

Effects of Molecular Sieving and Electrostatic-Enhancement in the Adsorption of Organic Compounds on the Zeolitic Imidazolate Framework, ZIF-8

Corresponding Author: Richard I. Masel

Additional Authors: Matthew T. Luebbers, Tianjiao Wu, Lingjuan Shen

Theory Employed in IGC Analysis

IGC data was analyzed through well-established calculations to obtain values for the corrected specific retention time of a given analyte at a specific temperature. The inlet pressure (p_i), column temperature (T_c), corresponding measured flow rate (F_m), and the time between injection and elution (t_R) were first measured for methane at elevated temperatures. The corrected dead volume, V_M , was calculated by Equation SI-1 below in which j (defined in Equation SI-2) is the James-Martin “compressibility correction factor”. The outlet pressure, p_o , is assumed to be atmospheric pressure, and the temperature correction term of 294.25K is the calibration temperature of the flow meter.

$$V_M = t_R \times F_M \times \left(\frac{T_c}{294.25K} \right) \times j \quad \text{Equation SI-1}$$

$$j = \frac{3}{2} \times \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \quad \text{Equation SI-2}$$

After determining the dead volume of the column setup, the corrected specific net retention volume, V_N , (Equation SI-3) and the number of theoretical plates, N (Equation SI-4), can be calculated for Gaussian, symmetrical peaks using t_R , the width at the half maximum of the peak (d_i) and the mass of adsorbent in the column (m).

$$V_N = \frac{I}{m} \times \left(F \times \frac{T_C}{294.25K} \times t_R \right) - V_M \quad \text{Equation SI-3}$$

$$N = 5.54 \times \left(\frac{t_R}{t_0} \right)^2 \quad \text{Equation SI-4}$$

The specific retention volume at zero coverage can be converted into the Henry's constant (K_c) by assuming ideal gas behavior. The Henry's constant is the low coverage slope of the adsorption isotherm and is therefore the proportionality constant between the specific amount adsorbed and the gas phase concentration. Conversion of V_N to more familiar units of K_c (mole/kg/Pa) is by Equation SI-5 in which R is the universal gas constant.

$$K_c = \frac{V_N}{RT_c} \quad \text{Equation SI-5}$$

To calculate value for the enthalpy of adsorption, a technique commonly employed in gas adsorption IGC is to exploit the direct proportionality of the net retention volume and the equilibrium (Henry) constants for infinite dilution. This proportionality along with the van't Hoff relationship (Equation SI-6) leads to a straightforward method for calculating the differential enthalpy of adsorption, ΔH , from the slope of a plot of $\ln(V_N)$ versus the inverse absolute temperature.

$$\frac{d \ln K_c}{d \left(\frac{1}{T_c} \right)} = \frac{d \ln V_N}{d \left(\frac{1}{T_c} \right)} = - \frac{\Delta H}{R} \quad \text{Equation SI-6}$$

The standard free energy change of adsorption, ΔG , can be calculated from V_N from Equation SI-7 when adsorption is occurring in the Henry's region. In Equation SI-7, S is the specific surface area of the adsorbent, π_0 is the reference two-dimensional surface pressure and P^0 is the adsorbate vapor pressure in the gaseous standard state. The standard reference state

used is that proposed by de Boer in which P^0 is equal to 101.3 kPa and π_0 is equal to 0.338 mJ/m². The standard entropy change of adsorption, ΔS , is calculated by Equation SI-8.

$$\Delta G = -RT_c \ln \left(\frac{V_M P^0}{S \pi_0} \right) \quad \text{Equation SI-7}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_c} \quad \text{Equation SI-8}$$

The method of Dorris and Gray was used to calculate the dispersive component of the surface energy, γ_s^D , by plotting the free energies of a series of n-alkanes is plotted versus the chain length to yield a straight line with a slope of ΔG_{CH_2} . By then analyzing the contribution of each additional methylene group to the free energy, the area of the a methylene group ($a_{CH_2}=0.06$ nm²), Avogadro's number (N), and the surface energy of a polyethylene-like surface composed of closely packed methylene groups (γ_{CH_2}), γ_s^D of the material can be estimated by Equation SI-9. The value of γ_{CH_2} (mJ/m²) is commonly calculated at a temperature in °C, T, by Equation SI-10.

$$\gamma_s^D = \frac{1}{\gamma_{CH_2}} \left(\frac{-\Delta G_{CH_2}}{2Na_{CH_2}} \right)^2 \quad \text{Equation SI-9}$$

$$\gamma_{CH_2} = 35.6 + 0.058(293 - T) \quad \text{Equation SI-10}$$

In a similar manner, the free energies can be plotted against the values of other molecular properties to identify the effects of “polarity” upon the specific component of the free energy. It is common to plot the free energy of adsorption versus the vapor pressure or the deformation polarizability of the sorbate, resulting in a linear relationship for the nonpolar n-alkane probes. In literature, the offset between the n-alkane reference line and the value of polar probes is equal to the specific component of the free energy and is due to the effects of the adsorbate's

“polarity”. Values for the molecular polarizability, dipole moments, acentric factors, and critical temperatures and pressures were all obtained from either the CRC Handbook of Chemistry and Physics or Perry’s Chemical Engineering Handbook.

In this work, the vapor pressure at a particular temperature is estimated by the method of Lee and Kesler using the critical temperatures and pressures and the acentric factor (ω) using Equations SI 11-13 in which T_r and P_r are the reduced temperatures which result from dividing the temperature and pressure of interest by the critical temperature and pressure respectively. Typical error from this calculation has been shown to be less than 2%.

$$\ln P_r = f^{(0)} + \omega \times f^{(1)} \quad \text{Equation SI-11}$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \times \ln T_r + 0.169347 \times T_r^6 \quad \text{Equation SI-12}$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \times \ln T_r + 0.43577 \times T_r^6 \quad \text{Equation SI-13}$$

The failure of the above methodology for materials with relatively high London dispersion energies, like carbon blacks and graphite powders, is often reported and led to the work first proposed by Donnet et al in which the deformation polarizability is used in place of the vapor pressure. Deriving from the fundamental London Equation, the free energy of adsorption can be plotted against a term of combining the characteristic electronic frequency of a molecule, ν , and the deformation polarizability, α_0 . Deformation polarizabilities can be obtained directly from the CRC Handbook of Chemistry and Physics and ν can be calculated from Equation SI-14 below where e is the elementary charge and m_e is the mass of an electron.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{e^2}{\alpha_0 m_e}} \quad \text{Equation SI-14}$$

Temperature (°C)	GC Inlet Pressure (PSI)			
	30	40	50	60
40	1.11	1.63	2.19	2.61
50	0.87	1.31	1.79	2.30
60	0.78	1.18	1.62	2.13
70	0.72	1.09	1.53	2.02
80	0.68	1.05	1.45	1.92
180	0.50	0.72	1.02	1.33
190	0.47	0.71	0.98	1.29
200	0.45	0.68	0.95	1.25
210	0.44	0.67	0.94	1.22
220	0.44	0.65	0.91	1.18
230	0.41	0.62	0.88	1.15
240	0.40	0.61	0.85	1.11
250	0.40	0.60	0.82	1.08
260	0.38	0.58	0.80	1.05
270	0.37	0.57	0.78	1.02

Table SI-1. Helium flow rates (SCCM) measured through the packed column of ZIF-8 at the given conditions (temperature and inlet pressure).

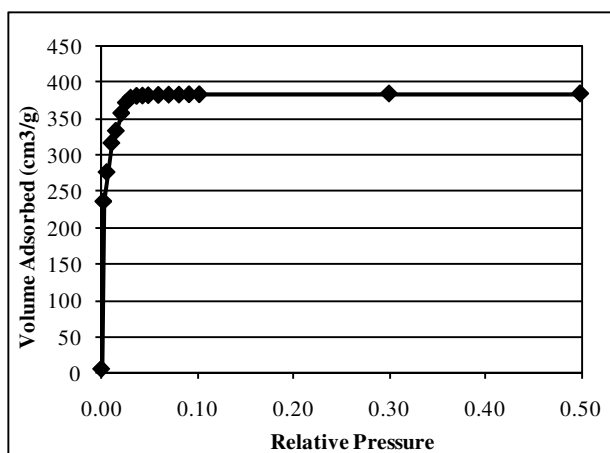


Figure SI-1. The measured nitrogen adsorption isotherm shown at liquid nitrogen temperatures.

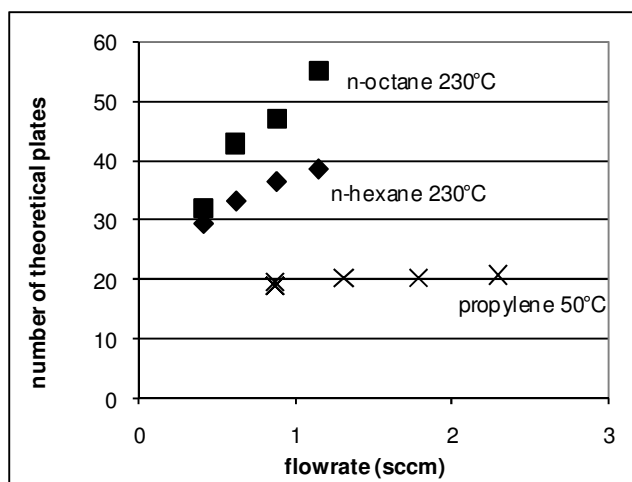


Figure SI-2. The effect of chromatographic flow rate through the packed column of ZIF-8 is shown in terms of the calculated number of theoretical plates for a few select compounds.

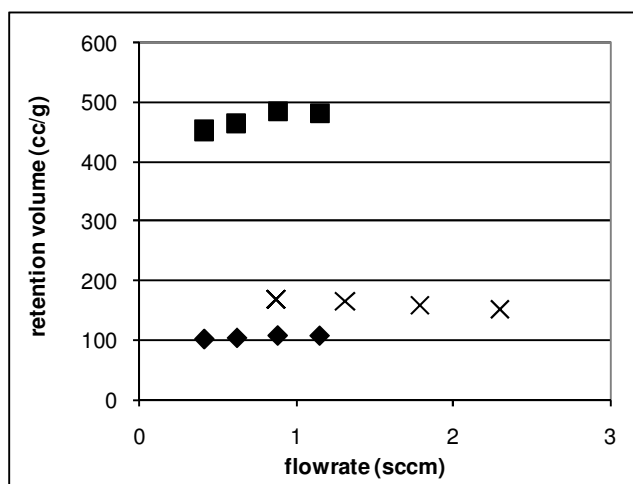


Figure SI-3. The effect of chromatographic flow rate through the packed column of ZIF-8 is shown in terms of the corrected specific retention volumes for a few select compounds.

Henry Constants (mmol/kg/kPa)	Temperature (°C)														
Adsorbed species	40	50	60	70	80	180	190	200	210	220	230	240	250	260	270
ethane	4.14	2.91	2.27	1.67											
ethylene	16.1	9.78	7.21	5.64	4.66										
propane	20.2	14.5	11.1	8.98	7.33										
propylene	105.	63.1	44.2	32.5	24.9										
n-butane	91.3	54.7	38.5	28.3	21.8										
isobutane	34.3	30.6	17.1	14.5	8.97										
n-pentane						29.3	24.0	19.6	16.3	13.5	11.5	9.61	8.17	6.97	5.99
n-hexane						77.3	60.8	48.2	39.0	31.5	26.0	21.3	17.7	14.8	12.4
n-heptane						194.	148.	114.	89.5	70.4	56.8	45.4	36.9	30.1	24.6
n-octane											115.	89.3	72.0	56.7	45.2
n-nonane											220.	167.	129.	101.	80.0
diethylether						22.7	18.2	14.8	12.3	10.2	8.68	7.26	6.13	5.27	4.51
ethylacetate						61.0	43.0	32.0	24.6	19.3	16.2	12.8	10.3	8.55	7.13
1,2-						16.5	13.6	11.4	9.67	8.12	6.95	5.90	5.04	4.34	3.76
acetone						22.7	16.2	11.9	9.34	7.33	6.31	5.03	4.14	3.46	2.92
MEK						47.2	33.6	25.1	19.6	15.5	13.0	10.3	8.59	7.14	6.05
trichloroethylene						41.5	33.3	27.1	22.5	18.4	15.3	12.5	10.7	9.09	7.69
acetaldehyde						5.52	4.31	3.46	2.91	2.43	2.19	1.80	1.56	1.30	1.11
bromoform											108.	81.1	63.4	51.9	42.3
THF											12.7	9.81	7.87	6.38	5.31
dichloromethane						9.77	8.24	7.05	6.01	5.14	4.22	3.61	3.08	2.66	2.28

Table SI-2. The table above lists all calculated values of the Henry constants (mmole/kg/kPa) for adsorbates on ZIF-8 measured chromatographically.

Corrected Retention Volumes (L/g)	Temperature (°C)														
Adsorbed species	40	50	60	70	80	180	190	200	210	220	230	240	250	260	270
ethane	0.011	0.008	0.006	0.005											
ethylene	0.042	0.026	0.020	0.016	0.014										
propane	0.053	0.039	0.031	0.026	0.022										
propylene	0.275	0.170	0.123	0.093	0.073										
n-butane	0.238	0.147	0.107	0.081	0.064										
isobutane	0.089	0.082	0.047	0.042	0.026										
n-pentane						0.111	0.092	0.077	0.066	0.056	0.048	0.041	0.036	0.031	0.027
n-hexane						0.292	0.234	0.190	0.157	0.129	0.109	0.091	0.077	0.066	0.056
n-heptane						0.731	0.571	0.450	0.360	0.289	0.238	0.194	0.161	0.133	0.111
n-octane											0.483	0.381	0.313	0.251	0.204
n-nonane											0.921	0.713	0.564	0.450	0.361
diethylether						0.086	0.070	0.058	0.050	0.042	0.036	0.031	0.027	0.023	0.020
ethylacetate						0.230	0.166	0.126	0.099	0.079	0.068	0.055	0.045	0.038	0.032
1,2-dichloroethylene						0.062	0.053	0.045	0.039	0.033	0.029	0.025	0.022	0.019	0.017
acetone						0.086	0.062	0.047	0.038	0.030	0.026	0.021	0.018	0.015	0.013
MEK						0.178	0.130	0.099	0.079	0.064	0.055	0.044	0.037	0.032	0.027
trichloroethylene						0.156	0.128	0.107	0.091	0.075	0.064	0.054	0.047	0.040	0.035
acetaldehyde						0.021	0.017	0.014	0.012	0.010	0.009	0.008	0.007	0.006	0.005
bromoform											0.455	0.346	0.276	0.230	0.191
THF											0.054	0.042	0.034	0.028	0.024
dichloromethane						0.037	0.032	0.028	0.024	0.021	0.018	0.015	0.013	0.012	0.010

Table SI-3. The table above lists all of the calculated values for the corrected retention volumes (L/g) for adsorbates studied on ZIF-8 and measured chromatographically. The data points in bold represent those with retention volumes less than the dead volume of the column assembly and greater experimental uncertainty is present in these data points.

	Table values are $\ln(V_N)$ (L/g)												
Temperature (°C)	40	50	60	70	80	230	240	250	260	270	RSQ	SLOPE	ΔH
Inverse Temp (1/K) \times	3.19	3.09	3.00	2.91	2.83	1.99	1.95	1.91	1.88	1.84			(kJ/mole)
ethane	-4.53	-4.85	-5.07	-5.35							0.996	2.869	23.85
ethylene	-3.17	-3.64	-3.91	-4.13	-4.29						0.969	3.045	25.32
propane	-2.94	-3.24	-3.48	-3.66	-3.84						0.994	2.460	20.46
propylene	-1.29	-1.77	-2.10	-2.38	-2.61						0.988	3.610	30.02
n-butane	-1.44	-1.92	-2.24	-2.51	-2.75						0.988	3.579	29.75
isobutane	-2.41	-2.50	-3.05	-3.18	-3.64						0.946	3.445	28.64
n-pentane						-3.03	-3.19	-3.34	-3.48	-3.61	1.000	3.938	32.74
n-hexane						-2.22	-2.40	-2.56	-2.72	-2.88	1.000	4.522	37.59
n-heptane						-1.44	-1.64	-1.83	-2.01	-2.19	1.000	5.163	42.93
n-octane						-0.73	-0.96	-1.16	-1.38	-1.59	0.999	5.839	48.54
n-nonane						-0.08	-0.34	-0.57	-0.80	-1.02	1.000	6.372	52.98
diethylether						-3.32	-3.47	-3.63	-3.76	-3.89	1.000	3.923	32.62
ethylacetate						-2.69	-2.91	-3.10	-3.27	-3.44	0.999	5.103	42.43
1,2-dichloroethylene						-3.54	-3.68	-3.82	-3.95	-4.08	1.000	3.678	30.58
Acetone						-3.63	-3.84	-4.02	-4.18	-4.33	0.998	4.707	39.13
MEK						-2.91	-3.12	-3.29	-3.45	-3.60	0.998	4.701	39.08
trichloroethylene						-2.75	-2.93	-3.07	-3.21	-3.36	0.999	4.137	34.40
Acetaldehyde						-4.69	-4.87	-5.00	-5.16	-5.30	0.998	4.094	34.03
Bromoform						-0.79	-1.06	-1.29	-1.47	-1.65	0.995	5.867	48.77
THF						-2.93	-3.17	-3.37	-3.56	-3.73	0.997	5.467	45.45
dichloromethane						-4.04	-4.17	-4.31	-4.44	-4.58	1.000	3.668	30.50

Table SI-4. The table above lists the values of the natural logarithm of retention volume and temperatures used to calculate the differential enthalpy of adsorption for ZIF-8 using the van't Hoff relationship. Calculated values of enthalpy (kJ/mole) and the quality of fit (R^2) are also listed.

	polarizability			$(h\nu)^{0.5} \alpha_0 \times 10^{49}$			ω	250C	250C	ΔG 250°C
	($\times 10^{24} \text{ cm}^3$)	α_0 (C m ² /V)	h ν (eV)		T _c (K)	P _c (Mpa)		P ⁰ (Mpa)	ln(P ⁰)	(kJ/mole)
n-pentane	9.99	1.112E-39	3.31	8.10	469.7	3.36	0.251	7.295	1.987	8.38
n-hexane	11.90	1.324E-39	3.04	9.23	507.6	3.04	0.304	3.790	1.332	11.75
n-heptane	13.61	1.514E-39	2.84	10.21	540.2	2.72	0.346	2.138	0.760	14.93
n-octane	15.90	1.769E-39	2.63	11.48	568.7	2.47	0.396	1.285	0.251	17.84
n-nonane	17.36	1.932E-39	2.51	12.26	594.6	2.31	0.446	0.809	-0.212	20.39
diethylether*	8.73	9.713E-40	3.54	7.32	466.7	3.64	0.281	8.442	2.133	7.13
ethylacetate*	8.62	9.591E-40	3.57	7.25	523.3	3.85	0.363	3.842	1.346	9.43
1,2-dichloroethylene	8.03	8.935E-40	3.70	6.88	508	5.19	0.264	6.396	1.856	6.28
acetone*	6.33	7.043E-40	4.16	5.75	508.2	4.71	0.307	5.823	1.762	5.43
MEK*	8.13	9.046E-40	3.67	6.94	535.5	4.12	0.32	3.469	1.244	8.60
trichloroethylene	10.03	1.116E-39	3.31	8.12	571	4.91	0.217	2.673	0.983	9.56
acetaldehyde	4.59	5.107E-40	4.89	4.52	466	5.57	0.292	13.155	2.577	1.17
bromoform	11.80	1.313E-39	3.05	9.18	696	6.09	0.156	0.784	-0.243	17.29
THF	NA	NA	NA	NA	540.5	5.19	0.225	4.141	1.421	8.22
dichloromethane	6.48	7.210E-40	4.11	5.85	510	6.1	0.19	7.244	1.980	4.14

Table SI-5. The table above lists the values used for the fit of the retention data to vapor pressure and deformation polarizability.

Critical constants and acentric factors were used to calculate vapor pressure through the Lee-Kesler Method and molecular polarizability were used to calculate the deformation polarizability term. The free energy values at 250°C used in the fit are also listed.

Free Energy of Adsorption (kJ/mole) calculated at the temperature (°C) listed															
Adsorbed species	40	50	60	70	80	180	190	200	210	220	230	240	250	260	270
ethane	1.91	1.11	0.54	-0.24											
ethylene	5.45	4.37	3.74	3.23	2.86										
propane	6.04	5.43	4.95	4.56	4.18										
propylene	10.34	9.37	8.76	8.24	7.78										
n-butane	9.96	8.99	8.38	7.84	7.38										
isobutane	7.42	7.43	6.14	5.95	4.78										
n-pentane						11.53	11.10	10.63	10.21	9.73	9.34	8.83	8.38	7.92	7.47
n-hexane						15.18	14.68	14.17	13.70	13.19	12.75	12.23	11.75	11.26	10.77
n-heptane						18.64	18.10	17.56	17.03	16.48	16.01	15.45	14.93	14.40	13.86
n-octane											18.97	18.34	17.84	17.21	16.60
n-nonane											21.67	21.01	20.39	19.79	19.17
diethylether						10.57	10.04	9.53	9.08	8.58	8.15	7.63	7.13	6.68	6.19
ethylacetate						14.29	13.35	12.56	11.85	11.19	10.78	10.06	9.43	8.82	8.25
1,2-dichloroethylene						9.37	8.94	8.50	8.10	7.63	7.22	6.75	6.28	5.82	5.36
acetone						10.57	9.59	8.68	7.95	7.21	6.81	6.07	5.43	4.82	4.23
MEK						13.33	12.40	11.61	10.93	10.30	9.85	9.16	8.60	8.03	7.51
trichloroethylene						12.84	12.36	11.91	11.50	10.99	10.53	9.97	9.56	9.10	8.60
acetaldehyde						5.24	4.49	3.80	3.27	2.68	2.39	1.68	1.17	0.48	-0.15
bromoform											18.72	17.92	17.29	16.82	16.29
THF											9.77	8.92	8.22	7.53	6.92
dichloromethane						7.39	6.98	6.60	6.18	5.76	5.13	4.66	4.14	3.66	3.11

Table SI-6. The table above lists all of the measured free energies of adsorption on ZIF-8 which were calculated from chromatographic data.