1207. Available at: <http://dx.doi.org/10.1021/ci010323u>.
- Yeo, S.-D. & Akgerman, A., 1990. Supercritical extraction of organic mixtures from aqueous solutions. *AIChE Journal*, 36(11), pp.1743–1747. Available at: <http://dx.doi.org/10.1002/aic.690361116>.

**Chapter 7: Summary, Major Contributions, and Limitations of this Thesis, Broader Impacts, and Future Work**

## 7.1 Summary of this Thesis

This thesis was divided into two parts. Part I contained three objectives and was concerned with the salting-out effect of organic compounds in saline solutions. Part II contained one objective and was focused on the partitioning of organic compounds between water and supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>). Both parts produced fundamental experimental partitioning data, which was then used to calibrate models to predict Setschenow constants (Part I) and water-sc-CO<sub>2</sub> partitioning coefficients (Part II). Here is a brief summary of these objectives.

*Objective 1 (Chapter 3)* was to determine the validity of the Setschenow Equation for selected hydrophilic compounds in the range of 2 – 5 M NaCl, 1.5 – 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines. This covers the range of salt concentrations typical of oil and gas reservoirs. The salting-out effect in these salt solutions was investigated for three polycyclic aromatic hydrocarbons (PAHs), naphthalene, fluorene, and phenanthrene, and three sulfur heterocyclics, thiophene, benzothiophene, and dibenzothiophene. The salting-out effect was measured using solid phase microextraction (SPME) fibers and analyzed by a gas chromatograph, coupled with a flame ionization detector (GC-FID). The salting-out effect was shown to be log-linear up to 2 – 5 M NaCl and 1.5 – 2 M CaCl<sub>2</sub> for the compounds studied here. The Setschenow constants were additive for thiophene and fluorene in mixed electrolyte solutions ranging from moderate to high ionic strengths of NaCl and CaCl<sub>2</sub>.

*Objective 2 (Chapter 4).* Determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines.

Objective 2 is similar to Objective 1, except it measures the salting-out effect of hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines. The hydrophilic compounds of concern were phenol, p-cresol, hydroquinone, pyrrole, hexanoic acid, and 9-hydroxyfluorene. These were chosen because they would also provide mechanistic insights into differences in salting-out between hydrophobic and hydrophilic compounds. The same SPME and GC-FID method was used to measure the salting-out effect. All of the organic compounds studied here exhibited log-linear salting-out behavior up to 5 M NaCl and 2 M CaCl<sub>2</sub>. The Setschenow constants of p-cresol and 9-hydroxyfluorene were additive up to high ionic strengths of NaCl and CaCl<sub>2</sub>.

*Objective 3 (Chapter 5).* Evaluate, update, and create new models for the prediction of Setschenow constants.

This objective was to evaluate the two available models for predicting NaCl Setschenow constants. The first model is a single parameter linear free energy relationship (sp-LFER) that uses octanol-water partitioning coefficients ( $\log K_{ow}$ ) of the organic compound to predict its NaCl Setschenow constants. The second model is a poly-parameter linear free energy relationship (pp-LFER) that uses the Abraham solvation parameters (ASPs) to predict the NaCl Setschenow constants. Both models produced predictions that had good agreement with the experimental NaCl Setschenow constants measured here (i.e. most predictions were lower than the root mean square error (RMSE) of the model). The  $\log K_{ow}$ -LFER and the pp-LFER were updated with data from this study and literature data, which increased confidence and the breadth of classes of organic compounds in those models. Finally, no useful models exist for the prediction of Setschenow constants for other salts, so four new sp-LFERs were developed using

literature data and data from this study (only in the case of the sp-CaCl<sub>2</sub>-LFER) to predict CaCl<sub>2</sub>, KCl, LiCl, and NaBr Setschenow constants. The developed models showed good predictive capability for these other salts based on regressed values and published data.

*Objective 4 (Chapter 6).* Develop New Linear Partitioning Models based on Experimental Water-Supercritical CO<sub>2</sub> Partitioning Data of Selected Organic Compounds.

There is a limited number of available partitioning coefficients for partitioning of organic compounds between sc-CO<sub>2</sub> and water in the literature; therefore models are needed to fill these experimental gaps. The partitioning coefficients of three organic compounds, thiophene, pyrrole, and anisole, between sc-CO<sub>2</sub> and water were measured over a range of temperature and pressure conditions. These partitioning coefficients followed respective thermodynamic trends in both the sc-CO<sub>2</sub> and H<sub>2</sub>O(aq) phases. A pp-LFER that uses the ASPs to predict partitioning coefficients was updated with data from this study and literature data. However, many organic compounds have no reported ASPs, so five new models were developed to predict water-sc-CO<sub>2</sub> partitioning coefficients from vapor pressure, aqueous solubility, and CO<sub>2</sub> density. One model was created using all of the organic compound that fell into the respective training range of each predictor variable in the model. The other four models are developed for specific classes of organic compounds, which include monopolar substituted benzenes, polar substituted benzenes, chlorinated phenols, and nitrogen-containing compounds.

## **7.2 Major Contributions of this Thesis**

This thesis will benefit the scientific and engineering community by providing fundamental partitioning constants and models for predicting the decrease in aqueous solubility due to salt and partitioning from water to sc-CO<sub>2</sub>. In addition, this is the largest collection of

solubility measurements on organic compounds in brines in the scientific literature. It will serve as a valuable source of data and models for studying and managing impaired (salty) waters such as desalination brines, agricultural runoff, produced waters, and CCUS environments.

Part I was accomplished in Objectives 1 – 3 (Chapter 3 – 5) and produced five major findings:

1. New NaCl and CaCl<sub>2</sub> Setschenow constants were measured for selected hydrophobic and hydrophilic organic compounds. Hundreds of polar, monopolar and apolar organic compounds are present in oil and gas reservoir brines (Carter, et al. 2012), so aqueous solubility data are needed in NaCl and CaCl<sub>2</sub> solutions. This work produced new NaCl and CaCl<sub>2</sub> Setschenow constants for 12 hydrophobic and hydrophilic organic compounds. This was especially important for hydrophilic organic compounds, as there are few reported NaCl and CaCl<sub>2</sub> Setschenow constants for those compounds relevant to oil and gas brines. In addition, this work gave insights into mechanisms of the salting-out effect. The addition of polar groups to an organic compound leads to a decrease in the salting-out effect, despite an increase in molar volume of the organic compound
2. The Setschenow Equation was shown to be valid up to 2 – 5 M NaCl, 1.5 – 2 M CaCl<sub>2</sub>, and in moderate to high concentrations of mixtures of NaCl and CaCl<sub>2</sub> in predicting the salting-out effect. The salting-out effect was log-linear for the 12 organic compounds in this study, which included thiophenes, PAHs, phenolic compounds, a carboxylic acid, and a nitrogen containing compound up to 2 – 5 M NaCl, 1.5 – M 2 NaCl, and up to an ionic strength of 5 M. This is important as 2 – 3 M NaCl represents the expected median salt concentrations of oil and gas brines and 5 M NaCl and 2 M CaCl<sub>2</sub> represent the highest expected salt concentrations of these brines. The Setschenow constants were

additive for  $\text{Na}^+$  and  $\text{Ca}^{2+}$  for moderate (1 – 3 M) to high ionic strengths (5 M). For most of the hydrophobic and hydrophilic organic compounds studied here, they exhibited log-linear salting-out behavior up to 5 M NaCl and 2 M  $\text{CaCl}_2$ .

3. The Setschenow Constant data measured in low salt concentrations can reliably be extrapolated to high salt concentrations. Since the NaCl and  $\text{CaCl}_2$  Setschenow constant data were valid in predicting the salting-out effect up to 5 M NaCl and 2 M  $\text{CaCl}_2$ , then this means that the Setschenow constants measured in low salt concentrations of NaCl and  $\text{CaCl}_2$  are extractable up the high salt concentrations typical of oil and gas reservoirs. Since these Setschenow constants do not have to be re-measured, this will save time, money, and effort.
4. Both the  $\log K_{ow}$  and pp-LFER were updated with more NaCl Setschenow constants, which increased the applicability of both LFERs and range of both LFERs. Both models displayed good agreement with experimental NaCl Setschenow constants, with the majority of the predictions producing residuals that were less than the RMSEs of each of the models. The pp-LFER, on average, provided for more accurate predictions. However, the pp-LFER requires use of Abraham solvation parameters (ASPs), which are not available for every organic compound. In addition, the  $\log K_{ow}$  LFER has a better balance of goodness of fit with simplicity than the pp-LFER. The updates of both of these models resulted in an increase in confidence in the LFERs, because there are now more classes of organic compounds in both those LFERs. In addition, both models can be easily incorporated into reactive transport models for prediction of NaCl Setschenow constants.
5. New single parameter (sp-) LFERs were developed for the prediction of  $\text{CaCl}_2$ , KCl, LiCl, and NaBr Setschenow constants from NaCl Setschenow constants. These new sp-

LFERs used available literature data, as well as NaCl and CaCl<sub>2</sub> Setschenow constant data estimated in this study to train and test these models. These sp-LFERs display good agreement with experimental Setschenow constants, and can be used with the pp-LFER or log K<sub>ow</sub> LFER to predict Setschenow constants for organic compounds with no reported Setschenow constants.

Part II was accomplished in Objective 4 (Chapter 6) and produced two major findings.

1. New partitioning coefficients were measured for thiophene, pyrrole, and anisole over a range of temperature and pressure conditions using a state-of-the-art *in-situ* batch reactor with dual spectroscopic detectors. No depressurization or dilution had to occur for organic analysis, making the measurements and resulting Setchenow constants more reliable than other methods that require depressurization. The measured partitioning coefficients for thiophene, pyrrole, and anisole followed expected trends based on their volatility and aqueous solubility. In addition, the partitioning coefficients for each organic compound exhibited an increase in partitioning to sc-CO<sub>2</sub> with increasing CO<sub>2</sub> density.
2. Models updated and developed for the prediction of water-sc-CO<sub>2</sub> partitioning coefficients. The pp-LFER was updated with the partitioning coefficients from this study, as well as additional literature data. There are organic compounds of interest with no reported ASPs, so five additional models were developed that use inputs of vapor pressure, aqueous solubility, and CO<sub>2</sub> density. Four of those models are applicable to four distinct organic compound classes. These four new LFERs are for monopolar substituted benzenes, polar substituted benzenes, chlorinated phenols, and nitrogen containing

compounds. The fifth model was also trained with available water-sc-CO<sub>2</sub> partitioning coefficient data against vapor pressure, aqueous solubility, and CO<sub>2</sub> density data. This model is available to all organic compounds that fall within the range against which the trained data was measured.

### **7.3 Limitations of this Thesis**

#### **7.3.1 Validity of the Setschenow Equation**

The Setschenow Equation was proven to be valid up to 2 – 5 M NaCl and 1.5 – 2 M CaCl<sub>2</sub> concentrations for selected hydrophobic and hydrophilic compounds in this study, however the extension of the Setschenow Equation may not be applicable to every class of organic compound. The compounds studied here were all small to moderately sized, ranging in molecular weights from 67.1 – 184.3 g/mol. It is possible that there are deviations from the Setschenow Equation for larger organic compounds (See Chapter 7.5.1, Future Work). Here, heterocyclic sulfur and nitrogen substituents, and hydroxyl groups (maximum of two polar groups) were investigated. There are many more substituents, such as halogenated functional groups and additional polar groups that could possibly lead to deviations from log-linear salting-out behavior (See Chapter 7.5.2, Future Work).

This work, along with previous studies, have shown that the Setschenow Equation is valid in predicting the salting-out effect up to 2 – 5 M NaCl and 1.5 – 2 M CaCl<sub>2</sub> concentrations of monopolar substituted benzenes, low molecular weight PAHs, hydroxylated PAHs, and heterocyclics (i.e. up to three rings), polar substituted benzenes with a maximum of two polar substituents, and carboxylic acids up to C<sub>6</sub>.

### **7.3.2 Modeling of Setschenow Constants**

The update of both the pp-LFER and the log  $K_{ow}$  LFER increased the breadth of organic compounds applicable to each LFER. The number of organic compounds used to train the pp-LFER increased from 43 to 160 compounds and from 101 to 194 for the log  $K_{ow}$  LFER. Despite the increase in organic compounds, there are still limitations to each of these models. Appendix C.2 details the ranges of log  $K_{ow}$  values for the log  $K_{ow}$  LFER and NaCl Setschenow constants for each of these models. Appendix C.2 also provides ranges of inputs for Setschenow constants in the sp-LFERs, and lists some relevant classes of organic compounds used to train these models. These include ketones, PAHs, chlorinated ethanes and ethenes, substituted benzenes, alcohols, chlorinated benzenes, alkanes and cycloalkanes, substituted phenols, carboxylic acids, polar nitrogens, carboxylic acid esters, pharmaceuticals and personal care products (PPCPs), and dioxins and amino acids (log  $K_{ow}$  LFER applicable only). There are many other compounds used in these models, under the “other” designation. Some key classes of organic compounds missing from these models include larger organic compounds, especially those large compounds found in oil and gas reservoirs (i.e. long-chained alkanes and other aromatic and heterocyclic biomarkers) and large PPCPs, which will be found in desalination brines (See Chapter 7.5.1, Future Work). Despite improvements in the models after they were updated with additional compounds, the errors in estimates of Setchenow constants that they provide should be considered when are used.

### **7.3.3 Modeling of Water – Supercritical Carbon Dioxide Partitioning Coefficients**

The development of the new water-sc-CO<sub>2</sub> partitioning coefficient models that use vapor pressure, aqueous solubility, and CO<sub>2</sub> density as inputs will enable prediction of more organic compounds than can be predicted from the ASP-LFER. However, there are still limitations to these models that must be considered. There are ranges of vapor pressures, aqueous solubility,

and CO<sub>2</sub> density inputs that were used to regress these models. The ranges are reported in Appendix D.6, and it is cautioned against exceeding those ranges. In addition, the four single compound class LFERs are only applicable to monopolar substituted benzenes, polar substituted benzenes, chlorinated phenols, and nitrogen containing compounds. Also, it should be noted that these models contain inherent error that must be considered in their applications to additional compounds.

## **7.4 Significance and Broader Impacts**

### **7.4.1 Carbon capture, utilization, and storage**

This work will have direct impacts on the risk assessment modeling for CCUS technologies. These data and models can be input into reactive transport models, such as STOMP (Ward et al. 2005) or TOUGHREACT (Xu et al. 2006) to predict the concentrations of organic compounds that will transport with water and/or CO<sub>2</sub> into overlying geologic formations.

### **7.4.2 Produced Water Management**

The data and models produced in this thesis will help with produced water management and modeling, especially for waters derived from extraction of unconventional oil and gas resources, such as shale gas extraction and oil sands process waters.

The hydraulic fracturing of many unconventional oil and gas formations, such as the Marcellus and Barnett shales, results in large volumes of produced water. These produced waters contain high levels of salts and natural petroleum hydrocarbons, and synthetic organic compounds such as 2,2-dibromo-3-nitilopropionamide and ethylene glycol (Carter, et al. 2013), whose aqueous solubility is expected to decrease due to the salting-out effect. Treatment and disposal of these large volumes of produced water is of utmost environmental importance due to the toxicity associated with constituents in these waters and this knowledge on the salting-out effect will provide useful knowledge on removal of those compounds, especially for the polar

organic compounds, which are more difficult to extract from water. Knowledge on the salting-out effect could be exploited for higher removal rates of hydrophilic organic compounds from water. The treatment and above-ground disposal of unconventional oil and gas produced water is likely to expand in the near future. Underground injection wells are used in many oil and gas producing areas to dispose of produced waters, but those wells have been linked to increased seismic activity in those areas (Keranen et al. 2014). This suggests that the oil and gas operators will need alternative options, such as treatment before disposal or reuse.

The extraction of bitumen from the Alberta oil sands requires large volumes of water for extraction, and therefore create large volumes of wastewater, termed oil sands process water, which will contain levels of electrolytes from dissolution of the rock and gypsum (Renault et al. 1998). The high levels of PAHs and naphthenic acids found in the oil sands process waters and the Athabasca River and tributaries (Kelly et al. 2009; Ross et al. 2012) could be better managed with knowledge on the salting-out effect, as removal of these organic compounds from water could be exploited with salt present. However, this will require additional research on naphthenic acids, which are in higher concentration in oil sands process waters, which may have unique salting-out behavior due to their multiple polar groups (See **Chapter 7.5.1.2**).

### **7.4.3 Water Treatment Industries**

There will be an increasing use of impaired salty water in the future, requiring a better understanding of the fate of organic chemicals in those waters. Water scarcity is a major issue in both the developed and developing world. Freshwater resources are dwindling, and this is only expected to be exacerbated by climate change in water-stressed areas (Vörösmarty et al. 2000). Desalination technologies, such as reverse osmosis and membrane desalination, are expected to become more widespread, which will result in the production of more concentrated waste brines. In addition, this water is expected to contain dissolved organic compounds, including

pharmaceuticals and personal care products, surfactants, pesticides, and other emerging and legacy contaminants of concern (Ozaki & Li 2002; Al-Rifai et al. 2007). Treatment of those waste brines will be based on the concentrations of the organic compounds in those waters. This work indicated that the Setschenow Equation will be valid in predicting the aqueous solubility of these dissolved organic compounds in these reject brines.

In addition, there has been research that has indicated that produced water with relatively low concentrations of total dissolved solids may be treated by reverse osmosis or nanofiltration (Mondal & Wickramasinghe 2008); this will result in concentration of both salts and organic compounds in these waters, and will require further treatment; which will be aided by knowledge on the solubility of those organic compounds in saline solutions.

Finally, knowledge on both the salting-out effect and the partitioning of organic compounds from water to sc-CO<sub>2</sub> can be combined to extract organic compounds from brines and therefore treat contaminated waters using sc-CO<sub>2</sub>. The LFERs developed here can be used in the design of optimal removal of organic compounds from these wastewaters. Supercritical CO<sub>2</sub> will be an ideal solvent for extraction, because after depressurization the organic compounds will precipitate and the CO<sub>2</sub> can be reused, requiring no solvent disposal, recharge, or cleanup. However, some additional research on the Setschenow Equation in supercritical fluid phase equilibria and a thorough cost analysis is necessary to ensure that this is an economically viable treatment alternative (**Chapter 7.6**).

#### **7.4.4 Organic Aerosols**

This work will also benefit air pollution sciences and engineering, because organic aerosols have been known to have high concentrations of salts and toxic organic compounds, such as PAHs. These are mechanisms for which these organic compounds are transported

through the atmosphere. Risk assessment of these aerosols requires methods to model the salting-out effect (Chang & Pankow 2006; Zuend et al. 2010).

## **7.5 Future Research Related to Part I**

The work in Part I of this study demonstrated that the Setschenow Equation predicts log-linear salting-out behavior for selected groups of organic compounds in NaCl and CaCl<sub>2</sub> brines. These groups include the lower molecular weight PAHs (including a hydroxylated PAH) and thiophenes (maximum of three rings for both of these groups), small phenolic compounds (i.e. one ring), small nitrogen containing compounds (one ring), and small carboxylic acids (<C<sub>6</sub>). Other studies have shown that the BTEX compounds (all one ring) exhibited log-linear salting-out behavior to 5 M NaCl (Keeley et al. 1991; Keeley et al. 1988). These organic compounds represent a wide range of organic compounds; however there are still more systems that require investigation.

### **7.5.1 The Validity of the Setschenow Equation For Additional Organic Compounds**

There are two proposed extensions of this work in regards to the size and structure of organic compounds. Specifically, this includes assessing the validity of the Setschenow Equation up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and mixtures for compounds with relatively larger molar volumes and for organic compounds with unique functional groups.

The validity of the Setschenow Equation needs to be examined for higher molecular weight compounds, such as larger PAHs, pharmaceuticals and pesticides, up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines. All organic compounds listed here are less than 182 g/mol; future work needs to focus on the salting-out behavior of larger PAHs, phenols, carboxylic acids, NSO-compounds, and alkanes up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in those mixed electrolytes. In addition, this future work needs to focus on the salting-out behavior of emerging

contaminants including pharmaceuticals, personal care products, surfactants, pesticides, and other larger organic compounds not naturally found in oil and gas reservoirs. These organic compounds may be found in desalination reject brines, which can have concentrations of salt up to 2 – 3 M NaCl. It is possible that the salting-out behavior may exhibit deviations, due to the size of these compounds, because partial molar volumes differences, which are changing due to the presence of salt may affect the salting-out behavior of these organic compounds.

The validity of the Setschenow Equation needs to be examined for organic compounds with differing functional groups, as deviations may arise due to the presence of those groups. For example, studies on the salting-out behavior of amino acids showed that organic compounds with multiple polar groups may exhibit deviations from log-linear behavior (Khoshkbarchi & Vera 1997; Baldwin 1996). The amino acid backbone has two polar groups, a carboxylic acid group, and an amino group. When an additional hydroxyl group is added to an amino acid, deviations from log-linear salting-out behavior occur (Khoshkbarchi & Vera 1997; Baldwin 1996). The addition of a third polar group results in favorable interactions with  $\text{Na}^+$  and  $\text{Cl}^-$  in solution, which results in salting-in behavior. It is unknown whether this will occur for aromatic compounds, such as benzenetriol (i.e. 1,3,5-trihydroxybenzene), which has three hydroxyl groups on the aromatic ring, hydroxylated PAHs with multiple hydroxyl groups, or other emerging contaminants with multiple polar groups, such as the antibiotic tetracycline.

### **7.5.2 The Validity of the Setschenow Equation for other Salts**

Another focus of future work should be on the salting-out effect due to electrolytes other than NaCl or  $\text{CaCl}_2$ . For example, Janado et al. (1983) showed the naphthalene and biphenyl exhibited both salting-out and salting-in behavior with increasing concentrations of aqueous NaSCN and KSCN solutions, but benzene exhibited only salting-out behavior. The authors

hypothesized that the solutes interfered with ion-ion electrostatic interactions, causing these deviations. However, this deviation in log-linear behavior from the salting-out effect has not been determined for any other organic compounds. In addition, the validity of the Setschenow Equation needs to be examined in a variety of other saline solutions, such as  $\text{MgCl}_2$ , among others.

### **7.5.3 The Additivity of the Setschenow Equation in Mixed Electrolyte Systems**

Future research should also focus on the additivity of the Setschenow Equation, which has not been investigated for a variety of organic compounds in mixed electrolyte systems. For example, this work showed that Setschenow constants are additive up to high ionic strength mixtures of  $\text{NaCl}$  and  $\text{CaCl}_2$ . This is important for oil and gas reservoir brines, however both of these salts have a common ion. It is unknown whether organic compounds are additive in mixed electrolytes with different anions and cations, i.e. solutions with high concentrations of  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , among others. This may create differing interactions that may result in deviations from additive behavior at high salt concentrations.

The additivity of the Setschenow Equation has not been examined in multi-mixed electrolyte systems, apart from seawater, which is 80%  $\text{NaCl}$ . It is unknown if Setschenow constants will be valid in predicting the salting-out effect with large percentages of three, four, or more salts.

Another important example of future work on the additivity of the Setschenow Equation could be a follow up on Gordon and Thorne's work on the salting-out of naphthalene in mixed electrolyte solutions (Gordon & Thorne 1967). The additivity of the Setschenow constants of a mixture of inorganic and organic salts was only valid at low ionic strengths. However, at higher concentrations of the organic and inorganic salts, the additivity failed. In the presence of organic

and inorganic salts, naphthalene exhibited a larger aqueous solubility than was predicted from the individual Setschenow constants. The organic salts that were investigated are not expected to be naturally present in any oil and gas reservoir brine. More work should focus on organic salts, such as how the salts of carboxylic and dicarboxylic acids (which are present in these reservoir brines) affect the solubility of neutral dissolved organic compounds, such as BTEX, PAHs, and phenols.

#### **7.5.4 Molecular Modeling of Salting-Out Effect Mechanisms**

Future work also needs to address determining mechanisms that cause salting-out on a molecular level. There are additional intermolecular forces (i.e. in addition to van der Waals forces and hydrogen bonding) that are controlling the salting-out effect, which include ion-dipole and ion-induced dipole interactions. Abraham solvation parameters are accurate at predicting other environmental partitioning coefficients because they represent the all the van der Waals and hydrogen bonding forces between the solute and solvents, however the presence of ions introduces more complicated intermolecular forces, and the ASPs cannot predict those interactions. Therefore an additional parameter representative of organic compound interactions with ions may be useful in future modeling efforts. Future work should be focused on these issues. Molecular dynamics simulations may provide insights into these mechanisms, which may provide for better models for predictions of Setschenow constants.

#### **7.6 Future Research Related to Part II**

The work in Part II demonstrated that partitioning coefficients of organic compounds from water to sc-CO<sub>2</sub> follow trends in vapor pressure and aqueous solubility. Specifically, these parameters can be used to predict these water-sc-CO<sub>2</sub> partitioning coefficients. However, there are still experimental, and therefore, modeling gaps on this topic, described here.

### **7.6.1 Additional Partitioning Coefficients for Solid Organic Compounds**

The work in Part II demonstrated the applicability of an *in-situ* measurement device, which provides for accurate and precise partitioning coefficients. Currently, this batch reactor has only been used to measure partitioning coefficients of liquid compounds; however there are many solid toxic and carcinogenic organic compounds, such as polycyclic aromatic hydrocarbons that will require water-sc-CO<sub>2</sub> partitioning coefficients. These measured partitioning coefficients could be used to further increase the applicability of the ASP-LFER and the VP-AS-LFER. These PAHs of interest exhibit much lower aqueous solubility than the current range of the aqueous solubility applicable to the VP-AS-LFER, so representative PAH compounds will need to be measured to further calibrate this model. This will require additional method development to determine ways to introduce the organic compound into the reactor, as currently the pure liquid organic compound is titrated in the vessel from a reservoir of the organic liquid using both the high pressure syringe pump and the HPLC pump. This cannot be done with solids, so additional steps for accurate measurements will need to be taken. In addition, this may require the use of a fluorescence detector for the analysis of PAHs, which will have better sensitivity in measuring the concentration of the PAHs than a UV detector.

### **7.6.2. Co-Solvency Effect**

The co-solvency effect involves the enhancement of solubility of one organic compound due to the presence of another, more volatile organic compound (Burant et al. 2013). The solubility enhancement of one organic compound due to the presence of another can have a significant effect on the partitioning behavior of the organic compounds into sc-CO<sub>2</sub> as reported solubility enhancements have been greater than 100% (Burant et al. 2013). The solubility enhancement depends on the concentration of the enhancer in sc-CO<sub>2</sub>.

First, for the measurement of the co-solvency effect on target organic compounds using the *in-situ* batch reactor, additional method development will be required to allow for proper measurement of the organic compound in both the aqueous-rich and CO<sub>2</sub>-rich phases.

For the measurement of the organic compounds in the CO<sub>2</sub>-rich phase, the FT-NIR spectra will need to be able to differentiate between the different organic compounds present. This will not be a problem if the bands, or absorbance wavelengths on the FT-NIR spectra do not overlap.

However, measuring the co-solvency effect poses a larger problem for measuring the concentrations of organic compounds in the aqueous phase. The UV detector is set up to measure aqueous solubility of the target analyte at one specific wavelength; this will require additional engineering to be able to measure the aqueous solubility of these organic compounds in the aqueous phase. A diode array detector should be able to make measurements of the aqueous phase at different wavelengths, possibly allowing this system to be able to be used to measure the co-solvency effect

This co-solvency effect will need to be incorporated into LFERs to predict changes in partitioning behavior to sc-CO<sub>2</sub>. This perhaps may be achieved by incorporating another term that is based on the predicted mole percentage of the solubility enhancer in the CO<sub>2</sub> and this will account for the co-solvency effect. However, before this can be incorporated into LFERs, more experimental work will be needed, especially since most experimental work on the co-solvency effect is not measured in water-sc-CO<sub>2</sub> partitioning coefficients.

### **7.7 Future Work on Brine to sc-CO<sub>2</sub> Partitioning**

A synthesis of both parts of this thesis, on both the salting-out effect and the partitioning behavior of organic compounds into sc-CO<sub>2</sub> is necessary for future research. The Setschenow Equation is only valid in predicting changes in partitioning to another phase only if the salt

changes the activity coefficient of the organic compound in the aqueous phase, i.e. the second phase is not significantly impacted by the salt. This assumption may be violated in the presence of sc-CO<sub>2</sub>. First, salt will impact the mutual solubility of water and CO<sub>2</sub>. This could possibly change the partitioning behavior of organic compounds in sc-CO<sub>2</sub> that cannot be accounted for by the Setschenow Equation. Second, it is possible that high system pressures may change the partitioning behavior of the organic compound in water, which may not be able to be accounted for by the Setschenow Equation. It is necessary to determine if the Setschenow Equation will be valid in predicting the salting-out effect for brine-sc-CO<sub>2</sub> partitioning coefficients.

There is one available study on the effect of salt on the partitioning of phenol between water and sc-CO<sub>2</sub>. This study found that the Setschenow Equation was valid in predicting the salting-out of phenol into sc-CO<sub>2</sub> (Wagner et al. 2003). The authors of that study asserted that the Setschenow constants increased with increasing pressure; however a closer examination of their reported Setschenow constants shows that the Setschenow constants measured at different pressures fall within the standard error of each other, and therefore are not statistically different. However, they did find that at 313 K and 80 Bar, there was no increase in partitioning with salt addition (Wagner et al. 2003). This temperature and pressure point is close to the critical point of CO<sub>2</sub>, so it is possible that the salting-out effect close to that point deviates from expected values. However this will require more research to determine the exact mechanism for why this deviation is occurring, and to determine if the Setschenow Equation will be valid in predicting changes in partitioning from water to sc-CO<sub>2</sub> for a variety of organic compounds.

## **7.8 Future Work on Modeling of Organic Compounds in CCUS Systems**

There have been several studies on the modeling of organic compounds with water or CO<sub>2</sub> that are leaking from geologic carbon storage sites to overlying aquifers (Zheng et al. 2013; Lirong Zhong et al. 2014; L. Zhong et al. 2014). However, there still is a considerable lack of

modeling studies on the transport of organic compounds in these systems, especially for hydrophilic organic compounds. Zheng et al. (2013) modeled the transport of benzene in CO<sub>2</sub> into an overlying aquifer, and found that benzene will accumulate in those formations. However, they did not consider the presence of many parameters, such as dissolved salts and the formation solids (Zheng et al. 2013), which should have opposing effects on the transport of organic compounds. This research will allow prediction of the water-sc-CO<sub>2</sub> partitioning coefficients of organic compounds over a range of temperatures and pressures using the different LFERs, which can now be incorporated into these larger reactive transport models. Modeling of transport of organic compounds can be applied to a variety of organic compounds because the LFERs do not require previously measured data, such as PR-EOS. This will allow for more accurate predictions of partitioning of organic compounds into sc-CO<sub>2</sub>, which will reduce uncertainty in modeling levels of organic compounds transporting with brines and/or CO<sub>2</sub>.

## 7.9 References

- Al-Rifai, J.H., Gabelish, C.L. & Schäfer, A.I., 2007. Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. *Chemosphere*, 69(5), pp.803–815. Available at: <http://www.sciencedirect.com/science/article/pii/S0045653507005966>.
- Baldwin, R.L., 1996. How Hofmeister ion interactions affect protein stability. *Biophysical Journal*, 71(4), pp.2056–2063. Available at: <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1233672/>.
- Burant, A., Lowry, G.V. & Karamalidis, A.K., 2013. Partitioning behavior of organic contaminants in carbon storage environments: a critical review. *Environmental science & technology*, 47(1), pp.37–54. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/23211055>.
- Carter, Kimberly E.; Hakala, J. Alexandra; Hammack, R.W., 2013. Hydraulic Fracturing and Organic Compounds - Uses, Disposal and Challenges. In *Society of Petroleum Engineers*. pp. 1–11.
- Chang, E.I. & Pankow, J.F., 2006. Prediction of activity coefficients in liquid aerosol particles containing organic compounds, dissolved inorganic salts, and water—Part 2: Consideration of phase separation effects by an X-UNIFAC model. *Atmospheric Environment*, 40(33), pp.6422–6436. Available at: <http://www.sciencedirect.com/science/article/pii/S1352231006004171>.
- Gordon, J.E. & Thorne, R.L., 1967. Salt effects on the activity coefficient of naphthalene in mixed aqueous electrolyte solutions. I. Mixtures of two salts. *The Journal of Physical*

- Chemistry*, 71(13), pp.4390–4399. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/j100872a035>.
- Janado, M. et al., 1983. Peculiar effects of alkali thiocyanates on the activity coefficients of aromatic hydrocarbons in water. *Journal of Solution Chemistry*, 12(10), pp.741–754. Available at: <http://dx.doi.org/10.1007/BF00647385>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1988. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: benzene and toluene. *Journal of Chemical & Engineering Data*, 33(2), pp.87–89. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00052a006>.
- Keeley, D.F., Hoffpauir, M.A. & Meriwether, J.R., 1991. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: C<sub>2</sub>-Substituted benzenes. *Journal of Chemical & Engineering Data*, 36(4), pp.456–459. Available at: <http://pubs.acs.org/doi/abs/10.1021/je00004a032>.
- Kelly, E.N. et al., 2009. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. *Proceedings of the National Academy of Sciences of the United States of America*, 106(52), pp.22346–51. Available at: <http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2789758&tool=pmcentrez&rendertype=abstract>.
- Keranen, K.M. et al., 2014. Sharp increase in central Oklahoma seismicity since 2008 induced by massive wastewater injection. *Science*, 345 (6195), pp.448–451. Available at: <http://www.sciencemag.org/content/345/6195/448.abstract>.
- Khoshkbarchi, M.K. & Vera, J.H., 1997. Effect of NaCl and KCl on the Solubility of Amino Acids in Aqueous Solutions at 298.2 K: Measurements and Modeling. *Industrial & Engineering Chemistry Research*, 36(6), pp.2445–2451. Available at: <http://dx.doi.org/10.1021/ie9606395>.
- Mondal, S. & Wickramasinghe, S.R., 2008. Produced water treatment by nanofiltration and reverse osmosis membranes. *Journal of Membrane Science*, 322(1), pp.162–170. Available at: <http://www.sciencedirect.com/science/article/pii/S0376738808004729> [Accessed June 8, 2015].
- Ozaki, H. & Li, H., 2002. Rejection of organic compounds by ultra-low pressure reverse osmosis membrane. *Water Research*, 36(1), pp.123–130. Available at: <http://www.sciencedirect.com/science/article/pii/S004313540100197X> [Accessed June 30, 2015].
- Reddy, C.M. et al., 2012. Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. *Proceedings of the National Academy of Sciences*, 109 (50), pp.20229–20234. Available at: <http://www.pnas.org/content/109/50/20229.abstract>.
- Renault, S. et al., 1998. Effect of high salinity tailings waters produced from gypsum treatment of oil sands tailings on plants of the boreal forest. *Environmental Pollution*, 102(2–3), pp.177–184. Available at: <http://www.sciencedirect.com/science/article/pii/S0269749198000992>.
- Ross, M.S. et al., 2012. Quantitative and Qualitative Analysis of Naphthenic Acids in Natural Waters Surrounding the Canadian Oil Sands Industry. *Environmental Science & Technology*, 46(23), pp.12796–12805. Available at: <http://pubs.acs.org/doi/abs/10.1021/es303432u>.

- Vörösmarty, C.J. et al., 2000. Global Water Resources: Vulnerability from Climate Change and Population Growth. *Science*, 289 (5477), pp.284–288. Available at: <http://www.sciencemag.org/content/289/5477/284.abstract>.
- Wagner, K.-D., Dahmen, N. & PiaGriesheimer, 2003. Salt effects on the partition coefficients of phenol in two-phase mixtures of water and carbon dioxide at pressures from 8 to 30 MPa at a temperature of 313 K. *The Journal of Chemical Thermodynamics*, 35(4), pp.677–687. Available at: <http://www.sciencedirect.com/science/article/pii/S0021961402002392>.
- Ward, A.L. et al., 2005. *STOMP: Subsurface Transport Over Multiple Phases. Version 1.0: Addendum: Sparse Vegetation, Evapotranspiration Model for the Water-Air-Energy Operational Mode. (PNNL-15465)*, Available at: [http://www.pnl.gov/main/publications/external/technical\\_reports/PNNL-15465.pdf](http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15465.pdf).
- Xu, T. et al., 2006. TOUGHREACT—A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration. *Computers & Geosciences*, 32(2), pp.145–165. Available at: <http://www.sciencedirect.com/science/article/pii/S0098300405001500> [Accessed April 17, 2015].
- Zheng, L. et al., 2013. On modeling the potential impacts of CO<sub>2</sub> sequestration on shallow groundwater: Transport of organics and co-injected H<sub>2</sub>S by supercritical CO<sub>2</sub> to shallow aquifers. *International Journal of Greenhouse Gas Control*, 14, pp.113–127. Available at: <http://www.sciencedirect.com/science/article/pii/S1750583613000303> [Accessed May 21, 2014].
- Zhong, L. et al., 2014. Mobilization and transport of organic compounds from reservoir rock and caprock in geological carbon sequestration sites. *Environmental Earth Sciences*, 71(9), pp.4261–4272. Available at: <http://dx.doi.org/10.1007/s12665-013-2823-z>.
- Zhong, L. et al., 2014. Transport of organic contaminants mobilized from coal through sandstone overlying a geological carbon sequestration reservoir. *International Journal of Greenhouse Gas Control*, 21, pp.158–164. Available at: <http://www.sciencedirect.com/science/article/pii/S1750583613004386> [Accessed May 2, 2014].
- Zuend, a. et al., 2010. Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols. *Atmospheric Chemistry and Physics*, 10(16), pp.7795–7820. Available at: <http://www.atmos-chem-phys.net/10/7795/2010/> [Accessed December 9, 2013].

## Appendix A

### Chapter 3:

Determine the validity of the Setschenow Equation for selected hydrophobic compounds in the range of 2 - 5 M NaCl, 1.5 - 2 M CaCl<sub>2</sub>, and mixed electrolyte brines.

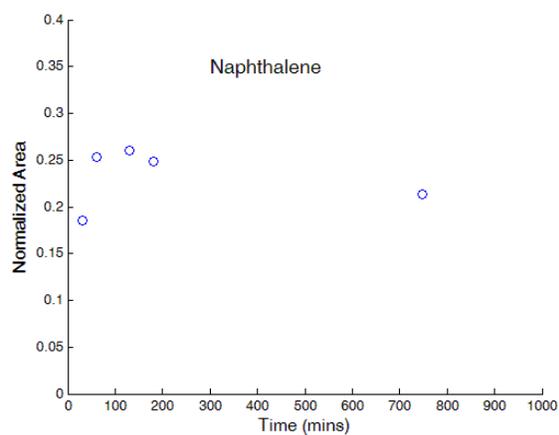
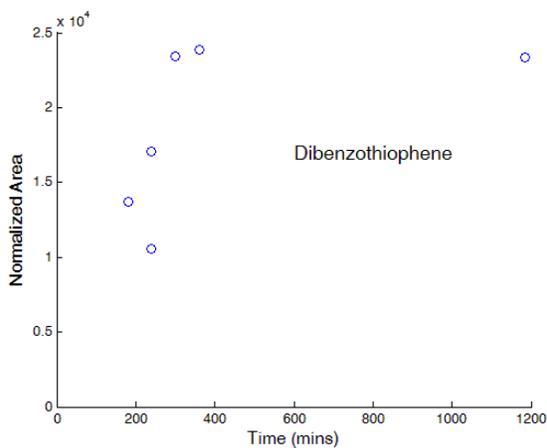
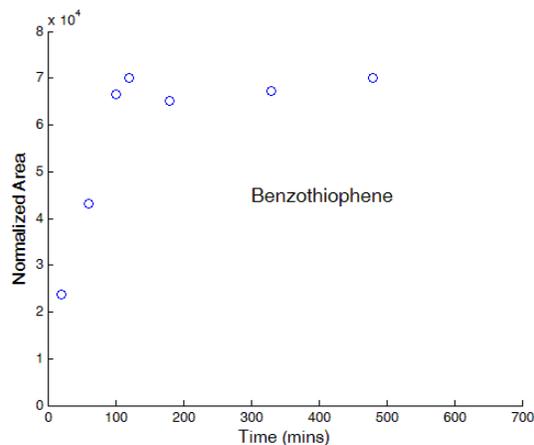
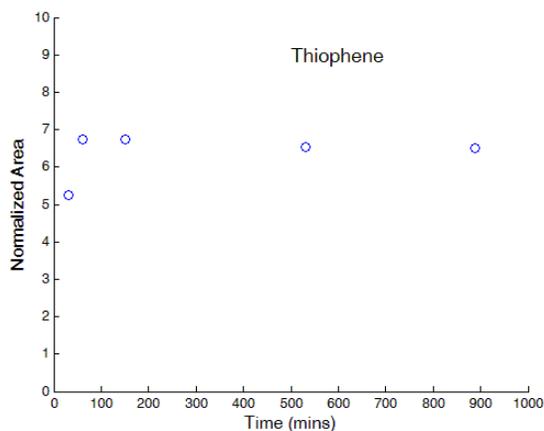
## A.1 Solid Phase Microextraction

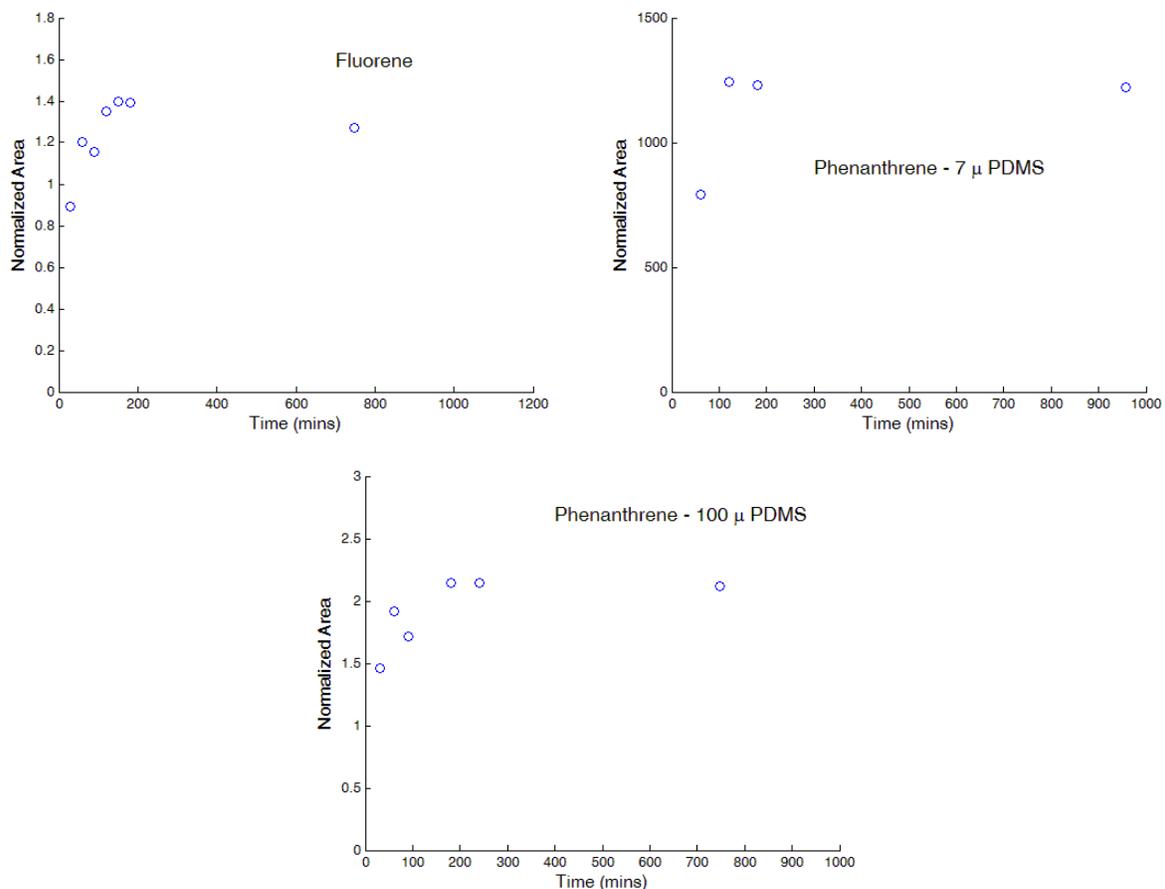
**Table A.1.1** Fibers, time to equilibrium, and concentrations associated with the organic compounds in this study.

Organic Compound	Type of Fiber Used	Time to Equilibrium (mins)	Concentration in Water (mg/L)
Thiophene	85 $\mu\text{m}$ PA <sup>a</sup>	60	~22
Benzothiophene	85 $\mu\text{m}$ PA	120	~0.75
Dibenzothiophene	100 $\mu\text{m}$ PDMS <sup>b</sup>	300	~0.2
Naphthalene	100 $\mu\text{m}$ PDMS	60	~1.3
Fluorene	100 $\mu\text{m}$ PDMS	150	~0.5
Phenanthrene	7 and 100 $\mu\text{m}$ PDMS	120, 240	~0.2

<sup>a</sup>PA: Polyacrylate

<sup>b</sup>PDMS: Polydimethylsiloxane





**Figure A.1.1** Time to equilibrium uptake curves for the compounds of interest in this study.

Time to equilibrium increased with increasing salt addition. For example, at 1 M NaCl, the time to equilibrium doubled. Time to equilibrium for the 2 M and 3 M NaCl solutions, was achieved in 12 hours. Time to equilibrium for the 4 M solutions was achieved in 24 hours. For the 5 M NaCl concentrations the aqueous solutions were equilibrated with the fiber for 24-48 hours. The time to equilibrium was confirmed by having longer exposure times. The 1 -3 M NaCl time was confirmed by 12-18 hour exposure time, the 4 M NaCl concentrations were confirmed by 48 hour exposure.

Only one measurement occurred per sample vial; however three replicates per salt concentration were taken (four replicates for naphthalene to ensure validity of the method). Although no internal standards were used because the validity of the Setschenow Equation could

not be confirmed for those standards, a calibration curve was constructed to ensure linearity over the concentration range of interest. With one notable exception, all Setschenow constants were close to either predicted and/or previous experimental Setschenow constants (see Results and Discussion in Chapter 3).

## **A.2. Removal of Data Points: Depletion and Aqueous Solubility Tables**

After all the data was collected for the study, an analysis of depletion and aqueous solubility for the systems was investigated, and it was found that some of the data exhibited errors. We conducted a rigorous assessment of each data point, and have only presented the most accurate data in the published manuscript. This is a discussion of that data assessment.

### **Aqueous solubility**

If the initial amount of organic compound resulted in an aqueous concentration that exceeded the aqueous solubility limits at the salt concentration at which it was measured, it was removed. See criteria for removal below. This only occurred for NaCl solutions of phenanthrene and fluorene, and coincided with exceedances of depletion for all but two points (the measurement of phenanthrene at 4 M NaCl and fluorene at 2 M CaCl<sub>2</sub>, which have been removed from the manuscript).

### **Depletion**

To accurately measure the salting-out effect of organic compounds using solid phase microextraction, the system must be non-depleting. Each of these tables (**Tables A.2.3-A2.3.8**) and figures (*Figures A.2.1-A2.1.6*) compares the predicted salting-out effect assuming an infinite bath (i.e. no depletion), the salting-out effect with depletion (this was based on the volume of the solution used), and the experimental data.

This assessment is based on work of non-depletion SPME theory. The salting-out effect measured by SPME should be non-depleting. Based on this, the amount of moles of organic fiber extracted by the fiber is given by Eqn. A.2.1:

$$n_{SPME} = K_{SPME-Water}^i \cdot V_{SPME} \cdot C_{0,water}^i \quad \text{Eqn. A.2.1.}$$

Here,  $n_{SPME}$  is the number of moles extracted by the SPME fiber,  $K_{SPME-Water}^i$  is the fiber-water partition coefficient,  $V_{SPME}$  is the volume of the SPME fiber, and  $C_{0,water}^i$  is the initial concentration in the water.

However in reality, there is always a small amount of the organic compound removed by the fiber. This is given by Eqn. A.2.2:

$$n_{SPME} = \frac{K_{SPME-Water}^i \cdot V_{SPME} \cdot V_{water} \cdot C_{0,water}^i}{K_{SPME-Water}^i \cdot V_{SPME} + V_{water}} \quad \text{Eqn. A.2.2}$$

Here,  $V_{water}$  is the volume of the water in the system.

If SPME is considered “non-depleting,” the amount removed given Eq. A.2.1 is close to the amount given by Eqn A.2.2. This definition of “close” is different for different researchers (Heringa & Hermens 2003). We have defined a window. The criteria and procedure for determining which points were accurate are as follows:

1. Calculate the amount removed by fibers for each case (depleting and non-depleting). Divide the value by the initial amount removed for each case (i.e. no salt added), and then log that value. Compare those two values to the log change in area count measured.

2. Those values were compared to the standard errors on those calculated and measured values.
3. The standard errors on the total Setschenow constants (i.e. the standard errors reported in Table 1 in the manuscript) were used as the standard errors for the predicted salting-out with and with-out depletions.
4. The standard errors on the experimental data points were the standard errors of the triplicates at each salinity measurement.
5. The log change in “salting-out” for the non-depleted data point plus or minus the standard error was considered the total window by which a data point was deemed acceptable and included in the regression. If both the experimental data and the depleted data point (plus or minus the standard error) fell within that window, the data was deemed accurate.
6. Aqueous solubility data was evaluated by both the standard error on the experimental aqueous solubility point and the experimental Setschenow constant. If the aqueous solubility was outside the window, the data were excluded.
7. If data points were excluded, then the Setschenow constant was re-regressed. These criteria were evaluated once again. No data points were excluded after the re-regression, providing more evidence that the data presented in the manuscript was accurate.

This resulted in removal of points from benzothiophene, dibenzothiophene, fluorene, and phenanthrene. These removed points are highlighted in *Figures A.2.3-6*.

The volumes of the fiber, as given by the manufacturer are given in **Table A.2.1**.

**Table A.2.1.** Volumes of fibers used in this study.

<b>Fiber</b>	<b>Volume (<math>\mu\text{L}</math>)</b>
100 $\mu\text{m}$ PDMS	0.612
7 $\mu\text{m}$ PDMS	0.028
85 $\mu\text{m}$ PA	0.52

Fiber-water partition coefficients for the PDMS fibers were estimated using a model (Mayer et al. 2000) that predicted the partition coefficients from their octanol water partition coefficients (Appendix A.4). The fiber-water partition coefficients for the PA fibers were estimated using Eqn. A.2.4 (Endo et al. 2011). Abraham solvation parameters are listed in Appendix A.3.

$$\log K_{PDMS-Water}^i = 1.00 \log K_{o/w}^i - 0.91 \quad \text{Eqn. A.2.3.}$$

$$\log K_{PA-Water}^i = -0.12 + 0.50R_2 - 0.16\pi_2 + 0.16\alpha_2 - 4\beta_2 + 3.28V_2 \quad \text{Eqn. A.2.4.}$$

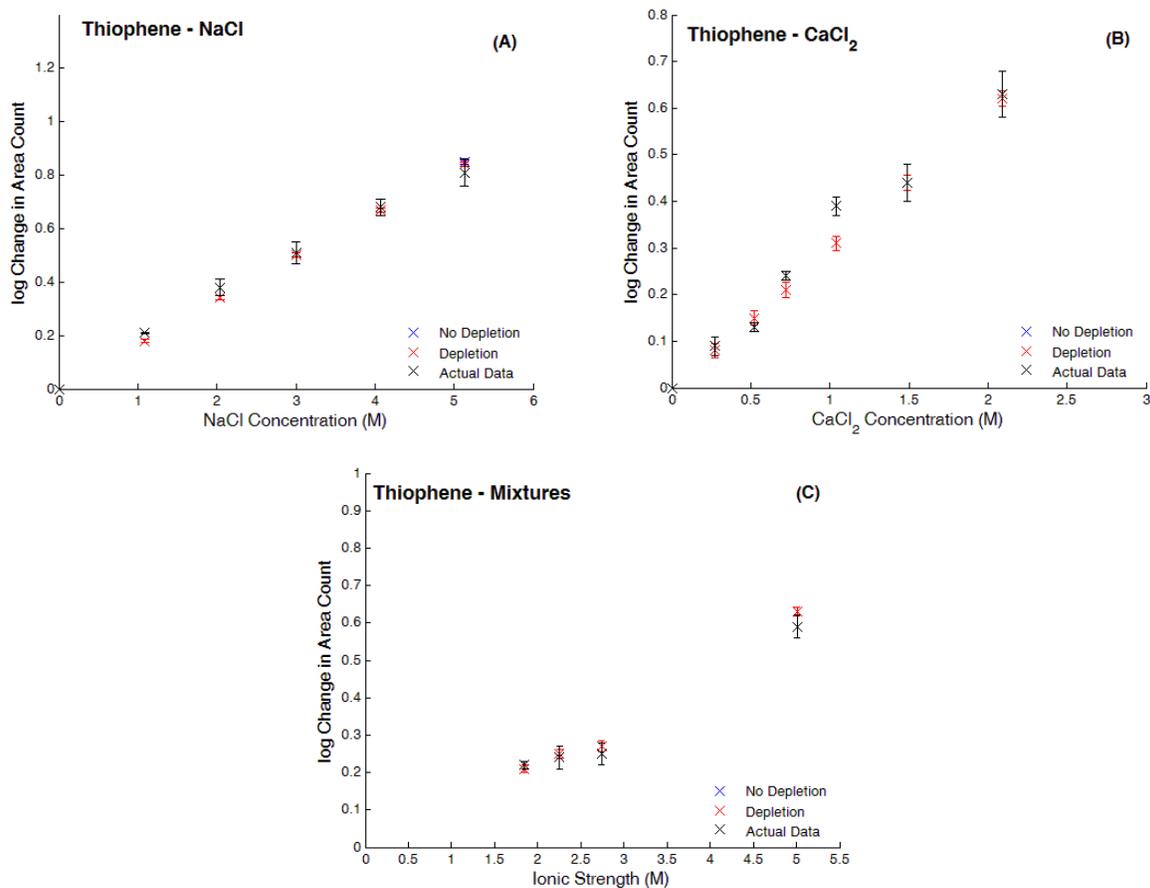
**Table A.2.2** Fiber-Water Partitioning Coefficients and Aqueous Solubility Sources for Each Compound.

Organic Compound	Log Fiber – Water partitioning Coefficient	Type of Fiber	Aqueous Solubility (mg/L)
Thiophene	1.67 (Endo et al. 2011)	85 μm PA	2984 (Valvani et al. 1981)
Benzothiophene	2.82 (Endo et al. 2011)	85 μm PA	160±6 (Seymour et al. 1997)
Dibenzothiophene	3.55 (Mayer et al. 2000)	100 μm PDMS	1±0.15 (Seymour et al. 1997)
Naphthalene	2.42 (Mayer et al. 2000)	100 μm PDMS	31.7±0.3 (Mackay & Shiu 1977)
Fluorene	3.41 (Mayer et al. 2000)	100 μm PDMS	1.98±0.04 (Mackay & Shiu 1977)
Phenanthrene	3.66 (Mayer et al. 2000)	7 and 100 μm PDMS	1.29±0.07 (Mackay & Shiu 1977)

**Table A.2.3.** Depletion and Aqueous Solubility of Thiophene in Salt Solutions

NaCl Concentration (M)	Salting Out No Depletion ( $M^{-1}$ )	SE <sup>a</sup> ( $M^{-1}$ )	Salting Out with Depletion ( $M^{-1}$ )	SE ( $M^{-1}$ )	Actual Salting-Out Data ( $M^{-1}$ )	SE ( $M^{-1}$ )	Aqueous Solubility (mg/L)
0	0.00	0	0.00	0	0.00	0.00	2984
1.09	0.18	0.008	0.18	0.008	0.21	0.00	1337
2.04	0.34	0.008	0.34	0.008	0.38	0.03	664
3.00	0.50	0.008	0.49	0.008	0.51	0.04	327
4.07	0.67	0.008	0.67	0.008	0.68	0.03	149
5.13	0.85	0.008	0.84	0.008	0.81	0.05	68
CaCl <sub>2</sub> Concentration (M)	Salting Out No Depletion ( $M^{-1}$ )	SE ( $M^{-1}$ )	Salting Out with Depletion ( $M^{-1}$ )	SE ( $M^{-1}$ )	Actual Salting-Out Data ( $M^{-1}$ )	SE ( $M^{-1}$ )	Aqueous Solubility (mg/L)
0	0.00	0	0.00	0	0.00	0.00	2984
0.27	0.08	0.016	0.08	0.016	0.09	0.02	2482
0.52	0.15	0.016	0.15	0.016	0.13	0.01	2101
0.72	0.21	0.016	0.21	0.016	0.24	0.01	1827
1.04	0.31	0.016	0.31	0.016	0.29	0.02	1470
1.49	0.44	0.016	0.44	0.016	0.44	0.04	1082
2.09	0.62	0.016	0.62	0.016	0.63	0.05	719
Ionic Strength (M)	Salting Out No Depletion ( $M^{-1}$ )	SE ( $M^{-1}$ )	Salting Out with Depletion ( $M^{-1}$ )	SE ( $M^{-1}$ )	Actual Salting-Out Data ( $M^{-1}$ )	SE ( $M^{-1}$ )	Aqueous Solubility (mg/L)
1.85	0.21	0.010	0.21	0.010	0.22	0.01	1828
2.25	0.25	0.012	0.25	0.012	0.24	0.03	1668
2.74	0.27	0.014	0.27	0.014	0.25	0.03	1590
5.01	0.63	0.011	0.63	0.011	0.59	0.03	703

<sup>a</sup>SE: Standard Error

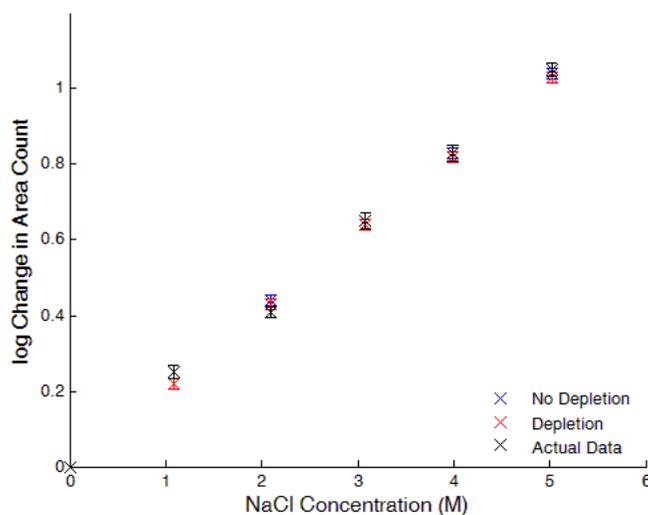


**Figure A.2.1** The change in “salting-out” for thiophene in A) NaCl, B) CaCl<sub>2</sub>, and C) Mixed electrolyte solutions. The actual log change in area count data are in black, the calculated salting-out with no depletion is in blue, and the calculated salting-out with depletion is in red.

**Table A.2.4.** Depletion and Aqueous Solubility of Naphthalene in Salt Solutions

NaCl Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE <sup>a</sup> (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0	0.00	0	0.00	0.00	31.7	32.0	31.4
1.08	0.22	0.015	0.22	0.015	0.25	0.017	14.30	19.8	18.1
2.1	0.44	0.015	0.43	0.015	0.41	0.014	6.75	12.6	10.7
3.09	0.64	0.015	0.64	0.015	0.65	0.021	3.25	8.1	6.4
3.99	0.83	0.015	0.82	0.015	0.83	0.021	1.68	5.4	4.1
5.02	1.04	0.015	1.03	0.015	1.05	0.018	0.78	3.4	2.4

<sup>a</sup>SE: Standard Error

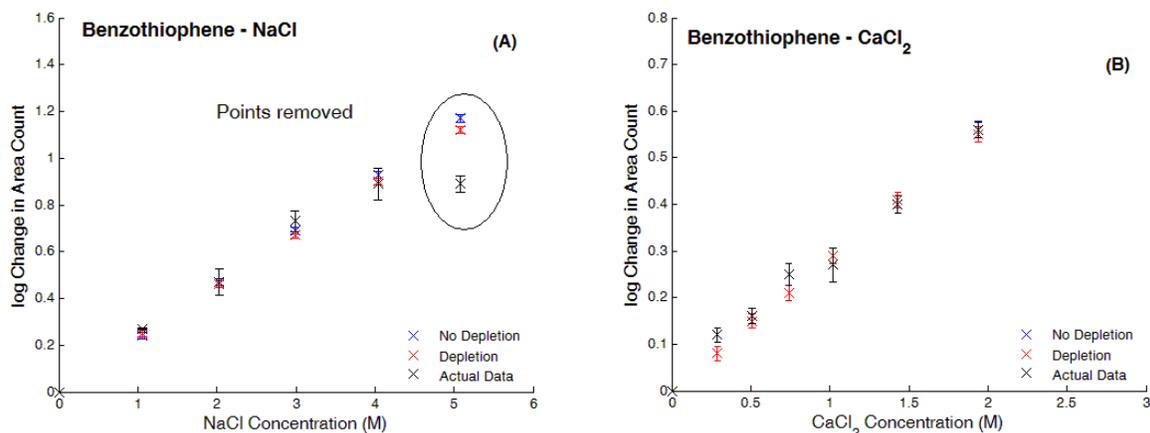


**Figure A.2.2.** The change in “salting-out” for naphthalene in NaCl. The actual log change in area count data are in black, the calculated salting-out with no depletion is in blue, and the calculated salting-out with depletion is in red.

**Table A.2.5.** Depletion and Aqueous Solubility of Benzothiophene in Salt Solutions

NaCl Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE <sup>a</sup> (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0	0.00	0	0.00	0.000	160.0	166.0	154.0
1.06	0.24	0.015	0.24	0.015	0.27	0.003	73.3	98.2	84.7
2.03	0.47	0.015	0.46	0.015	0.47	0.055	35.9	60.8	49.0
2.99	0.69	0.015	0.67	0.015	0.73	0.045	17.7	37.8	28.5
4.04	0.93	0.015	0.90	0.015	0.89	0.069	8.2	22.5	15.8
5.08	1.17	0.015	1.12	0.015	0.89	0.035	3.8	13.4	8.8
CaCl <sub>2</sub> Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0	0.00	0	0.00	0.00	160.0	166.0	154.0
0.29	0.08	0.016	0.08	0.016	0.12	0.016	131.9	136.9	127.0
0.51	0.15	0.016	0.15	0.016	0.16	0.016	114.0	118.2	109.7
0.74	0.21	0.016	0.21	0.016	0.25	0.024	97.8	101.4	94.1
1.02	0.29	0.016	0.29	0.016	0.27	0.036	81.2	84.2	78.1
1.43	0.41	0.016	0.41	0.016	0.40	0.019	61.8	64.1	59.5
1.94	0.56	0.016	0.55	0.016	0.56	0.018	44.0	45.7	42.4

<sup>a</sup>SE: Standard Error



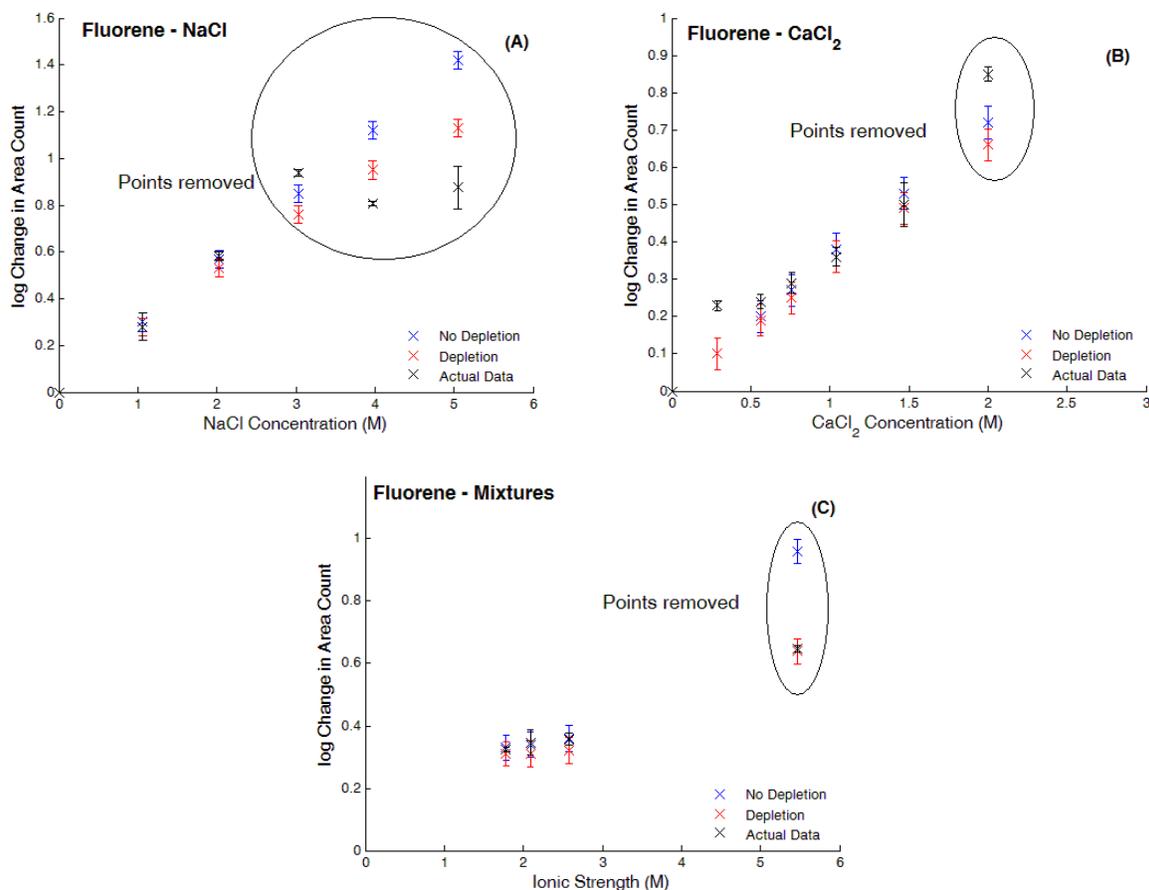
**Figure A.2.3.** The change in “salting-out” for benzothiophene in A) NaCl and B) CaCl<sub>2</sub>. The actual log change in area count data are in black, the calculated salting-out with no depletion is in blue, and the calculated salting-out with depletion is in red. The points removed from the regression in the manuscript are encircled.

**Table A.2.6.** Depletion and Aqueous Solubility of Fluorene in Salt Solutions

NaCl Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE <sup>a</sup> (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0.000	0.00	0.00	0.00	0.00	1.98	2.02	1.94
1.06	0.30	0.038	0.28	0.04	0.28	0.06	1.00	1.12	0.89
2.03	0.57	0.038	0.53	0.04	0.58	0.02	0.53	0.65	0.44
3.03	0.85	0.038	0.76	0.04	0.94	0.01	0.28	0.37	0.21
3.97	1.12	0.038	0.95	0.04	0.81	0.01	0.15	0.22	0.10
5.05	1.42	0.038	1.13	0.04	0.87	0.09	0.08	0.12	0.05
CaCl <sub>2</sub> Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0.000	0.00	0.00	0.00	0.00	1.98	2.02	1.94
0.29	0.10	0.043	0.10	0.04	0.23	0.01	1.56	1.59	1.53
0.56	0.20	0.043	0.19	0.04	0.24	0.02	1.25	1.25	1.25
0.76	0.27	0.043	0.26	0.04	0.29	0.03	1.05	1.05	1.05
1.04	0.38	0.043	0.36	0.04	0.36	0.02	0.83	0.83	0.83
1.47	0.53	0.043	0.49	0.04	0.50	0.06	0.58	0.59	0.58
2.00	0.72	0.043	0.66	0.04	0.85	0.02	0.38	0.38	0.37
Ionic Strength (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
1.78	0.54	0.039	0.43	0.039	0.32	0.006	0.58	0.59	0.56
2.09	0.67	0.041	0.42	0.041	0.35	0.041	0.42	0.43	0.41
2.58	0.88	0.042	0.36	0.042	0.36	0.019	0.26	0.27	0.25

5.47	1.68	0.040	0.82	0.040	0.65	0.011	0.04	0.04	0.04
------	------	-------	------	-------	------	-------	------	------	------

<sup>a</sup>SE: Standard Error



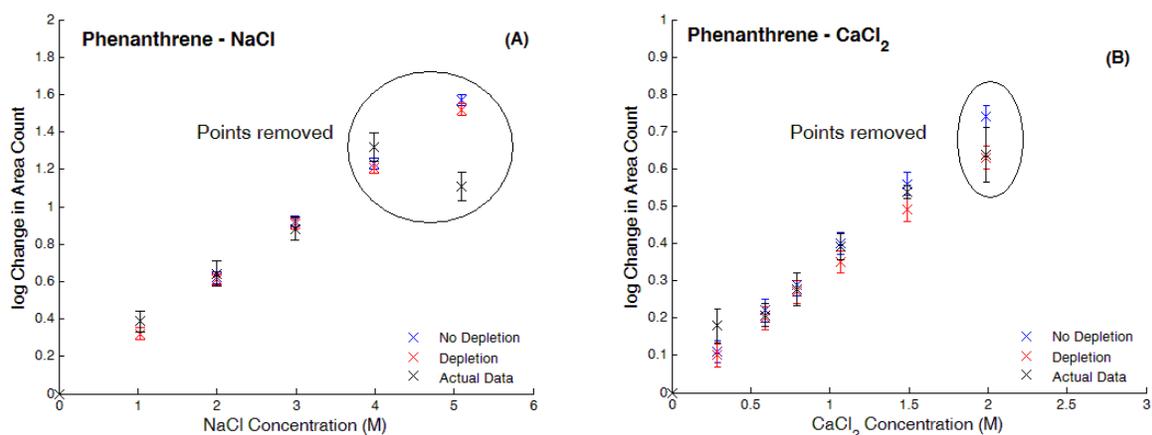
**Figure A.2.4.** The change in “salting-out” for fluorene in A) NaCl, B) CaCl<sub>2</sub>, and C) Mixed electrolyte solutions. The actual log change in area count data are in black, the calculated salting-out with no depletion is in blue, and the calculated salting-out with depletion is in red. The points removed from the regression in the manuscript are encircled. The points removed from the regression in the manuscript are encircled.

**Table A.2.7.** Depletion and Aqueous Solubility of Phenanthrene in Salt Solutions

NaCl Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE <sup>a</sup> (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0	0.00	0	0	0	1.29	1.36	1.22
1.03	0.32	0.031	0.32	0.031	0.387	0.057	0.62	0.71	0.55
2	0.62	0.031	0.61	0.031	0.643	0.065	0.31	0.38	0.26
2.99	0.92	0.031	0.91	0.031	0.882	0.063	0.15	0.20	0.12

3.99	1.23	0.031	1.21	0.031	1.317	0.076	0.08	0.11	0.05
5.1	1.57	0.031	1.52	0.031	1.108	0.077	0.03	0.05	0.02
CaCl <sub>2</sub> Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0	0.03	0	0.03	0	0.000	1.29	1.36	1.22
0.29	0.11	0.03	0.10	0.03	0.179	0.045	1.01	1.08	0.93
0.59	0.22	0.03	0.20	0.03	0.208	0.032	0.78	0.85	0.71
0.79	0.29	0.03	0.27	0.03	0.276	0.044	0.65	0.73	0.59
1.07	0.40	0.03	0.36	0.03	0.392	0.036	0.51	0.58	0.45
1.49	0.56	0.03	0.49	0.03	0.538	0.017	0.36	0.42	0.31
1.99	0.74	0.03	0.63	0.03	0.638	0.074	0.23	0.28	0.19

<sup>a</sup>SE: Standard Error



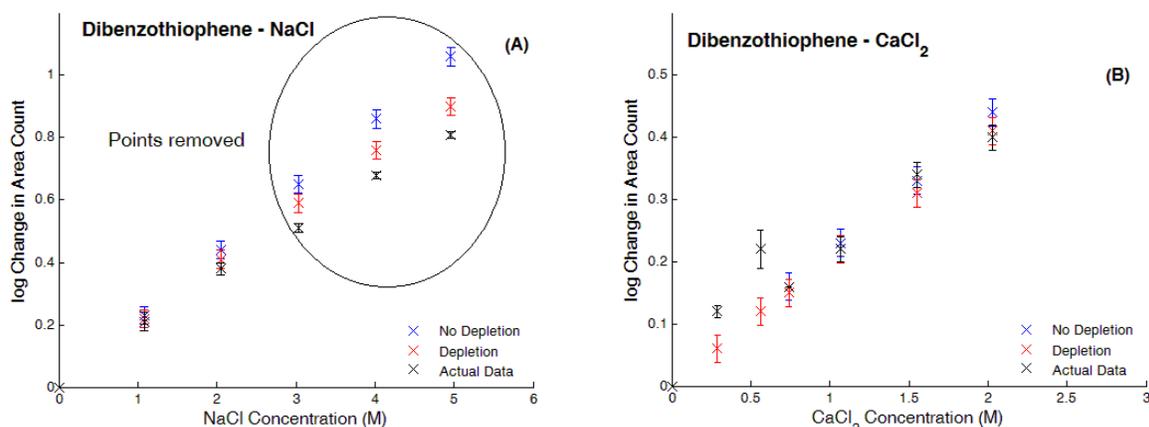
**Figure A.2.5.** The change in “salting-out” for phenanthrene in A) NaCl and B) CaCl<sub>2</sub>. The actual log change in area count data are in black, the calculated salting-out with no depletion is in blue, and the calculated salting-out with depletion is in red. The points removed from the regression in the manuscript are encircled

**Table A.2.8.** Depletion and Aqueous Solubility of Dibenzothiophene in Salt Solutions

NaCl Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE <sup>a</sup> (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0	0.00	0	0.00	0.00	1	1.15	0.85
1.08	0.23	0.0286	0.22	0.03	0.21	0.03	0.59	0.73	0.47
2.05	0.44	0.0286	0.41	0.03	0.38	0.02	0.37	0.48	0.27
3.03	0.65	0.0286	0.59	0.03	0.51	0.01	0.23	0.32	0.16
4.02	0.86	0.0286	0.76	0.03	0.68	0.01	0.14	0.21	0.09
4.96	1.06	0.0286	0.90	0.03	0.81	0.01	0.09	0.14	0.05

CaCl <sub>2</sub> Concentration (M)	Salting Out No Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Salting Out with Depletion (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Actual Salting-Out Data (M <sup>-1</sup> )	SE (M <sup>-1</sup> )	Aqueous Solubility (mg/L)	Aqueous Solubility + SE (mg/L)	Aqueous Solubility - SE (mg/L)
0	0.00	0	0.00	0	0.00	0.00	1	1.15	0.85
0.29	0.06	0.022	0.06	0.022	0.12	0.01	0.87	1.00	0.74
0.56	0.12	0.022	0.12	0.022	0.22	0.03	0.76	0.87	0.64
0.74	0.16	0.022	0.15	0.022	0.16	0.00	0.69	0.80	0.59
1.07	0.23	0.022	0.22	0.022	0.22	0.02	0.59	0.68	0.50
1.55	0.33	0.022	0.31	0.022	0.34	0.02	0.46	0.53	0.39
2.03	0.44	0.022	0.41	0.022	0.40	0.02	0.36	0.42	0.31

<sup>a</sup>SE: Standard Error



**Figure A.2.6.** The change in “salting-out” for dibenzothiophene in A) NaCl and B) CaCl<sub>2</sub>. The actual log change in area count data are in black, the calculated salting-out with no depletion is in blue, and the calculated salting-out with depletion is in red. The points removed from the regression in the manuscript are encircled

### A.3 Abraham Solvation Parameters

**Table A.3.1.** Abraham Solvation Parameters of Organic Compounds in this Study

Organic Compound	$R_2$	$\pi_2$	$\alpha_2$	$\beta_2$	$V_x$
Thiophene	0.687	0.56	0	0.15	0.6411
Benzothiophene	1.323	0.88	0	0.2	0.9821
Dibenzothiophene	1.959	1.31	0	0.18	1.3791
Naphthalene	1.34	0.92	0	0.2	1.085
Fluorene	1.59	1.06	0	0.25	1.357
Phenanthrene	2.06	1.29	0	0.29	1.454

#### A.4 Aqueous solubility, octanol-water partitioning coefficients, and experimentally determined NaCl and CaCl<sub>2</sub> Setschenow Constants and Associated Measurement Error.

**Table A.4.1.** Partitioning information of organic compounds used in this study.

Organic Compound	Log K <sub>ow</sub>	NaCl K <sub>s</sub> (M <sup>-1</sup> )	R <sup>2</sup>	Std Error (M <sup>-1</sup> )	CaCl <sub>2</sub> K <sub>s</sub> (M <sup>-1</sup> )	R <sup>2</sup>	Std Error (M <sup>-1</sup> )
Thiophene	1.81 (Johansen & Pawliszyn 1996)	0.165	0.962	0.008	0.295	0.959	0.016
Benzothiophene	3.17 (Andersson & Schröder 1999)	0.230 <sup>b</sup>	0.928	0.017	0.289	0.943	0.018
Naphthalene	3.33 (Schwarzenbach et al. 2003)	0.208	0.885	0.015	N/A	N/A	N/A
Dibenzothiophene	4.36 (Andersson & Schröder 1999)	0.213 <sup>a</sup>	0.880	0.029	0.217	0.868	0.022
Phenanthrene	4.32 (Schwarzenbach et al. 2003)	0.308 <sup>b</sup>	0.902	0.031	0.373 <sup>d</sup>	0.903	0.03
Fluorene	4.57 (Schwarzenbach et al. 2003)	0.281 <sup>a</sup>	0.895	0.038	0.362 <sup>d</sup>	0.816	0.043

<sup>a</sup>Determined using data up to 2 M NaCl

<sup>b</sup>Determined using data up to 3 M NaCl

<sup>c</sup>Determined using data up to 4 M NaCl

<sup>d</sup>Determined using data up to 1.5 M CaCl<sub>2</sub>

\*Measured in a different study.

#### A.5 References

- Andersson, J.T. & Schröder, W., 1999. A Method for Measuring 1-Octanol–Water Partition Coefficients. *Analytical Chemistry*, 71(16), pp.3610–3614. Available at: <http://dx.doi.org/10.1021/ac9902291>.
- Endo, S., Droge, S.T.J. & Goss, K.-U., 2011. Polyparameter Linear Free Energy Models for Polyacrylate Fiber–Water Partition Coefficients to Evaluate the Efficiency of Solid-Phase Microextraction. *Analytical Chemistry*, 83(4), pp.1394–1400. Available at: <http://dx.doi.org/10.1021/ac102868e>.
- Heringa, M.B. & Hermens, J.L.M., 2003. Measurement of free concentrations using negligible depletion-solid phase microextraction (nd-SPME). *TrAC Trends in Analytical Chemistry*, 22(9), pp.575–587. Available at: <http://www.sciencedirect.com/science/article/pii/S0165993603010069> [Accessed June 8, 2015].
- Johansen, S. & Pawliszyn, J., 1996. Trace analysis of hetero aromatic compounds (NSO) in water and polluted groundwater by Solid phase micro-extraction (SPME). *Journal of High*

- Resolution ...*, 19, pp.627–632. Available at:  
<http://onlinelibrary.wiley.com/doi/10.1002/jhrc.1240191107/full>.
- Mackay, D. & Shiu, W.Y., 1977. Aqueous solubility of polynuclear aromatic hydrocarbons. *Journal of Chemical & Engineering Data*, 22(4), pp.399–402. Available at:  
<http://dx.doi.org/10.1021/je60075a012>.
- Mayer, P., Vaes, W.H.J. & Hermens, J.L.M., 2000. Absorption of Hydrophobic Compounds into the Poly(dimethylsiloxane) Coating of Solid-Phase Microextraction Fibers: High Partition Coefficients and Fluorescence Microscopy Images. *Analytical Chemistry*, 72(3), pp.459–464. Available at: <http://dx.doi.org/10.1021/ac990948f>.
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Seymour, D.T. et al., 1997. Acute toxicity and aqueous solubility of some condensed thiophenes and their microbial metabolites. *Environmental Toxicology and Chemistry*, 16(4), pp.658–665. Available at: <http://dx.doi.org/10.1002/etc.5620160409>.
- Valvani, S.C., Yalkowsky, S.H. & Roseman, T.J., 1981. Solubility and partitioning IV: Aqueous solubility and octanol-water partition coefficients of liquid nonelectrolytes. *Journal of Pharmaceutical Sciences*, 70(5), pp.502–507. Available at:  
<http://dx.doi.org/10.1002/jps.2600700510>.

## **Appendix B**

### Chapter 4:

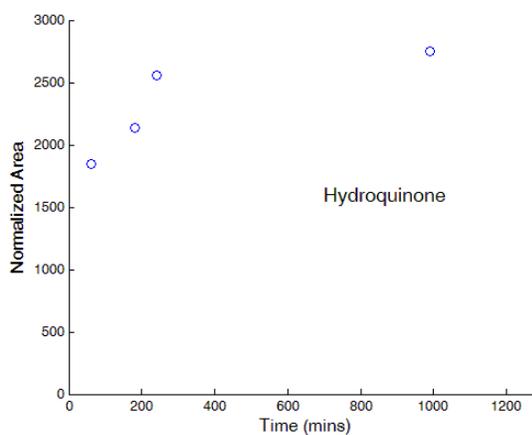
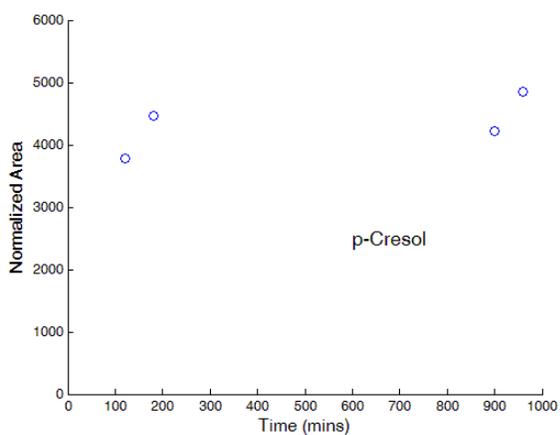
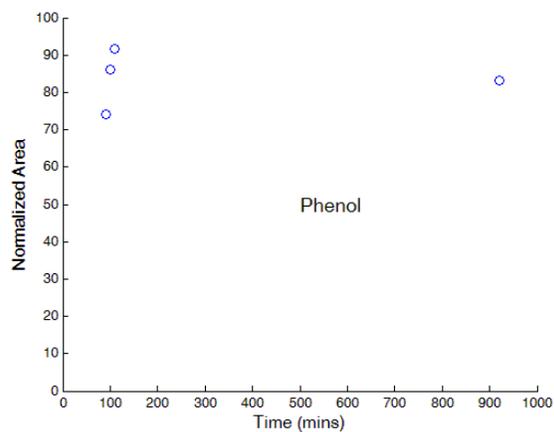
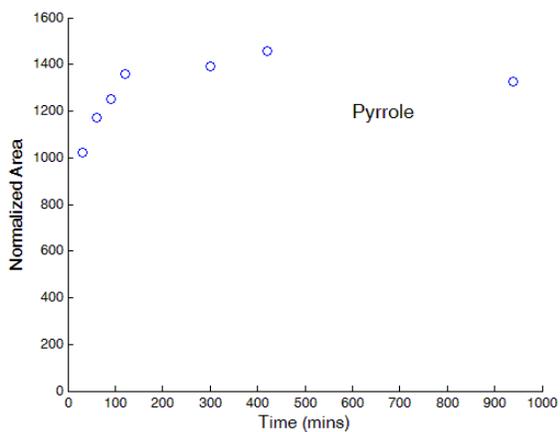
Determine the validity of the Setschenow Equation for selected hydrophilic compounds up to 5 M NaCl, 2 M CaCl<sub>2</sub>, and in mixed electrolyte brines.

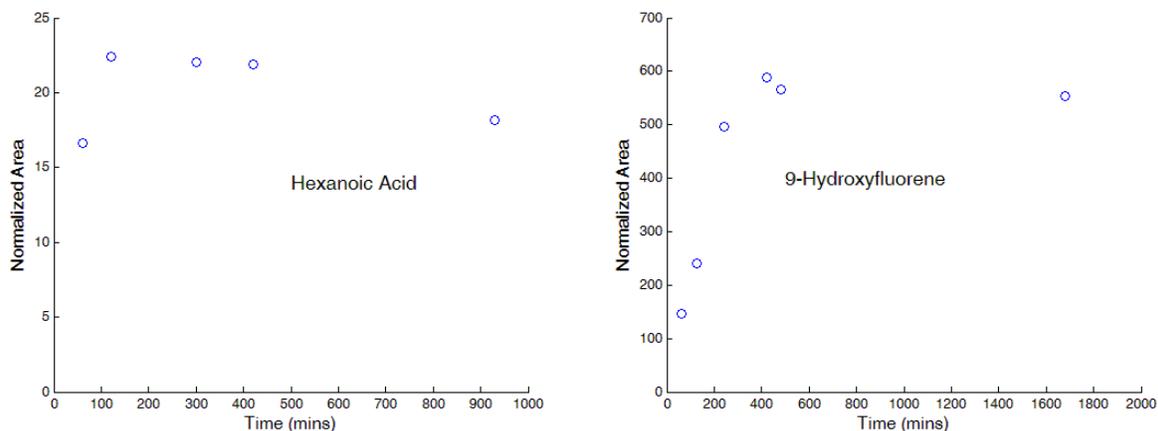
## B.1. Solid Phase Microextraction

**Table B.1.1** Fibers, time to equilibrium, and concentrations associated with the organic compounds in this study.

Organic Compound	Type of Fiber Used	Time to Equilibrium (mins)	Concentration in Water (mg/L)
Pyrrole	85 $\mu$ m PA <sup>a</sup>	120	~300
Phenol	85 $\mu$ m PA	120	~45
p-Cresol	85 $\mu$ m PA	180	~8.5
Hydroquinone	85 $\mu$ m PA	240	~45
Hexanoic Acid	85 $\mu$ m PA	240	~160
9-HydroxyFluorene	85 $\mu$ m PA	420	~6

<sup>a</sup>PA: Polyacrylate





**Figure B.1.1** Time to equilibrium uptake curves for the compounds of interest in this study.

Time to equilibrium increased with increasing salt addition. For example, at 1 M NaCl, the time to equilibrium doubled. Time to equilibrium for both 2 M and 3 M NaCl, was achieved in 12 hours (this was achieved in 18 hours for 9-hydroxyfluorene in both the 2 M and 3 M NaCl solutions). Time to equilibrium for the 4 M solutions was achieved in 24 hours. For the 5 M NaCl concentrations the aqueous solutions were equilibrated with the fiber for 24 - 48 hours. The times to equilibrium were all confirmed by having longer exposure times. The 1 -3 M NaCl times were confirmed by 12-24 hour exposure times, the 4 M NaCl concentrations were confirmed by 48 exposure times. Only one measurement occurred per sample vial; however three replicates per salt concentration were taken.

## B.2. Depletion and Aqueous Solubility Tables

The given fiber-water partition coefficients are estimated from the pp-LFER published by Endo et al. (2011). It uses Abraham solvation parameters to estimate partition coefficients for 85  $\mu\text{m}$  PA fibers. There are no available ASPs for 9-hydroxyfluorene so its  $\log K_{ow}$  was used instead. Fiber-water partition coefficients are typically smaller than  $\log K_{ow}$ , so this is expected to be a conservative estimate. Depletion and aqueous solubility did not lead to any issues with deviations from the Setschenow Equation.

$$\log K_{PA-Water}^i = -0.12 + 0.50R_2 - 0.16\pi_2 + 0.16\alpha_2 - 4\beta_2 + 3.28V_2 \quad \text{B.2 Eqn. 1}$$

**Table B.2.1** Depletion and Aqueous Solubility of Pyrrole in Salt Solutions

Salt Concentration (mol/L)	Initial Concentration in Water (mg/L)	$K_{f/w}$ at Salt Conc.	Amount on Fiber (mols)	Amount in Water (mols)	% Depleted	Aqueous Solubility at Salt Concentration (g/L)	Average Salting-out
<b>NaCl</b>							
0	300.00	0.868	1.73E-08	1.80E-04	0.010	47.50	0
1.00	300.00	1.02	2.43E-08	1.80E-04	0.013	33.78	0.125
1.99	300.00	1.16	3.40E-08	1.80E-04	0.019	24.10	0.237
3.04	300.00	1.32	4.87E-08	1.80E-04	0.027	16.84	0.437
3.98	300.00	1.46	6.70E-08	1.80E-04	0.037	12.23	0.613
5.03	300.00	1.61	9.60E-08	1.80E-04	0.053	8.54	0.767
<b>CaCl<sub>2</sub></b>							
0.26	300.00	0.92	1.93E-08	1.80E-04	0.011	42.54	0.045
0.52	300.00	0.96	2.14E-08	1.80E-04	0.012	38.24	0.090
0.76	300.00	1.01	2.37E-08	1.80E-04	0.013	34.59	0.128
1.10	300.00	1.07	2.74E-08	1.80E-04	0.015	29.98	0.191
1.52	300.00	1.15	3.27E-08	1.80E-04	0.018	25.10	0.259
1.93	300.00	1.22	3.88E-08	1.80E-04	0.022	21.13	0.377

Initial H <sub>2</sub> O Concentration =	4.50E-03	mol/L
Volume of Water =	0.04	L
Type of Fiber =	85	μm PA
Volume of Fiber =	5.20E-07	L
Molecular Weight of HC =	67.2	g/mol
NaCl $K_s$ =	0.148	L/mol
SE of NaCl $K_s$ =	0.012	L/mol
CaCl <sub>2</sub> $K_s$ =	0.182	L/mol
SE of CaCl <sub>2</sub> $K_s$ =	0.009	L/mol

**Table B.2.2.** Depletion and Aqueous Solubility of Phenol in Salt Solutions

Salt Concentration (mol/L)	Initial Concentration in Water (mg/L)	$K_{f/w}$ at Salt Conc.	Amount on Fiber (mols)	Amount in Water (mols)	% Depleted	Aqueous Solubility at Salt Concentration (g/L)	Average Salting-out
<b>NaCl</b>							
0	45.00	1.6	9.89E-09	1.91E-05	0.05	93.00	0
1.01	45.00	1.74	1.37E-08	1.91E-05	0.07	67.27	0.108
1.88	45.00	1.86	1.80E-08	1.91E-05	0.09	50.96	0.250
3.06	45.00	2.02	2.63E-08	1.91E-05	0.14	34.97	0.419
3.96	45.00	2.15	3.51E-08	1.91E-05	0.18	26.15	0.565
5.09	45.00	2.31	5.02E-08	1.91E-05	0.26	18.27	0.712
<b>CaCl<sub>2</sub></b>							
0.58	45.00	1.78	1.50E-08	1.91E-05	0.08	61.38	0.138

1.03	45.00	1.92	2.08E-08	1.91E-05	0.11	44.18	0.323
1.49	45.00	2.06	2.88E-08	1.91E-05	0.15	31.89	0.462
1.93	45.00	2.20	3.97E-08	1.91E-05	0.21	23.13	0.618
		Initial H <sub>2</sub> O Concentration =		4.78E-04	mol/L		
		Volume of Water =		0.04	L		
		Type of Fiber =		85	μm PA		
		Volume of Fiber =		5.20E-07	L		
		Molecular Weight of HC =		94.1	g/mol		
		NaCl K <sub>s</sub> =		0.139	L/mol		
		SE of NaCl K <sub>s</sub> =		0.012	L/mol		
		CaCl <sub>2</sub> K <sub>s</sub> =		0.313	L/mol		
		SE of CaCl <sub>2</sub> K <sub>s</sub> =		0.031	L/mol		

**Table B.2.3. Depletion and Aqueous Solubility of p-Cresol in Salt Solutions**

Salt Concentration (mol/L)	Initial Concentration in Water (mg/L)	K <sub>f/w</sub> at Salt Conc.	Amount on Fiber (mols)	Amount in Water (mols)	% Depleted	Aqueous Solubility at Salt Concentration (mg/L)	Average Salting-out
<b>NaCl</b>							
0	8.00	1.89	2.98E-09	2.96E-06	0.10	19.20	0
1.08	8.00	2.10	4.82E-09	2.96E-06	0.16	11.87	0.262
1.96	8.00	2.27	7.14E-09	2.95E-06	0.24	8.02	0.375
3.03	8.00	2.48	1.15E-08	2.95E-06	0.39	4.96	0.515
4.03	8.00	2.67	1.80E-08	2.94E-06	0.61	3.18	0.745
5.13	8.00	2.89	2.93E-08	2.93E-06	0.99	1.94	1.058
<b>CaCl<sub>2</sub></b>							
0.51	8.00	2.04	4.24E-09	2.96E-06	0.14	13.49	0.158
1.06	8.00	2.21	6.20E-09	2.95E-06	0.21	9.23	0.285
1.58	8.00	2.37	8.90E-09	2.95E-06	0.30	6.43	0.443
2.02	8.00	2.50	1.20E-08	2.95E-06	0.41	4.75	0.594
<b>Mixtures</b>							
1.01	8.00	2.11	4.97E-09	2.96E-06	0.17	11.51	0.229
1.07	8.00	2.15	5.47E-09	2.95E-06	0.18	10.46	0.288
1.05	8.00	2.18	5.77E-09	2.95E-06	0.19	9.92	0.304
3.19	8.00	2.62	1.61E-08	2.94E-06	0.55	3.53	0.690
		Initial H <sub>2</sub> O Concentration =		7.40E-05	mol/L		
		Volume of Water =		0.04	L		
		Type of Fiber =		85	μm PA		
		Volume of Fiber =		5.20E-07	L		
		Molecular Weight of HC =		110.2	g/mol		
		NaCl K <sub>s</sub> =		0.194	L/mol		
		SE of NaCl K <sub>s</sub> =		0.011	L/mol		

CaCl <sub>2</sub> K <sub>s</sub> =	0.3	L/mol
SE of CaCl <sub>2</sub> K <sub>s</sub> =	0.027	L/mol

**Table B.2.4.** Depletion and Aqueous Solubility of Hydroquinone in Salt Solutions

Salt Concentration (mol/L)	Initial Concentration in Water (mg/L)	K <sub>f/w</sub> at Salt Conc.	Amount on Fiber (mols)	Amount in Water (mols)	% Depleted	Aqueous Solubility at Salt Concentration (g/L)	Average Salting-out
<b>NaCl</b>							
0	45.00	0.672	9.99E-10	1.64E-05	0.006	69.50	0
1.12	45.00	0.76	1.22E-09	1.64E-05	0.007	56.79	0.077
1.99	45.00	0.83	1.43E-09	1.64E-05	0.009	48.57	0.134
3.01	45.00	0.91	1.71E-09	1.64E-05	0.010	40.50	0.213
4.03	45.00	0.99	2.06E-09	1.64E-05	0.013	33.69	0.322
5.03	45.00	1.06	2.46E-09	1.64E-05	0.015	28.18	0.411
<b>CaCl<sub>2</sub></b>							
0.55	45.00	0.73	1.15E-09	1.64E-05	0.007	60.28	0.058
1.07	45.00	0.79	1.32E-09	1.64E-05	0.008	52.70	0.112
1.52	45.00	0.84	1.48E-09	1.64E-05	0.009	46.94	0.178
2.00	45.00	0.90	1.67E-09	1.64E-05	0.010	41.48	0.222
			Initial H <sub>2</sub> O Concentration =	4.09E-04	mol/L		
			Volume of Water =	0.04	L		
			Type of Fiber =	85	μm PA		
			Volume of Fiber =	5.20E-07	L		
			Molecular Weight of HC =	110.1	g/mol		
			NaCl K <sub>s</sub> =	0.078	L/mol		
			SE of NaCl K <sub>s</sub> =	0.0044	L/mol		
			CaCl <sub>2</sub> K <sub>s</sub> =	0.112	L/mol		
			SE of CaCl <sub>2</sub> K <sub>s</sub> =	0.007	L/mol		

**Table B.2.5.** Depletion and Aqueous Solubility of Hexanoic Acid in Salt Solutions

<b>Hexanoic Acid</b>							
Salt Concentration (mol/L)	Initial Concentration in Water (mg/L)	K <sub>f/w</sub> at Salt Conc.	Amount on Fiber (mols)	Amount in Water (mols)	% Depleted	Aqueous Solubility at Salt Concentration (mg/L)	Average Salting-out
<b>NaCl</b>							
0	175.00	1.54	2.70E-08	6.00E-05	0.05	9.80	0
1.07	175.00	1.80	4.89E-08	6.00E-05	0.08	5.41	0.21
2.00	175.00	2.02	8.16E-08	5.99E-05	0.14	3.25	0.43
3.11	175.00	2.29	1.50E-07	5.98E-05	0.25	1.76	0.85
3.97	175.00	2.49	2.42E-07	5.98E-05	0.40	1.09	0.85
5.14	175.00	2.77	4.59E-07	5.95E-05	0.77	0.57	1.28

CaCl <sub>2</sub>							
0.56	175.00	1.74	4.30E-08	6.00E-05	0.07	6.16	0.19
1.04	175.00	1.91	6.37E-08	5.99E-05	0.11	4.16	0.39
1.52	175.00	2.08	9.46E-08	5.99E-05	0.16	2.80	0.53
1.97	175.00	2.25	1.38E-07	5.99E-05	0.23	1.92	0.71
		Initial H <sub>2</sub> O Concentration =		1.50E-03	mol/L		
		Volume of Water =		0.04	L		
		Type of Fiber =		85	µm PA		
		Volume of Fiber =		5.20E-07	L		
		Molecular Weight of HC =		116.1	g/mol		
		NaCl K <sub>s</sub> =		0.24	L/mol		
		SE of NaCl					
		K <sub>s</sub> =		0.019	L/mol		
		CaCl <sub>2</sub> K <sub>s</sub> =		0.359	L/mol		
		SE of CaCl <sub>2</sub>					
		K <sub>s</sub> =		0.021	L/mol		

**Table B.2.6.** Depletion and Aqueous Solubility of 9-Hydroxyfluorene in Salt Solutions

9-Hydroxyfluorene							
Salt Concentration (mol/L)	Initial Concentration in Water (mg/L)	K <sub>f/w</sub> at Salt Conc. (log K <sub>ow</sub> )	Amount on Fiber (mols)	Amount in Water (mols)	% Depleted	Aqueous Solubility at Salt Concentration (mg/L)	Average Salting-out
NaCl							
0.00	6.00	2.56	6.20E-09	1.31E-06	0.47	4700.00	0.00
1.05	6.00	2.80	1.09E-08	1.31E-06	0.82	2675.04	0.33
1.94	6.00	3.01	1.75E-08	1.30E-06	1.33	1648.96	0.48
3.02	6.00	3.27	3.09E-08	1.29E-06	2.34	924.78	0.76
4.01	6.00	3.50	5.19E-08	1.27E-06	3.93	542.32	1.01
5.02	6.00	3.73	8.70E-08	1.23E-06	6.59	314.51	1.05
CaCl <sub>2</sub>							
0.54	6.00	2.72	8.92E-09	1.31E-06	0.68	3259.06	0.22
1.04	6.00	2.87	1.25E-08	1.31E-06	0.95	2313.04	0.36
1.54	6.00	3.01	1.75E-08	1.30E-06	1.32	1655.16	0.45
2.05	6.00	3.16	2.46E-08	1.30E-06	1.86	1168.58	0.57
Mixtures							
1.01	6.00	2.81	1.10E-08	1.31E-06	0.84	2631.13	0.28
1.07	6.00	2.84	1.18E-08	1.31E-06	0.90	2455.32	0.28
1.03	6.00	2.85	1.20E-08	1.31E-06	0.91	2417.19	0.30
3.11	6.00	3.35	3.74E-08	1.28E-06	2.83	761.65	0.77
		Initial H <sub>2</sub> O Concentration =		3.30E-05	mol/L		
		Volume of Water =		0.04	L		
		Type of Fiber =		85	µm PA		

Volume of Fiber =	5.20E-07	L
Molecular Weight of HC =	182.2	g/mol
NaCl $K_s$ =	0.234	L/mol
SE of NaCl $K_s$ =	0.019	L/mol
CaCl <sub>2</sub> $K_s$ =	0.295	L/mol
SE of CaCl <sub>2</sub> $K_s$ =	0.029	L/mol

### B.3. Abraham Solvation Parameters and log $K_{ow}$ of Organic Compounds

**Table B.3.1.** Abraham Solvation Parameters and log  $K_{ow}$  of Organic Compounds in this Study

Organic Compound	$R_2$	$\pi_2$	$\alpha_2$	$\beta_2$	$V_x$	Log $K_{ow}$
Pyrrole	0.613	0.73	0.41	0.29	0.577	0.75 (Poole et al. 2000)
Phenol	0.805	0.89	0.6	0.31	0.7751	1.44 (Schwarzenbach et al. 2003)
p-Cresol	0.82	0.87	0.52	0.31	0.916	1.93 (Schwarzenbach et al. 2003)
Hydroquinone	1	1	1.16	0.6	0.834	0.59 (Schwarzenbach et al. 2003)
Hexanoic Acid	0.174	0.6	0.6	0.45	1.0284	1.92 (Schwarzenbach et al. 2003)
9-HydroxyFluorene	N/A	N/A	N/A	N/A	N/A	2.56* (Substance Identifier n.d.)

\*Estimated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)

### B.4. Change in pKa with salt concentration

The calculated  $pK_a^{salt}$  for hexanoic acid are given in Table B.4.1. See Barriada et al. (2000) for the relevant equations and parameters.

**Table B.4.1.** Change in pKa with NaCl Concentration

NaCl Conc. (M)	pKa*
0	4.89
0.5	4.60
1	4.62
2	4.72
3	4.86

4	5.01
5	5.18

### B.5 List of oil and gas reservoirs with calculations for percent of organic acid in the neutral form.

The percent of the acid in the neutral form (B.5 Eqn. 1) was also calculated for hexanoic acid (the organic acid investigated in this study), acetic and benzoic acids, which are important organic carboxylic acids.

$$\alpha_{i,a} = \frac{1}{a + 10^{pH-pK_a}} \quad \text{B.5 Eqn. 1}$$

**Table B.5.1.** Reservoir fluid baseline and post-injection pH, total dissolved solids, and percent of an organic compound in the neutral form.

Formation	TDS (mg/L)	Brine Type	Baseline pH	Injected pH	Percent in Neutral Form Hexanoic Acid	Percent in Neutral Form Acetic Acid	Percent in Neutral Form Benzoic Acid
Frio Formation (Kharaka et al. 2006)	93000	Na-Ca-Cl	6.5	5.7	13.4	10.1	3.00
Lower Tuscaloosa (Lu et al. 2012)	150000	Na-Ca-Cl	5.7	5.2	32.9	26.2	8.9
Weyburn (Emberley et al. 2004)	70000	Na - Cl	6	5.9	8.9	6.6	1.9
Central Mississippi Salt Dome (Kharaka & Hanor 2003)	320000	Na - Ca - Cl	5.08	N/A	39.2	31.9	11.4
San Joaquin Valley (Kharaka & Hanor 2003)	44300	Na - Ca - Cl	6.9	N/A	0.97	0.70	0.19
Marcellus shale flowback water, Day 14, median (Haluszczak et al. 2013)	157000	Na - Ca - Cl	6.2	N/A	4.7	3.4	0.97

### B.6 References

Barriada, J.L., Brandariz, I. & de Vicente, M.E., 2000. Acid–Base Equilibria of Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations. *Journal of Chemical & Engineering Data*, 45(6), pp.1173–1178. Available at: <http://dx.doi.org/10.1021/je000150p>.

- Emberley, S. et al., 2004. Geochemical monitoring of fluid-rock interaction and CO<sub>2</sub> storage at the Weyburn CO<sub>2</sub>-injection enhanced oil recovery site, Saskatchewan, Canada. *Energy*, 29(9-10), pp.1393–1401. Available at: <http://www.sciencedirect.com/science/article/pii/S0360544204001562> [Accessed February 21, 2014].
- Endo, S., Droge, S.T.J. & Goss, K.-U., 2011. Polyparameter Linear Free Energy Models for Polyacrylate Fiber–Water Partition Coefficients to Evaluate the Efficiency of Solid-Phase Microextraction. *Analytical Chemistry*, 83(4), pp.1394–1400. Available at: <http://dx.doi.org/10.1021/ac102868e>.
- Haluszczak, L.O., Rose, A.W. & Kump, L.R., 2013. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry*, 28, pp.55–61. Available at: <http://www.sciencedirect.com/science/article/pii/S0883292712002752> [Accessed December 1, 2014].
- Kharaka, Y.K., Cole, D.R. & Hovorka, S.D., 2006. Gas-water-rock interactions in Frio Formation following CO<sub>2</sub> injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology*, 34(7), p.577. Available at: <http://geology.gsapubs.org/cgi/doi/10.1130/G22357.1> [Accessed February 13, 2014].
- Kharaka, Y.K. & Hanor, J.S., 2003. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In E.-C. H. D. Holland & K. K. Turekian, eds. *Treatise on Geochemistry*. Oxford: Pergamon, pp. 1–48. Available at: <http://www.sciencedirect.com/science/article/pii/B0080437516050854>.
- Lu, J. et al., 2012. CO<sub>2</sub>–rock–brine interactions in Lower Tuscaloosa Formation at Cranfield CO<sub>2</sub> sequestration site, Mississippi, U.S.A. *Chemical Geology*, 291, pp.269–277. Available at: <http://www.sciencedirect.com/science/article/pii/S0009254111004293> [Accessed July 7, 2014].
- Poole, S.K., Durham, D. & Kibbey, C., 2000. Rapid method for estimating the octanol–water partition coefficient (log Pow) by microemulsion electrokinetic chromatography. *Journal of Chromatography B: Biomedical Sciences and Applications*, 745(1), pp.117–126. Available at: <http://www.sciencedirect.com/science/article/pii/S0378434700000724> [Accessed June 10, 2015].
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Substance Identifier, S.S., Advanced Chemistry Development (ACD/Labs) Software V11.02. Columbus, OH. Available at: <https://scifinder.cas.org>.

## **Appendix C**

### Chapter 5:

Evaluate, update, and create new models for the prediction of Setschenow constants.

### C.1. Outlier and Influential Point Tests and Removal

Two outlier tests were completed to determine if there were any influential and outlier points in the pp-LFER and the log  $K_{ow}$ . Both these outlier tests had to be satisfied to remove a Setschenow constant from a model. Potential outliers were first identified using Cook's Distance (C.1 Eqn. 1), which is used to estimate the influence of a data point when performing OLS regression. This is calculated by:

$$D_i = \sum_{j=1}^n \frac{(\hat{y}_j - \hat{y}_{j(i)})^2}{p \cdot MSE} \quad \text{C.1 Eqn. 1}$$

Here  $D_i$  is Cook's Distance,  $\hat{y}_j$  is the prediction from the full regression model for observation  $j$ ,  $\hat{y}_{j(i)}$  is the prediction for the observation  $j$  from a refitted regression model when it has been removed from the dataset,  $p$  is the number of predictor variables, and  $MSE$  is the mean square error of the original model. The threshold for determining whether  $D_i$  may be an outlier is given by  $D_i \geq \frac{4}{n-p-1}$ , where  $n$  is the number of observations in the model.

The second outlier test uses studentized deleted residuals (SDR), using a threshold determined by the Bonferroni Correction test to determine outliers. This is a jack-knifing procedure, in which the residual for each observation is standardized to the mean square error of the model, with the observation  $i$  deleted from the model, to determine the influence of that point on the model itself. The SDR follows a t-distribution and is given by C.1 Eqn. 2, with input equations given in C.1 Eqns. 3,4,5:

$$t_i = \frac{e_i}{\sqrt{MSE_i(1-h_i)}} = \frac{d_i}{s\{d_i\}} \quad \text{C.1 Eqn. 2}$$

$$d_i = \frac{e_i}{(1-h_i)} \quad \text{C.1 Eqn. 3}$$

$$s\{d_i\} = \sqrt{\frac{MSE_i}{1-h_i}} \quad \text{C.1 Eqn. 4}$$

$$e_i = y_j - \hat{y}_{i(i)} \quad \text{C.1 Eqn. 5}$$

Here  $e_i$  is the calculation of the deleted residual, where  $\hat{y}_i$  is the prediction, or fitted value from the full regression model for observation  $i$ ,  $y_i$  is the observation for  $i$ .  $MSE_i$  is the mean square error of the model,  $h_i$  is the  $i$ th element on the main diagonal of the hat matrix between 0 and 1. Hat values measure influence of a point on a model, which is based on the calculation of the fitted values ( $\hat{y}_i$ ), which is described elsewhere (Hoaglin & Welsch 1978).

The SDRs follow a t-distribution, so therefore the threshold for determining whether an observation is an outlier is done with the Bonferroni Correction. A p-value of 0.05 predicts that 5% of the values in this model should be greater than  $2 \pm t_{0.025}$  by chance, so the Bonferroni correction adjusts the p-value to account for that chance:

$$t_{n-p-1} \cdot \left(1 - \frac{\alpha}{2n}\right) \geq t_i \quad \text{C.1 Eqn. 6}$$

Here  $t_{n-p-1}$  is the t-distribution value, n is the number of observations, p is the number of predictor variables, and  $\alpha$  is the p-value, set to 0.05. If the magnitude of the SDR ( $t_i$ ) is larger than the magnitude of the threshold value ( $t_{n-p-1} \cdot \left(1 - \frac{\alpha}{2n}\right)$ ) and is deemed to have significant

influence on the model. If this data point was indicated by Cook's Distance in C.1 Eqn. 1 as an influential point, then it is considered an outlier.

Both these influence and outlier tests were used on the pp-LFER, log  $K_{ow}$  LFER, and each sp-LFER for predicting  $CaCl_2$ ,  $KCl$ ,  $LiCl$ , and  $NaBr$  Setschenow constants. These outlier tests were completed in Matlab.

The new pp-LFER and log  $K_{ow}$  LFER before the outliers were removed are presented in C.1 Eqn. 7 and 8. Plots of predicted versus experimental values are given in *Figure C.1.1*. The accuracy of both models significantly decreased (pp-LFER  $R^2_{adj} = 0.687$ , log  $K_{ow}$  LFER  $R^2_{adj} = 0.596$ ) with the addition of more data.

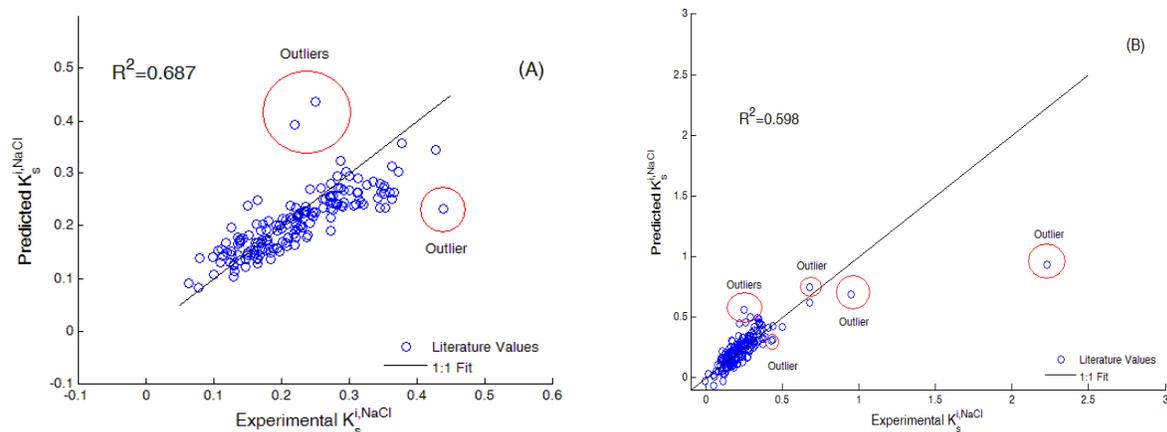
$$K_s^{i,NaCl} = -0.023(\pm 0.01)\pi_2 - 0.055(\pm 0.02)\alpha_2 - 0.082(\pm 0.02)\beta_2 + 0.159(\pm 0.01)V_2 + 0.107(\pm 0.01) \quad \text{C.1 Eqn. 7}$$

$$n=163, R^2_{adj} = 0.687, RMSE = 0.045$$

$$K_s^{i,NaCl} = 0.062(\pm 0.004)\log K_{ow} + 0.072(\pm 0.013) \quad \text{C.1 Eqn. 8}$$

$$n=200, R^2_{adj} = 0.596, RMSE = 0.098$$

This finding was contrary to expectations, and it was hypothesized that this may be due to the experimental uncertainty of these  $NaCl$  Setschenow constants, which caused some data points to heavily influence the results of the model (*Figure C.1.1*). Experimental estimation of Setschenow constants is difficult and can lead to errors, and other researchers have discussed that there is some experimental uncertainty in the dataset (Endo et al. 2012). This knowledge, as well as qualitative observations of the data, led to these outlier tests.



**Figure C.1.1.** Plots of comparisons between the A) pp-LFER predicted and experimental NaCl Setschenow constant values, B)  $\log K_{ow}$  predicted and experimental NaCl Setschenow constant values. Lines represent model fit, so distance from the line is indicative of error in the model. Outliers removed from the final fit are circled in red.

In the pp-LFER, three organic compounds were deemed to be outliers, 1-methylnaphthalene, n-dodecane, and n-tetradecane. Those points are circled in *Figure C.1.1.A*. In the  $\log K_{ow}$  LFER, six organic compounds were deemed to be outliers, 1-methylnaphthalene, n-dodecane, n-tetradecane, n-hexadecane, n-octadecane, and n-hexacosane. Those points are circled in *Figure C.1.1.B*. Please note that m-hexadecane, n-octadecane, and n-hexacosane were not in the pp-LFER, as they do not have reported ASPs. A list of organic compounds that met the criteria for Cook's Distance can be found in **Table C.1.1**. The compounds that met the SDR criteria, and were removed from the LFERs are in bold; the other compounds were kept in the LFERs. The list of organic compounds that exceeded the threshold for Cook's Distance for the  $\log K_{ow}$  are listed in **Table C.2.1**, along with the experimental and predicted NaCl Setschenow constant. The removal of these points led to an improvement of regression statistics, and therefore confidence in the models, which are detailed in Chapter 5.

**Table C.1.1** Organic compounds which exceeded the threshold for Cook's Distance in the pp-LFER

Organic Compound	Experimental $K_s$ ( $M^{-1}$ )	pp-LFER predicted $K_s$ ( $M^{-1}$ )
Benzo(ghi)perylene (Jonker & Muijs 2010)	0.292	0.345
<b>1-methylnaphthalene (Xie et al. 1997)</b>	<b>0.440</b>	<b>0.260</b>
Perylene (Schlautman et al. 2004)	0.259	0.337
<b>Dodecane (Xie et al. 1997)</b>	<b>0.220</b>	<b>0.441</b>
<b>Tetradecane (Xie et al. 1997)</b>	<b>0.250</b>	<b>0.496</b>
4-Nitroaniline (Endo et al. 2012)	0.099	0.147
Lindane (Xie et al. 1997)	0.166	0.285
Progesterone (Ni & Yalkowsky 2003)	0.288	0.353
Bisphenol A (Endo et al. 2012)	0.174	0.249
Tri-n-butyl phosphate (Endo et al. 2012)	0.428	0.373
4-Nitroanisole (Endo et al. 2012)	0.126	0.206
Metolachlor (Endo et al. 2012)	0.296	0.346
2-Ethyl-1-hexanol (Jochmann et al. 2006)	0.150	0.263

**Table C.1.2** Organic compounds which exceeded the threshold for Cook's Distance in the log  $K_{ow}$ .

Organic Compound	Experimental $K_s$ ( $M^{-1}$ )	log $K_{ow}$ predicted $K_s$ ( $M^{-1}$ )
Benzo(ghi)perylene (Jonker & Muijs 2010)	0.292	0.403
Dibenz(a,h)anthracene (Jonker & Muijs 2010)	0.337	0.397
<b>1-Methylnaphthalene (Xie et al. 1997)</b>	<b>0.440</b>	<b>0.276</b>
Perylene (Schlautman et al. 2004)	0.259	0.376
<b>Dodecane (Xie et al. 1997)</b>	<b>0.220</b>	<b>0.369</b>
<b>Tetradecane (Xie et al. 1997)</b>	<b>0.250</b>	<b>0.442</b>
Tri-n-butyl phosphate (Endo et al. 2012)	0.428	0.274
Leucine (Ni & Yalkowsky 2003)	0.114	-0.043
2-monochlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007)	0.440	0.352

2,7-dichlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007)	0.498	0.347
<b>Hexadecane</b> (Xie et al. 1997)	<b>0.680</b>	<b>0.485</b>
<b>Octadecane</b> (Xie et al. 1997)	<b>0.950</b>	<b>0.528</b>
Eicosane( Xie et al. 1997)	0.680	0.571
<b>Hexacosane</b> (Xie et al. 1997)	<b>2.23</b>	<b>0.699</b>

## C.2 Published NaCl Setschenow Constants along with New Model Predictions

The first cited reference is for the NaCl  $K_s$ , the second is for the  $\log K_{ow}$ . The outliers left out of the models are italicized in the first column.

**Table C.2.1** Abraham Solvation Parameters (ASP),  $\log K_{ow}$ , published NaCl  $K_s$ , and new model predictions.

Organic Compound	$R_2$	$\pi_2$	$\alpha_2$	$\beta_2$	$V_2$	$\log K_{ow}$	NaCl $K_s$ ( $M^{-1}$ )	New pp-LFER prediction ( $M^{-1}$ )	New $\log K_{ow}$ prediction ( $M^{-1}$ )
<b>Ketones</b>									
2-Hexanone (Endo et al. 2012; Schwarzenbach et al. 2003)	0.14	0.68	0	0.51	0.97	1.38	<b>0.198</b>	0.202	0.171
2-Heptanone (Endo et al. 2012; Substance Identifier n.d.)	0.12	0.68	0	0.51	1.111	1.98	<b>0.233</b>	0.230	0.196
2-Octanone (Endo et al. 2012; Substance Identifier n.d.)	0.11	0.68	0	0.51	1.252	2.51	<b>0.273</b>	0.257	0.218
2-Nonanone (Endo et al. 2012; Substance Identifier n.d.)	0.12	0.68	0	0.51	1.392	3.16	<b>0.301</b>	0.284	0.246
2-Decanone (Endo et al. 2012; Substance Identifier n.d.)	0.11	0.68	0	0.51	1.533	3.77	<b>0.314</b>	0.312	0.271
2-Undecanone (Endo et al. 2012; Substance Identifier n.d.)	0.1	0.68	0	0.51	1.674	4.09	<b>0.364</b>	0.340	0.285
Cyclohexanone (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.4	0.86	0	0.56	0.861	0.71	<b>0.202</b>	0.167	0.143
Acetone (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.18	0.7	0.04	0.49	0.547	-0.24	<b>0.11</b>	0.119	0.103
<b>Alkylated Benzenes</b>									
Benzene (Endo et al. 2012; Schwarzenbach et al. 2003)	0.61	0.52	0	0.14	0.716	2.17	<b>0.152</b>	0.191	0.204
Toluene (Endo et al. 2012; Schwarzenbach et al. 2003)	0.6	0.52	0	0.14	0.857	2.69	<b>0.221</b>	0.219	0.226

et al. 2003)									
n-Propylbenzene (Endo et al. 2012; Schwarzenbach et al. 2003)	0.6	0.5	0	0.15	1.139	3.69	<b>0.262</b>	0.273	0.268
n-Butylbenzene (Endo et al. 2012; Schwarzenbach et al. 2003)	0.6	0.51	0	0.15	1.28	4.38	<b>0.285</b>	0.301	0.297
n-Pentylbenzene (Endo et al. 2012; Schwarzenbach et al. 2003)	0.59	0.51	0	0.15	1.421	4.9	<b>0.3</b>	0.328	0.319
Ethylbenzene (Endo et al. 2012; Schwarzenbach et al. 2003)	0.61	0.51	0	0.15	0.998	3.2	<b>0.234</b>	0.245	0.247
o-Xylene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.66	0.56	0	0.16	0.998	3.16	<b>0.227</b>	0.242	0.246
m-Xylene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.62	0.52	0	0.16	0.998	3.3	<b>0.248</b>	0.244	0.252
p-Xylene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.61	0.52	0	0.16	0.998	3.27	<b>0.251</b>	0.273	0.250
Isopropylbenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.6	0.49	0	0.16	1.139	3.66	<b>0.316</b>	0.266	0.267
1,2,4-Trimethylbenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.68	0.56	0	0.19	1.139	3.65	<b>0.293</b>	0.254	0.266
1,2,3-Trimethylbenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.73	0.61	0	0.19	1.139	3.6	<b>0.321</b>	0.264	0.264
1,3,5-Trimethylbenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.65	0.52	0	0.19	1.139	3.42	<b>0.318</b>	0.268	0.257
sec-Butylbenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.6	0.48	0	0.16	1.28	4.44	<b>0.288</b>	0.301	0.299
tert-Butylbenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.62	0.49	0	0.18	1.28	4.11	<b>0.243</b>	0.298	0.286
Anisole (Görgényi et al. 2006; Schwarzenbach et al. 2003)	0.71	0.75	0	0.29	0.916	2.11	<b>0.225</b>	0.206	0.202
Benzaldehyde (Zhou & Mopper 1990; Schwarzenbach et al. 2003)	0.82	1	0	0.39	0.873	1.48	<b>0.20</b>	0.177	0.175
<b>Chlorinated Ethane and Ethenes</b>									
trans-1,2-Dichloroethene (Jochmann et al. 2007; Schwarzenbach et al. 2003)	0.43	0.41	0.09	0.05	0.592	2.09	<b>0.179</b>	0.178	0.201
cis-1,2-Dichloroethene (Jochmann et al. 2007; Schwarzenbach et al. 2003)	0.44	0.61	0.11	0.05	0.592	1.86	<b>0.137</b>	0.169	0.191
Trichloroethene (Jochmann et al. 2007; Schwarzenbach et al. 2003)	0.52	0.37	0.08	0.03	0.715	2.42	<b>0.178</b>	0.205	0.215
Tetrachloroethene (Jochmann et al. 2007; Schwarzenbach et al. 2003)	0.64	0.44	0	0	0.837	2.88	<b>0.213</b>	0.231	0.234
1,1,1-Trichloroethane	0.37	0.41	0	0.09	0.758	2.49	<b>0.193</b>	0.211	0.218

(Gossett 1987; Schwarzenbach et al. 2003)									
1,1-Dichloroethane (Gossett 1987; Schwarzenbach et al. 2003)	0.32	0.49	0.1	0.1	0.635	1.79	<b>0.145</b>	0.179	0.188
Chloroform (Gossett 1987; Schwarzenbach et al. 2003)	0.43	0.49	0.15	0.02	0.617	1.95	<b>0.14</b>	0.180	0.195
Dichloromethane (Gossett 1987; Schwarzenbach et al. 2003)	0.39	0.57	0.1	0.05	0.494	1.31	<b>0.107</b>	0.153	0.168
<b>Alcohols</b>									
Ethanol (Jochmann et al. 2006; Sangster 1989)	0.25	0.42	0.37	0.48	0.449	-0.3	<b>0.13</b>	0.096	0.100
1-Propanol (Jochmann et al. 2006; Sangster 1989)	0.24	0.42	0.37	0.48	0.59	0.25	<b>0.13</b>	0.124	0.124
2-Propanol (Jochmann et al. 2006; Sangster 1989)	0.21	0.36	0.33	0.56	0.59	0.05	<b>0.13</b>	0.120	0.115
1-Butanol (Jochmann et al. 2006; Sangster 1989)	0.22	0.42	0.37	0.48	0.731	0.84	<b>0.12</b>	0.152	0.148
2-Butanol (Jochmann et al. 2006; Sangster 1989)	0.22	0.36	0.33	0.56	0.731	0.65	<b>0.15</b>	0.148	0.140
iso-Butanol (Jochmann et al. 2006; Sangster 1989)	0.22	0.39	0.37	0.48	0.731	0.76	<b>0.15</b>	0.153	0.145
tert-Butanol (Jochmann et al. 2006; Sangster 1989)	0.28	0.3	0.31	0.6	0.731	0.35	<b>0.16</b>	0.1546	0.128
1-Pentanol (Jochmann et al. 2006; Sangster 1989)	0.22	0.42	0.37	0.48	0.872	1.51	<b>0.14</b>	0.179	0.176
3-Pentanol (Jochmann et al. 2006; Sangster 1989)	0.22	0.36	0.33	0.56	0.872	1.21	<b>0.14</b>	0.175	0.164
2-ethyl-1-Hexanol (Endo et al. 2012; Substance Identifier n.d.)	0.21	0.39	0.37	0.48	1.295	2.72	<b>0.15</b>	0.263	0.227
1-Hexanol (Endo et al. 2012; Substance Identifier n.d.)	0.21	0.42	0.37	0.48	1.013	1.86	<b>0.221</b>	0.207	0.191
4-ethyl-3-Hexanol (Endo et al. 2012; Substance Identifier n.d.)	0.17	0.36	0.33	0.57	1.295	2.56	<b>0.291</b>	0.257	0.221
2-Butoxyethanol (Endo et al. 2012; Substance Identifier n.d.)	0.2	0.53	0.26	0.83	1.071	0.83	<b>0.211</b>	0.184	0.148
<b>Polycyclic Aromatic Hydrocarbons</b>									
Phenanthrene (Schwarzenbach et al. 2003)	2.06	1.29	0	0.29	1.454	4.57	<b>0.308</b>	0.278	0.305
Anthracene (Jonker & Muijs 2010; Schwarzenbach et al. 2003)	2.29	1.34	0	0.28	1.454	4.68	<b>0.346</b>	0.276	0.310
Fluoranthene (Jonker & Muijs 2010; Schwarzenbach et al. 2003)	2.38	1.55	0	0.24	1.585	5.23	<b>0.364</b>	0.297	0.333

\*  
\*  
\*  
\*

Pyrene (Jonker & Muijs 2010; Schwarzenbach et al. 2003)	2.81	1.71	0	0.28	1.585	5.13	<b>0.354</b>	0.283	0.328	
Benz[a]anthracene (Jonker & Muijs 2010; Schwarzenbach et al. 2003)	2.99	1.7	0	0.33	1.823	5.91	<b>0.361</b>	0.323	0.361	
Chrysene (Jonker & Muijs 2010; Schwarzenbach et al. 2003)	3.03	1.73	0	0.33	1.823	5.81	<b>0.367</b>	0.321	0.357	
Benzo[e]pyrene (Jonker & Muijs 2010; Substance Identifier n.d.)	3.63	1.99	0	0.35	1.954	6.19	<b>0.348</b>	0.330	0.373	*
Benzo[b]fluoranthene (Jonker & Muijs 2010; Substance Identifier n.d.)	3.19	1.82	0	0.4	1.954	6.19	<b>0.351</b>	0.335	0.373	*
Benzo[k]fluoranthene (Jonker & Muijs 2010; Substance Identifier n.d.)	3.19	1.91	0	0.33	1.954	6.19	<b>0.353</b>	0.339	0.373	*
Benzo[a]pyrene (Jonker & Muijs 2010; Schwarzenbach et al. 2003)	3.63	1.96	0	0.37	1.954	6.13	<b>0.352</b>	0.329	0.370	
Benzo[ghi]perylene (Jonker & Muijs 2010; Sangster 1989)	4.07	1.9	0	0.45	2.084	6.9	<b>0.292</b>	0.345	0.403	
Dibenz[a,h]anthracene (Jonker & Muijs 2010; Sangster 1989)	4	2.04	0	0.44	2.192	6.75	<b>0.336</b>	0.336	0.397	
Indeno[123,cd]pyrene (Jonker & Muijs 2010; Substance Identifier n.d.)	3.61	1.93	0	0.42	2.084	6.65	<b>0.346</b>	0.346	0.392	*
Naphthalene (Schwarzenbach et al. 2003)	1.34	0.92	0	0.2	1.085	3.33	<b>0.208</b>	0.208	0.253	
<i>1-methylnaphthalene</i> (Xie et al. 1997; Schwarzenbach et al. 2003)	1.34	0.94	0	0.22	1.226	3.87	<b>0.44</b>	0.260	0.276	
Biphenyl (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	1.36	0.99	0	0.26	1.324	4.01	<b>0.276</b>	0.274	0.281	
Acenaphthene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	1.6	1.05	0	0.22	1.259	4.2	<b>0.238</b>	0.260	0.289	
Fluorene (Schwarzenbach et al. 2003)	1.59	1.06	0	0.25	1.357	4.32	<b>0.281</b>	0.274	0.294	
1-Methylphenanthrene (Xie et al. 1997; Sangster 1989)	2.06	1.25	0	0.26	1.595	5.08	<b>0.313</b>	0.310	0.326	
1-Ethyl naphthalene (Ni & Yalkowsky 2003; Sangster 1989)	1.371	0.88	0	0.2	1.367	4.4	<b>0.273</b>	0.292	0.298	
Perylene (Schlautman et al. 2004; Schwarzenbach et al. 2003)	3.256	1.76	0	0.4	1.954	6.25	<b>0.259</b>	0.337	0.376	
2-Methyl anthracene (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	5.09	<b>0.336</b>	N/A	0.327	
1-Ethyl anthracene (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	5.6	<b>0.313</b>	N/A	0.348	
<b>Chlorinated Benzenes</b>										
Chlorobenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.72	0.65	0	0.07	0.839	2.78	<b>0.209</b>	0.216	0.230	

o-Dichlorobenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.87	0.78	0	0.04	0.961	3.4	<b>0.247</b>	0.237	0.256
m-Dichlorobenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.85	0.73	0	0.02	0.961	3.47	<b>0.226</b>	0.241	0.259
p-Dichlorobenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.83	0.75	0	0.02	0.961	3.45	<b>0.245</b>	0.240	0.258
1,2,4-Trichlorobenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.98	0.81	0	0	1.084	4.06	<b>0.29</b>	0.263	0.284
<b>Alkanes and Cycloalkanes</b>									
n-Pentane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0	0	0	0	0.813	3.39	<b>0.221</b>	0.249	0.255
n-Hhexane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0	0	0	0	0.954	4	<b>0.276</b>	0.276	0.281
Cyclopentane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.26	0.1	0	0	0.705	3	<b>0.182</b>	0.222	0.239
Cyclohexane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.31	0.1	0	0	0.845	3.44	<b>0.277</b>	0.248	0.257
Cycloheptane (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.35	0.1	0	0	0.986	3.69	<b>0.343</b>	0.276	0.268
Methylcyclopentane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.23	0.1	0	0	0.845	3.37	<b>0.273</b>	0.249	0.255
Methylcyclohexane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.24	0.06	0	0	0.986	3.88	<b>0.274</b>	0.278	0.276
Methane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0	0	0	0	0.25	1.09	<b>0.127</b>	0.139	0.159
Ethane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0	0	0	0	0.39	1.81	<b>0.162</b>	0.166	0.189
Ethylene (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.107	0.1	0	0.07	0.3474	1.32	<b>0.127</b>	0.146	0.168
Butane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0	0	0	0	0.672	2.89	<b>0.217</b>	0.221	0.234
Propane (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0	0	0	0	0.531	2.36	<b>0.194</b>	0.194	0.212
<i>Dodecane</i> (Substance Identifier n.d.; Xie et al. 1997)	0	0	0	0	1.799	6.1	<b>0.22</b>	0.441	0.369
<i>Tetradecane</i> (Substance Identifier n.d.; Xie et al. 1997)	0	0	0	0	2.081	7.84	<b>0.25</b>	0.496	0.442
<i>Hexadecane</i> (Xie et al. 1997; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	8.86	<b>0.68</b>	N/A	0.485
<i>Octadecane</i> (Xie et al. 1997; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	9.88	<b>0.95</b>	N/A	0.528

\*

\*

\*

\*

\*

\*

Eicosane (Xie et al. 1997; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	10.9	<b>0.68</b>	N/A	0.571	*
Hexacosane (Xie et al. 1997; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	13.95	<b>2.23</b>	N/A	0.699	*
<b>Substituted Phenols</b>										
4-Iodophenol (Endo et al. 2012; Substance Identifier n.d.)	1.38	1.22	0.68	0.2	1.033	2.99	<b>0.162</b>	0.186	0.239	*
4-Fluorophenol (Endo et al. 2012; Substance Identifier n.d.)	0.67	0.97	0.63	0.23	0.813	1.84	<b>0.168</b>	0.157	0.190	*
Phenol (Schwarzenbach et al. 2003)	0.81	0.89	0.6	0.3	0.775	1.44	<b>0.139</b>	0.146	0.173	
2,4-Dichlorophenol (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.96	0.82	0.54	0.17	1.02	3.09	<b>0.218</b>	0.210	0.243	
2,4,6-Trichlorophenol (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	1.01	0.8	0.68	0.15	1.142	3.67	<b>0.228</b>	0.231	0.267	
o-Nitrophenol (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	1.02	1.05	0.05	0.37	0.949	1.78	<b>0.136</b>	0.188	0.188	
m-Nitrophenol (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	1.05	1.57	0.79	0.23	0.949	2	<b>0.147</b>	0.152	0.197	
p-Nitrophenol (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	1.07	1.72	0.82	0.26	0.949	1.96	<b>0.165</b>	0.142	0.195	
Benzoic acid (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.73	0.9	0.59	0.4	0.932	1.89	<b>0.177</b>	0.165	0.192	
o-Chlorobenzoic acid (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.84	1.01	0.68	0.4	1.054	2.1	<b>0.182</b>	0.177	0.201	*
m-Chlorobenzoic acid (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.84	0.95	0.63	0.32	1.054	2.7	<b>0.18</b>	0.182	0.226	*
o-Hydroxybenzoic acid (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.9	0.85	0.73	0.37	0.99	2.24	<b>0.172</b>	0.18	0.201	
Phenylacetic acid (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.73	0.97	0.6	0.61	1.073	1.41	<b>0.19</b>	0.171	0.172	
m-Cresol (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.822	0.88	0.57	0.34	0.916	1.98	<b>0.182</b>	0.171	0.196	
p-Cresol (Schwarzenbach et al. 2003)	0.82	0.87	0.57	0.31	0.916	1.93	<b>0.194</b>	0.174	0.194	
Hydroquinone (Schwarzenbach et al. 2003)	1	1	1.16	0.6	0.834	0.59	<b>0.078</b>	0.098	0.138	
Vanillin (Noubigh, Abderrabba, et al. 2007; Substance Identifier n.d.)	1.04	1.04	0.32	0.67	1.131	1.21	<b>0.118</b>	0.182	0.164	*
<b>Carboxylic Acids</b>										
Propionic acid (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.233	0.65	0.6	0.45	0.606	0.33	<b>0.132</b>	0.112	0.127	
Butanoic acid	0.21	0.62	0.6	0.45	0.747	0.79	<b>0.166</b>	0.141	0.146	

(Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)									
Hexanoic acid (Schwarzenbach et al. 2003)	0.174	0.6	0.6	0.45	1.028	1.92	<b>0.24</b>	0.197	0.194
Heptanoic acid (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.149	0.6	0.6	0.45	1.169	2.22	<b>0.242</b>	0.224	0.206
Acetic acid (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.265	0.65	0.61	0.44	0.465	-0.25	<b>0.064</b>	0.085	0.103
Suberic acid (Bretti et al. 2006; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	0.69	<b>0.132</b>	N/A	0.142
Azelaic acid (Bretti et al. 2006; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	1.19	<b>0.128</b>	N/A	0.163
Sebacic acid (Bretti et al. 2006; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	1.7	<b>0.164</b>	N/A	0.184
<b>Polar Nitrogens</b>									
4-Nitroaniline (Endo et al. 2012; Substance Identifier n.d.)	1.22	1.92	0.46	0.35	0.99	1.2	<b>0.099</b>	0.147	0.163
Aniline (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.955	0.96	0.26	0.41	0.816	0.95	<b>0.136</b>	0.153	0.153
Benzylamine (Ni & Yalkowsky 2003; Sangster 1989)	0.829	0.88	0.1	0.72	0.957	1.09	<b>0.112</b>	0.161	0.159
Piperidine (Ni & Yalkowsky 2003; Sangster 1989)	0.422	0.46	0.1	0.69	0.804	0.84	<b>0.156</b>	0.153	0.148
Pyrrole (Poole et al. 2000)	0.613	0.73	0.41	0.29	0.577	0.75	<b>0.148</b>	0.124	0.145
Acetanilide (Endo et al. 2012; Sangster 1989)	0.9	1.37	0.48	0.67	1.114	1.24	<b>0.197</b>	0.161	0.165
p-Toluidine (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.92	0.95	0.23	0.45	0.957	1.39	<b>0.17</b>	0.179	0.171
Theophylline (Ni & Yalkowsky 2003; Substance Identifier n.d.)	1.5	1.6	0.54	1.15	1.2223	-0.28	<b>0.1</b>	0.118	0.101
<b>Carboxylic Acid Esters</b>									
Methyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.142	0.64	0	0.45	0.606	0.2	<b>0.185</b>	0.138	0.121
Ethyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.11	0.62	0	0.45	0.747	0.69	<b>0.172</b>	0.167	0.142
Propyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.092	0.6	0	0.45	0.888	1.24	<b>0.201</b>	0.195	0.165
Butyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.071	0.6	0	0.45	1.028	1.8	<b>0.224</b>	0.223	0.189
iso-Butyl acetate (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.052	0.57	0	0.47	1.028	1.65	<b>0.225</b>	0.222	0.182
Pentyl acetate (Ni & Yalkowsky 2003; Substance Identifier n.d.)	0.067	0.6	0	0.45	1.169	2.31	<b>0.283</b>	0.250	0.210

Identifier n.d.)										
Hexyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.056	0.6	0	0.45	1.31	2.83	<b>0.312</b>	0.278	0.232	
sec-Butyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	N/A	N/A	N/A	N/A	N/A	1.65	<b>0.241</b>	N/A	0.182	
tert-Butyl acetate (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	N/A	N/A	N/A	N/A	N/A	1.55	<b>0.269</b>	N/A	0.178	
<b>Amino Acids</b>										
Cystine (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-4.46	<b>-0.068</b>	N/A	-0.074	*
Tyrosine (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-2.22	<b>0.048</b>	N/A	0.020	*
Leucine (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-1.67	<b>0.114</b>	N/A	0.043	*
Glycine (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-3.21	<b>0.002</b>	N/A	-0.022	*
Cytosine (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-1.65	<b>-0.005</b>	N/A	0.044	*
<b>Dioxins and Furans</b>										
Dibenzofuran (Oleszek-Kudlak et al. 2007; Schwarzenbach et al. 2003)	1.407	1.02	0	0.17	1.274	4.31	<b>0.311</b>	0.271	0.294	
Dibenzo-p-dioxin (Oleszek-Kudlak et al. 2007; Schwarzenbach et al. 2003)	N/A	N/A	N/A	N/A	N/A	4.3	<b>0.389</b>	N/A	0.294	
2-Monochlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	5.7	<b>0.44</b>	N/A	0.352	*
2,7-Dichlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	5.58	<b>0.498</b>	N/A	0.347	*
2,8-Dichlorodibenzofuran (Oleszek-Kudlak et al. 2007; Schwarzenbach et al. 2003)	N/A	N/A	N/A	N/A	N/A	5.44	<b>0.409</b>	N/A	0.341	
<b>Pharmaceuticals and Personal Care Products</b>										
Testosterone (Ni & Yalkowsky 2003; Substance Identifier n.d.)	1.54	2.59	0.32	1.19	2.383	3.18	<b>0.326</b>	0.313	0.247	*
Progesterone (Ni & Yalkowsky 2003; Substance Identifier n.d.)	1.45	3.29	0	1.14	2.623	3.83	<b>0.288</b>	0.353	0.274	*
Caffeine (Endo et al. 2012; Substance Identifier n.d.)	1.5	1.82	0.08	1.25	1.363	-0.63	<b>0.114</b>	0.147	0.087	*
Phenylthiourea (Ni & Yalkowsky 2003; Substance Identifier n.d.)	1.25	1.69	0.48	0.79	1.177	0.6	<b>0.184</b>	0.147	0.138	*
5-Fluorouracil (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-0.65	<b>0.014</b>	N/A	0.086	*
6-Mercaptopurine	N/A	N/A	N/A	N/A	N/A	-0.81	<b>0.048</b>	N/A	0.079	*

(Ni & Yalkowsky 2003; Substance Identifier n.d.)										
Sulfanilamide (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-0.67	<b>0.124</b>	N/A	0.085	*
Theobromine (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	-1.06	<b>0.056</b>	N/A	0.068	*
Phenytoin (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	1.42	<b>0.191</b>	N/A	0.173	*
<b>Others</b>										
p-Nitrotoluene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	0.87	1.11	0	0.28	1.032	2.38	<b>0.163</b>	0.215	0.213	
Heptanal (Endo et al. 2012; Substance Identifier n.d.)	0.14	0.65	0	0.45	1.111	2.44	<b>0.237</b>	0.237	0.215	*
Octanal (Endo et al. 2012; Substance Identifier n.d.)	0.16	0.65	0	0.45	1.252	2.95	<b>0.265</b>	0.264	0.237	*
Decanal (Endo et al. 2012; Substance Identifier n.d.)	0.15	0.65	0	0.45	1.533	3.97	<b>0.283</b>	0.319	0.280	*
Metolachlor (Endo et al. 2012; Schwarzenbach et al. 2003)	1.15	1.01	0.07	1.38	2.281	3.13	<b>0.296</b>	0.346	0.244	
Methyl tert-butylether (Jochmann et al. 2006; Schwarzenbach et al. 2003)	0.02	0.21	0	0.59	0.872	0.94	<b>0.17</b>	0.193	0.152	
Tetrahydrofuran (Jochmann et al. 2006; Schwarzenbach et al. 2003)	0.29	0.52	0	0.48	0.622	0.46	<b>0.16</b>	0.142	0.132	
1,4-Dioxane (Jochmann et al. 2006; Schwarzenbach et al. 2003)	0.33	0.75	0	0.64	0.681	-0.27	<b>0.08</b>	0.128	0.102	
Lindane (Xie et al. 1997; Schwarzenbach et al. 2003)	1.45	0.88	0	0.68	1.5798	3.78	<b>0.166</b>	0.285	0.272	
1-Naphthol (Ni & Yalkowsky 2003; Sangster 1989)	1.52	1.05	0.61	0.37	1.144	2.84	<b>0.207</b>	0.198	0.232	
2-Naphthol (Ni & Yalkowsky 2003; Substance Identifier n.d.)	1.52	1.08	0.61	0.4	1.144	2.72	<b>0.22</b>	0.194	0.227	*
Thiophene (Johansen & Pawliszyn 1996)	0.687	0.56	0	0.15	0.641	1.81	<b>0.165</b>	0.173	0.189	
Benzothiophene (Andersson & Schröder 1999)	1.323	0.88	0	0.2	1.01	3.12	<b>0.23</b>	0.223	0.244	
Dibenzothiophene (Andersson & Schröder 1999)	1.959	1.31	0	0.18	1.379	4.38	<b>0.213</b>	0.275	0.297	
Carbazole (Endo et al. 2012; Sangster 1989)	1.79	1.42	0.47	0.26	1.315	3.72	<b>0.232</b>	0.232	0.269	
2,2,2-Trifluoroethanol (Endo et al. 2012; Substance Identifier n.d.)	0.02	0.6	0.57	0.25	0.562	0.2	<b>0.125</b>	0.128	0.121	*
1,1,1,3,3,3-Hexafluoro-2-propanol (Endo et al. 2012; Substance Identifier n.d.)	-0.24	0.55	0.77	0.1	0.816	2.62	<b>0.222</b>	0.189	0.223	*
C4:2 Fluorotelomer Alcohol (Endo et al. 2012; Substance Identifier n.d.)	-0.67	0.2	0.55	0.25	1.352	1.57	<b>0.273</b>	0.304	0.179	*

Identifler n.d.)										
C6:2 Fluorotelomer Alcohol (Endo et al. 2012; Substance Identifler n.d.)	-1.04	0.2	0.55	0.25	1.785	4.08	<b>0.378</b>	0.392	0.284	*
1-Nitropentane (Endo et al. 2012; Substance Identifler n.d.)	0.21	0.95	0	0.29	0.987	2.01	<b>0.203</b>	0.217	0.197	*
1-Nitrohexane (Endo et al. 2012; Substance Identifler n.d.)	0.2	0.95	0	0.29	1.128	2.47	<b>0.236</b>	0.244	0.217	*
Bisphenol A (Endo et al. 2012; Substance Identifler n.d.)	1.61	1.56	0.99	0.91	1.864	3.64	<b>0.174</b>	0.249	0.266	*
2-Phenylphenol (Endo et al. 2012; Substance Identifler n.d.)	1.55	1.4	0.56	0.49	1.383	3.29	<b>0.274</b>	0.222	0.251	*
4-Aminobiphenyl (Endo et al. 2012; Schwarzenbach et al. 2003)	1.57	1.48	0.26	0.48	1.424	2.86	<b>0.208</b>	0.240	0.233	
2,5-Dimethylpyrazine (Endo et al. 2012; Substance Identifler n.d.)	0.63	0.9	0	0.69	0.916	0.69	<b>0.209</b>	0.161	0.142	*
Methyl-phenyl sulfoxide (Endo et al. 2012; Substance Identifler n.d.)	1.1	1.8	0	0.91	1.08	0.31	<b>0.166</b>	0.133	0.126	*
4-Nitroanisole (Endo et al. 2012; Substance Identifler n.d.)	0.97	1.29	0	0.4	1.09	2.12	<b>0.126</b>	0.206	0.202	*
Valerophenone (Endo et al. 2012; Substance Identifler n.d.)	0.8	0.95	0	0.5	1.437	3.2	<b>0.271</b>	0.278	0.247	*
Benzophenone (Endo et al. 2012; Schwarzenbach et al. 2003)	1.45	1.5	0	0.5	1.481	3.18	<b>0.262</b>	0.260	0.247	
di-n-propyl Phthalate (Endo et al. 2012; Schwarzenbach et al. 2003)	0.71	1.4	0	0.88	1.992	3.27	<b>0.374</b>	0.332	0.250	
tri-n-butyl Phosphate (Endo et al. 2012; Substance Identifler n.d.)	-0.1	0.9	0	1.21	2.239	3.83	<b>0.428</b>	0.373	0.274	*
Atrazine (Endo et al. 2012; Schwarzenbach et al. 2003)	1.22	1.29	0.17	1.01	1.62	2.65	<b>0.274</b>	0.239	0.224	
Diethylether (Xie et al. 1997; Schwarzenbach et al. 2003)	0.04	0.25	0	0.45	0.731	0.89	<b>0.238</b>	0.178	0.150	
Bromomethane (De Bruyn & Saltzman 1997; Schwarzenbach et al. 2003)	0.399	0.43	0	0.1	0.425	1.19	<b>0.15</b>	0.144	0.163	
Dimethyl sulfide (Schwarzenbach et al. 2003)	0.404	0.38	0	0.29	0.554	0.98	<b>0.17</b>	0.152	0.154	
9-Hydroxyfluorene (Substance Identifler n.d.)	N/A	N/A	N/A	N/A	N/A	2.56	<b>0.234</b>	N/A	0.221	*
1-NO-2-Naphthol (Bretti et al. 2011; Substance Identifler n.d.)	N/A	N/A	N/A	N/A	N/A	2.37	<b>0.108</b>	N/A	0.213	*
1,5-Dihydroxynaphthalene (Bretti et al. 2011; Substance Identifler n.d.)	N/A	N/A	N/A	N/A	N/A	1.57	<b>0.177</b>	N/A	0.179	*
o-Dinitrobenzene (Ni & Yalkowsky 2003; Substance	N/A	N/A	N/A	N/A	N/A	1.87	<b>0.124</b>	N/A	0.193	*

Identifier n.d.)									
m-Dinitrobenzene (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	N/A	N/A	N/A	N/A	N/A	1.49	<b>0.109</b>	N/A	0.176
p-Dinitrobenzene (Ni & Yalkowsky 2003; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	1.43	<b>0.097</b>	N/A	0.173
Phthalic acid (Ni & Yalkowsky 2003; Schwarzenbach et al. 2003)	N/A	N/A	N/A	N/A	N/A	0.73	<b>0.178</b>	N/A	0.144
Protocatechuic Acid (Noubigh, Abderrabba, et al. 2007; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	1.01	<b>0.0967</b>	N/A	0.155
Gallic Acid (Noubigh, Abderrabba, et al. 2007; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	0.53	<b>0.092</b>	N/A	0.135
Ferrulic Acid (Noubigh, Abderrabba, et al. 2007; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	0.96	<b>0.171</b>	N/A	0.153
Syringic Acid (Noubigh, Abderrabba, et al. 2007; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	1.28	<b>0.105</b>	N/A	0.167
Diacetone alcohol (Susana Bidner & de Santiago 1971; Substance Identifier n.d.)	N/A	N/A	N/A	N/A	N/A	0.03	<b>0.139</b>	N/A	0.114

\* log  $K_{ow}$  estimated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)

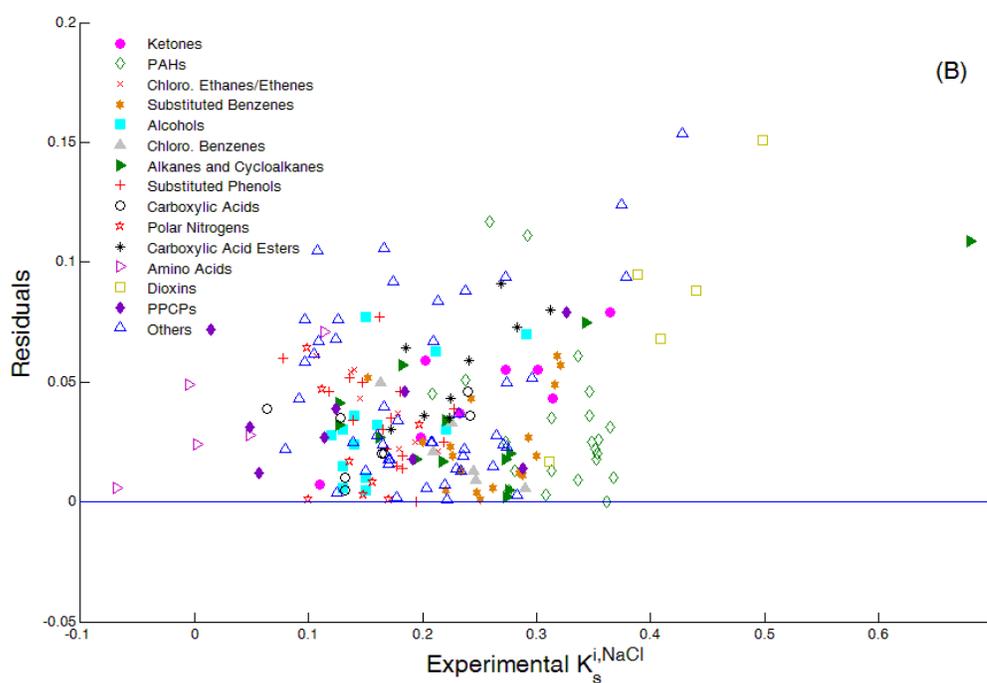
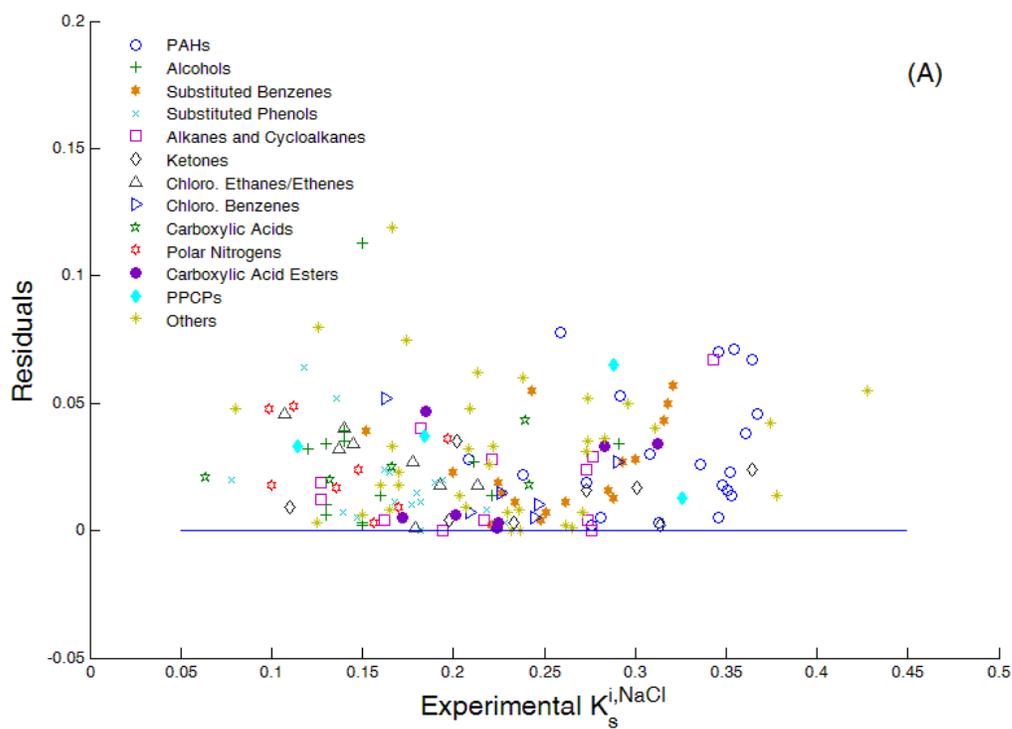
**Table C.2.2.** Range of Regressions for the NaCl Setschenow constant LFERs

<b>log <math>K_{ow}</math> LFER</b>	
log $K_{ow}$ Range	-4.46 – 10.9
NaCl Setschenow Constant Range	-0.068 – 0.68 M <sup>-1</sup>
<b>pp-LFER</b>	
NaCl Setschenow Constant Range	0.0640 – 0.428

### C.3 Plots and Breakdown of Residuals

**Table C.3.1.** Number and Percentages of Organic Compounds in Residuals Bins per LFER

<b>Residual Bin</b>	<b>log <math>K_{ow}</math> LFER</b>	<b>pp-LFER</b>
≥0.20	0 (0 %)	0 (0 %)
0.15 – 0.20	2 (1 %)	0 (0 %)
0.10 – 0.15	6 (3 %)	2 (1 %)
0.05 – 0.10	45 (23 %)	19 (12 %)
0.025 – 0.05	57 (30 %)	47 (29 %)
≤0.025	84 (43%)	92 (58 %)



**Figure C.3.1.** Plots of absolute values of residuals between the A) pp-LFER predicted and experimental NaCl Setschenow constant values, B) log  $K_{ow}$  predicted and experimental NaCl Setschenow constant values.

#### C.4 Data for the CaCl<sub>2</sub>, KCl, LiCl and NaBr sp-LFERs.

**Table C.4.1.** Range of Regressions for the CaCl<sub>2</sub>, KCl, LiCl, and NaBr constant LFERs

<b>sp-CaCl<sub>2</sub>-LFER</b>	
NaCl Setschenow Constant Range	0.0740 – 0.498 M <sup>-1</sup>
CaCl <sub>2</sub> Setschenow Constant Range	0.112 – 0.712 M <sup>-1</sup>
<b>sp-KCl-LFER</b>	
NaCl Setschenow Constant Range	0.0570 – 0.498 M <sup>-1</sup>
KCl Setschenow Constant Range	0.0280 – 0.482 M <sup>-1</sup>
<b>sp-LiCl-LFER</b>	
NaCl Setschenow Constant Range	0.092 – 0.276 M <sup>-1</sup>
LiCl Setschenow Constant Range	0.0560 – 0.218 M <sup>-1</sup>
<b>sp-NaBr-LFER</b>	
NaCl Setschenow Constant Range	0.0820 – 0.308 M <sup>-1</sup>
NaBr Setschenow Constant Range	0.0890 – 0.233 M <sup>-1</sup>

**Table C.4.2** Organic compounds used in CaCl<sub>2</sub> LFER

Compound of Interest	NaCl K <sub>s</sub> (M <sup>-1</sup> )	CaCl <sub>2</sub> K <sub>s</sub> (M <sup>-1</sup> )	sp-LFER predicted CaCl <sub>2</sub> K <sub>s</sub>
Chlorobenzene (Xie et al. 1997)	0.209	0.286	0.296
o-Dichlorobenzene (Xie et al. 1997)	0.247	0.357	0.342
m-Dichlorobenzene (Xie et al. 1997)	0.226	0.357	0.317
p-Dichlorobenzene (Xie et al. 1997)	0.245	0.344	0.340
1,2,4-Trichlorobenzene (Xie et al. 1997)	0.29	0.349	0.395
Naphthalene (Gordon & Thorne 1967)	0.208	0.322	0.295
1-Naphthol (Schwarzenbach et al. 2003)	0.21	0.35	0.297
<i>Hexachlorobenzene</i> (Oleszek-Kudlak et al. 2007)	0.343	0.707	0.478
2-Monochlorodibenzo-o-dioxin (Oleszek-Kudlak et al. 2007)	0.44	0.632	0.578
2,7-Dichlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007)	0.498	0.712	0.649
Dibenzofuran (Oleszek-Kudlak et al. 2007)	0.311	0.435	0.420
2,8-Dichlorodibenzofuran (Oleszek-Kudlak et al. 2007)	0.409	0.495	0.540
Benzene (Boddu et al. 2001)	0.19	0.33	0.273
Toluene (Poulson et al. 1999)	0.224	0.289	0.314
Pyrene (Schlautman et al. 2004)	0.208	0.218	0.295
Perylene (Schlautman et al. 2004)	0.259	0.3	0.357

Carbaryl (Long & McDevit 1952)	0.247	0.353	0.342
Acetic Acid (Prideaux & Millott 1926)	0.074	0.165	0.131
1-Butanol (Long & McDevit 1952)	0.19	0.25	0.273
Thiophene	0.165	0.295	0.242
Dibenzothiophene	0.213	0.217	0.301
Fluorene	0.281	0.362	0.384
Benzothiophene	0.23	0.289	0.322
Phenanthrene	0.308	0.373	0.417
Pyrrole	0.148	0.182	0.222
p-Cresol	0.194	0.3	0.278
Phenol	0.139	0.313	0.211
Hydroquinone	0.078	0.112	0.136
Hexanoic Acid	0.24	0.359	0.334
9-HydroxyFluorene	0.234	0.295	0.326

**Table C.4.3.** Organic compounds used in KCl LFER

Compound of Interest	NaCl $K_s$ ( $M^{-1}$ )	KCl $K_s$ ( $M^{-1}$ )	sp-LFER predicted KCl $K_s$
Benzene (Xie et al. 1997)	0.195	0.166	0.166
Toluene (Xie et al. 1997)	0.225	0.206	0.193
o-Xylene (Xie et al. 1997)	0.227	0.205	0.195
p-Xylene (Xie et al. 1997)	0.251	0.217	0.217
Naphthalene (Xie et al. 1997)	0.208	0.204	0.189
Biphenyl (Xie et al. 1997)	0.276	0.255	0.239
n-Hexane (Xie et al. 1997)	0.276	0.244	0.239
Chlorobenzene (Xie et al. 1997)	0.209	0.176	0.179
o-Dichlorobenzene (Xie et al. 1997)	0.247	0.207	0.213
m-Dichlorobenzene (Xie et al. 1997)	0.226	0.201	0.194
1,2,4-Trichlorobenzene (Xie et al. 1997)	0.25	0.239	0.216
Benzoic Acid (Xie et al. 1997)	0.176	0.138	0.149
m-Chlorobenzene (Xie et al. 1997)	0.18	0.142	0.152
Lindane (Xie et al. 1997)	0.166	0.149	0.140
H <sub>2</sub> (Pawlikowski & Prausnitz 1983)	0.092	0.078	0.072
N <sub>2</sub> O Pawlikowski & Prausnitz 1983)	0.101	0.099	0.081
O <sub>2</sub>	0.14	0.159	0.116

(Pawlikowski & Prausnitz 1983)			
Helium (Pawlikowski & Prausnitz 1983)	0.082	0.068	0.063
2-Monochlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007)	0.44	0.323	0.388
2,7-Dichlorodibenzo-p-dioxin (Oleszek-Kudlak et al. 2007)	0.498	0.482	0.441
2,8-Dichlorodibenzofuran (Oleszek-Kudlak et al. 2007)	0.409	0.384	0.360
Hexachlorobenzene (Oleszek-Kudlak et al. 2007)	0.343	0.266	0.300
Perylene (Schlautman et al. 2004)	0.259	0.225	0.224
Pyrene (Schlautman et al. 2004)	0.208	0.187	0.178
Phenol (Morrison 1944)	0.183	0.147	0.090
Phenylacetic Acid (Morrison 1944)	0.15	0.133	0.125
Anisole (Görgényi et al. 2006)	0.225	0.15	0.193
Chloroform (Görgényi et al. 2006)	0.208	0.121	0.178
Propylbenzene (Sanemasa et al. 1984)	0.281	0.256	0.244
Ethylbenzene (Sanemasa et al. 1984)	0.280	0.250	0.243
m-Xylene (Xie et al. 1997)	0.249	0.222	0.215
Phenanthrene (Xie et al. 1997)	0.308	0.279	0.268
p-Dichlorobenzene (Xie et al. 1997)	0.245	0.192	0.211
2-Chlorobenzene (Xie et al. 1997)	0.182	0.139	0.154
Argon (Pawlikowski & Prausnitz 1983)	0.133	0.125	0.110
Dibenzofuran (Oleszek-Kudlak et al. 2007)	0.311	0.266	0.271
1-Naphthol (Almeida et al. 1983)	0.209	0.179	0.179
Protocatechuic Acid (Noubigh, Mgaidi, et al. 2007)	0.0967	0.05	0.077
Vanillin (Noubigh, Mgaidi, et al. 2007)	0.118	0.102	0.096
Gallic Acid (Noubigh, Mgaidi, et al. 2007)	0.092	0.039	0.072
Ferrulic Acid (Noubigh, Abderrabba, et al. 2007)	0.171	0.138	0.144
Syringic Acid (Noubigh, Abderrabba, et al. 2007)	0.105	0.037	0.084
Acetone (Susana Bidner & de Santiago 1971)	0.11	0.101	0.089
Diacetone alcohol (Susana Bidner & de Santiago 1971)	0.139	0.118	0.115
Ethyl Acetate (Susana Bidner & de Santiago 1971)	0.172	0.151	0.145
Diethyl ether (Susana Bidner & de Santiago 1971)	0.238	0.223	0.205
γ-butyrolactone	0.057	0.028	0.041

(Susana Bidner & de Santiago 1971)			
------------------------------------	--	--	--

**Table C.4.4.** NaCl and LiCl Setschenow constants used in sp-LiCl-LFER

Compound	NaCl K <sub>s</sub> (M <sup>-1</sup> )	LiCl K <sub>s</sub> (M <sup>-1</sup> )	Pred. LiCl K <sub>s</sub> (M <sup>-1</sup> )
n-Butane (Morrison & Billett 1952)	0.217	0.171	0.159
Propane (Morrison & Billett 1952)	0.194	0.152	0.140
Ethane (Morrison & Billett 1952)	0.162	0.124	0.114
Methane (Morrison & Billett 1952)	0.127	0.097	0.085
H <sub>2</sub> (Morrison & Billett 1952)	0.092	0.065	0.057
N <sub>2</sub> (Morrison & Billett 1952)	0.121	0.095	0.080
Ethylene (Morrison & Billett 1952)	0.127	0.089	0.085
Benzene (Xie et al. 1997)	0.195	0.141	0.141
Toluene (Xie et al. 1997)	0.227	0.168	0.167
o-Xylene (Xie et al. 1997)	0.227	0.18	0.167
m-Xylene (Xie et al. 1997)	0.248	0.185	0.185
p-Xylene (Xie et al. 1997)	0.251	0.187	0.187
Naphthalene (Xie et al. 1997)	0.22	0.18	0.162
Biphenyl (Xie et al. 1997)	0.276	0.218	0.208
Chloroform (Görgényi et al. 2006)	0.208	0.131	0.152
Chlorobenzene (Görgényi et al. 2006)	0.257	0.17	0.192
Anisole (Görgényi et al. 2006)	0.225	0.119	0.166
1-Naphthol (Almeida et al. 1983)	0.209	0.193	0.153
Phenol (Bergen & Long 1956)	0.172	0.143	0.122
Caffeine (Perez-Tejeda et al. 1987)	0.142	0.086	0.098
Lindane (Xie et al. 1997)	0.166	0.135	0.117
Aniline (Bergen & Long 1956)	0.136	0.07	0.093
Benzylamine (Bergen & Long 1956)	0.112	0.084	0.073
Piperidine (Bergen & Long 1956)	0.156	0.056	0.109
Diacetone alcohol (Susana Bidner & de Santiago 1971)	0.139	0.0774	0.095
Diethyl ether (Susana Bidner & de Santiago 1971)	0.238	0.176	0.176
Acetone (Susana Bidner & de Santiago 1971)	0.11	0.063	0.071

**Table C.4.5** NaCl and NaBr Setschenow constants used in sp-NaBr-LFER

Compound	NaCl K <sub>s</sub> (M <sup>-1</sup> )	NaBr K <sub>s</sub> (M <sup>-1</sup> )	Pred. NaBr K <sub>s</sub> (M <sup>-1</sup> )
H <sub>2</sub> (Pawlikowski & Prausnitz 1983)	0.092	0.089	0.091
O <sub>2</sub> (Pawlikowski & Prausnitz 1983)	0.14	0.11	0.122
Argon (Pawlikowski & Prausnitz 1983)	0.133	0.142	0.118
Methane (Pawlikowski & Prausnitz 1983)	0.127	0.117	0.114
Helium (Pawlikowski & Prausnitz 1983)	0.082	0.089	0.085
Benzene (Xie et al. 1997)	0.19	0.155	0.155
Toluene (Xie et al. 1997)	0.206	0.191	0.165
o-Xylene (Xie et al. 1997)	0.205	0.178	0.164
m-Xylene (Xie et al. 1997)	0.222	0.144	0.175
p-Xylene (Xie et al. 1997)	0.217	0.198	0.172
Naphthalene (Xie et al. 1997)	0.208	0.162	0.166
Biphenyl (Xie et al. 1997)	0.255	0.209	0.197
Phenanthrene (Xie et al. 1997)	0.308	0.211	0.231
n-Hexane (Xie et al. 1997)	0.244	0.161	0.190
Chlorobenzene (Xie et al. 1997)	0.209	0.129	0.167
p-Dichlorobenzene (Xie et al. 1997)	0.245	0.174	0.190
Lindane (Xie et al. 1997)	0.166	0.131	0.139
Ethylbenzene (Sanemasa et al. 1984)	0.28	0.232	0.213
Propylbenzene (Sanemasa et al. 1984)	0.281	0.233	0.214
1-Naphthol (Almeida et al. 1983)	0.209	0.155	0.167
Diacetone alcohol (Susana Bidner & de Santiago 1971)	0.139	0.109	0.122
Ethyl acetate (Susana Bidner & de Santiago 1971)	0.172	0.123	0.143

#### C.4 References

Almeida, M.B. et al., 1983. Setchenow coefficients for naphthols by distribution method. *Canadian Journal of Chemistry*, 61(2), pp.244–248. Available at: <http://www.nrcresearchpress.com/doi/abs/10.1139/v83-043>.

- Andersson, J.T. & Schröder, W., 1999. A Method for Measuring 1-Octanol–Water Partition Coefficients. *Analytical Chemistry*, 71(16), pp.3610–3614. Available at: <http://dx.doi.org/10.1021/ac9902291>.
- Bergen, R.L. & Long, F.A., 1956. The Salting in of Substituted Benzenes by Large Ion Salts. *The Journal of Physical Chemistry*, 60(8), pp.1131–1135. Available at: <http://dx.doi.org/10.1021/j150542a024>.
- Boddu, V.M., Krishnaiah, A. & Viswanath, D.S., 2001. Liquid–Liquid Equilibria of the Benzene + Water + Acetic Acid Ternary System and Solubility of Benzene in Water: Effect of Calcium Chloride. *Journal of Chemical & Engineering Data*, 46(5), pp.1172–1175. Available at: <http://pubs.acs.org/doi/abs/10.1021/je000196i>.
- Bretti, C. et al., 2006. Solubility and Activity Coefficients of Acidic and Basic Nonelectrolytes in Aqueous Salt Solutions. 2. Solubility and Activity Coefficients of Suberic, Azelaic, and Sebacic Acids in NaCl(aq), (CH<sub>3</sub>)<sub>4</sub>NCl(aq), and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NI(aq) at Different Ionic Strengths a. *Journal of Chemical & Engineering Data*, 51(5), pp.1660–1667. Available at: <http://dx.doi.org/10.1021/je060132t>.
- Bretti, C. et al., 2011. Solubility, activity coefficients and acid–base properties of three naphthol derivatives in NaCl(aq) at different ionic strengths and at T=298.15K. *Journal of Molecular Liquids*, 158(1), pp.50–56. Available at: <http://www.sciencedirect.com/science/article/pii/S0167732210003041> [Accessed June 11, 2015].
- De Bruyn, W.J. & Saltzman, E.S., 1997. The solubility of methyl bromide in pure water, 35% sodium chloride and seawater. *Marine Chemistry*, 56(1-2), pp.51–57. Available at: <http://www.sciencedirect.com/science/article/pii/S0304420396000898> [Accessed August 11, 2015].
- Endo, S., Pfennigsdorff, A. & Goss, K.-U., 2012. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. *Environmental science & technology*, 46(3), pp.1496–503. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22191628>.
- Gordon, J.E. & Thorne, R.L., 1967. Salt effects on the activity coefficient of naphthalene in mixed aqueous electrolyte solutions. I. Mixtures of two salts. *The Journal of Physical Chemistry*, 71(13), pp.4390–4399. Available at: <http://pubs.acs.org/doi/abs/10.1021/j100872a035>.
- Görgényi, M. et al., 2006. Aqueous salting-out effect of inorganic cations and anions on non-electrolytes. *Chemosphere*, 65(5), pp.802–10. Available at: <http://www.sciencedirect.com/science/article/pii/S0045653506003377> [Accessed November 19, 2014].
- Gossett, J.M., 1987. Measurement of Henry’s law constants for C<sub>1</sub> and C<sub>2</sub> chlorinated hydrocarbons. *Environmental Science & Technology*, 21(2), pp.202–208. Available at: <http://dx.doi.org/10.1021/es00156a012>.
- Hoaglin, D.C. & Welsch, R.E., 1978. The Hat Matrix in Regression and ANOVA. *The American Statistician*, 32(1), pp.17–22. Available at: <http://www.tandfonline.com/doi/abs/10.1080/00031305.1978.10479237>.
- Jochmann, M., Yuan, X. & Schmidt, T., 2007. Determination of volatile organic hydrocarbons in water samples by solid-phase dynamic extraction. *Analytical and Bioanalytical Chemistry*, 387(6), pp.2163–2174. Available at: <http://dx.doi.org/10.1007/s00216-006-1066-1>.
- Jochmann, M.A., Kmiecik, M.P. & Schmidt, T.C., 2006. Solid-phase dynamic extraction for the enrichment of polar volatile organic compounds from water. *Journal of chromatography. A*,

- 1115(1-2), pp.208–16. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0021967306004535> [Accessed April 18, 2014].
- Johansen, S. & Pawliszyn, J., 1996. Trace analysis of hetero aromatic compounds (NSO) in water and polluted groundwater by Solid phase micro- extraction (SPME). *Journal of High Resolution ...*, 19(November), pp.627–632. Available at:  
<http://onlinelibrary.wiley.com/doi/10.1002/jhrc.1240191107/full> [Accessed December 10, 2013].
- Jonker, M.T.O. & Muijs, B., 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere*, 80, pp.223–227.
- Long, F.A. & McDevit, W.F., 1952. Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions. *Chemical Reviews*, 51(1), pp.119–169. Available at:  
<http://pubs.acs.org/doi/abs/10.1021/cr60158a004>.
- Morrison, T.J., 1944. The salting-out effect. *Trans. Faraday Soc.*, 40(0), pp.43–48. Available at:  
<http://dx.doi.org/10.1039/TF9444000043>.
- Morrison, T.J. & Billett, F., 1952. 730. The salting-out of non-electrolytes. Part II. The effect of variation in non-electrolyte. *J. Chem. Soc.*, (0), pp.3819–3822. Available at:  
<http://dx.doi.org/10.1039/JR9520003819>.
- Ni, N. & Yalkowsky, S.H., 2003. Prediction of Setschenow constants. *International journal of pharmaceutics*, 254, pp.167–172.
- Noubigh, A., Mgaidi, A., et al., 2007. Effect of salts on the solubility of phenolic compounds: experimental measurements and modelling. *Journal of the Science of Food and Agriculture*, 87(5), pp.783–788. Available at: <http://dx.doi.org/10.1002/jsfa.2762>.
- Noubigh, A., Abderrabba, M. & Provost, E., 2007. Temperature and salt addition effects on the solubility behaviour of some phenolic compounds in water. *The Journal of Chemical Thermodynamics*, 39(2), pp.297–303. Available at:  
<http://www.sciencedirect.com/science/article/pii/S0021961406001546> [Accessed December 11, 2014].
- Oleszek-Kudlak, S., Shibata, E. & Nakamura, T., 2007. Solubilities of Selected PCDDs and PCDFs in Water and Various Chloride Solutions. *Journal of Chemical & Engineering Data*, 52(5), pp.1824–1829. Available at: <http://pubs.acs.org/doi/abs/10.1021/jc700185m>.
- Pawlikowski, E.M. & Prausnitz, J.M., 1983. Estimation of Setchenow constants for nonpolar gases in aqueous solutions of common salts at moderate temperatures. *Industrial & Engineering Chemistry Fundamentals*, 22(1), pp.86–90. Available at:  
<http://dx.doi.org/10.1021/i100009a015>.
- Perez-Tejeda, P. et al., 1987. Setschenow coefficients for caffeine, theophylline and theobromine in aqueous electrolyte solutions. *J. Chem. Soc., Faraday Trans. 1*, 83(4), pp.1029–1039. Available at: <http://dx.doi.org/10.1039/F19878301029>.
- Poole, S.K., Durham, D. & Kibbey, C., 2000. Rapid method for estimating the octanol–water partition coefficient (log Pow) by microemulsion electrokinetic chromatography. *Journal of Chromatography B: Biomedical Sciences and Applications*, 745(1), pp.117–126. Available at: <http://www.sciencedirect.com/science/article/pii/S0378434700000724> [Accessed June 10, 2015].
- Poulson, S., Harrington, R. & Drever, J., 1999. The solubility of toluene in aqueous salt solutions. *Talanta*, 48, pp.633–641.

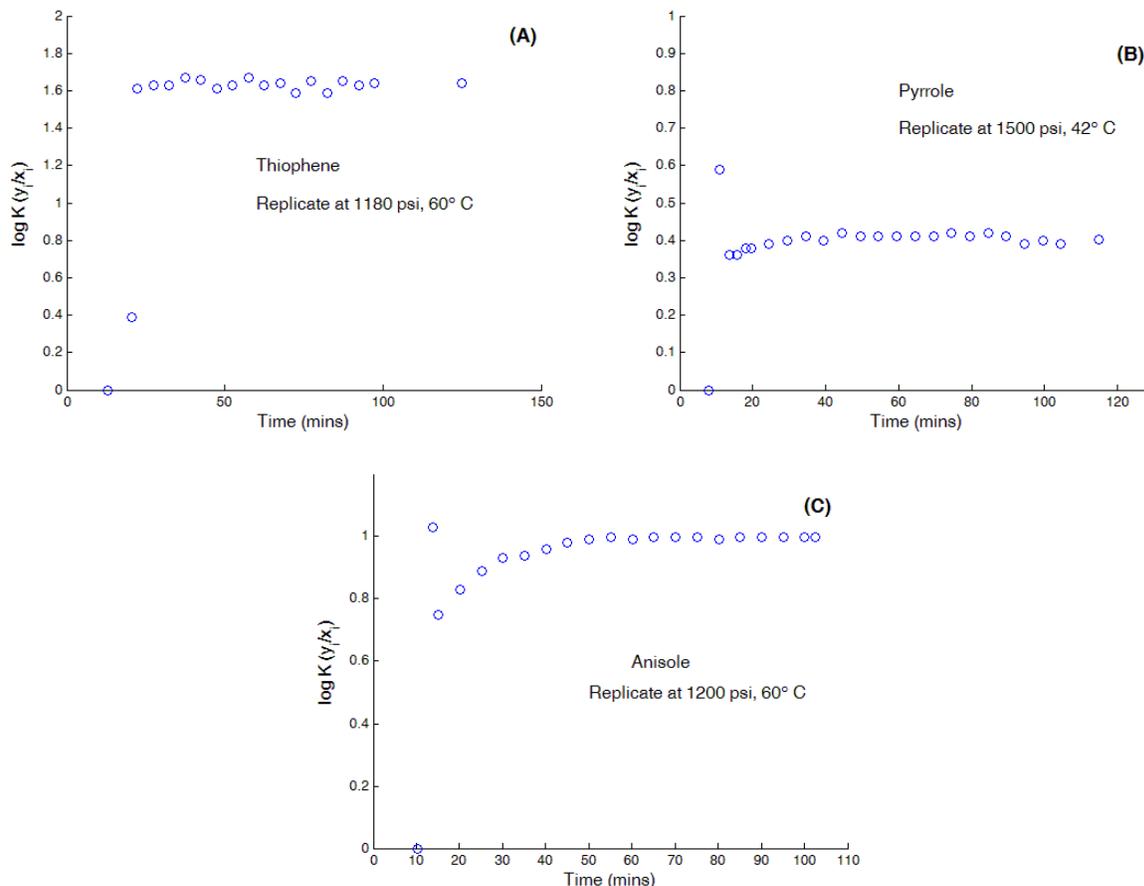
- Prideaux, E.B.R. & Millott, J.O., 1926. XXVII.-Action of hydrogen fluoride on compounds of selenium and tellurium. Part I. Selenium dioxide. *J. Chem. Soc.*, 129(0), pp.167–174. Available at: <http://dx.doi.org/10.1039/JR9262900167>.
- Sanemasa, I. et al., 1984. The Effects of Salts on the Solubilities of Benzene, Toluene, Ethylbenzene, and Propylbenzene in Water. *Bulletin of the Chemical Society of Japan*, 57(6), pp.1539–1544.
- Sangster, J., 1989. Octanol-Water Partition Coefficients of Simple Organic Compounds. *Journal of Physical and Chemical Reference Data*, 18(3).
- Schlautman, M.A. et al., 2004. Testing a surface tension-based model to predict the salting out of polycyclic aromatic hydrocarbons in model environmental solutions. *Water Research*, 38(14–15), pp.3331–3339. Available at: <http://www.sciencedirect.com/science/article/pii/S0043135404002350>.
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Substance Identifier, S.S., Advanced Chemistry Development (ACD/Labs) Software V11.02. Columbus, OH. Available at: <https://scifinder.cas.org>.
- Susana Bidner, M. & de Santiago, M., 1971. Solubilité de liquides non-électrolytes dans des solutions aqueuses d'électrolytes. *Chemical Engineering Science*, 26(9), pp.1484–1488. Available at: <http://www.sciencedirect.com/science/article/pii/0009250971800702> [Accessed May 12, 2015].
- Xie, W.-H., Shiu, W.-Y. & Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research*, 44(4), pp.429–444. Available at: <http://www.sciencedirect.com/science/article/pii/S0141113697000172>.
- Zhou, X. & Mopper, K., 1990. Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; implications for air-sea exchange. *Environmental Science & Technology*, 24(12), pp.1864–1869. Available at: <http://dx.doi.org/10.1021/es00082a013>.

## **Appendix D**

Chapter 6:  
New Linear Partitioning Models based on Experimental Water – Supercritical CO<sub>2</sub> Partitioning  
Data of Selected Organic Compounds

## D.1 Time to Equilibrium Curves for Organic Compound Partitioning

Here are examples of partitioning coefficient versus time curves for the organic compounds in this study. These show that the system obtained equilibrium two hours for the compounds.



**Figure D.1.1.** Partitioning coefficients of organic compounds versus time to equilibrium for A) Thiophene, B) Pyrrole, and C) Anisole.

## D.2 Equation of State Modeling and Binary Interaction Parameters

Equation of state modeling is typically the most common modeling technique used in supercritical fluid phase equilibria. There are a variety of EOS that can be used in supercritical fluid phase equilibria, including Soave-Redlich-Kwong (SRK) (Soave 1972; Redlich & Kwong 1949), Peng & Robinson (1976) (PR), Patel & Teja (1982) and Adachi & Lu (1984) SRK and PR are commonly used to calibrate data measured in sc-CO<sub>2</sub>.

The PR-EOS is given by Eqn. D.2.1, where,  $P$  is the pressure of the system,  $R$  is the universal gas constant,  $T$  is the temperature of the system,  $\nu$  is the molar volume of the compound of interest,  $a$  and  $b$  are parameters used to account for the deviations from ideality of the compounds of interest (i.e., they account for all attractive and repulsive forces of all of the species in the system). Any units can be used as long as they are consistent. The PR-EOS, described in greater detail elsewhere (Burant et al. 2013; Peng & Robinson 1976; Sandler 2006), requires inputs of critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), and acentric factors ( $\omega$ ) of all components to determine phase equilibria (**Table D.2.1**).

$$P = \frac{RT}{\nu - b} - \frac{a}{\nu(\nu + b) + b(\nu - b)} \quad \text{Eqn. D.2.1}$$

In a multi-component system, such as the organic compound-water-sc-CO<sub>2</sub> system of interest here; the above PR-EOS needs mixing rules and binary interaction parameters (BIPs) to account for the interactions between each component in the system. BIPs are required for every possible component pair in the system. In EOS modeling, an array of mixing rules have been used, including Panagiotopoulos & Reid (1986), Wong & Sandler (1992) and Mathias–Klotz–Prausnitz (Mathias et al. 1991), but these mixing rules often require more sophisticated regression techniques and additional BIPs for implementation. The simplest mixing rules are the van der Waals (vdW) mixing rules, described elsewhere (Sandler 2006), which are used in this study as an example of EOS modeling with BIPs.

Binary interaction parameters based on the experimental data from this study were estimated using the regression software on Aspen Plus Properties V7.0®. This uses (experimental and model data) to determine the BIPs by reducing the error of the PR-EOS with a

maximum likelihood function. The PR-EOS was run on MATLAB R2013A with the regressed BIPs.

**Table D.2.1.** Critical properties, vapor pressures, and aqueous solubilities of compounds of interest in this study.

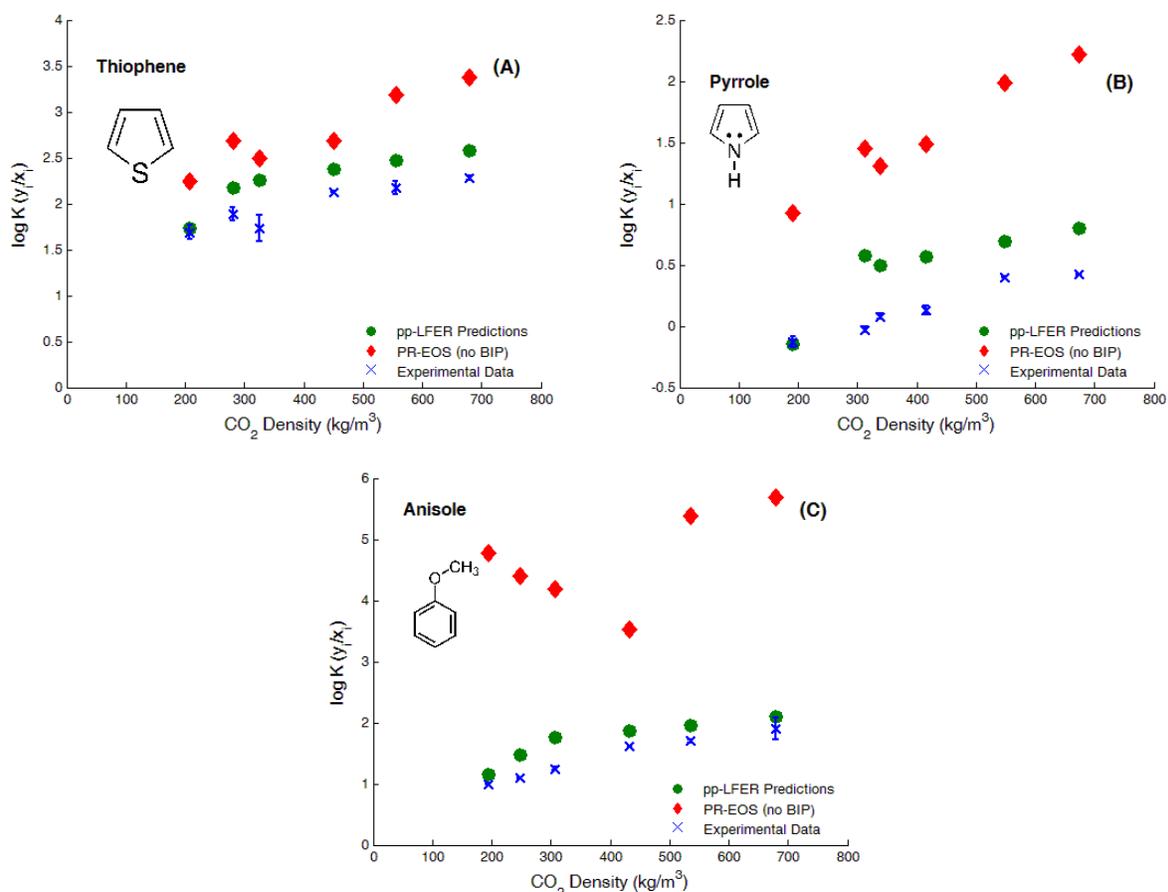
Component	T <sub>c</sub> (K)	P <sub>c</sub> (bar)	Ω	T <sub>b</sub> (K)	MW (g/mol)
Carbon Dioxide	304.2	73.8	0.255	194.7	44
Water	647	220.6	0.344	373	18
Thiophene	579.4	57	0.193	357	84
Pyrrole	639.8	62.1	0.288	402	67.1
Anisole	643	42	0.369	427	108.1

\*T<sub>b</sub>: Boiling Point

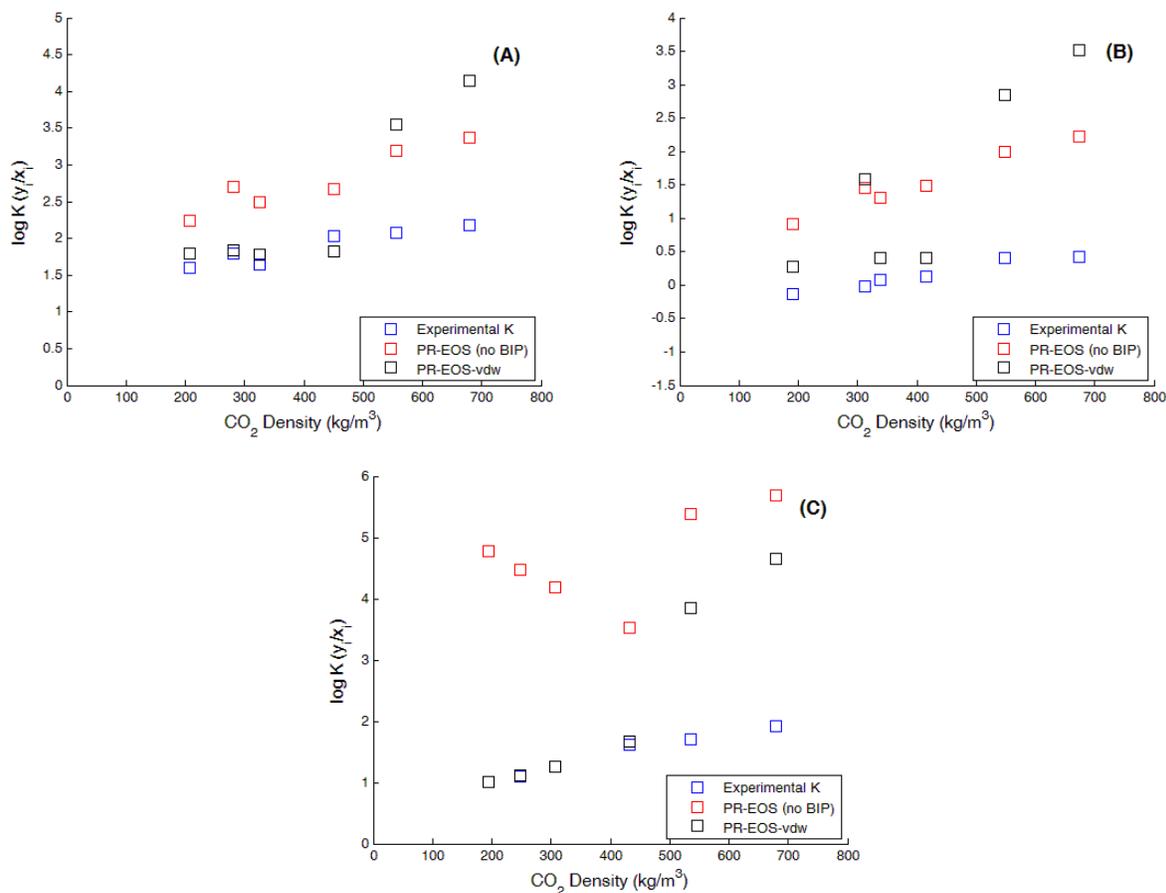
The calculation of BIPs requires the mole fractions of each component in each phase; the experimental work was focused on measuring only the mole fraction of the organic compounds in the sc-CO<sub>2</sub> and aqueous phases, so two models were used to calculate the mole fractions of the CO<sub>2</sub> and water in each respective phase. The CO<sub>2</sub> mole fraction in the water-rich phase was estimated by a CO<sub>2</sub> solubility calculator based on the work of Wang et al. (2013) The calculator (<http://co2calculator.ce.cmu.edu/9/NineModels.aspx>) is based on a multi-model predictive system, which calculates the solubility of CO<sub>2</sub> in conditions of interest considering the most accurate EOS or empirical model for the given conditions among nine mathematical models across a wide range of temperature, pressure, and salinity conditions. Mole fractions of water in sc-CO<sub>2</sub> were calculated using the model of Spycher et al. (2003).

Binary interaction parameters were regressed after experimental data collection on Aspen Plus Properties V7.0®, and the BIPs, which are temperature dependent, were determined for each data point. All of the BIPs are found in **Table D.2.1**. The PR-EOS with vdW mixing rules typically has higher errors for polar components. The CO<sub>2</sub>-H<sub>2</sub>O-pyrrole system has the highest RMSE of the PR-EOS with vdW mixing rules, due to the fact that two relatively polar components are present.

In addition, the use of existing BIPs is best for interpolating between data points and typically cannot be extrapolated beyond the original data set (Valderrama 2003), so these BIPs are only applicable to the data range shown here. Since this data set is linear ( $\log K_{i,c/w}$  versus  $\text{CO}_2$  density), one could just create a linear regression of experimental data points, and use that fit to interpolate for new partitioning coefficients. However, such an approach does not solve the problem of *a priori* prediction of partitioning coefficients.



**Figure D.2.1.** Comparison of experimental partitioning coefficients to the previous pp-LFER and PR-EOS, without binary interaction parameters for (A) Thiophene, (B) Pyrrole, and (C) Anisole. The two models represent models available to predict partitioning coefficients *a priori*; binary interaction parameters for EOS modeling are not available until after measurements are taken.



**Figure D.2.2.** Partitioning coefficients versus  $CO_2$  density for (A) Thiophene, (B) Pyrrole, and (C) Anisole. This is a comparison of  $\log K$  values, PR-EOS without BIP values, and PR-EOS with vdW-BIPs.

**Table D.2.2.** Binary Interaction Parameter for All Components in this Study

Parameter	Component i	Component j	Value (SI units)	Standard deviation
PRKBV/1	THIOPHENE	$CO_2$	1.35E+03	1.03E+01
PRKBV/2	THIOPHENE	$CO_2$	-2.03E+00	1.54E-02
PRKBV/3	THIOPHENE	$CO_2$	-2.24E+05	1.73E+03
PRKBV/1	THIOPHENE	$H_2O$	3.49E+01	1.08E+00
PRKBV/2	THIOPHENE	$H_2O$	-4.79E-02	1.67E-03
PRKBV/3	THIOPHENE	$H_2O$	-6.31E+03	1.77E+02
PRKBV/1	$CO_2$	$H_2O$	1.17E+00	5.69E-02
PRKBV/2	$CO_2$	$H_2O$	-1.62E-03	8.74E-05
PRKBV/3	$CO_2$	$H_2O$	-2.37E+02	9.27E+00
PRKBV/1	ANISOLE	$CO_2$	1.66E+03	4.60E+00

PRKBV/2	ANISOLE	CO <sub>2</sub>	-2.52E+00	6.97E-03
PRKBV/3	ANISOLE	CO <sub>2</sub>	-2.74E+05	7.64E+02
PRKBV/1	ANISOLE	H <sub>2</sub> O	1.16E+02	2.35E-01
PRKBV/2	ANISOLE	H <sub>2</sub> O	-1.75E-01	3.69E-04
PRKBV/3	ANISOLE	H <sub>2</sub> O	-1.93E+04	3.87E+01
PRKBV/1	CO <sub>2</sub>	H <sub>2</sub> O	4.42E+00	5.71E-02
PRKBV/2	CO <sub>2</sub>	H <sub>2</sub> O	-6.56E-03	8.77E-05
PRKBV/3	CO <sub>2</sub>	H <sub>2</sub> O	-7.71E+02	9.30E+00
PRKBV/1	PYRROLE	CO <sub>2</sub>	2.02E+03	9.89E+00
PRKBV/2	PYRROLE	CO <sub>2</sub>	-3.07E+00	1.52E-02
PRKBV/3	PYRROLE	CO <sub>2</sub>	-3.34E+05	1.62E+03
PRKBV/1	PYRROLE	H <sub>2</sub> O	9.36E+01	1.07E+00
PRKBV/2	PYRROLE	H <sub>2</sub> O	-1.40E-01	1.68E-03
PRKBV/3	PYRROLE	H <sub>2</sub> O	-1.56E+04	1.72E+02
PRKBV/1	CO <sub>2</sub>	H <sub>2</sub> O	-1.29E+02	5.88E-02
PRKBV/2	CO <sub>2</sub>	H <sub>2</sub> O	1.96E-01	1.13E-04
PRKBV/3	CO <sub>2</sub>	H <sub>2</sub> O	2.12E+04	1.22E+01

These binary interactions are calculated using the following equation:

$$k_{ij} = PRKBV / 1 + PRKBV / 2 \cdot T + \frac{PRKBV / 3}{T} \quad \text{Eqn. D.2.2}$$

Once the binary BIP is calculated, it is inputted into the Peng-Robinson equation of state (PR-EOS). The procedure for calculating the (PR-EOS) is given in **Chapter 2.7.1**).

### D.3 Iterations of the ASP-LFERs.

Here are the ASP-LFERs with all the Abraham solvation parameters. Note that the  $\pi_2$  is insignificant in this equation. The regression statistics remain the same as the reported ASP-LFER in the main body of the study (Eqn. 6.8).

$$\log K_{i,c/w} = 1.35(\pm 0.10) - 0.79R_2(\pm 0.08) - 0.017\pi_2(\pm 0.01) - 3.06\alpha_2(\pm 0.07) - 3.99\beta_2(\pm 0.09) + 3.16V_2(\pm 0.13) + 1.90\pi_1(\pm 0.13)$$

Eqn. D.3.1

Here is the ASP-LFER with both the  $R_2$  and the  $\pi_2$ . The  $R^2$  of the regression is 0.897, and the RMSE is 0.347.

$$\log K_{i,c/w} = 1.43(\pm 0.11) - 0.036\pi_2(\pm 0.01) - 3.37\alpha_2(\pm 0.08) - 4.26\beta_2(\pm 0.1) + 2.67V_2(\pm 0.15) + 1.43\pi_1(\pm 0.12)$$

Eqn. D.3.2

#### D.4. Lists of organic compounds partitioning coefficients from this study and the literature.

**Table D.4.1.** Lists of Monopolar Substituted Benzenes

Organic Compound	log VP <sub>25</sub> °C (Pa)	log AS <sub>25</sub> <sup>o</sup> c (M)	log ρCO <sub>2</sub> (kg/m <sup>3</sup> )	R <sub>2</sub>	α <sub>2</sub>	β <sub>2</sub>	V <sub>2</sub>	π <sub>1</sub>	log K	ASP- LFER log K	VP- AS LFER log K	Mono. Ben. LFER log K
Ethylbenzoate (Timko et al. 2004; Schwarzenbach et al. 2003)	1.38	-2.63	2.88	0.689	0	0.46	1.214	-0.09	2.74	2.60	2.20	2.80
Toluene (Timko et al. 2004; Yeo & Akgerman 1990; Schwarzenbach et al. 2003)	3.57	-2.22	2.88	0.601	0	0.14	0.857	-0.09	3.08	2.82	2.80	3.14
	3.57	-2.22	2.37	0.601	0	0.14	0.857	-0.40	2.93	2.24	2.12	2.59
	3.57	-2.22	2.53	0.601	0	0.14	0.857	-0.24	3.21	2.53	2.34	2.76
	3.57	-2.22	2.71	0.601	0	0.14	0.857	-0.18	3.44	2.66	2.58	2.96
Benzene (Schwarzenbach et al. 2003)	4.10	-1.65	1.69	0.61	0	0.14	0.716	-0.86	1.49	0.94	0.97	1.23
	4.10	-1.65	2.12	0.61	0	0.14	0.716	-0.65	1.54	1.32	1.55	1.71
	4.10	-1.65	2.30	0.61	0	0.14	0.716	-0.49	1.69	1.62	1.78	1.90
	4.10	-1.65	2.71	0.61	0	0.14	0.716	-0.18	1.81	2.20	2.33	2.35
	4.10	-1.65	2.84	0.61	0	0.14	0.716	-0.12	2.50	2.32	2.51	2.49
	4.10	-1.65	2.89	0.61	0	0.14	0.716	-0.08	2.26	2.37	2.57	2.54
	4.10	-1.65	2.91	0.61	0	0.14	0.716	-0.07	2.19	2.40	2.60	2.57
	4.10	-1.65	1.66	0.61	0	0.14	0.716	-0.87	1.50	0.92	0.93	1.19
	4.10	-1.65	2.07	0.61	0	0.14	0.716	-0.69	1.64	1.25	1.47	1.64
	4.10	-1.65	2.21	0.61	0	0.14	0.716	-0.59	1.71	1.45	1.66	1.79
	4.10	-1.65	2.35	0.61	0	0.14	0.716	-0.29	1.88	2.00	1.86	1.96
	4.10	-1.65	2.77	0.61	0	0.14	0.716	-0.15	2.11	2.25	2.42	2.42
	4.10	-1.65	1.63	0.61	0	0.14	0.716	-0.87	1.68	0.91	0.89	1.16
	4.10	-1.65	2.02	0.61	0	0.14	0.716	-0.72	1.66	1.20	1.41	1.59
	4.10	-1.65	2.15	0.61	0	0.14	0.716	-0.63	1.68	1.36	1.58	1.73
	4.10	-1.65	2.27	0.61	0	0.14	0.716	-0.52	1.83	1.56	1.74	1.86
4.10	-1.65	2.38	0.61	0	0.14	0.716	-0.40	1.90	1.80	1.89	1.98	
4.10	-1.65	2.74	0.61	0	0.14	0.716	-0.17	2.22	2.22	2.37	2.38	

	4.10	-1.65	2.78	0.61	0	0.14	0.716	-0.15	2.40	2.26	2.42	2.42
2-Methoxyacetophenone (Timko et al. 2004; Substance Identifier n.d.)	0.59*	-1.96*	2.88	N/A	N/A	N/A	N/A	N/A	1.67	N/A	1.31	1.48
3-Methoxyacetophenone (Timko et al. 2004; Substance Identifier n.d.)	0.71*	-2.00*	2.88	N/A	N/A	N/A	N/A	N/A	1.92	N/A	1.39	1.59
Methylbenzoate (Timko et al. 2004; Schwarzenbach et al. 2003)	1.72	-1.81	2.88	0.733	0	0.48	1.073	-0.09	2.31	2.04	1.67	1.74
Propiophenone (Timko et al. 2004; Schwarzenbach et al. 2003)	1.24	-2.09	2.88	0.804	0	0.51	1.155	-0.09	2.08	2.12	1.69	1.95
Propylbenzoate (Timko et al. 2004; Schwarzenbach et al. 2003; Jain & Yalkowsky 2001)	0.92	-3.37	2.88	0.675	0	0.46	1.354	-0.09	3.02	3.06	2.62	3.69
Acetophenone (Timko et al. 2004; Schwarzenbach et al. 2003)	1.67	-1.35	2.88	0.818	0	0.49	1.014	-0.09	1.69	1.74	1.26	1.05
Benzaldehyde (Wagner et al. 1999; Schwarzenbach et al. 2003)	2.24	-1.55	2.88	0.82	0	0.39	0.873	-0.09	1.59	1.69	1.67	1.59
	2.24	-1.55	2.46	0.82	0	0.39	0.873	-0.26	0.75	1.37	1.12	1.13
	2.24	-1.55	2.80	0.82	0	0.39	0.873	-0.13	1.48	1.61	1.58	1.51
	2.24	-1.55	2.86	0.82	0	0.39	0.873	-0.10	1.56	1.67	1.65	1.57
	2.24	-1.55	2.90	0.82	0	0.39	0.873	-0.08	1.66	1.72	1.70	1.61
	2.24	-1.55	2.93	0.82	0	0.39	0.873	-0.06	1.71	1.75	1.74	1.64
	2.24	-1.55	2.95	0.82	0	0.39	0.873	-0.04	1.75	1.78	1.77	1.66
	2.24	-1.55	2.96	0.82	0	0.39	0.873	-0.03	1.80	1.80	1.79	1.68
	2.24	-1.55	2.37	0.82	0	0.39	0.873	-0.40	0.51	1.12	1.00	1.03
	2.24	-1.55	2.65	0.82	0	0.39	0.873	-0.20	1.13	1.48	1.37	1.34
	2.24	-1.55	2.79	0.82	0	0.39	0.873	-0.14	1.38	1.60	1.56	1.49
	2.24	-1.55	2.85	0.82	0	0.39	0.873	-0.11	1.52	1.66	1.64	1.56
	2.24	-1.55	2.90	0.82	0	0.39	0.873	-0.08	1.60	1.72	1.71	1.61
	2.24	-1.55	2.92	0.82	0	0.39	0.873	-0.06	1.64	1.75	1.74	1.64
	2.24	-1.55	2.94	0.82	0	0.39	0.873	-0.05	1.67	1.77	1.76	1.66
	2.24	-1.55	2.30	0.82	0	0.39	0.873	-0.49	0.40	0.96	0.90	0.95
	2.24	-1.55	2.46	0.82	0	0.39	0.873	-0.26	0.72	1.37	1.12	1.13
	2.24	-1.55	2.65	0.82	0	0.39	0.873	-0.20	1.15	1.48	1.38	1.34
	2.24	-1.55	2.78	0.82	0	0.39	0.873	-0.14	1.41	1.59	1.55	1.49
	2.24	-1.55	2.86	0.82	0	0.39	0.873	-0.10	1.53	1.67	1.65	1.57
	2.24	-1.55	2.89	0.82	0	0.39	0.873	-0.08	1.61	1.71	1.70	1.61
	2.24	-1.55	2.92	0.82	0	0.39	0.873	-0.06	1.65	1.74	1.73	1.63
	2.24	-1.55	2.55	0.82	0	0.39	0.873	-0.24	0.88	1.42	1.24	1.23
2.24	-1.55	2.80	0.82	0	0.39	0.873	-0.14	1.44	1.60	1.57	1.50	
2.24	-1.55	2.89	0.82	0	0.39	0.873	-0.08	1.64	1.71	1.70	1.61	
2.24	-1.55	2.93	0.82	0	0.39	0.873	-0.06	1.67	1.76	1.74	1.64	
2.24	-1.55	2.95	0.82	0	0.39	0.873	-0.04	1.74	1.78	1.77	1.66	

	2.24	-1.55	2.96	0.82	0	0.39	0.873	-0.03	1.79	1.80	1.79	1.68
	2.24	-1.55	2.65	0.82	0	0.39	0.873	-0.20	1.25	1.48	1.37	1.34
	2.24	-1.55	2.85	0.82	0	0.39	0.873	-0.11	1.52	1.66	1.64	1.56
	2.24	-1.55	2.89	0.82	0	0.39	0.873	-0.08	1.61	1.71	1.70	1.60
	2.24	-1.55	2.92	0.82	0	0.39	0.873	-0.06	1.70	1.75	1.74	1.64
	2.24	-1.55	2.94	0.82	0	0.39	0.873	-0.05	1.67	1.77	1.76	1.66
	2.24	-1.55	2.53	0.82	0	0.39	0.873	-0.25	0.99	1.41	1.21	1.20
	2.24	-1.55	2.80	0.82	0	0.39	0.873	-0.14	1.40	1.60	1.57	1.50
	2.24	-1.55	2.87	0.82	0	0.39	0.873	-0.10	1.55	1.68	1.66	1.57
	2.24	-1.55	2.90	0.82	0	0.39	0.873	-0.08	1.61	1.71	1.70	1.61
Anisole (Schwarzenbach et al. 2003)	2.31	-1.80	2.39	0.71	0	0.29	0.916	-0.37	1.09	1.79	1.26	1.45
	2.31	-1.80	2.73	0.71	0	0.29	0.916	-0.17	1.03	2.16	1.71	1.82
	2.31	-1.80	2.83	0.71	0	0.29	0.916	-0.12	1.86	2.26	1.85	1.93
	2.31	-1.80	2.29	0.71	0	0.29	0.916	-0.50	0.943	1.55	1.12	1.34
	2.31	-1.80	2.49	0.71	0	0.29	0.916	-0.23	1.19	2.06	1.39	1.55
	2.31	-1.80	2.64	0.71	0	0.29	0.916	-0.21	1.55	2.09	1.59	1.72

**Table D.4.2. Lists of Polar Substituted Benzenes**

Organic Compound	log VP 25 °C (Pa)	log AS <sub>25°C</sub> (M)	log ρCO <sub>2</sub> (kg/m <sup>3</sup> )	R <sub>2</sub>	α <sub>2</sub>	β <sub>2</sub>	V <sub>2</sub>	π <sub>1</sub>	log K	ASP-LFER log K	VP-AS LFER log K	Polar Subs. Ben. LFER log K
Benzoic Acid (Brudi et al. 1996; Schwarzenbach et al. 2003)	-0.96	-1.33	2.43	0.73	0.59	0.4	0.932	-0.32	-0.21	-0.30	-0.49	-0.75
	-0.96	-1.33	2.80	0.73	0.59	0.4	0.932	-0.14	-0.05	0.04	0.01	-0.21
	-0.96	-1.33	2.86	0.73	0.59	0.4	0.932	-0.10	0.11	0.11	0.10	-0.12
	-0.96	-1.33	2.89	0.73	0.59	0.4	0.932	-0.08	0.15	0.14	0.14	-0.08
	-0.96	-1.33	2.92	0.73	0.59	0.4	0.932	-0.06	0.23	0.18	0.18	-0.03
	-0.96	-1.33	2.94	0.73	0.59	0.4	0.932	-0.04	0.30	0.21	0.21	0.00
	-0.96	-1.33	2.96	0.73	0.59	0.4	0.932	-0.03	0.32	0.23	0.22	0.02
	-0.96	-1.33	2.63	0.73	0.59	0.4	0.932	-0.21	-0.27	-0.10	-0.22	-0.46
	-0.96	-1.33	2.78	0.73	0.59	0.4	0.932	-0.15	-0.08	0.02	-0.01	-0.24
	-0.96	-1.33	2.85	0.73	0.59	0.4	0.932	-0.11	0.03	0.09	0.07	-0.14
	-0.96	-1.33	2.90	0.73	0.59	0.4	0.932	-0.08	0.17	0.15	0.14	-0.07
	-0.96	-1.33	2.92	0.73	0.59	0.4	0.932	-0.06	0.24	0.18	0.17	-0.03
	-0.96	-1.33	2.94	0.73	0.59	0.4	0.932	-0.05	0.23	0.20	0.20	-0.01
	-0.96	-1.33	2.48	0.73	0.59	0.4	0.932	-0.23	-0.40	-0.14	-0.41	-0.68
	-0.96	-1.33	2.66	0.73	0.59	0.4	0.932	-0.20	-0.30	-0.08	-0.17	-0.41
	-0.96	-1.33	2.79	0.73	0.59	0.4	0.932	-0.14	-0.05	0.04	0.00	-0.22
	-0.96	-1.33	2.86	0.73	0.59	0.4	0.932	-0.10	0.09	0.11	0.09	-0.12
-0.96	-1.33	2.90	0.73	0.59	0.4	0.932	-0.08	0.16	0.15	0.14	-0.07	
-0.96	-1.33	2.92	0.73	0.59	0.4	0.932	-0.06	0.20	0.17	0.17	-0.04	
3-Methylphenol (Ghonasgi et al. 1991; Schwarzenbach et	1.30	-0.67	2.78	0.822	0.57	0.34	0.9169	-0.15	-0.22	0.20	0.41	0.45
	1.30	-0.67	2.84	0.822	0.57	0.34	0.9169	-0.12	0.15	0.25	0.49	0.53
	1.30	-0.67	2.86	0.822	0.57	0.34	0.9169	-0.10	0.34	0.29	0.52	0.57

al. 2003)	1.30	-0.67	2.88	0.822	0.57	0.34	0.9169	-0.09	0.43	0.31	0.55	0.59
	1.30	-0.67	2.89	0.822	0.57	0.34	0.9169	-0.08	0.48	0.32	0.56	0.61
	1.30	-0.67	2.90	0.822	0.57	0.34	0.9169	-0.07	0.59	0.33	0.58	0.63
	1.30	-0.67	2.55	0.822	0.57	0.34	0.9169	-0.24	0.00	0.03	0.10	0.11
	1.30	-0.67	2.70	0.822	0.57	0.34	0.9169	-0.18	0.05	0.13	0.31	0.34
	1.30	-0.67	2.79	0.822	0.57	0.34	0.9169	-0.14	0.25	0.20	0.42	0.45
	1.30	-0.67	2.82	0.822	0.57	0.34	0.9169	-0.12	0.49	0.24	0.47	0.51
	1.30	-0.67	2.85	0.822	0.57	0.34	0.9169	-0.11	0.70	0.27	0.50	0.55
	1.30	-0.67	2.87	0.822	0.57	0.34	0.9169	-0.10	0.78	0.29	0.52	0.57
Salicylic acid (Karásek et al. 2002; Schwarzenbach et al. 2003)	-1.70	-1.47	2.89	0.89	0.72	0.41	0.9904	-0.08	-0.62	-0.24	-0.07	-0.40
	-1.70	-1.47	2.92	0.89	0.72	0.41	0.9904	-0.06	-0.49	-0.19	-0.02	-0.35
	-1.70	-1.47	2.94	0.89	0.72	0.41	0.9904	-0.04	-0.40	-0.17	0.00	-0.32
	-1.70	-1.47	2.96	0.89	0.72	0.41	0.9904	-0.03	-0.39	-0.15	0.02	-0.30
	-1.70	-1.47	2.85	0.89	0.72	0.41	0.9904	-0.11	-0.77	-0.29	-0.13	-0.47
	-1.70	-1.47	2.89	0.89	0.72	0.41	0.9904	-0.08	-0.57	-0.23	-0.06	-0.39
	-1.70	-1.47	2.92	0.89	0.72	0.41	0.9904	-0.06	-0.42	-0.20	-0.03	-0.36
	-1.70	-1.47	2.94	0.89	0.72	0.41	0.9904	-0.05	-0.41	-0.17	0.00	-0.33
	-1.70	-1.47	2.78	0.89	0.72	0.41	0.9904	-0.15	-0.92	-0.36	-0.21	-0.56
	-1.70	-1.47	2.86	0.89	0.72	0.41	0.9904	-0.10	-0.68	-0.27	-0.11	-0.45
	-1.70	-1.47	2.90	0.89	0.72	0.41	0.9904	-0.08	-0.48	-0.23	-0.06	-0.39
	-1.70	-1.47	2.92	0.89	0.72	0.41	0.9904	-0.06	-0.42	-0.20	-0.03	-0.36
	-1.70	-1.47	2.71	0.89	0.72	0.41	0.9904	-0.18	-1.10	-0.42	-0.32	-0.67
	-1.70	-1.47	2.82	0.89	0.72	0.41	0.9904	-0.13	-0.77	-0.32	-0.16	-0.51
	-1.70	-1.47	2.87	0.89	0.72	0.41	0.9904	-0.10	-0.52	-0.27	-0.10	-0.43
	-1.70	-1.47	2.90	0.89	0.72	0.41	0.9904	-0.08	-0.43	-0.23	-0.06	-0.39
	-1.70	-1.47	2.63	0.89	0.72	0.41	0.9904	-0.21	-1.40	-0.48	-0.42	-0.78
	-1.70	-1.47	2.77	0.89	0.72	0.41	0.9904	-0.15	-0.85	-0.36	-0.22	-0.57
	-1.70	-1.47	2.84	0.89	0.72	0.41	0.9904	-0.12	-0.59	-0.30	-0.14	-0.48
	-1.70	-1.47	2.87	0.89	0.72	0.41	0.9904	-0.09	-0.46	-0.26	-0.09	-0.43
-1.70	-1.47	2.73	0.89	0.72	0.41	0.9904	-0.17	-1.00	-0.41	-0.29	-0.64	
-1.70	-1.47	2.80	0.89	0.72	0.41	0.9904	-0.13	-0.68	-0.33	-0.18	-0.53	
-1.70	-1.47	2.85	0.89	0.72	0.41	0.9904	-0.11	-0.51	-0.29	-0.13	-0.46	
Phenol (Ghonasgi et al. 1991; Brudi et al. 1996; Karásek et al. 2002; Schwarzenbach et al. 2003)	1.79	-0.01	2.78	0.805	0.6	0.31	0.775	-0.15	-0.34	-0.21	0.07	-0.07
	1.79	-0.01	2.84	0.805	0.6	0.31	0.775	-0.12	0.05	-0.15	0.14	0.00
	1.79	-0.01	2.86	0.805	0.6	0.31	0.775	-0.10	0.10	-0.12	0.18	0.04
	1.79	-0.01	2.90	0.805	0.6	0.31	0.775	-0.08	0.19	-0.08	0.23	0.09
	1.79	-0.01	2.91	0.805	0.6	0.31	0.775	-0.07	0.24	-0.07	0.24	0.11
	1.79	-0.01	2.55	0.805	0.6	0.31	0.775	-0.24	-0.47	-0.38	-0.24	-0.42
	1.79	-0.01	2.70	0.805	0.6	0.31	0.775	-0.18	-0.44	-0.28	-0.03	-0.19
	1.79	-0.01	2.79	0.805	0.6	0.31	0.775	-0.14	-0.11	-0.21	0.08	-0.07
	1.79	-0.01	2.85	0.805	0.6	0.31	0.775	-0.11	0.12	-0.14	0.17	0.03
	1.79	-0.01	2.87	0.805	0.6	0.31	0.775	-0.09	0.22	-0.11	0.19	0.06
	1.79	-0.01	2.46	0.805	0.6	0.31	0.775	-0.26	-0.25	-0.42	-0.35	-0.54

	1.79	-0.01	2.82	0.805	0.6	0.31	0.775	-0.13	-0.06	-0.17	0.12	-0.02
	1.79	-0.01	2.90	0.805	0.6	0.31	0.775	-0.08	0.00	-0.08	0.23	0.10
	1.79	-0.01	2.93	0.805	0.6	0.31	0.775	-0.06	0.01	-0.05	0.26	0.14
	1.79	-0.01	2.95	0.805	0.6	0.31	0.775	-0.04	0.02	-0.02	0.29	0.17
	1.79	-0.01	2.37	0.805	0.6	0.31	0.775	-0.40	-0.66	-0.67	-0.47	-0.67
	1.79	-0.01	2.64	0.805	0.6	0.31	0.775	-0.21	-0.37	-0.32	-0.12	-0.28
	1.79	-0.01	2.85	0.805	0.6	0.31	0.775	-0.11	-0.06	-0.14	0.16	0.02
	1.79	-0.01	2.90	0.805	0.6	0.31	0.775	-0.08	0.03	-0.08	0.22	0.09
	1.79	-0.01	2.92	0.805	0.6	0.31	0.775	-0.06	0.08	-0.05	0.26	0.13
	1.79	-0.01	2.94	0.805	0.6	0.31	0.775	-0.05	0.11	-0.03	0.28	0.16
	1.79	-0.01	2.28	0.805	0.6	0.31	0.775	-0.51	-0.51	-0.88	-0.60	-0.80
	1.79	-0.01	2.51	0.805	0.6	0.31	0.775	-0.18	-0.66	-0.28	-0.29	-0.47
	1.79	-0.01	2.79	0.805	0.6	0.31	0.775	-0.14	-0.13	-0.20	0.08	-0.07
	1.79	-0.01	2.86	0.805	0.6	0.31	0.775	-0.10	0.01	-0.13	0.18	0.04
	1.79	-0.01	2.90	0.805	0.6	0.31	0.775	-0.08	0.10	-0.08	0.22	0.09
	1.79	-0.01	2.92	0.805	0.6	0.31	0.775	-0.06	0.14	-0.05	0.26	0.13
	1.79	-0.01	2.89	0.805	0.6	0.31	0.775	-0.08	0.04	-0.09	0.22	0.09
	1.79	-0.01	2.92	0.805	0.6	0.31	0.775	-0.06	0.12	-0.05	0.26	0.13
	1.79	-0.01	2.94	0.805	0.6	0.31	0.775	-0.04	0.13	-0.02	0.29	0.16
	1.79	-0.01	2.96	0.805	0.6	0.31	0.775	-0.03	0.13	0.00	0.31	0.18
	1.79	-0.01	2.85	0.805	0.6	0.31	0.775	-0.11	-0.04	-0.14	0.16	0.02
	1.79	-0.01	2.89	0.805	0.6	0.31	0.775	-0.08	0.05	-0.09	0.22	0.09
	1.79	-0.01	2.92	0.805	0.6	0.31	0.775	-0.06	0.13	-0.05	0.26	0.13
	1.79	-0.01	2.94	0.805	0.6	0.31	0.775	-0.05	0.15	-0.03	0.28	0.16
	1.79	-0.01	2.78	0.805	0.6	0.31	0.775	-0.15	-0.07	-0.21	0.07	-0.07
	1.79	-0.01	2.86	0.805	0.6	0.31	0.775	-0.10	0.10	-0.13	0.18	0.04
	1.79	-0.01	2.90	0.805	0.6	0.31	0.775	-0.08	0.20	-0.08	0.22	0.09
	1.79	-0.01	2.92	0.805	0.6	0.31	0.775	-0.06	0.24	-0.05	0.26	0.13
	1.79	-0.01	2.71	0.805	0.6	0.31	0.775	-0.18	-0.12	-0.28	-0.03	-0.19
	1.79	-0.01	2.82	0.805	0.6	0.31	0.775	-0.13	0.10	-0.17	0.12	-0.02
	1.79	-0.01	2.87	0.805	0.6	0.31	0.775	-0.10	0.18	-0.12	0.19	0.05
	1.79	-0.01	2.90	0.805	0.6	0.31	0.775	-0.08	0.22	-0.08	0.23	0.09
	1.79	-0.01	2.63	0.805	0.6	0.31	0.775	-0.21	-0.20	-0.33	-0.13	-0.29
	1.79	-0.01	2.77	0.805	0.6	0.31	0.775	-0.15	0.03	-0.22	0.06	-0.09
	1.79	-0.01	2.84	0.805	0.6	0.31	0.775	-0.12	0.16	-0.15	0.15	0.01
	1.79	-0.01	2.87	0.805	0.6	0.31	0.775	-0.09	0.20	-0.11	0.19	0.06
	1.79	-0.01	2.57	0.805	0.6	0.31	0.775	-0.23	-0.28	-0.37	-0.21	-0.38
	1.79	-0.01	2.73	0.805	0.6	0.31	0.775	-0.17	0.00	-0.26	0.00	-0.15
	1.79	-0.01	2.80	0.805	0.6	0.31	0.775	-0.13	0.14	-0.19	0.10	-0.04
	1.79	-0.01	2.85	0.805	0.6	0.31	0.775	-0.11	0.21	-0.14	0.16	0.02
Benzyl Alcohol (Brudi et al. 1996; Substance Identifier n.d.;	1.32*	-0.45	2.43	0.595	0.16	0.12	0.88	-0.15	-0.39	2.39	-0.23	-0.33
	1.32*	-0.45	2.81	0.803	0.33	0.56	0.916	-0.13	0.04	0.08	0.27	0.22
	1.32*	-0.45	2.86	0.803	0.33	0.56	0.916	-0.10	0.14	0.15	0.35	0.30

Valvani et al. 1981)	1.32*	-0.45	2.89	0.803	0.33	0.56	0.916	-0.08	0.19	0.18	0.38	0.34
	1.32*	-0.45	2.92	0.803	0.33	0.56	0.916	-0.06	0.27	0.22	0.43	0.39
	1.32*	-0.45	2.94	0.803	0.33	0.56	0.916	-0.04	0.31	0.25	0.46	0.42
	1.32*	-0.45	2.96	0.803	0.33	0.56	0.916	-0.03	0.36	0.27	0.48	0.44
	1.32*	-0.45	2.32	0.803	0.33	0.56	0.916	-0.47	-0.55	-0.53	-0.38	-0.49
	1.32*	-0.45	2.60	0.803	0.33	0.56	0.916	-0.22	-0.33	-0.08	0.00	-0.08
	1.32*	-0.45	2.77	0.803	0.33	0.56	0.916	-0.15	0.02	0.05	0.23	0.17
	1.32*	-0.45	2.85	0.803	0.33	0.56	0.916	-0.11	0.16	0.13	0.33	0.28
	1.32*	-0.45	2.89	0.803	0.33	0.56	0.916	-0.08	0.29	0.18	0.39	0.35
	1.32*	-0.45	2.92	0.803	0.33	0.56	0.916	-0.06	0.34	0.22	0.43	0.39
	1.32*	-0.45	2.94	0.803	0.33	0.56	0.916	-0.05	0.37	0.24	0.45	0.41
	1.32*	-0.45	2.27	0.803	0.33	0.56	0.916	-0.53	-0.51	-0.64	-0.45	-0.57
	1.32*	-0.45	2.45	0.803	0.33	0.56	0.916	-0.28	-0.38	-0.19	-0.20	-0.30
	1.32*	-0.45	2.65	0.803	0.33	0.56	0.916	-0.20	-0.03	-0.04	0.07	0.00
	1.32*	-0.45	2.78	0.803	0.33	0.56	0.916	-0.14	0.18	0.06	0.24	0.19
	1.32*	-0.45	2.86	0.803	0.33	0.56	0.916	-0.10	0.32	0.14	0.35	0.30
	1.32*	-0.45	2.90	0.803	0.33	0.56	0.916	-0.08	0.38	0.19	0.39	0.35
	1.32*	-0.45	2.92	0.803	0.33	0.56	0.916	-0.06	0.43	0.22	0.42	0.38
Vanillin (Brudi et al. 1996; Substance Identifier n.d.; Noubigh et al. 2007)	-0.59*	-1.19	2.80	1.04	0.32	0.67	1.131	-0.14	-0.17	0.16	0.05	-0.14
	-0.59*	-1.19	2.86	1.04	0.32	0.67	1.131	-0.10	0.02	0.23	0.14	-0.05
	-0.59*	-1.19	2.89	1.04	0.32	0.67	1.131	-0.08	0.15	0.26	0.18	-0.01
	-0.59*	-1.19	2.93	1.04	0.32	0.67	1.131	-0.06	0.29	0.31	0.22	0.04
	-0.59*	-1.19	2.94	1.04	0.32	0.67	1.131	-0.04	0.38	0.33	0.25	0.07
	-0.59*	-1.19	2.96	1.04	0.32	0.67	1.131	-0.03	0.42	0.35	0.27	0.09
	-0.59*	-1.19	2.41	1.04	0.32	0.67	1.131	-0.35	-0.70	-0.23	-0.47	-0.71
	-0.59*	-1.19	2.63	1.04	0.32	0.67	1.131	-0.21	-0.54	0.02	-0.18	-0.39
	-0.59*	-1.19	2.78	1.04	0.32	0.67	1.131	-0.15	-0.23	0.14	0.02	-0.18
	-0.59*	-1.19	2.85	1.04	0.32	0.67	1.131	-0.11	0.01	0.21	0.12	-0.07
	-0.59*	-1.19	2.90	1.04	0.32	0.67	1.131	-0.08	0.20	0.27	0.18	0.00
	-0.59*	-1.19	2.92	1.04	0.32	0.67	1.131	-0.06	0.30	0.30	0.22	0.04
	-0.59*	-1.19	2.94	1.04	0.32	0.67	1.131	-0.05	0.38	0.33	0.24	0.06
	-0.59*	-1.19	2.24	1.04	0.32	0.67	1.131	-0.55	-0.77	-0.61	-0.70	-0.96
	-0.59*	-1.19	2.44	1.04	0.32	0.67	1.131	-0.31	-0.47	-0.16	-0.43	-0.67
	-0.59*	-1.19	2.65	1.04	0.32	0.67	1.131	-0.21	-0.43	0.03	-0.15	-0.37
	-0.59*	-1.19	2.79	1.04	0.32	0.67	1.131	-0.14	-0.12	0.15	0.04	-0.16
	-0.59*	-1.19	2.86	1.04	0.32	0.67	1.131	-0.10	0.13	0.23	0.14	-0.05
-0.59*	-1.19	2.90	1.04	0.32	0.67	1.131	-0.08	0.26	0.27	0.18	0.00	
-0.59*	-1.19	2.92	1.04	0.32	0.67	1.131	-0.06	0.34	0.30	0.21	0.03	

**Table D.4.3. Lists of Chlorinated Phenols**

Organic Compound	log VP <sub>25</sub> °C (Pa)	log AS <sub>25</sub> °C (M)	log ρCO <sub>2</sub> (kg/m <sup>3</sup> )	R <sub>2</sub>	α <sub>2</sub>	β <sub>2</sub>	V <sub>2</sub>	π <sub>1</sub>	log K	ASP- LFER log K	VP-AS LFER log K	Chlorinated Phenols LFER log K
2,4,6-	0.37	-2.37	2.86	1.01	0.82	0.08	1.142	-0.10	2.16	1.123	1.529	1.752

Trichlorophenol (Karásek et al. 2002; Schwarzenbach et al. 2003)	0.37	-2.37	2.82	1.01	0.82	0.08	1.142	-0.13	1.83	1.078	1.474	1.589
	0.37	-2.37	2.77	1.01	0.82	0.08	1.142	-0.15	1.66	1.034	1.414	1.410
2,4-Dichlorophenol (Karásek et al. 2002; Schwarzenbach et al. 2003)	1.20	-1.57	2.86	0.96	0.53	0.19	1.02	-0.10	1.83	1.216	1.222	1.495
	1.20	-1.57	2.82	0.96	0.53	0.19	1.02	-0.13	1.36	1.171	1.167	1.332
	1.20	-1.57	2.77	0.96	0.53	0.19	1.02	-0.15	1.23	1.127	1.107	1.153
2-Chlorophenol (Karásek et al. 2002; Schwarzenbach et al. 2003)	2.50	-0.65	2.86	0.853	0.32	0.31	0.8975	-0.10	1.11	1.072	1.017	1.466
	2.50	-0.65	2.82	0.853	0.32	0.31	0.8975	-0.13	1.00	1.027	0.963	1.303
	2.50	-0.65	2.77	0.853	0.32	0.31	0.8975	-0.15	0.92	0.983	0.902	1.123
4-Chlorophenol (Ghonasgi et al. 1991; Schwarzenbach et al. 2003)	1.27	-0.68	2.78	0.915	0.67	0.21	0.8975	-0.15	0.29	0.278	0.409	0.243
	1.27	-0.68	2.84	0.915	0.67	0.21	0.8975	-0.12	0.48	0.332	0.481	0.455
	1.27	-0.68	2.86	0.915	0.67	0.21	0.8975	-0.10	0.54	0.363	0.518	0.565
	1.27	-0.68	2.88	0.915	0.67	0.21	0.8975	-0.09	0.70	0.384	0.541	0.636
	1.27	-0.68	2.89	0.915	0.67	0.21	0.8975	-0.08	0.72	0.400	0.559	0.689
	1.27	-0.68	2.90	0.915	0.67	0.21	0.8975	-0.07	0.73	0.412	0.572	0.728
	1.27	-0.68	2.55	0.915	0.67	0.21	0.8975	-0.24	0.36	0.104	0.093	-0.698
	1.27	-0.68	2.70	0.915	0.67	0.21	0.8975	-0.18	0.17	0.209	0.304	-0.072
	1.27	-0.68	2.79	0.915	0.67	0.21	0.8975	-0.14	0.12	0.281	0.413	0.253
	1.27	-0.68	2.82	0.915	0.67	0.21	0.8975	-0.12	0.30	0.320	0.465	0.409
	1.27	-0.68	2.85	0.915	0.67	0.21	0.8975	-0.11	0.38	0.346	0.498	0.506
Pentachlorophenol (Curren & Burk 1998; Schwarzenbach et al. 2003)	1.27	-0.68	2.87	0.915	0.67	0.21	0.8975	-0.10	0.44	0.365	0.520	0.571
	-2.04	-4.15	2.81	1.22	0.96	0.01	1.3871	-0.13	1.08	1.527	1.898	1.674
	-2.04	-4.15	2.88	1.22	0.96	0.01	1.3871	-0.09	1.95	1.602	1.990	1.949
	-2.04	-4.15	2.91	1.22	0.96	0.01	1.3871	-0.07	2.23	1.640	2.031	2.071
	-2.04	-4.15	2.92	1.22	0.96	0.01	1.3871	-0.06	2.18	1.664	2.056	2.146
	-2.04	-4.15	2.94	1.22	0.96	0.01	1.3871	-0.05	2.11	1.683	2.075	2.203
	-2.04	-4.15	2.95	1.22	0.96	0.01	1.3871	-0.04	2.36	1.699	2.091	2.250
	-2.04	-4.15	2.76	1.22	0.96	0.01	1.3871	-0.16	1.23	1.480	1.837	1.495
	-2.04	-4.15	2.83	1.22	0.96	0.01	1.3871	-0.12	1.36	1.555	1.935	1.784
	-2.04	-4.15	2.84	1.22	0.96	0.01	1.3871	-0.12	1.69	1.558	1.938	1.795
-2.04	-4.15	2.87	1.22	0.96	0.01	1.3871	-0.10	1.85	1.597	1.984	1.931	
-2.04	-4.15	2.89	1.22	0.96	0.01	1.3871	-0.08	1.98	1.624	2.014	2.022	

**Table D.4.4.** Lists of Nitrogen Containing Compounds

Organic Compound	log VP <sub>25</sub> °C (Pa)	log AS <sub>25</sub> °C (M)	log ρCO <sub>2</sub> (kg/m <sup>3</sup> )	R <sub>2</sub>	α <sub>2</sub>	β <sub>2</sub>	V <sub>2</sub>	π <sub>1</sub>	log K	ASP- LFER log K	VP-AS LFER log K	Nitrogen Containing LFER log K
Aniline (Wagner et al. 1999; Schwarzenbach et al. 2003)	1.92	-0.44	2.48	0.955	0.26	0.41	0.816	-0.23	-0.44	0.28	0.09	-0.25
	1.92	-0.44	2.81	0.955	0.26	0.41	0.816	-0.13	0.05	0.43	0.52	0.22
	1.92	-0.44	2.86	0.955	0.26	0.41	0.816	-0.10	0.26	0.48	0.59	0.30
	1.92	-0.44	2.89	0.955	0.26	0.41	0.816	-0.08	0.30	0.52	0.64	0.35
	1.92	-0.44	2.93	0.955	0.26	0.41	0.816	-0.06	0.35	0.56	0.68	0.39
	1.92	-0.44	2.94	0.955	0.26	0.41	0.816	-0.04	0.38	0.58	0.71	0.42

	1.92	-0.44	2.96	0.955	0.26	0.41	0.816	-0.03	0.38	0.60	0.73	0.45
	1.92	-0.44	2.34	0.955	0.26	0.41	0.816	-0.44	-0.68	-0.09	-0.10	-0.46
	1.92	-0.44	2.63	0.955	0.26	0.41	0.816	-0.21	0.11	0.30	0.28	-0.04
	1.92	-0.44	2.85	0.955	0.26	0.41	0.816	-0.11	0.28	0.47	0.58	0.28
	1.92	-0.44	2.89	0.955	0.26	0.41	0.816	-0.08	0.31	0.52	0.64	0.34
	1.92	-0.44	2.92	0.955	0.26	0.41	0.816	-0.06	0.39	0.55	0.68	0.39
	1.92	-0.44	2.94	0.955	0.26	0.41	0.816	-0.05	0.45	0.58	0.70	0.42
	1.92	-0.44	2.30	0.955	0.26	0.41	0.816	-0.49	-0.64	-0.17	-0.16	-0.52
	1.92	-0.44	2.50	0.955	0.26	0.41	0.816	-0.20	-0.35	0.32	0.11	-0.23
	1.92	-0.44	2.67	0.955	0.26	0.41	0.816	-0.20	0.04	0.32	0.34	0.02
	1.92	-0.44	2.79	0.955	0.26	0.41	0.816	-0.14	0.23	0.41	0.50	0.19
	1.92	-0.44	2.86	0.955	0.26	0.41	0.816	-0.10	0.38	0.49	0.60	0.30
	1.92	-0.44	2.90	0.955	0.26	0.41	0.816	-0.08	0.44	0.53	0.65	0.36
	1.92	-0.44	2.92	0.955	0.26	0.41	0.816	-0.06	0.48	0.55	0.67	0.39
2-Nitrophenol (Karásek et al. 2002; Schwarzenbach et al. 2003)	1.26	-2.03	2.86	1.015	0.05	0.37	0.949	-0.10	1.86	1.59	1.63	1.95
	1.26	-2.03	2.82	1.015	0.05	0.37	0.949	-0.13	1.63	1.55	1.57	1.89
	1.26	-2.03	2.77	1.015	0.05	0.37	0.949	-0.15	1.48	1.51	1.51	1.82
4-Nitrophenol (Karásek et al. 2002; Schwarzenbach et al. 2003)	-2.26	-0.98	2.86	1.07	0.82	0.26	0.949	-0.10	-0.74	-0.24	-0.76	-0.60
	-2.26	-0.98	2.82	1.07	0.82	0.26	0.949	-0.13	-0.77	-0.28	-0.81	-0.66
	-2.26	-0.98	2.77	1.07	0.82	0.26	0.949	-0.15	-0.80	-0.32	-0.87	-0.73
Pyrrole (Dearden 2003; Yaffe et al. 2001)	3.04	-0.15	2.50	0.613	0.41	0.29	0.577	-0.21	-0.08	-0.15	0.35	-0.16
	3.04	-0.15	2.74	0.613	0.41	0.29	0.577	-0.17	0.343	-0.07	0.68	0.19
	3.04	-0.15	2.83	0.613	0.41	0.29	0.577	-0.12	0.351	0.02	0.80	0.32
	3.04	-0.15	2.28	0.613	0.41	0.29	0.577	-0.51	-0.192	-0.70	0.06	-0.48
	3.04	-0.15	2.53	0.613	0.41	0.29	0.577	-0.24	0.003	-0.21	0.39	-0.11
	3.04	-0.15	2.62	0.613	0.41	0.29	0.577	-0.22	0.076	-0.16	0.51	0.02
2-Methyl-2,6- dinitrophenol (Karásek et al. 2002; Substance Identifier n.d.)	-2.00*	-2.57*	2.86	N/A	N/A	N/A	N/A	N/A	1.74	N/A	0.67	1.38
	-2.00*	-2.57*	2.82	N/A	N/A	N/A	N/A	N/A	1.56	N/A	0.62	1.32
	-2.00*	-2.57*	2.77	N/A	N/A	N/A	N/A	N/A	1.32	N/A	0.56	1.26

**Table D.4.5.** Lists of Other Organic Compounds

Organic Compound	log VP <sub>25°C</sub> (Pa)	log AS <sub>25°C</sub> (M)	log ρCO <sub>2</sub> (kg/m <sup>3</sup> )	R <sub>2</sub>	α <sub>2</sub>	β <sub>2</sub>	V <sub>2</sub>	π <sub>1</sub>	log K	ASP- LFER log K	VP-AS LFER log K
Naphthalene (Yeo & Akgerman 1990; Schwarzenbach et al. 2003)	1.05	-3.60	2.40	1.34	0	0.2	1.085	-0.37	2.10	2.18	2.22
	1.05	-3.60	2.53	1.34	0	0.2	1.085	-0.24	2.32	2.41	2.40
	1.05	-3.60	2.70	1.34	0	0.2	1.085	-0.18	2.54	2.52	2.63
Parathion (Yeo & Akgerman 1990; Schwarzenbach et al. 2003)	-3.22	-4.30	2.38	N/A	N/A	N/A	N/A	N/A	1.11	N/A	0.95
	-3.22	-4.30	2.53	N/A	N/A	N/A	N/A	N/A	1.16	N/A	1.15
	-3.22	-4.30	2.77	N/A	N/A	N/A	N/A	N/A	1.26	N/A	1.47
2-Hexanone (Brudi et al. 1996; Schwarzenbach et al. 2003)	3.20	-0.76	2.48	0.136	0	0.51	0.97	-0.23	1.46	1.83	0.91
	3.20	-0.76	2.81	0.136	0	0.51	0.97	-0.13	1.91	2.01	1.35
	3.20	-0.76	2.86	0.136	0	0.51	0.97	-0.10	2.10	2.07	1.42
	3.20	-0.76	2.90	0.136	0	0.51	0.97	-0.08	2.12	2.11	1.46

	3.20	-0.76	2.93	0.136	0	0.51	0.97	-0.06	2.15	2.14	1.50
	3.20	-0.76	2.95	0.136	0	0.51	0.97	-0.04	2.14	2.17	1.52
	3.20	-0.76	2.96	0.136	0	0.51	0.97	-0.03	2.15	2.19	1.54
	3.20	-0.76	2.34	0.136	0	0.51	0.97	-0.44	1.27	1.44	0.71
	3.20	-0.76	2.63	0.136	0	0.51	0.97	-0.21	1.93	1.86	1.10
	3.20	-0.76	2.78	0.136	0	0.51	0.97	-0.15	1.97	1.98	1.30
	3.20	-0.76	2.85	0.136	0	0.51	0.97	-0.11	2.06	2.05	1.40
	3.20	-0.76	2.90	0.136	0	0.51	0.97	-0.08	2.07	2.11	1.46
	3.20	-0.76	2.92	0.136	0	0.51	0.97	-0.06	2.11	2.14	1.49
	3.20	-0.76	2.94	0.136	0	0.51	0.97	-0.05	2.14	2.16	1.52
	3.20	-0.76	2.27	0.136	0	0.51	0.97	-0.53	1.08	1.28	0.61
	3.20	-0.76	2.67	0.136	0	0.51	0.97	-0.20	1.77	1.89	1.15
	3.20	-0.76	2.79	0.136	0	0.51	0.97	-0.14	1.99	1.99	1.32
	3.20	-0.76	2.87	0.136	0	0.51	0.97	-0.10	2.04	2.07	1.42
	3.20	-0.76	2.90	0.136	0	0.51	0.97	-0.08	2.09	2.11	1.46
	3.20	-0.76	2.92	0.136	0	0.51	0.97	-0.06	2.06	2.14	1.49
3-Methyl-4-chlorophenol (Karásek et al. 2002; Wang et al. 2012)	1.24	-2.46	2.86	0.92	0.65	0.22	1.038	-0.10	0.77	0.82	1.97
	1.24	-2.46	2.82	0.92	0.65	0.22	1.038	-0.13	0.68	0.78	1.92
	1.24	-2.46	2.77	0.92	0.65	0.22	1.038	-0.15	0.58	0.73	1.86
Cyclohexanone (Brudi et al. 1996; Schwarzenbach et al. 2003)	2.78	-0.63	2.53	0.403	0	0.56	0.861	-0.24	0.75	1.03	0.68
	2.78	-0.63	2.80	0.403	0	0.56	0.861	-0.14	1.48	1.23	1.03
	2.78	-0.63	2.86	0.403	0	0.56	0.861	-0.10	1.56	1.30	1.12
	2.78	-0.63	2.89	0.403	0	0.56	0.861	-0.08	1.66	1.34	1.16
	2.78	-0.63	2.92	0.403	0	0.56	0.861	-0.06	1.71	1.38	1.21
	2.78	-0.63	2.94	0.403	0	0.56	0.861	-0.04	1.75	1.40	1.23
	2.78	-0.63	2.96	0.403	0	0.56	0.861	-0.03	1.80	1.43	1.25
	2.78	-0.63	2.34	0.403	0	0.56	0.861	-0.44	0.56	0.67	0.43
	2.78	-0.63	2.63	0.403	0	0.56	0.861	-0.21	1.10	1.09	0.81
	2.78	-0.63	2.77	0.403	0	0.56	0.861	-0.15	1.39	1.21	1.00
	2.78	-0.63	2.85	0.403	0	0.56	0.861	-0.11	1.53	1.28	1.10
	2.78	-0.63	2.90	0.403	0	0.56	0.861	-0.08	1.61	1.34	1.17
	2.78	-0.63	2.92	0.403	0	0.56	0.861	-0.06	1.65	1.37	1.20
	2.78	-0.63	2.94	0.403	0	0.56	0.861	-0.05	1.67	1.40	1.23
	2.78	-0.63	2.33	0.403	0	0.56	0.861	-0.46	0.40	0.64	0.41
	2.78	-0.63	2.49	0.403	0	0.56	0.861	-0.22	0.72	1.08	0.63
	2.78	-0.63	2.65	0.403	0	0.56	0.861	-0.20	1.15	1.11	0.85
	2.78	-0.63	2.79	0.403	0	0.56	0.861	-0.14	1.41	1.22	1.03
	2.78	-0.63	2.86	0.403	0	0.56	0.861	-0.10	1.53	1.30	1.12
	2.78	-0.63	2.90	0.403	0	0.56	0.861	-0.08	1.61	1.34	1.17
2.78	-0.63	2.92	0.403	0	0.56	0.861	-0.06	1.65	1.37	1.20	
Caffeine (Brudi et al. 1996; Substance Identifier n.d.; Yalkowsky et al. 1983)	-3.92*	-0.98	2.80	1.5	0	1.35	1.363	-0.14	-1.00	-1.22	-1.55
	-3.92*	-0.98	2.86	1.5	0	1.35	1.363	-0.10	-0.96	-1.16	-1.47
	-3.92*	-0.98	2.89	1.5	0	1.35	1.363	-0.08	-0.89	-1.13	-1.43

	-3.92*	-0.98	2.93	1.5	0	1.35	1.363	-0.06	-0.77	-1.08	-1.38
	-3.92*	-0.98	2.94	1.5	0	1.35	1.363	-0.05	-0.72	-1.06	-1.36
	-3.92*	-0.98	2.96	1.5	0	1.35	1.363	-0.03	-0.66	-1.03	-1.34
	-3.92*	-0.98	2.61	1.5	0	1.35	1.363	-0.22	-0.96	-1.37	-1.80
	-3.92*	-0.98	2.79	1.5	0	1.35	1.363	-0.14	-1.05	-1.24	-1.57
	-3.92*	-0.98	2.85	1.5	0	1.35	1.363	-0.11	-1.05	-1.17	-1.48
	-3.92*	-0.98	2.89	1.5	0	1.35	1.363	-0.08	-0.85	-1.12	-1.42
	-3.92*	-0.98	2.92	1.5	0	1.35	1.363	-0.06	-0.72	-1.08	-1.39
	-3.92*	-0.98	2.94	1.5	0	1.35	1.363	-0.05	-0.66	-1.06	-1.36
	-3.92*	-0.98	2.44	1.5	0	1.35	1.363	-0.31	-1.00	-1.54	-2.04
	-3.92*	-0.98	2.68	1.5	0	1.35	1.363	-0.19	-1.05	-1.33	-1.71
	-3.92*	-0.98	2.77	1.5	0	1.35	1.363	-0.15	-1.10	-1.25	-1.59
	-3.92*	-0.98	2.86	1.5	0	1.35	1.363	-0.10	-0.85	-1.16	-1.47
	-3.92*	-0.98	2.90	1.5	0	1.35	1.363	-0.08	-0.70	-1.12	-1.42
	-3.92*	-0.98	2.92	1.5	0	1.35	1.363	-0.06	-0.66	-1.09	-1.39
Tetrahydrofuran (Timko et al. 2004; Schwarzenbach et al. 2003)	4.33	1.15	2.88	0.289	0	0.48	0.6223	-0.09	0.93	0.97	0.33
Hexane (Timko et al. 2004; Schwarzenbach et al. 2003)	4.30	-3.83	2.88	0	0	0	0.954	-0.09	3.95	4.18	4.45
Bromobenzene (Timko et al. 2004; Mackay et al. 1982; Yalkowsky et al. 1979)	2.74	-2.64	2.88	0.882	0	0.09	0.8914	-0.09	3.04	2.90	2.80
Chlorobenzene (Timko et al. 2004; Schwarzenbach et al. 2003)	3.20	-2.39	2.88	0.718	0	0.07	0.8333	-0.09	3.06	2.93	2.78
Cyclohexane (Timko et al. 2004; Schwarzenbach et al. 2003)	4.10	-3.17	2.88	0.305	0	0	0.8454	-0.09	3.69	3.58	3.82
Cyclohexene (Timko et al. 2004; Schwarzenbach et al. 2003)	4.07	-2.60	2.88	0.395	0	0.1	0.8024	-0.09	3.28	2.97	3.33
Cyclopentene (Timko et al. 2004; Schwarzenbach et al. 2003)	4.70	-2.09	2.88	0.335	0	0.1	0.6615	-0.09	3.15	2.57	3.18
3-Buten-2-one (Timko et al. 2004; Substance Identifier n.d.)	4.04*	-0.24*	2.88	N/A	N/A	N/A	N/A	N/A	0.89	N/A	1.36
Fluorobenzene (Timko et al. 2004; Dearden 2003; Yalkowsky et al. 1979)	4.01	-1.79	2.88	0.477	0	0.1	0.734	-0.09	2.89	2.52	2.64
Thiophen (Dearden 2003; Valvani et al. 1981)	4.02	-1.45	2.45	0.687	0	0.15	0.6411	-0.29	1.67	1.64	1.78
	4.02	-1.45	2.74	0.687	0	0.15	0.6411	-0.16	2.04	1.87	2.18
	4.02	-1.45	2.83	0.687	0	0.15	0.6411	-0.12	2.13	1.96	2.30
	4.02	-1.45	2.32	0.687	0	0.15	0.6411	-0.47	1.54	1.31	1.61
	4.02	-1.45	2.51	0.687	0	0.15	0.6411	-0.25	1.59	1.71	1.87
	4.02	-1.45	2.65	0.687	0	0.15	0.6411	-0.20	1.97	1.80	2.06

\*Estimated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)

### D.5. Ranges of Vapor Pressure, Aqueous Solubility, CO<sub>2</sub> Density, and log K for LFERs

**Table D.5.1.** Range in Parameters for ASP-LFER

Parameter	Range in Values
CO <sub>2</sub> Density Range (log kg/m <sup>3</sup> )	1.63 – 2.96
log K range (mol/mol)	-1.40 – 3.95

**Table D.5.2.** Range in Parameters for VP-AS-LFER

Parameter	Range in Values
Vapor Pressure Range (log Pa)	-3.95 – 4.70
Aqueous Solubility Range (log M)	-4.30 – 1.15
CO <sub>2</sub> Density Range (log kg/m <sup>3</sup> )	1.63 – 2.96
log K range (mol/mol)	-1.40 – 3.95

**Table D.5.3.** Range in Parameters for Monopolar Substituted Benzene-LFER

Parameter	Range in Values
Vapor Pressure Range (log Pa)	0.59 – 4.10
Aqueous Solubility Range (log M)	-3.37 – -1.35
CO <sub>2</sub> Density Range (log kg/m <sup>3</sup> )	1.63 – 2.96
log K range (mol/mol)	0.40 – 3.44

**Table D.5.4.** Range in Parameters for Polar Substituted Benzene-LFER

Parameter	Range in Values
Vapor Pressure Range (log Pa)	-1.70 – 1.79
Aqueous Solubility Range (log M)	-1.47 – -0.01
CO <sub>2</sub> Density Range (log kg/m <sup>3</sup> )	2.24 – 2.96
log K range (mol/mol)	-1.40 – 0.78

**Table D.5.5.** Range in Parameters for Chlorinated Phenols LFER

Parameter	Range in Values
Vapor Pressure Range (log Pa)	-2.04 – 2.50
Aqueous Solubility Range (log M)	-4.15 – -0.65
CO <sub>2</sub> Density Range (log kg/m <sup>3</sup> )	2.55 – 2.95
log K range (mol/mol)	-0.36 – 2.36

**Table D.5.6.** Range in Parameters for Nitrogen Containing-LFER

Parameter	Range in Values
-----------	-----------------

Vapor Pressure Range (log Pa)	-2.26 – 3.04
Aqueous Solubility Range (log M)	-2.57 – -0.15
CO <sub>2</sub> Density Range (log kg/m <sup>3</sup> )	2.28 – 2.96
log K range (mol/mol)	-0.80 – 1.86

## D.6 Table of Root Mean Square Errors

**Table D.6.1.** Root Mean Square Errors

Organic Compound	pp-LFER	PR (no BIPs)	PR-vdW	ASP-LFER	VP-AS-LFER	Group LFER
Thiophene	0.504	0.98	1.04	0.19	0.16	N/A
Pyrrole	0.478	1.51	1.80	0.33	0.37	0.15
Anisole	0.412	3.33	1.46	0.63	0.15	0.27

There is an overall improvement for the organic compounds after the BIPs were regressed; however there was still considerable error with some of the points, which led to an increase in RMSE.

## D.7 References

- Adachi, Y. & Lu, B.C.-Y., 1984. Simplest equation of state for vapor-liquid equilibrium calculation: A modification of the van der waals equation. *AIChE Journal*, 30(6), pp.991–993. Available at: <http://dx.doi.org/10.1002/aic.690300619>.
- Brudi, K., Dahmen, N. & Schmieder, H., 1996. Partition coefficients of organic substances in two-phase mixtures of water and carbon dioxide at pressures of 8 to 30 MPa and temperatures of 313 to 333 K. *The Journal of Supercritical Fluids*, 9(3), pp.146–151. Available at: <http://www.sciencedirect.com/science/article/pii/S089684469690025X>.
- Burant, A., Lowry, G.V. & Karamalidis, A.K., 2013. Partitioning behavior of organic contaminants in carbon storage environments: a critical review. *Environmental science & technology*, 47(1), pp.37–54. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/23211055>.
- Curren, M.S. & Burk, R.C., 1998. Supercritical Fluid Extraction of Acidic, Polar Solutes from Aqueous Matrices: Partitioning Data for Pentachlorophenol between Carbon Dioxide and Water. *Journal of Chemical & Engineering Data*, 43(6), pp.978–982. Available at: <http://pubs.acs.org/doi/abs/10.1021/jc980099d>.
- Dearden, J.C., 2003. Quantitative structure-property relationships for prediction of boiling point, vapor pressure, and melting point. *Environmental Toxicology and Chemistry*, 22(8), pp.1696–1709. Available at: <http://dx.doi.org/10.1897/01-363>.
- Ghonasgi, D. et al., 1991. Supercritical CO<sub>2</sub> extraction of organic contaminants from aqueous streams. *AIChE Journal*, 37(6), pp.944–950. Available at: <http://dx.doi.org/10.1002/aic.690370617>.

- Jain, N. & Yalkowsky, S.H., 2001. Estimation of the aqueous solubility I: Application to organic nonelectrolytes. *Journal of Pharmaceutical Sciences*, 90(2), pp.234–252. Available at: [http://dx.doi.org/10.1002/1520-6017\(200102\)90:2<234::AID-JPS14>3.0.CO;2-V](http://dx.doi.org/10.1002/1520-6017(200102)90:2<234::AID-JPS14>3.0.CO;2-V).
- Karásek, P. et al., 2002. Partition Coefficients of Environmentally Important Phenols in a Supercritical Carbon Dioxide–Water System from Cocurrent Extraction without Analysis of the Compressible Phase. *Analytical Chemistry*, 74(16), pp.4294–4299. Available at: <http://pubs.acs.org/doi/abs/10.1021/ac025599v>.
- Mackay, D. et al., 1982. Vapor-pressure correlations for low-volatility environmental chemicals. *Environmental Science & Technology*, 16(10), pp.645–649. Available at: <http://dx.doi.org/10.1021/es00104a004>.
- Mathias, P.M., Klotz, H.C. & Prausnitz, J.M., 1991. Equation-of-State mixing rules for multicomponent mixtures: the problem of invariance. *Fluid Phase Equilibria*, 67, pp.31–44. Available at: <http://www.sciencedirect.com/science/article/pii/0378381291900459> [Accessed October 24, 2014].
- Noubigh, A. et al., 2007. Effect of salts on the solubility of phenolic compounds: experimental measurements and modelling. *Journal of the Science of Food and Agriculture*, 87(5), pp.783–788. Available at: <http://dx.doi.org/10.1002/jsfa.2762>.
- Panagiotopoulos, A.Z. & Reid, R.C., 1986. New Mixing Rule for Cubic Equations of State for Highly Polar, Asymmetric Systems. In *Equations of State*. pp. 571–582. Available at: <http://pubs.acs.org/doi/abs/10.1021/bk-1986-0300.ch028>.
- Patel, N.C. & Teja, A.S., 1982. A new cubic equation of state for fluids and fluid mixtures. *Chemical Engineering Science*, 37(3), pp.463–473. Available at: <http://www.sciencedirect.com/science/article/pii/0009250982800997>.
- Peng, D.-Y. & Robinson, D.B., 1976. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1), pp.59–64. Available at: <http://pubs.acs.org/doi/abs/10.1021/i160057a011>.
- Redlich, O. & Kwong, J.N.S., 1949. On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chemical Reviews*, 44(1), pp.233–244. Available at: <http://pubs.acs.org/doi/abs/10.1021/cr60137a013>.
- Sandler, S.I., 2006. *Chemical, Biochemical, and Engineering Thermodynamics* 4th ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Schwarzenbach, R.P., Gschwend, P.M. & Imboden, D.M., 2003. *Environmental Organic Chemistry* 2nd ed., Hoboken, NJ: John Wiley & Sons, Inc.
- Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, 27(6), pp.1197–1203. Available at: <http://www.sciencedirect.com/science/article/pii/0009250972800964>.
- Spycher, N., Pruess, K. & Ennis-King, J., 2003. CO<sub>2</sub>-H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. *Geochimica et Cosmochimica Acta*, 67(16), pp.3015–3031. Available at: <http://www.sciencedirect.com/science/article/pii/S0016703703002734> [Accessed December 17, 2014].
- Substance Identifier, S.S., Advanced Chemistry Development (ACD/Labs) Software V11.02. *Columbus, OH*. Available at: <https://scifinder.cas.org>.
- Timko, M.T. et al., 2004. Partition Coefficients of Organic Solutes between Supercritical Carbon Dioxide and Water: Experimental Measurements and Empirical Correlations. *Journal of*

- Chemical & Engineering Data*, 49(4), pp.768–778. Available at: <http://pubs.acs.org/doi/abs/10.1021/je030197l>.
- Valderrama, J.O., 2003. The State of the Cubic Equations of State. *Industrial & Engineering Chemistry Research*, 42(8), pp.1603–1618. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie020447b>.
- Valvani, S.C., Yalkowsky, S.H. & Roseman, T.J., 1981. Solubility and partitioning IV: Aqueous solubility and octanol-water partition coefficients of liquid nonelectrolytes. *Journal of Pharmaceutical Sciences*, 70(5), pp.502–507. Available at: <http://dx.doi.org/10.1002/jps.2600700510>.
- Wagner, K.-D. et al., 1999. Partition coefficients of aromatic organic substances in two-phase mixtures of water and carbon dioxide at pressures from 8 to 30 MPa and at temperatures of 313 to 333 K. Part II. *The Journal of Supercritical Fluids*, 15(2), pp.109–116. Available at: <http://www.sciencedirect.com/science/article/pii/S0896844699000042> [Accessed January 15, 2015].
- Wang, C. et al., 2012. Simulation and prediction of phenolic compounds fate in Songhua River, China. *The Science of the total environment*, 431, pp.366–74. Available at: <http://www.sciencedirect.com/science/article/pii/S0048969712007292> [Accessed January 30, 2015].
- Wang, Z., Small, M.J. & Karamalidis, A.K., 2013. Multimodel Predictive System for Carbon Dioxide Solubility in Saline Formation Waters. *Environmental Science & Technology*, 47(3), pp.1407–1415. Available at: <http://dx.doi.org/10.1021/es303842j>.
- Wong, D.S.H. & Sandler, S.I., 1992. A theoretically correct mixing rule for cubic equations of state. *AIChE Journal*, 38(5), pp.671–680. Available at: <http://dx.doi.org/10.1002/aic.690380505>.
- Yaffe, D. et al., 2001. A Fuzzy ARTMAP Based on Quantitative Structure–Property Relationships (QSPRs) for Predicting Aqueous Solubility of Organic Compounds. *Journal of Chemical Information and Computer Sciences*, 41(5), pp.1177–1207. Available at: <http://dx.doi.org/10.1021/ci010323u>.
- Yalkowsky, S.H., Orr, R.J. & Valvani, S.C., 1979. Solubility and Partitioning. 3. The Solubility of Halobenzenes in Water. *Industrial & Engineering Chemistry Fundamentals*, 18(4), pp.351–353. Available at: <http://dx.doi.org/10.1021/i160072a011>.
- Yalkowsky, S.H., Valvani, S.C. & Roseman, T.J., 1983. Solubility and partitioning VI: Octanol solubility and octanol–water partition coefficients. *Journal of Pharmaceutical Sciences*, 72(8), pp.866–870. Available at: <http://dx.doi.org/10.1002/jps.2600720808>.
- Yeo, S.-D. & Akgerman, A., 1990. Supercritical extraction of organic mixtures from aqueous solutions. *AIChE Journal*, 36(11), pp.1743–1747. Available at: <http://dx.doi.org/10.1002/aic.690361116>.