

Structure and Reactivity in Aqueous Systems.

A thesis submitted for the degree of Doctor of Philosophy in the
Faculty of Science.

by

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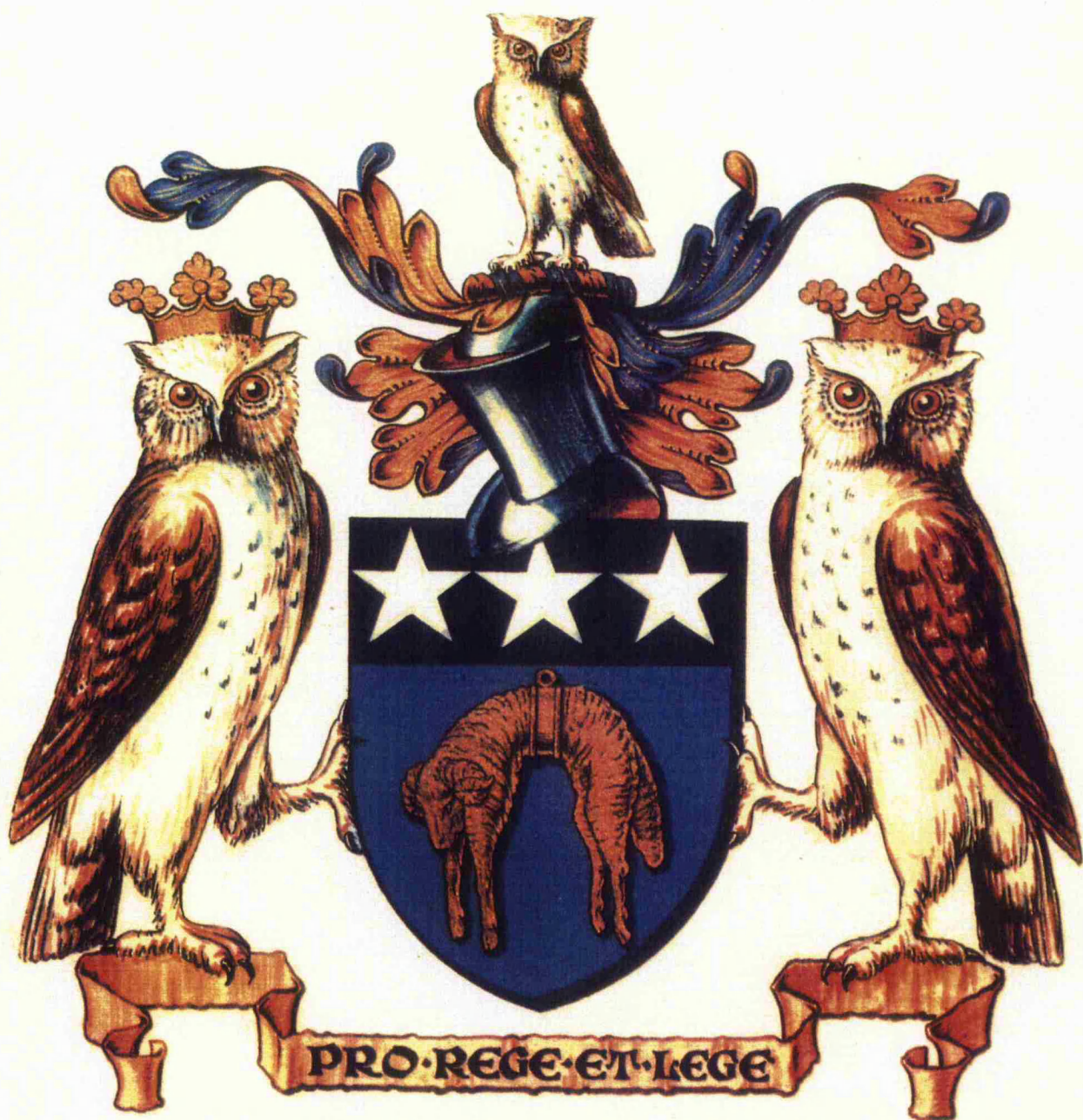
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*To Mum
Cheryl
Chris
and Nicki*

Statement

This thesis is based on work conducted by the author in the Department of Chemistry of the University of Leicester, during the period between October 1987 and June 1990.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by reference. This work is not being presented for any other degree.

June 1993

Ian Martin Horn
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Kinetics of Reactions in Aqueous Systems

Ian Martin Horn

Abstract

Rate constants for chemical reactions in various aqueous systems have been measured and analysed. Oxidations of a number of organic dyes by the compound sodium perborate tetrahydrate have been extensively studied kinetically. These rate constants are compared to those for hydrogen peroxide and sodium percarbonate, for similar oxidations under the same conditions. A general review of peroxyanion chemistry is included, and a computer simulation of the perborate species in solution is presented.

The theories of Debye and Hückel concerning kinetic salt effects are examined in the light of Desnoyer's theory of co-sphere interaction for ions in solution.

The effects of added salt on the alkaline hydrolysis of the disodium salt of bromophenol blue are reported and analysed using Pitzer's equations for the activity coefficients of single ions in aqueous salt solutions.

The Kirkwood-Buff theory of interactions in binary aqueous mixtures has been examined and extended according to the methods proposed by Ben-Naim. Calculated Kirkwood-Buff parameters are presented for ethanol + water, and t-butanol + water mixtures.

Theory is described for the calculation of the so-called g_k parameters for first- and second-order reactions. These parameters have been calculated for the alkaline hydrolysis of an iron(III) complex, and the spontaneous hydrolysis of 4-methoxyphenyl-2,2-dichloropropionate in t-butanol + water mixtures. The significance of the calculated parameters, in terms of the role of preferential solvation in the reaction mechanism, is discussed.

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My gratitude to Dr. Colin 'El' Hubbard and Dr. Bassem Shraydeh for permission to include their results in chapter 4.

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Chapter 1

Introduction

The literature contains a wealth of information on studies of liquid water, an effective summary is presented by Franks who describes water as 'a unique substance'.¹ The work in this thesis deals mainly with reactions in aqueous solutions, in particular, analysis of kinetic data for such reactions. The thesis is sub-divided into three distinct parts. Chapters 3 to 5 introduce the oxidative properties of some peroxyanion compounds going on to describe a detailed kinetic study on oxidations of organic dyes by sodium perborate tetrahydrate. Chapters 6 and 7 outline theory behind interactions between ionic species in solution, using kinetic salt effects as a probe. Finally, chapters 8 and 9 describe the application of the Kirkwood-Buff theory of interactions in binary aqueous mixtures,^{2,3} leading to an understanding of the role of preferential solvation in reaction mechanisms.

The compound sodium perborate tetrahydrate is the basis of many modern solid detergents. Crystallographic studies of perborate in the solid state have been carried out and the structure has been determined.⁴ However, the exact nature of this compound in aqueous solution remains somewhat unclear. Chapter 3 reviews oxidations by some common inorganic (and selected organic) peroxyanions that are relevant to the study presented in chapter 4. A summary of available literature information on sodium perborate tetrahydrate is also included in this chapter. A detailed kinetic study of the oxidation of some model organic dyes and 'real' stains by sodium perborate tetrahydrate is presented in chapter 4. Comparisons are made to oxidations of the same substrates by hydrogen peroxide and sodium percarbonate. The production of a number of substances by sodium perborate tetrahydrate on dissolution is explored in chapter 5. This chapter draws together obtained experimental data and literature information on the decomposition products of sodium perborate tetrahydrate in the form of a computer simulation. Written in FORTRAN, the program simulates equilibria between substances produced on dissolution of sodium perborate tetrahydrate, indicating predicted concentration at a specific time.

The theories describing kinetic salt effects are summarised in chapter 6. Comments on the short-falls in the theory proposed by Debye and Hückel,⁵ and subsequent modifications,^{6,7} are made in the light of proposed co-sphere co-sphere overlap effects involving added ions in aqueous solutions.^{8,9} Section 6.5 briefly introduces Pitzer's equations for activity coefficients of salts in solutions.^{10,11} Pitzer's theory is examined in more detail in chapter 7 and is applied to the alkaline hydrolysis of the dye bromophenol blue.¹² Calculations to obtain specific ion-ion interaction parameters for this hydrolysis are described. These parameters are then used to describe trends in rate constant upon addition of various added tetraalkyl-ammonium and alkali metal salts.

The final two chapters are concerned with the description and application of the Kirkwood-Buff theory of interactions in binary aqueous mixtures.^{2,3,13-15} Methods of calculating the Kirkwood-Buff integral function, using available thermodynamic parameters (obtained or calculated from literature information), are introduced in chapter 8. The theory is then applied to water + ethanol and water + t-butanol mixtures in chapter 9 and the significance of the calculated Kirkwood-Buff parameters is explained. Transition state theory¹⁶ and the Kirkwood-Buff analysis are then used to form a description of chemical reactions in aqueous solutions (both first- and second-order). Incorporated in this description are calculations to obtain the so-called g_k parameters, a function of affinity of a solute for a particular solvent in the mixture. The g_k values for the spontaneous hydrolysis of 4-methoxyphenyl-2,2-dichloropropionate (a first-order reaction)¹⁷ and the alkaline hydrolysis of $[\text{Fe}(\text{gmi})_3]^{2+}$ (a second-order reaction)¹⁸ in water + t-butanol mixtures are calculated. Both calculated Kirkwood-Buff and g_k parameters lead to a clearer understanding of the role of preferential solvation in the above reactions.

A detailed description of the instruments and methods used to collect kinetic data is presented in chapter 2.

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Chapter 2

Experimental

2.1 Introduction.

The following chapter describes details of the collection and analysis of kinetic data by the computer controlled spectrophotometers used by the kinetics group at Leicester University. The theory behind the analysis for a first order reaction is outlined and the computer programs used for data collection and analysis are outlined.

2.2 Analysis of kinetic data.

Rate constants reported in this thesis were all monitored under first order conditions. For a typical first order process reactant species A reacts to give product P; i.e. $A \longrightarrow P$. For such a reaction the integrated rate equation takes the form

$$\ln \left(\frac{[A]_0}{[A]_t} \right) = kt \quad 2.1$$

$[A]_0$ = concentration of substance A at time $t = 0$

$[A]_t$ = concentration of substance A at time t

Hence,

$$[A]_t = [A]_0 \exp(-kt) \quad 2.2$$

The dependence of concentration upon time, as the reaction proceeds, is exponential with the rate being determined by the rate constant k . The half life of a reaction, $t_{1/2}$, is defined as the time taken for the concentration of a substance to fall to half its original value. For the example above, when $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$. The half-life is defined in terms of rate constant k by equation 2.3.

$$t_{1/2} = \frac{\ln 2}{k} \quad 2.3$$

For second order reactions data were collected under pseudo first order conditions using the isolation method.

Consider a reaction $A + B \longrightarrow \text{Products, P}$ where k is the second order rate constant;

$$-\frac{d[A]}{dt} = k[A][B] \quad 2.4$$

The concentration of substance B can be assumed to be constant providing it is present in large excess over the concentration of A . In this case $[B]$ can be incorporated into the rate constant.

$$k_{\text{obs}} = k[B] \quad 2.5$$

where k_{obs} is the first order rate constant. Hence, the rate law can now be written in the form of equation 2.1.

$$-\frac{d[A]}{dt} = k_{\text{obs}}[A] \quad 2.6$$

This approach has been applied to the second order reactions reported in this thesis (e.g. bromophenol blue hydrolysis in chapter 7).

A convenient means of monitoring the progress of reactions involved following the change in concentration of either reactant or product with time. In spectrophotometric terms, this involved logging the changes in absorbance with time. The Beer-Lambert law establishes the relationship between concentration and absorbance. For a substance A , in dilute solution placed in the path of a beam of monochromatic light of wavelength λ , the absorbance is given by;

$$P = \log_{10} \left(\frac{I_0}{I_t} \right) = \epsilon_{\lambda} l [A] \quad 2.7$$

where, I_0 and I_t = incident and transmitted light at wavelength λ

ϵ_{λ} = molar extinction coefficient of A at wavelength λ

$[A]$ = Concentration of species A/mol dm⁻³
 l = path length/m

Over all substances present in solution, the absorbance at wavelength λ will be

$$P = \epsilon_a l[A] + \epsilon_b l[B] + \dots \quad 2.8$$

where the molar absorption coefficients of substances A and B at wavelength λ are ϵ_a and ϵ_b respectively.

For a simple first-order reaction, the rate constant can be directly obtained from collected absorbance/time data using a combination of equations 2.1 and 2.7.

When

$$\text{time} = 0 \quad P_0 = \epsilon_a [A]_0 l + \epsilon_b [B]_0 l$$

$$\text{time} = t \quad P_t = \epsilon_a [A]_t l + \epsilon_b [B]_t l$$

$$\begin{aligned} \text{time} = \infty \quad P_\infty &= \epsilon_b [B]_\infty l \\ &= \epsilon_b l ([A]_0 + [B]_0) \\ &= \epsilon_b l ([A]_t + [B]_t) \end{aligned}$$

and

$$\begin{aligned} [A]_0 &= \frac{(P_0 + P_\infty)}{(\epsilon_a l + \epsilon_b l)} \\ [A]_t &= \frac{(P_t + P_\infty)}{(\epsilon_a l + \epsilon_b l)} \end{aligned}$$

therefore

$$\ln(kt) = \frac{(P_0 + P_\infty)}{(P_t + P_\infty)} \quad 2.9$$

2.3 The HP8451A diode array spectrophotometer.

The Hewlett-Packard 8451A spectrophotometer is a single beam, microprocessor controlled instrument operating in the UV/visible region in the range 190 to 820 nm at 2 nm resolution ± 0.5 nm. This instrument is capable of measuring absorbances either every tenth of a second, for up to twenty five separate wavelengths, or every seven tenths of a second for a full spectrum. The essential features of this instrument are illustrated by the block diagram in figure 2.1.

Central to the operation of the HP8451A were two 8-bit microcomputers, the Z80 and HP85A. The former operates the internal hardware (lamp, shutter, pre-amp and analogue-to-digital converter) whereas the latter can be thought of as the interface between the user and the instrument itself, handling the collection of data.

Figure 2.1 shows how light emitted from the internal deuterium lamp is focused onto the sample cell (1cm^2 base and 3cm height) by an ellipsoidal mirror then, using a second ellipsoidal mirror, reflected onto a monozone holographic grating. The grating disperses the light onto a linear photodiode array consisting of 328 individual light sensitive cells and control circuits etched on a semiconductor chip (2mm x 18mm). The full wavelength range of 190 to 820 nm utilizes 316 of these cells, the remainder allowing for alignment of the array during instrument wavelength calibration.

A number of BASIC programs were written by Dr. M.J. Blandamer to collect absorbance data as a function of time which were then stored on disk for analysis at a later stage. Each kinetic run produced a spectrum displayed on the instruments cathode ray tube (CRT) and a hard copy of the collected spectra on the in-built thermal printer/plotter. The analysis program was based on the theory outlined in section 2.5 and recalled information stored on disk by the logging program. An example of output from the data logging

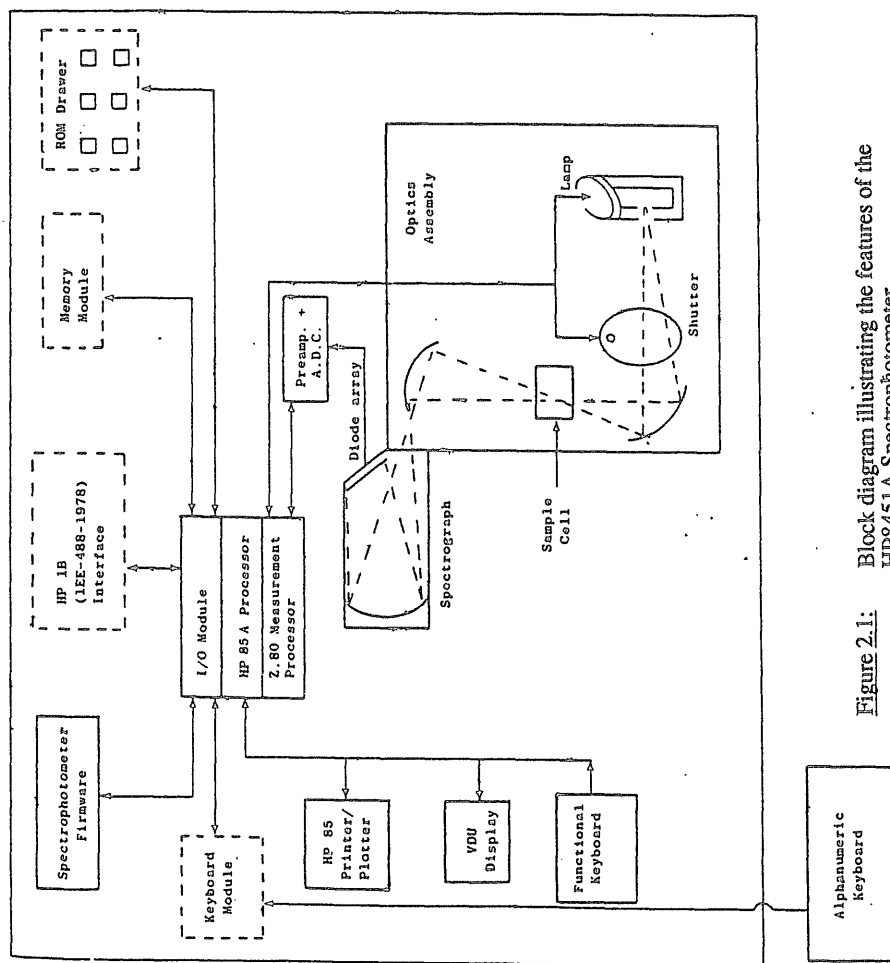


Figure 2.1: Block diagram illustrating the features of the HP8451A Spectrophotometer.

and analysis programs for the Hewlett-Packard is shown in figure 2.2 showing a complete spectrum, absorbance/time and first-order plots.

Temperature control of the sample is achieved by virtue of an insulated copper cell holder in the spectrophotometer. The cell holder (figure 2.3) was water cooled via a small bore copper pipe around the block and thermostatted by a platinum resistance thermometer connected to a Wheatstone bridge. Temperature values were set manually via a dial controlling the bridge setting. When the bridge was in balance, the system was at the correct temperature and the heater coil around the copper block was switched off. If the temperature fell below the set value the heater was switched on until the system returned to equilibrium. Temperature was monitored using a probe inserted into the insulation between the two copper blocks and connected to a digital thermometer, which displayed the temperature. The digital thermometer was accurate to ± 0.01 Celsius.

2.4 Pye-Unicam SP1800 spectrophotometer.

The SP1800 spectrophotometer is a double beam instrument operating in the UV/visible region over the range 190 to 820nm capable of monitoring three sample and three reference cells at one time. Initially this instrument was driven by software on an interfaced Hewlett-Packard 9825A minicomputer (written by Dr. M.J.Blandamer) but after the machine was destroyed by flood damage in the early months of 1988 it was necessary to write new software to interface the SP1800 to an IBM personal computer.

The spectrophotometer was directly connected to a Microprocessor Instrumentation of Kinetic Experiments (MIKE) interface which was, in turn, connected to an IBM PC via a digital voltmeter. Data collection and analysis programs written on the PC were similar to those used for the HP8451A but written in turbo-BASIC and incorporating enhanced

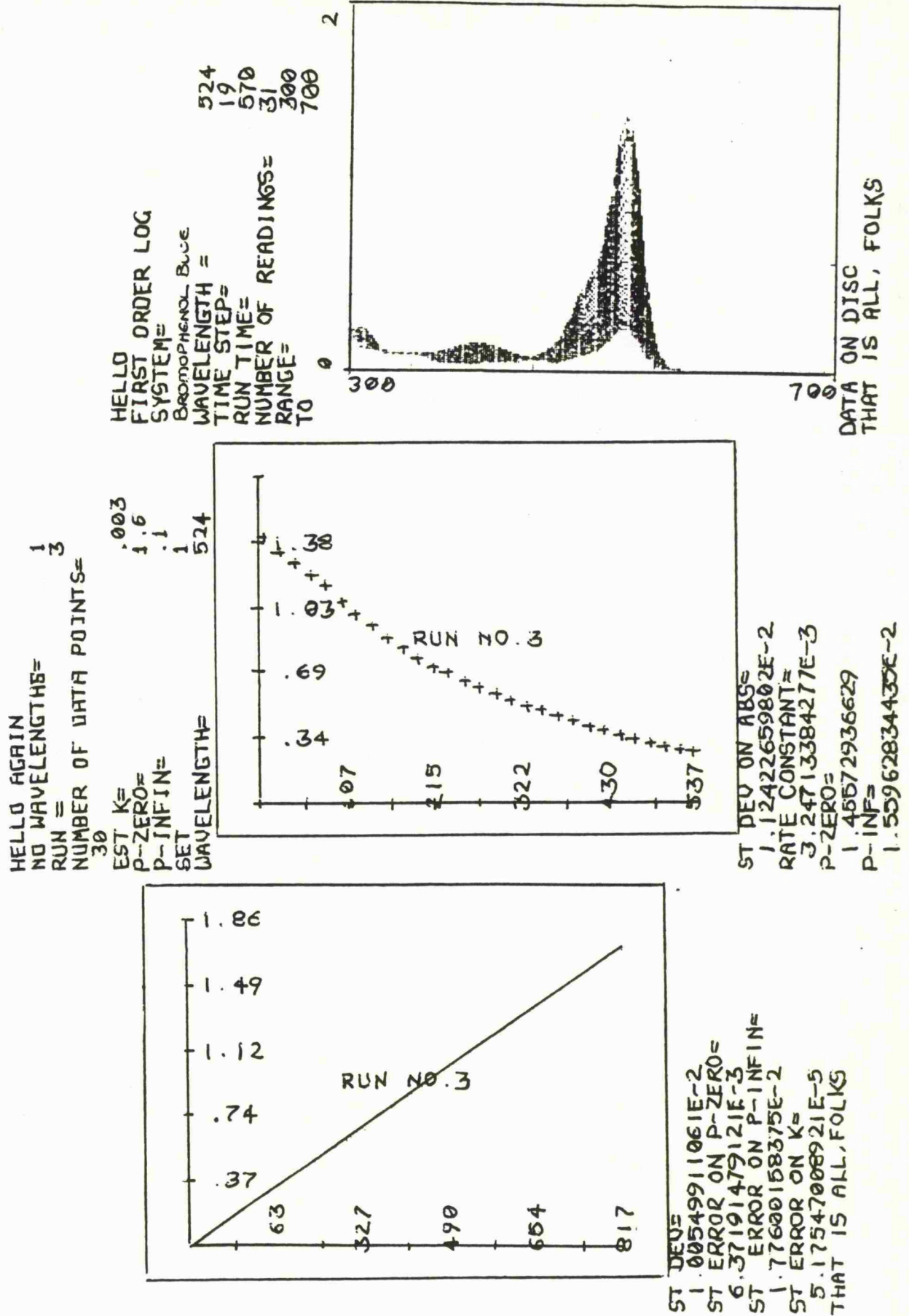


Figure 2.2: Example of the output produced by the data logging and analysis programs from the HP8451A.

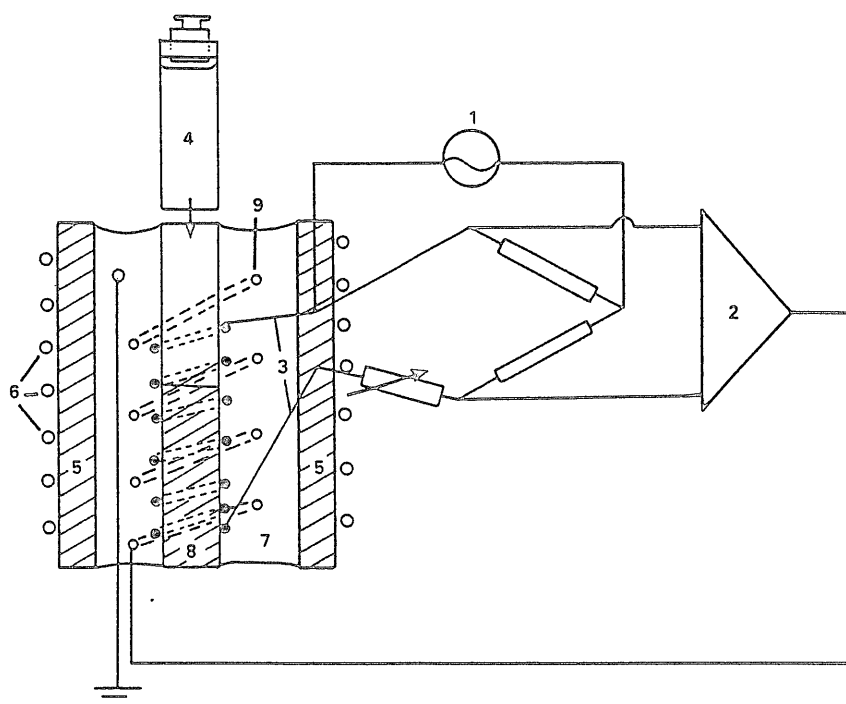
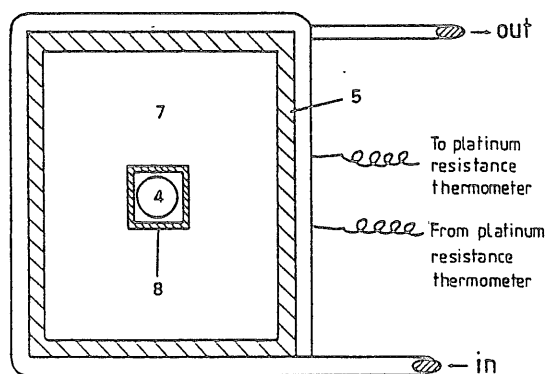


Figure 2.3: Diagram of the thermostatted cell block positioned in the HP8451A spectrophotometer.

1. Oscillator
2. Amplifier
3. Platinum Resistance Thermometer acting as an arm of Wheatstone Bridge
4. Sample Cell
5. Outer Copper Block
6. Water Pipes
7. Insulating Material
8. Inner Copper Block
9. Heater Coil



on-screen graphics facilities. The two-stage data collection and analysis programs are presented as flow diagrams in figures 2.4 and 2.5. After entering all required information into the logging program, absorbance/time data collection was initiated using a single keystroke. At time intervals calculated from input information, the computer sent a 'cell select' binary signal to the MIKE interface, each cell having a unique signal. A comparison was made between the 'cell select' signal and a 'cell identification' signal for the cell in the path of the spectrophotometer light beam. If the signals did not match, the multi-cell block in the spectrophotometer was moved until the two signals matched. A 'sample pulse' was then sent to the digital voltmeter to accept an analogue absorbance reading from the spectrophotometer (a short delay being incorporated into the system between 'cell ready' and 'sample pulse' signals to allow the spectrophotometer's analogue meter to provide an accurate reading) The final step involved the sending of a signal from the IBM PC to the MIKE interface to clear all lines in preparation for the next reading. Figure 2.6 illustrates the main features of the Pye-Unicam SP1800 spectrophotometer. Temperature control was achieved via the same method as used for the Hewlett-Packard.

The advantage of this new program over the old HP minicomputer version for the SP 1800 was the fact that progress of reaction could be monitored for each cell via individual absorbance/time plots. Facilities to store information on either the hard disk of the PC or a floppy disk to transfer to other computers were also incorporated. Printed output of absorbance/time and first-order plots from this program were obtained on a dot-matrix printer, and had a similar format to that produced by the Hewlett-Packard.

2.5 Method of processing absorbance/time data.

In order to analyse data collected by the two spectrophotometers, programs were written based on a non-linear least squares analysis proposed by Moore.¹

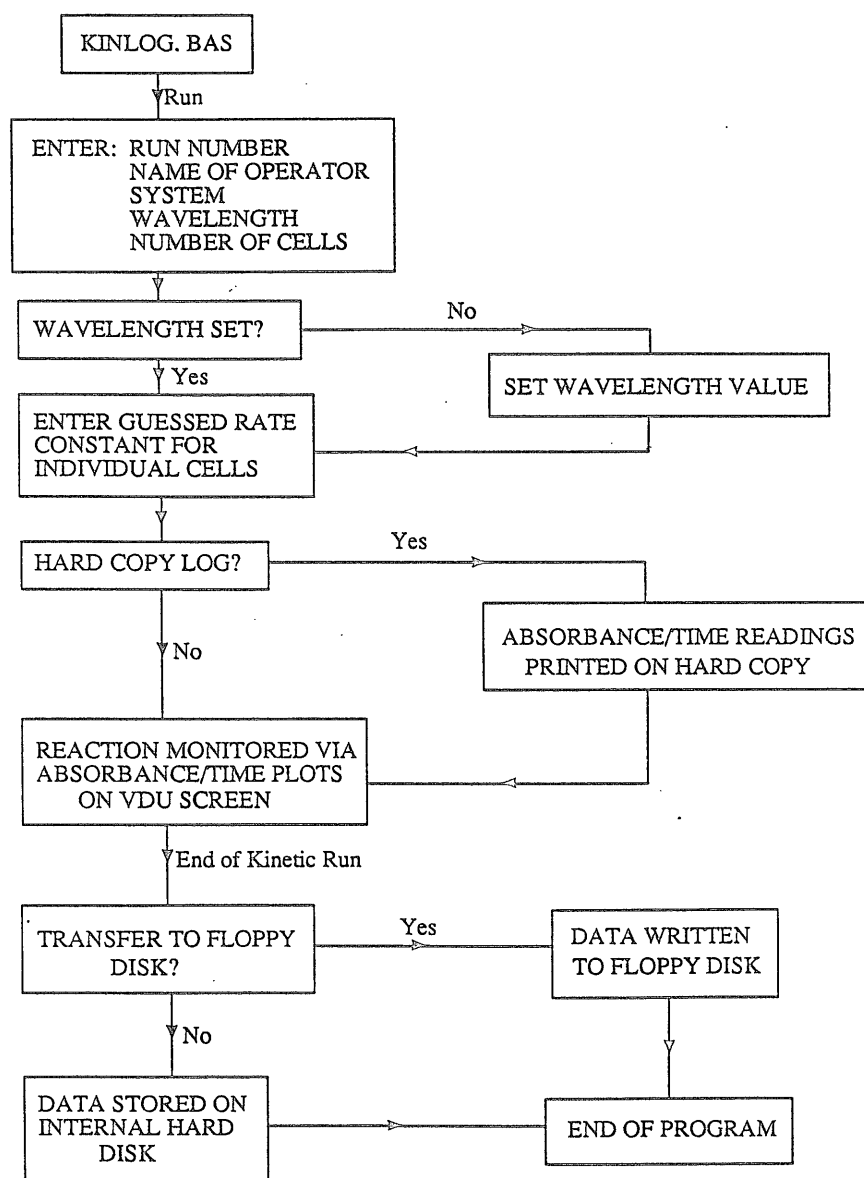


Figure 2-4: Flow diagram illustrating the data logging program KINLOG. BAS.

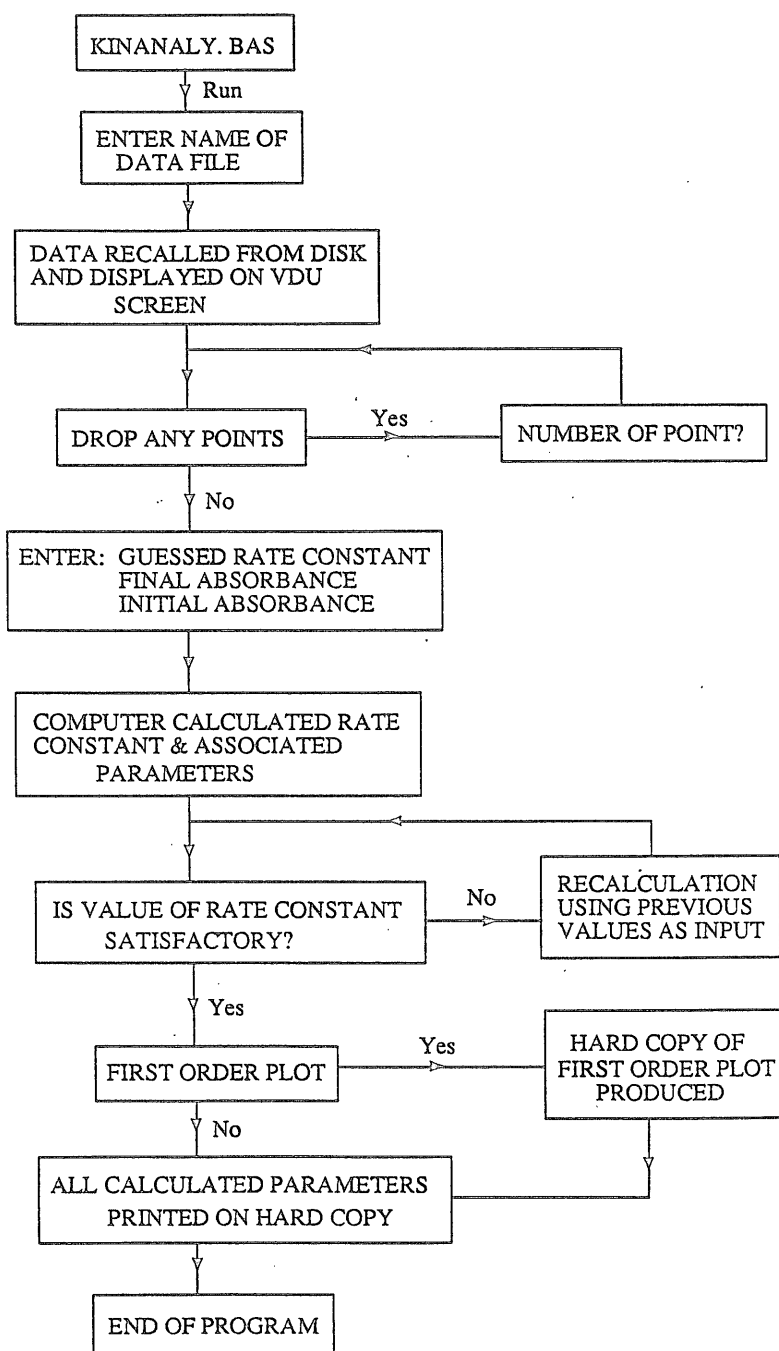


Figure 2-5: Flow diagram illustrating the data analysis program
KINANALY. BAS

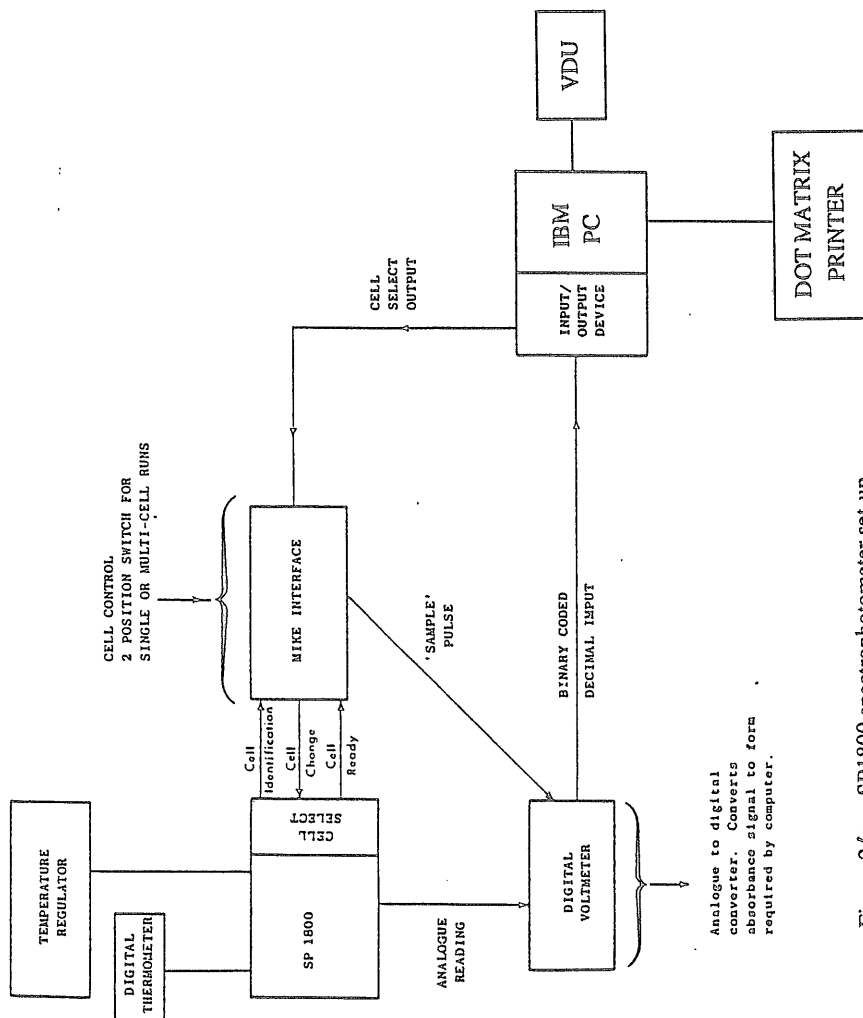


Figure 2.6: SP1800 spectrophotometer set-up.

Equation 2.9 can be rearranged to give an expression for the absorbance at time t , P_t ;

$$P_t = (P_o - P_\infty)\exp(-kt) + P_\infty \quad 2.10$$

Hence at a given time t it is possible to describe absorbance P_t in terms of three independent variables P_o , P_∞ and k . i.e.

$$P_t = P_t \left\{ P_o, P_\infty, k \right\} \quad 2.11$$

From this we can derive the general differential equation;

$$\begin{aligned} dP = & \left(\frac{\delta P_t}{\delta P_o} \right)_{t, P_\infty, k} \cdot dP_o + \left(\frac{\delta P_t}{\delta P_\infty} \right)_{t, P_o, k} \cdot dP_\infty \\ & + \left(\frac{\delta P_t}{\delta k} \right)_{P_o, P_\infty, t} \cdot dk \end{aligned} \quad 2.12$$

Equation 2.10 can be differentiated with respect to each of the independent variables giving the following expressions;

$$\left(\frac{\delta P_t}{\delta P_o} \right)_{P_\infty, k} = \exp(-kt) = \alpha_a \quad 2.13$$

$$\left(\frac{\delta P_t}{\delta P_\infty} \right)_{P_o, k} = 1 - \exp(-kt) = \alpha_b \quad 2.14$$

$$\left(\frac{\delta P_t}{\delta k} \right)_{P_o, P_\infty} = -t(P_o - P_\infty)\exp(-kt) = \alpha_c \quad 2.15$$

At the beginning of the program estimates of P_o , P_∞ and k are fed into the computer. These estimates are used to calculate absorbance at each time t , $P_t(\text{calc})$, and the difference between observed and calculated absorbances dP_t . The α quantities, as defined above, are used to improve the fit of observed to calculated data at each time interval. A quantity Q is defined by equation 2.16.

$$Q = \sum \left(dP_t - \alpha_a dP_o - \alpha_b dP_\infty - \alpha_c dk \right) \quad 2.16$$

When Q is at a minimum, $dQ/dX = 0$.

Hence

$$\frac{dQ}{dP_o} = \sum \alpha_a^2 dP_o + \sum \alpha_b \alpha_c dP_\infty + \sum \alpha_a \alpha_c dk - \sum \alpha_a dP_t = 0 \quad 2.17$$

$$\frac{dQ}{dP_\infty} = \sum \alpha_b \alpha_a dP_o + \sum \alpha_b^2 dP_\infty + \sum \alpha_b \alpha_c dk - \sum \alpha_b dP_t = 0 \quad 2.18$$

$$\frac{dQ}{dk} = \sum \alpha_c \alpha_a dP_o + \sum \alpha_c \alpha_b dP_\infty + \sum \alpha_c^2 dk - \sum \alpha_c dP_t = 0 \quad 2.19$$

Or, in matrix form;

$$\begin{array}{c} \left| \begin{array}{ccc} \sum \alpha_a^2 & \sum \alpha_b \alpha_c & \sum \alpha_c \alpha_a \\ \sum \alpha_b \alpha_a & \sum \alpha_b^2 & \sum \alpha_b \alpha_c \\ \sum \alpha_c \alpha_a & \sum \alpha_b \alpha_c & \sum \alpha_c^2 \end{array} \right| \left| \begin{array}{c} dP_o \\ dP_\infty \\ dk \end{array} \right| = \left| \begin{array}{c} \sum \alpha_a dP_t \\ \sum \alpha_b dP_t \\ \sum \alpha_c dP_t \end{array} \right| \\ X \quad \quad \quad \beta \quad \quad \quad Y \end{array}$$

Which can be written in the form of a linear equation;

$$Y = \beta X \quad 2.20$$

A linear least squares method² is used to solve equation 2.20 with calculated parameters α_a , α_b and α_c being placed in array X. Estimated values of P_o , P_∞ and k are revised and improved using calculated correctors

$$\text{i.e.} \quad P_o(\text{imp}) = P_o(\text{previous}) + dP_o$$

similarly for P_∞ and k. These improved values are then substituted into equation 2.10 to obtain improved values of absorbance at time t. A comparison is then made between

$P_t(\text{calc})$ and $P_t(\text{obs})$. If the agreement is unsatisfactory the cycle is repeated until the value of $\Sigma[P_t(\text{obs}) - P_t(\text{calc})]^2$ is at a minimum or is a comparable magnitude to that of the estimated experimental precision. The output produced by the program gives calculated values of P_o , P_∞ and k along with their associated standard errors. All rate constants presented in this thesis, unless otherwise indicated, are accurate to $\leq \pm 2.0\%$.

References.

- (1) P.Moore, J.Chem.Soc.,Faraday Trans.I,68,1890,(1972)
- (2) D.Z.Arbitton, A.L.Schmeltekoft, 'Modern Spectroscopy, Modern Research II', Ed. K.N.Rao, Academic Press, New York,(1976)

Chapter 3

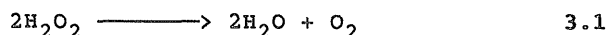
Peroxoanion oxidations of organic substrates

3.1 Introduction.

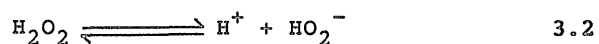
Several peroxyanions, and hydrogen peroxide, have found widespread use in commercial and household washing products. Although referred to as 'bleaching agents', the oxidative properties of these peroxy compounds make them useful as stain decolourants rather than harsh bleaches, such as hypochlorite, which tend to remove dyes intentionally present in the fabric. Interest at Leicester has centred on the behaviour of sodium perborate tetrahydrate in aqueous solutions and comparisons with hydrogen peroxide. Results of these studies are presented in chapter 4. However, to place such a study on a secure footing, it is necessary to review briefly the general chemistry of peroxyanion oxidation of organic species in solution, paying particular attention to the known properties of hydrogen peroxide and sodium perborate tetrahydrate.

3.2 Hydrogen Peroxide.

Hydrogen peroxide is one of the most common 'bleaching agents' used in textile¹ and domestic bleaching applications.² Pure hydrogen peroxide has an 'active oxygen' content of 47%. At low pH, hydrogen peroxide is relatively stable, the decomposition to water and oxygen (equation 3.1) having a high activation energy ($= 209 \text{ kJ mol}^{-1}$), which at ambient pressure is not achieved even at the boiling point temperature of the solution.

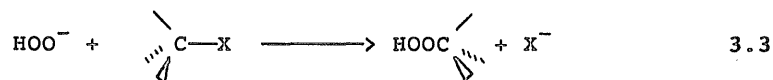


However, the rate of decomposition is greatly accelerated by the presence of metal ions,¹ especially Mn(II).³ Hydrogen peroxide is a very weak acid in aqueous solutions, equation 3.2 shows the equilibrium between hydrogen peroxide and the perhydroxyl ion.

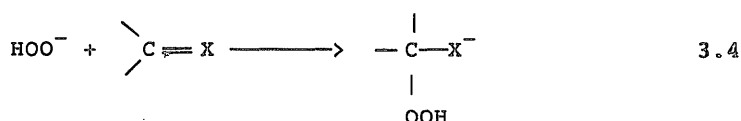


The dissociation constant for the equilibrium at 298K is $1.78 \times 10^{-2} \text{ mol dm}^{-3}$ and the pK_a of hydrogen peroxide is

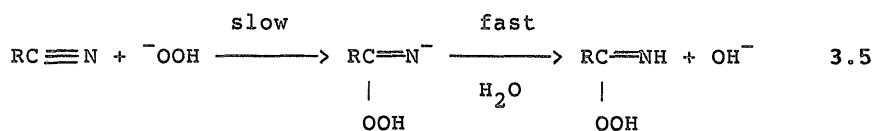
approximately 11.4. Hence, at high pH, hydrogen peroxide is predominantly in the form of HO_2^- - the perhydroxyl ion. It is widely accepted^{1,4} that the perhydroxyl ion is the active (bleaching) moiety and that the stain removing properties at high pHs are dominated by its action as a nucleophile. Reactions of this type are numerous and, in general, fall into two categories; reactions involving displacement of a group X in the substrate by the perhydroxyl anion, so-called $\text{S}_\text{N}2$ reactions (equation 3.3)



and reactions where the perhydroxyl ion adds to a multiple bond (equation 3.4)



A well established example of nucleophilic addition of the perhydroxyl ion to a multiple bond is shown in equation 3.5, where an alkyl nitrile is oxidised to produce the peroxy carboximidic acid.⁵

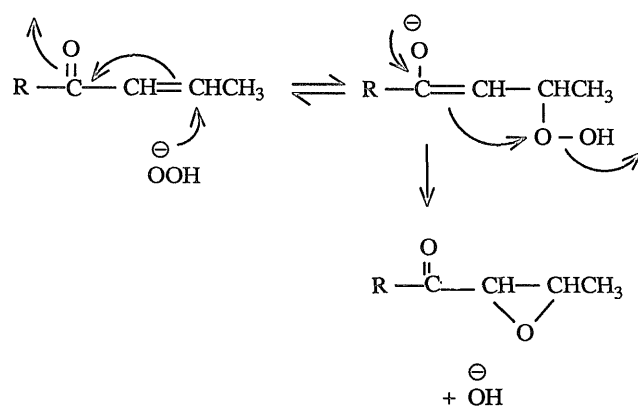


where $\text{pH} > 10.0$. Initial nucleophilic attack of the perhydroxyl ion is the rate limiting step, and the following rate equation was established by Ogata and co-workers;⁶

$$\text{Rate} = k[\text{RCN}][\text{HO}_2^-] \quad 3.6$$

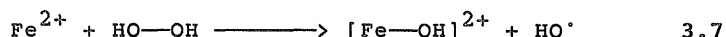
where k is in the range $10^{-3} < k/\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^{-3} < 31$ for the addition to nitriles at 298 K. Hydrogen peroxide can also be used in the synthesis of epoxides from alkenes. Figure 3.1 illustrates the proposed mechanism,⁷ the carboxy-alkene

Figure 3.1: Proposed mechanism for the epoxidation of alkenes (*after ref. 4*);
R=H, alkyl.



undergoing initial nucleophilic attack by the perhydroxyl ion.

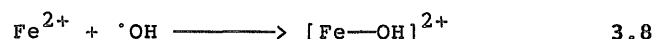
The bond energy of the O-O bond is relatively small (142 kJ mol^{-1})⁵ and one might therefore expect hydrogen peroxide readily to undergo homolytic bond fission. The O-O bond undergoes homolytic fission producing the hydroxy radical, a powerful oxidising species. Homolytic fission can be achieved by irradiating solutions of hydrogen peroxide, but a convenient alternative uses the so-called 'Fenton's reagent'.⁸ Fenton's reagent is a mixture of hydrogen peroxide and a reducing agent which acts as an electron donor (equation 3.7). Iron (II) is usually used as the reducing agent, although Hg(II) can be used due to the similarity in redox potentials;⁸ $\text{Fe(II)} \rightarrow \text{Fe(III)} = -0.77 \text{ V}$.



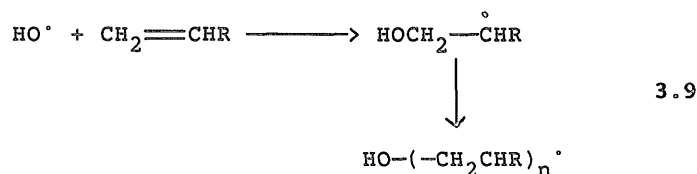
Oxidations involving hydroxy radicals produced by this method fall into two general classes:

- (i) Chain reactions, requiring only traces of reagent, the hydroxy radicals reacting to produce organic radicals;
- (ii) Non-chain reactions, in which oxidation is governed by hydroxy radical attack.

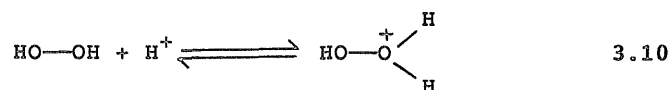
The latter of these is subject to radical loss via the side reaction described by equation 3.8.



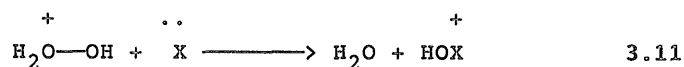
This method of producing hydroxy radicals was widely used in the 1950's to produce long chain alcohols from alkenes (equation 3.19).⁸



Heterolytic fission is only possible in the presence of an acid catalyst. The free oxy-cation, OH^+ , is thermodynamically unfavourable and reaction proceeds via the formation of a hydroperoxy cation.

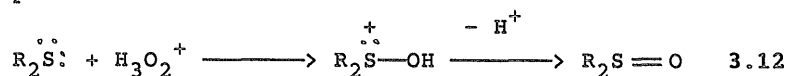


The hydroperoxy cation was proposed by Ross as an intermediate in the hydrogen peroxide oxidation of thiodiglycol.⁹ He observed an increase in rate of oxidation at $\text{pH} \leq 1$. Similar behaviour is reported for the oxidation of p,p-dichlorobenzyl sulphide.¹⁰ Both studies indicate that above this low pH, the equilibrium in equation 3.10 is not present. All heterolytic fission reactions of hydrogen peroxide are bimolecular;⁸ for example

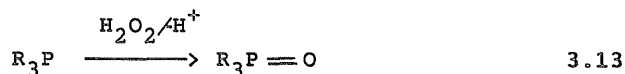


There are numerous examples of this type of oxidation of molecules containing lone pairs of electrons;

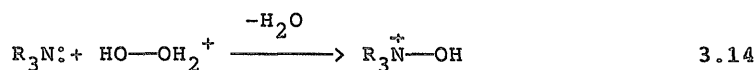
(i) sulphides



(ii) phosphines



(iii) tertiary amines



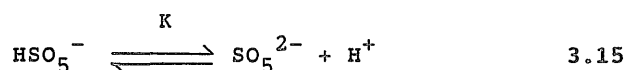
3.3 Peroxosulphates.

3.3(i) Peroxomonosulphate.

At a recent lecture on 'bleaching systems',⁴ the speaker

commented favourably on the commercial applications of peroxomonosulphate, SO_5^{2-} , as a bleaching agent. Indeed, its use in the bleaching of wool has advantages over hydrogen peroxide alone.³ However, for everyday laundry applications it is found to be somewhat aggressive, having detrimental effects on the fabric itself.¹¹

Peroxomonosulphate (PMS) is commercially available as 'Oxone', the triple salt $\text{KHSO}_5 \cdot \text{K}_2\text{SO}_4 \cdot \text{KHSO}_4$, and can be prepared in the laboratory using the method described by Flanagan et al.¹² PMS is a strong oxidant ($E^\circ = +1.82\text{V}$)¹³ and exists in solution as HSO_5^- and SO_5^{2-} according to the equilibrium described by equation 3.15.^{14,15}



The equilibrium has a pK_a of 9.4.¹⁵ Mechanisms of oxidation by PMS have been discussed in terms of direct oxygen atom transfer for aldehyde^{14,15} and metalloprotein¹³ oxidations. The mechanism for PMS oxidation is shown in figure 3.2, and indicates that the oxidation products for the two PMS species are the same. The rate equation for aldehyde oxidation is given by equation 3.16,¹⁵ and holds for oxidations at high pH (where the presence of any corresponding enol is not significant).

$$-\frac{d[\text{PMS}]}{dt} = k_1[\text{Aldehyde}][\text{HSO}_5^-] + k_2K[\text{Aldehyde}][\text{SO}_5^{2-}] \quad 3.16$$

where k_1 is the rate constant for HSO_5^- oxidation,

k_2 is the rate constant for SO_5^{2-} oxidation,

K is the equilibrium constant (equation 3.15)

The PMS oxidation of alkenes proceeds, in the presence of a manganese catalyst, via the formation of a manganese(V) porphyrin complex which acts as an oxygen transfer agent.¹³ The intermediate proposed by Robert and Meunier is shown in figure 3.3 and the rate law is as follows;

Figure 3.2: Mechanism of oxidation of aldehydes by peroxomonosulphate anions in solution.

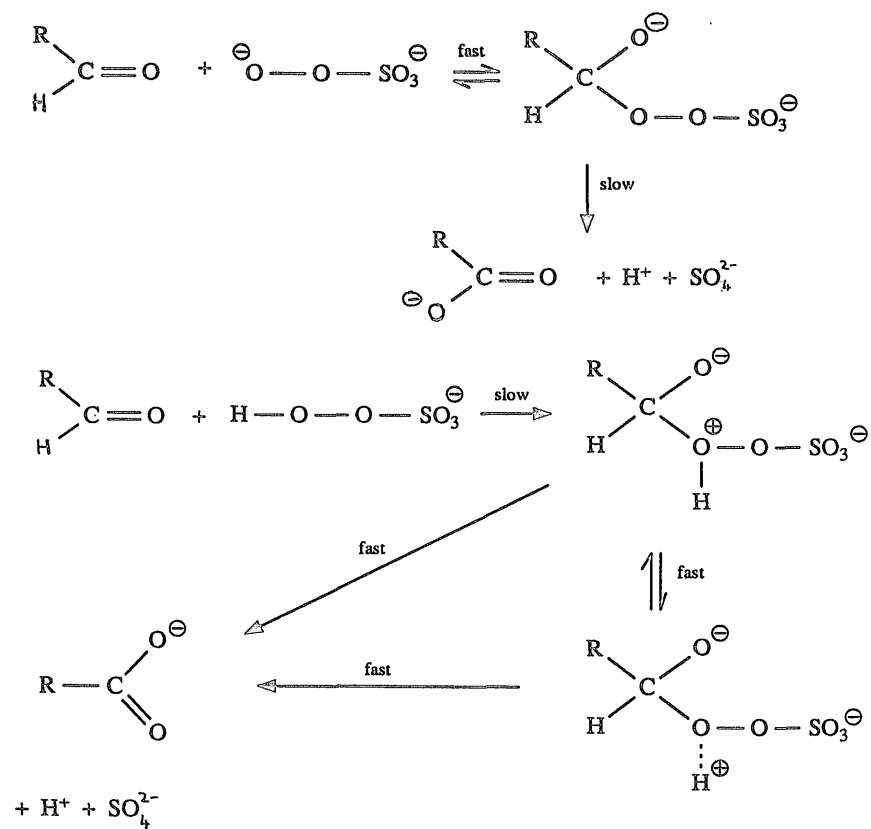
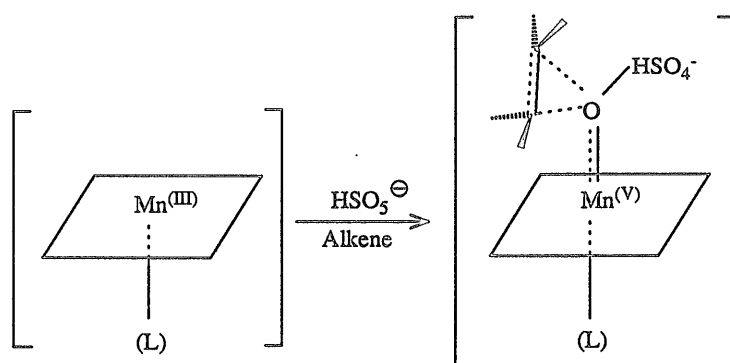


Figure 3.3: Proposed intermediate in the catalytic epoxidation of alkenes by peroxomonosulphate (L = ligand).



$$\frac{d[\text{Alkene}]}{dt} = k[\text{catalyst}] \cdot [\text{alkene}] \cdot [\text{P.T.A.}]^x \quad 3.17$$

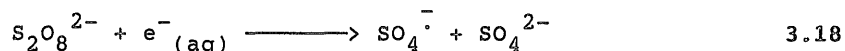
where P.T.A. is a phase transfer agent and $0.1 \leq x \leq 0.24$ at $[\text{catalyst}] = 10^{-4} \text{ mol dm}^{-3}$ and $[\text{alkene}] = 0.25 \text{ mol dm}^{-3}$.

A similar intermediate to that in figure 3.3 is proposed by the same authors for the PMS oxidation of alkanes via insertion of a single oxygen into the R-H bond.

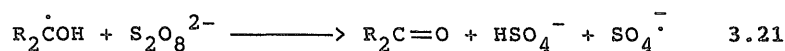
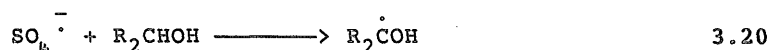
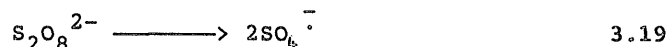
3.3(ii) Peroxodisulphate.

Although peroxodisulphate (PDS), $\text{S}_2\text{O}_8^{2-}$, is a strong oxidant ($E^\circ = +2.01 \text{ V}$) its reactions in solution are very slow, usually requiring the presence of a metal catalyst. Moreover, the only commercial application using peroxodisulphate involves its use in metal etching.

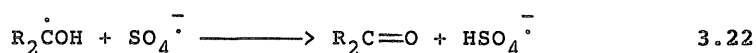
PDS is reduced by electrons derived from radiolysis of water to form the sulphate radical anion, a strongly oxidising species;¹⁶



Another more commonly used method of producing the sulphate radical anion is by direct thermolysis or radiolysis of PDS (however, thermolysis at 298 K is extremely slow). The literature contains many examples of PDS oxidations of organic compounds proceeding via a radical mechanism. An example is contained in a comprehensive review of PDS oxidations by House.¹⁷ He gives the mechanism for PDS oxidations of alcohols in aqueous solutions as follows;



or



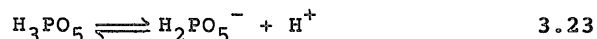
House dismisses any direct attack on the alcohol by PDS, quoting work performed by Kolthoff et al.¹⁸ Here the free radical capture agent, allyl acetate, was added to aqueous solutions of PDS and various alcohols. If PDS directly attacked the alcohol, the addition of allyl acetate would have no effect on the reaction rate. However, a decrease in reaction rate was observed giving evidence for a radical pathway.

Due to the nature of PDS oxidations one would expect variation of pH to have little effect on oxidation rate, due to lack of protonation of the S-O-O-S link. Literature studies of PDS oxidations seldom examine in any detail pH effects and so a brief examination of the effect of pH variation on the PDS oxidation of an organic dye is included in chapter 4.

3.4 Peroxophosphates.

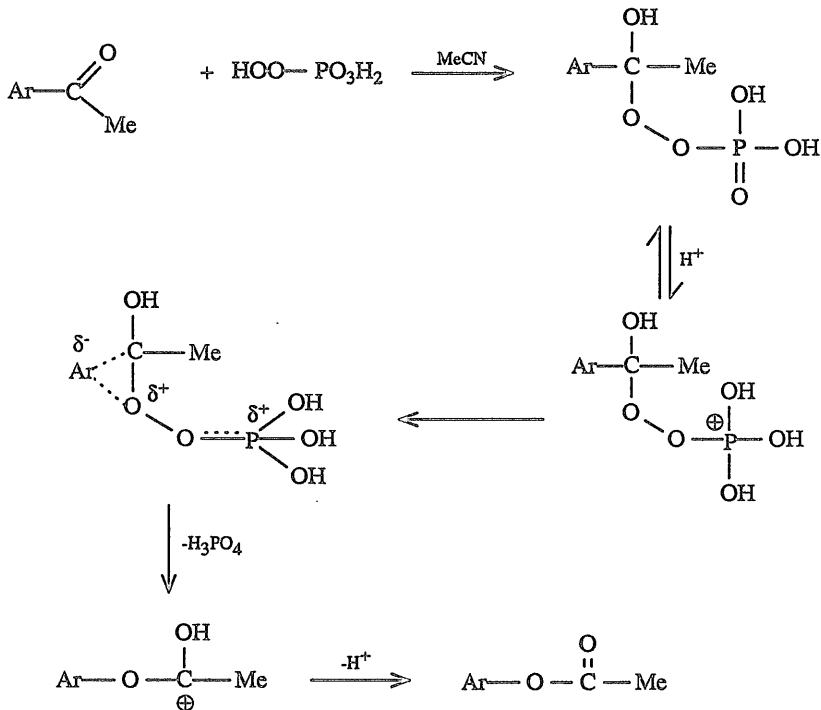
3.4(i) Peroxomonophosphate.

Preparations of peroxomonophosphate (PMP) have been reported since the early methods described by Schmidlin and Massini (1910).¹⁹ In solution, the PMP species exist according to the equilibrium described in equation 3.23.

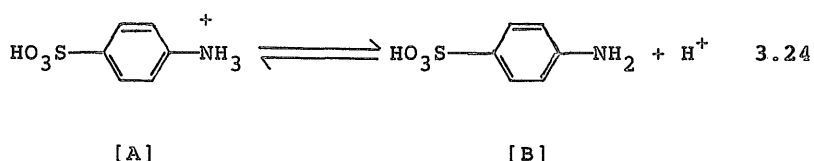


The pK_a of H_3PO_5 is 1.1. PMP oxidations of organic compounds proceed via similar pathways to those of PMS, usually involving single oxygen atom transfer. One recent illustration of PMP oxidation involved the acid catalysed oxidation of acetophenone (figure 3.4),²⁰ the rate being first-order in ketone and PMP.

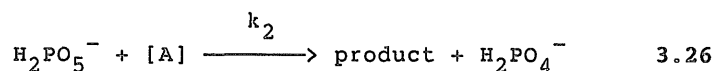
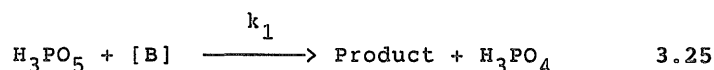
Figure 3.4: Proposed mechanism for the peroxomonophosphate oxidation of acetophenone .



The most recent study of the oxidative properties of PMP is reported by Panigrali and Paichha,²¹ and involves the oxidation of naphthionic acid ($pK_a = 2.81$)²¹. The protonation equilibria is given by equation 3.23.



Hence, the oxidation steps can be written as follows;



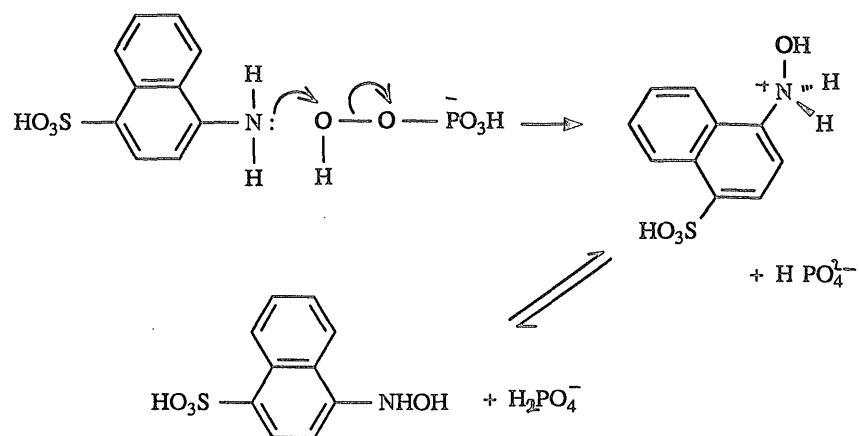
The overall rate of reaction is not informative as both processes produce the same rate law, e.g. $\text{HL}^+ + \text{X}$ gives the same rate law as $\text{L} + \text{HX}^+$.

The mechanism for the oxidation proposed by Panigrali and Paichha is illustrated in figure 3.5. H_2PO_5^- acts initially as a nucleophile, attacking the protonated form of naphthionic acid. Oxidation of the protonated form proceeds via rapid formation of the tetrahedral intermediate, followed by rate limiting decomposition to the amino alcohol. In contrast, the rate limiting step for the oxidation of the unprotonated form by H_3PO_5 involves rate limiting formation of the tetrahedral intermediate.

3.4(ii) Peroxodiphosphate.

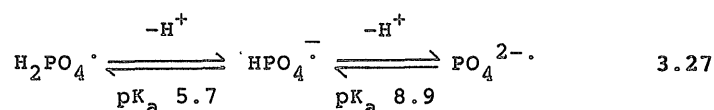
Methods of preparation of peroxodiphosphate (PDP) are again reported in the early study carried out by Schmidlin and Massini¹⁹ and more recently by Kasatkin.²² PDP is another strong oxidant ($E^\circ = 2.07 \text{ V}$).²³ The potassium compound

Figure 3.5: Proposed mechanism for the peroxomonophosphate oxidation for the unprotonated form of naphthionic acid.



contains 4.6% 'active oxygen' and is highly soluble in water (up to 50%).²⁴ The decomposition kinetics of PDP have been studied.²⁵ Catalytic amounts of Mn(II) and Mn(II)/Co(II) accelerate the decomposition, the kinetics being extremely complex.^{26,27}

As with PDS, the majority of PDP oxidations of organic compounds proceed via photolysed or radiolysed radical formation according to the following equilibrium;¹⁶

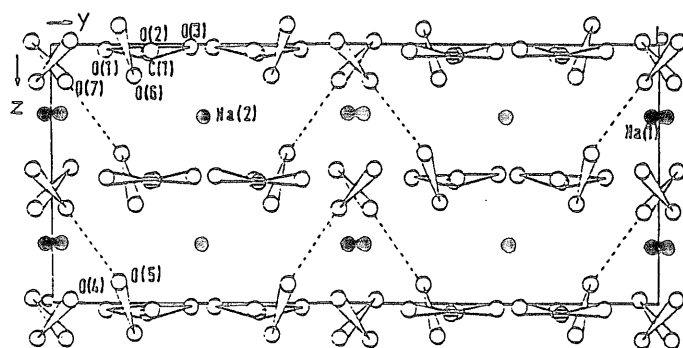


Such reactions are not relevant to the present study.

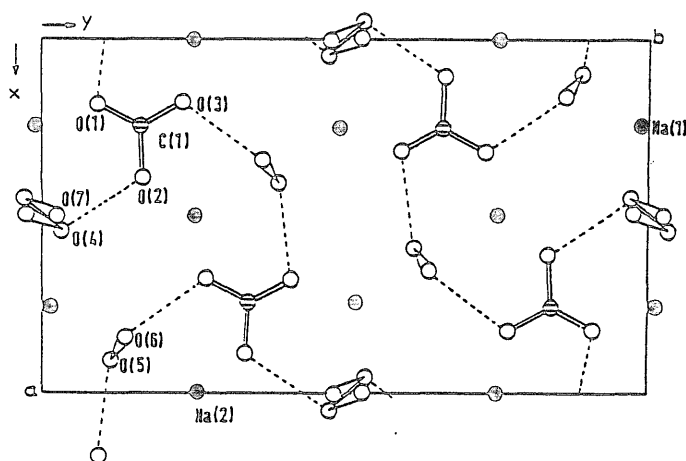
3.5 Percarbonate.

Alkali metal percarbonates have been known for over a century, a preparation being outlined in an 1896 textbook.²⁸ The formulae of percarbonates were often written as $\text{M}_2\text{CO}_4 \cdot n\text{H}_2\text{O}$ until the 1950s when it was argued that percarbonates were simply carbonates with hydrogen peroxide and water of crystallisation.²⁹ Subsequent X-ray crystal structure studies showed this to be the case (figure 3.6),³⁰ with sodium percarbonate having the formula $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$,³⁰ although the existence of $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ has been reported.³¹

General opinion appears to favour percarbonate producing hydrogen peroxide on dissolution.^{30,32,33} Kern stated that there was no evidence for the presence, in significant quantities, of percarbonate in carbonate + hydrogen peroxide solutions under conditions in which perborate + hydrogen peroxide solutions contained perborate. However, a kinetic study of benzil cleavage in water + t-butanol mixtures provided evidence for a carbonate-mediated path.³⁴ Kwart and Wegemer proposed that a rapid equilibrium is established by the carbonate ion in a basic solution of hydrogen peroxide and a percarbonate species (Equation 3.28). The mechanism favoured³⁴ for percarbonate formation involves reversion of



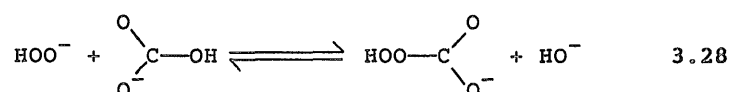
Projection of the structure onto (100). The hydrogen bonding between sheets is shown.



Projection of the structure onto (001), from $z = -0.2$ to $z = +0.3$. The hydrogen bonds in this layer are shown.

Figure 3.6: Crystal structure of sodium percarbonate .

the carbonate ion to CO_2 followed by rate determining nucleophilic attack of the hydroperoxy anion.

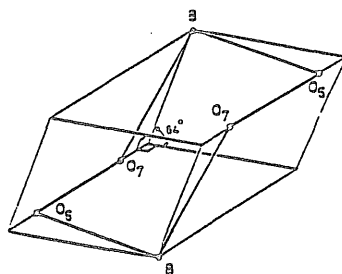
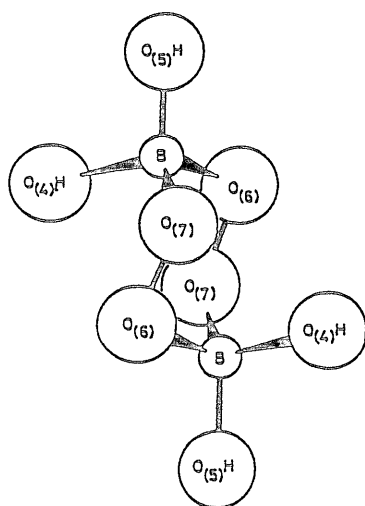


Other kinetic evidence for the existence of percarbonate species in solution involves observations on fresh, ice-cold solutions of electrolytically prepared percarbonates. Such solutions apparently liberate iodine from a solution of potassium iodide more slowly than would be expected if decomposition to hydrogen peroxide were instantaneous.

In general, for the purposes of the study in chapter 4, one may consider the oxidative properties of percarbonate to be that of hydrogen peroxide at the appropriate pH as will be shown by the measurements in section 4.7.

3.6 Perborates.

Perborates have been prepared for most of the alkaline and alkali earth metals; some appear to form several hydrates.³⁵ The only commercially significant perborates are the so-called sodium perborate tetra- and monohydrates. In the solid state, the perborate anion is shown to be binuclear with two peroxo bridges linking the two boron atoms (figure 3.7); the sodium cations are octahedrally co-ordinated by the oxygen of hydrating water molecules.³⁶ The formula of sodium perborate tetrahydrate has been written as $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ but is more accurately represented by $\text{Na}_2[\text{B}_2(\mu\text{-O}_2)_2(\text{OH})_4]^- \cdot 6\text{H}_2\text{O}$. Further X-ray studies have been carried out^{37,38} and they confirm the above. Solid sodium perborate tetrahydrate contains 10.4% 'active oxygen' and its solubility in water is 30 g dm^{-3} at 298 K (giving a solution of pH ca. 10.1).²⁴ At 298 K the saturated solution of sodium perborate tetrahydrate contains 0.23 mol dm^{-3} , here as elsewhere referring to moles of boron.



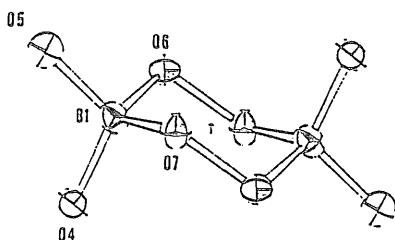
The double peroxo bridge connecting two boron atoms.

Bond distances within the peroxoborate ion.

B - O ₅	1.54 Å
B - O ₆	1.54 Å
B - O ₇	1.52 Å
B - O ₇	1.52 Å
O ₆ - O ₇	1.47 Å

Bond angles within the peroxoborate ion.

O ₅ -B-O ₆	101°
O ₅ -B-O ₇	116°
O ₆ -B-O ₇	115°
O ₅ -B-O ₇	104°
O ₆ -B-O ₇	113°
O ₆ -B-O ₇	108°
B-O ₆ -O ₇	107°
B-O ₇ -O ₆	107°



Structure of the cyclic $[B_2(O_2)_2(OH)_4]^{2-}$ anion. Thermal-vibration ellipsoids are scaled to enclose 50% probability.

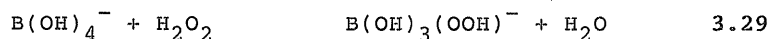
Figure 3.7: Crystal structure of hydrated sodium perborate.

3.6(i) Perborate in aqueous solution.

Whether the di- μ -peroxo structure of figure 3.7 persists in solution was until recently unclear. Some pH and ^{11}B NMR studies suggest that the perborate anion is predominantly mono-nuclear in solution, although the NMR spectra also indicated a binuclear species at high concentrations.^{39,40} However, ^{11}B NMR spectra of calcium perborate solutions were interpreted by Shchetinina et al in terms of a major role for binuclear species.⁴¹ At high concentrations and relatively low pH there were indications of species containing more than one peroxo group; this is in agreement with earlier potentiometric studies.⁴²

Borate (i.e. $\text{B}(\text{OH})_3$) solutions reacted with hydrogen peroxide have been shown to contain significant amounts of perborate.^{43-45,40} Attainment of equilibrium is claimed to be fairly rapid, with the equilibrium constant for the borate/hydrogen peroxide and perborate equilibrium being approximately 30 mol dm^{-3} ; a value of 37 has been derived in later work.⁴³ A recent study of the borate-hydrogen peroxide system, using pH and ^{11}B NMR data and allowing for all possible equilibria,³⁹ has been used to construct an equilibrium/pH diagram (figure 3.8).⁴⁷ As yet, this type of diagram has only been constructed for $T = 298 \text{ K}$ and will be referred to as the 'Pizer-Horvath' diagram.

A study of lithium borate-hydrogen peroxide solutions indicated that borate and hydrogen peroxide are in equilibrium with a perborate species according to equation 3.29;⁴⁸



The standard dissociation constant for the reaction is 25 at 298 K. These studies indicated that the maximum perborate concentration occurred at pH 10.2, over the range $8.5 < \text{pH} < 11.1$ the solutions contained significant amounts of perborate, whilst at a pH lower than 8.5 mononuclear borate

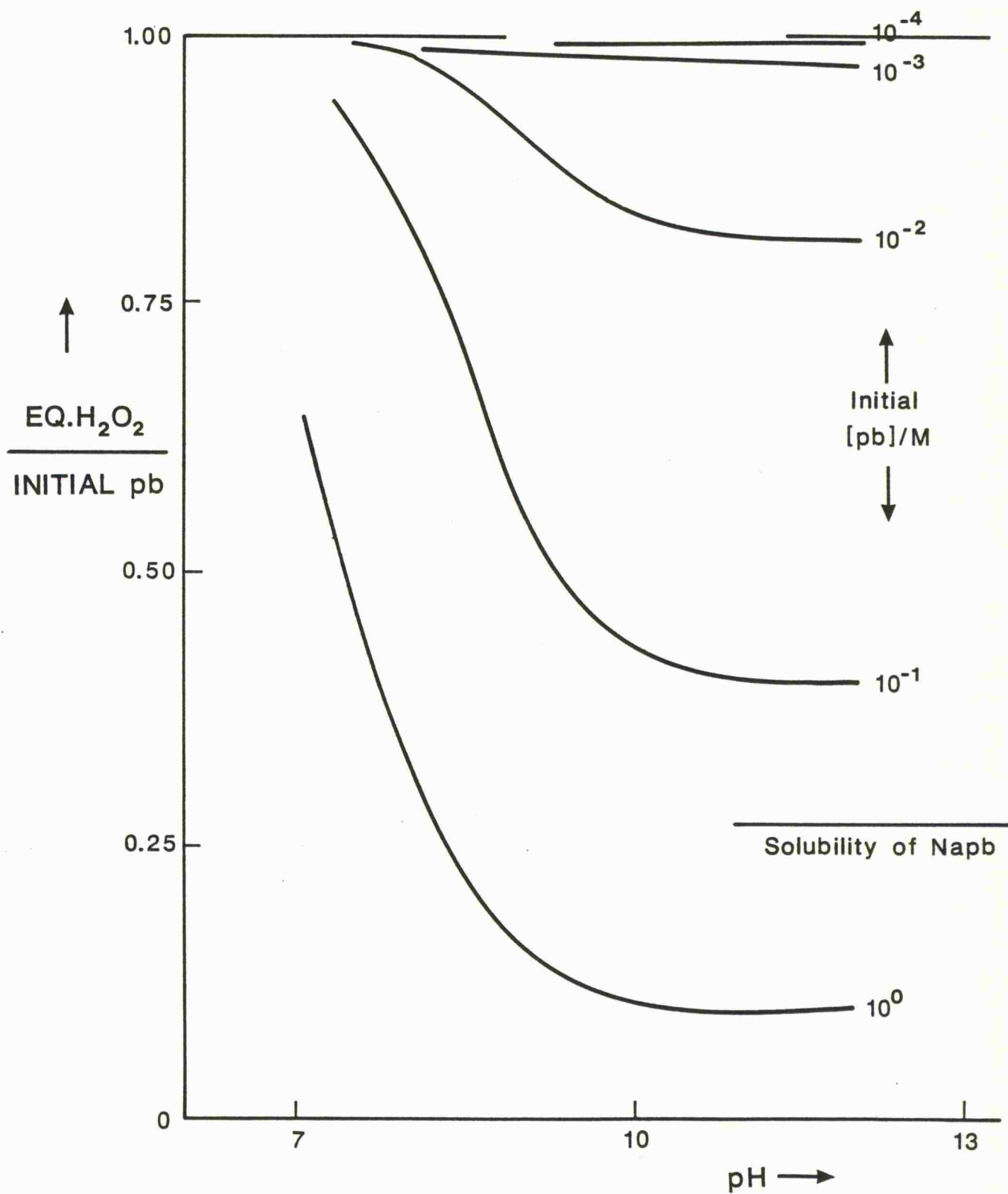


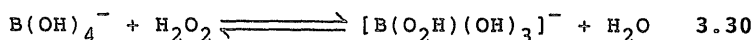
Figure 3.8: Hydrogen peroxide: perborate ratios for equilibrium at 298K, showing a range of initial perborate concentrations - the "Pizer-Horvath" diagram.

is present mainly as boric acid ($pK_a = 9.5$),⁴⁹ which does not interact significantly with hydrogen peroxide. At pH above 11.1, hydrogen peroxide exists as HO_2^- resulting in much reduced perborate formation.⁴⁸

A recent ^{11}B NMR study of the perborate species in aqueous solution appears to confirm the above and provides further information on which borate species predominate under various conditions.⁴⁰ Flanagan et al state that an aqueous solution of the perborate dimer (i.e. 0.1 mol dm^{-3} in moles of boron) produces the same ^{11}B NMR spectrum as a solution containing 0.1 mol dm^{-3} $B(OH)_3$ in 0.1 mol dm^{-3} hydrogen peroxide. This suggests the presence of identical species in both solutions.

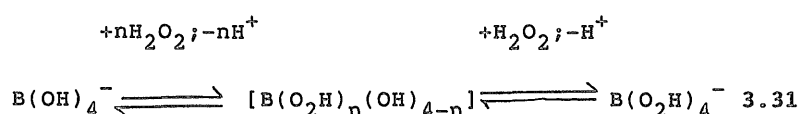
Flanagan et al also obtained further spectra for solutions containing hydrogen peroxide and borate at various concentrations and pHs. The spectra were interpreted as follows:

(i) Low borate, low hydrogen peroxide; At $[Borate] < 0.01 \text{ mol dm}^{-3}$ a rapid equilibrium is established according to equation 3.30



In the absence of hydrogen peroxide, at high pH, a sharp single peak is observed. This is attributed to $B(OH)_4^-$. On addition of hydrogen peroxide the peak is shifted downfield by $HO_2^-/\tilde{O}H$ exchange. This exchange is rapid on the ^{11}B NMR timescale, hence a single peak is observed. As pH decreases the peak broadens somewhat due to the loss of symmetry as the amount of $B(OH)_3$ becomes predominant.

(ii) Low borate, high hydrogen peroxide; At $[Borate]$ of $0.01 - 0.05$ in solutions of up to 34 mol dm^{-3} hydrogen peroxide Flanagan et al observed a number of species and proposed the following equilibrium;



where $n = 1-3$

At high pH, HO^- is present in significant quantities and competes more effectively than HO_2^- , hence B(OH)_4^- is predominant. Decrease in pH leads to exchange between HO^- and HO_2^- , and as the amount of HO^- decreases $\text{HO}_2^-/\text{H}_2\text{O}_2$ become more competitive in the exchange. $\text{HO}_2^-/\text{H}_2\text{O}_2$ are more competitive than water at lower pHs at these high concentrations hence, $\text{B(O}_2\text{H)}_4^-$ is predominant below a pH of 9. $\text{HO}^-/\text{HO}_2^-$ exchange in the tri- and tetra-substituted species is slow on the ^{11}B NMR time scale, leading to two distinct peaks that can be attributed to these species.

(iii) $[\text{Borate}] > 0.1 \text{ mol dm}^{-3}$; At higher concentrations of borate, complexes exist which contain more than one boron per species. These species are mostly bi-nuclear and Flanagan et al appear not to have observed the trimer for which Edwards offers evidence in an earlier study.⁴⁴

Comparisons were made between the ^{11}B NMR spectrum of 0.1 mol dm^{-3} borate in 1.0 mol dm^{-3} hydrogen peroxide and the raman/pH titration study performed by Pizer and Tihal for an identical solution.³⁹ The ^{11}B NMR spectrum of this solution contained a peak which was assigned to the species in equation 3.30, and also a peak assigned to the species $\text{B(O}_2\text{H)}_2(\text{OH)}_2^-$. Pizer and Tihal proposed that, between a pH of 8-13 and at the above concentrations of borate and hydrogen peroxide, the main perborate species present were $\text{B(O}_2\text{H)}(\text{OH)}_3^-$ and $\text{B(O}_2\text{H)}_2(\text{OH)}_2^-$. The study by Flanagan et al appears to confirm this.

As will be seen, the kinetic study presented in the following chapter details perborate oxidations at $[\text{Borate}] \leq 0.1 \text{ mol dm}^{-3}$, at pHs usually above 9.0 and without excess

hydrogen peroxide. Taking into account both the ^{11}B NMR and raman/pH studies,^{40,39} and considering the observations made by Edwards and Kern,^{44,45} it is clear that the species present under these conditions will be the mono-nuclear $\text{B}(\text{O}_2\text{H})(\text{OH})_3^-$ and associated equilibria species. However, if the concentration of borate is increased past 0.1 mol dm^{-3} , one must take into account poly-nuclear species and indeed, in excess peroxide various amounts of the di-hydroperoxo substituted borate will also be present.

A number of publications provide indirect data on the decomposition kinetics of perborate,⁵⁰⁻⁵³ and these data are summarised in table 3.1. The table shows that added MgSO_4 , NiSO_4 and ZnSO_4 retard perborate decomposition, whilst MnSO_4 and CoSO_4 have marked accelerating effects. The kinetics of decomposition are first order in perborate over the first half-life, but deviate significantly as the decomposition progresses. It has been possible to estimate dependencies of rate constant on temperature from references 50 to 52 leading to the Arrhenius plot illustrated in figure 3.9; the rate constants are summarised in table 3.2.

As is the case for some other peroxo anions, little information is available on the oxidative properties of perborate with regard to organic substrates in aqueous solutions. However, it seems likely that such reactions proceed via perborate, or liberated hydrogen peroxide, single oxygen atom transfer. Some suggestions that the oxidising species is in fact singlet oxygen, $^1\text{O}_2$, can be discounted as a result of the study conducted by Becker.⁵⁴ Indeed, an earlier study indicates that the breaking of the peroxo- bridge to produce $^1\text{O}_2$ would not be expected to be significant below 373K.⁵⁵

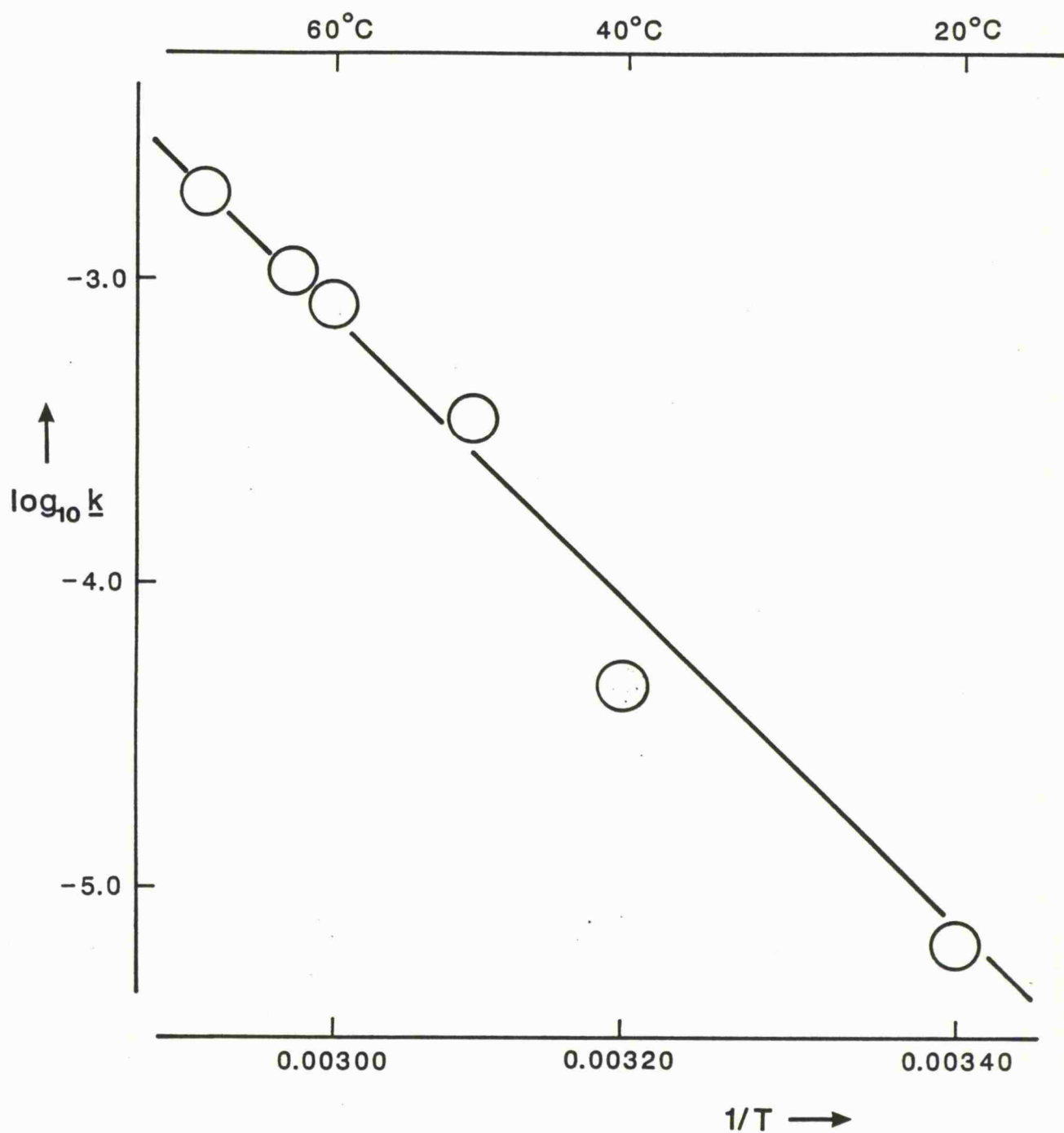


Figure 3.9: Arrhenius plot for decomposition of perborate in aqueous solution over the temperature range $293 \leq T/K \leq 343$.

Table 3.1: First-order rate constants for perborate decomposition in aqueous solution in the presence of various additives at 313 K.

Added Salt	[Added Salt] ^b	$\tau_{1/2}/\text{min}$	$10^5 k/\text{s}^{-1}$
		290	4.1
$\text{Al}_2(\text{SO}_4)_3$	0.01	300	3.9
MgSO_4	0.01	480	2.4
MnSO_4	0.0001	194	5.9
	0.001	60	19.2
FeSO_4	0.0001	165	7.0
	0.001	142	8.1
	0.01	71	16.2
	0.1	38	30.3
CoSO_4	0.01	13 ^c	88.0
NiSO_4	0.01	2735	0.4
CuSO_4	0.01	150	7.7
ZnSO_4	0.01	4270	0.3

^a For first half-life; initial [perborate] = 0.26 mol dm^{-3} of boron.

^b In weight percent.

^c Erratic dependence of k on $[\text{CoSO}_4]$

Table 3.2: Published and estimated rate constants for
perborate decomposition in aqueous solution.

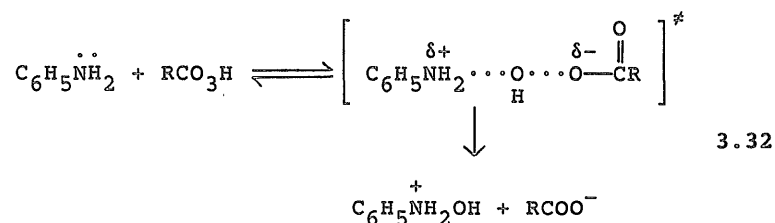
Temperature/K	Rate Constant/s ⁻¹	Note
293	6.1×10^{-6}	a
313	4.1×10^{-5}	ref.51
323	3.8×10^{-4}	a
333	8.0×10^{-4}	ref.52
333	8.4×10^{-4}	ref.53
333	9.0×10^{-4}	a
336	1.2×10^{-3}	a
343	2.0×10^{-3}	a

a These values have been estimated from results expressed in terms of percentage decomposition, half-lives, etc. from reference 50.

3.7 Organic peroxoanions.

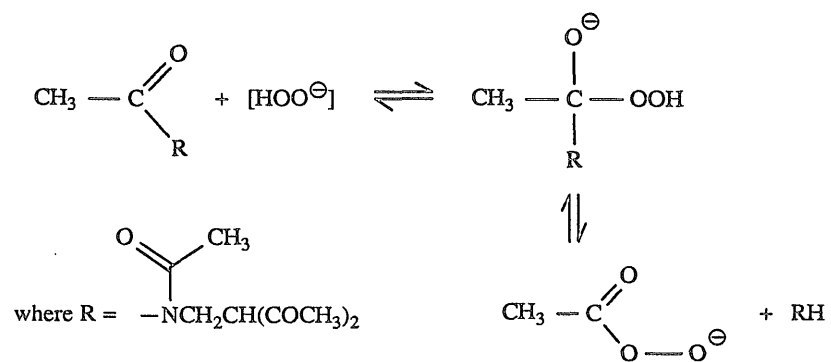
During the 1950's simple peroxo carboxylates were claimed to give high bleaching performance⁵⁶ and are still used as such in some areas today.⁴ Indeed, recent work has highlighted percarboxylate oxidations of iron(III) and chromium(III) porphyrin derivatives.⁵⁷ Of particular relevance to the kinetic study in chapter 4 is the observation by Becker that peracetic acid is liberated from a solution of perborate and TAED (N,N,N',N' - tetraacetyl ethylenediamine),⁵⁴ according to figure 3.10. TAED and other similar compounds are referred to as 'activators'. This is perhaps a little misleading as no activation of a perborate species, to produce an oxidising borate moiety, takes place. Section 4.4 details some kinetic results for the oxidation of organic dyes by solutions of perborate and TAED.

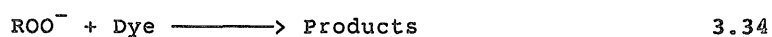
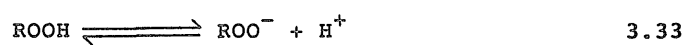
As with other inorganic peroxides, there are examples of percarboxylates oxidising via single oxygen atom transfer. The percarboxylate oxidation of aniline (equation 3.32) is a simple illustration of such an oxidation via an S_N2 transition state.



The oxidation of amaranth by (substituted) peroxybenzoates has been studied by Jones and Davies.⁵⁸ It is interesting to note that the repeat scan spectra for the oxidation of amaranth by m-chloroperoxybenzoic acid shows a sharp isosbestic point in contrast to those presented for the perborate oxidation in chapter 4. Jones and Davies conclude that the oxidation proceeds via nucleophilic attack by the peroxybenzoate anion on the unionised dye (equations 3.33 and 3.34). Products of oxidation absorb less in the UV/visible region of the spectra, which is probably due to attack at or near the nitrogen-nitrogen bond.⁵⁸

Figure 3.10: Mechanism of liberation of peracetic acid from a solution of TAED and perborate.





where $\text{R} = \text{C}_6\text{H}_4\text{R}'\text{-CO-}$ and $\text{R}' = \text{H}$, substituent group.

The rate of reaction is first order in both $[\text{dye}]$ and $[\text{ROO}^-]$. The rate of oxidation of amaranth is greatest at the pK_a of the peroxybenzoate species, values of pK_a for some substituted peroxybenzoates are give in table 3.3. ⁵⁹

Although, in general, percarboxylate oxidations of organic substrates in aqueous solution under normal conditions proceed via single oxygen atom transfer there is evidence to suggest alternative behaviour. A recent kinetic study indicates that diperoxydodecanoic acid (DPDDA), $\text{HO}_3\text{C}(\text{CH}_2)_{10}\text{CO}_3\text{H}$, oxidises 1,3-diphenylisobenzofuran via the formation of singlet oxygen.³⁷ The yield of $^1\text{O}_2$, observed as a result of DPDDA decomposition, was 88.3% at 298K.

Table 3.3: Some values of observed rate constant, k_{obs} , for oxidation of amaranth and erythrosin by substituted peroxybenzoate, $\text{C}_6\text{H}_4\text{R}'\text{CO}_3\text{H}$, at 298K. Ionic strength is 0.1 mol dm^{-3} using NaNO_3 as added electrolyte (after reference 59).

Substituent, r'	pK_a	Amaranth $k_{\text{obs}}/\text{s}^{-1}$	Erythrosin $k_{\text{obs}}/\text{s}^{-1}$
p-ome-	7.93	0.108	0.320
h-	7.64	0.156	0.242
p-Cl-	7.60	0.132	0.268
p-SO ₃ -	7.56	0.088	—
m-Cl-	7.53	0.206	0.295
m-NO ₂ -	7.23	0.161	0.235
o-CO ₂ -	7.14	0.142	0.267

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Chapter 4

Kinetics of reactions involving perborate ions in aqueous solutions.

4.1 Introduction.

Information on the kinetics and reactivity of sodium perborate tetrahydrate (perborate) is limited, as is information on its structure in solution. This lack of information comes as a surprise when one considers that perborate has been a major component of domestic and commercial laundry products for most of the present century, to the extent of figuring in some common brand names; e.g. 'Persil' is derived from the words perborate and silicate.¹

The kinetic study presented here provides information on the oxidation of some model organic dyes and real stains by perborate. A comparison is drawn with hydrogen peroxide and sodium percarbonate, and a brief comment on the effect of pH on oxidations involving peroxodisulphate is made. Most of the data presented involve oxidations of bromophenol blue, amaranth and erythrosin, but some limited information has been obtained for other organic substrates.

4.2 Experimental.

A cell of path length 1.0 cm containing a solution of the peroxo compound, buffers and any other additives was placed in the cell holder of a computer controlled spectrophotometer (either Pye-Unicam SP1800 or Hewlett-Packard HP8451A) and allowed to attain thermal equilibrium over a few minutes to the required temperature. To this solution was added one drop of concentrated dye solution such that the initial absorbance was approximately 1.0. The reaction was monitored over 2.5 half lives.

In order to minimise the decomposition of perborate to hydrogen peroxide prior to kinetic study solutions of perborate were used while 'fresh' (i.e. age of solution < 30 minutes). The decomposition half-life of aqueous perborate is approximately one day at 298 K (section 3.6). Measurements of pH were carried out using a WPA CD620 digital pH meter to an accuracy of ± 0.005 pH unit. Absorbance/time data were

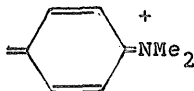
analysed as outlined in chapter 2.

4.3 Organic dyes and real stains.

Initial kinetic runs involved the perborate oxidation of amaranth and erythrosin-B, the repeat scan spectra being shown in figures 4.1a and 4.1b. Both dyes are permitted food colourants,² and were used in a study on the oxidative properties of (substituted) peroxybenzoates (section 3.7).³ Perborate oxidation of amaranth and erythrosin-B proceeded at reasonable rates at temperatures of 313 K and above, although the rates at 298 K were particularly slow. Hence, kinetic studies involving three other dyes were carried out; malachite green, crystal violet and bromophenol blue. The first two of these reacted extremely rapidly with perborate, even in dilute solution ($0.001 \text{ mol dm}^{-3}$). However, bromophenol blue oxidations proceeded at a convenient rate for kinetic observations and was therefore selected for extensive study at 298 K. The structure of these dyes and others used in the study are shown in figure 4.2. Throughout this study, reference will be made to the poor kinetic behaviour of amaranth when oxidised. Amaranth is an azo dye and as such stands apart from the other dyes used in the study, which are quinonoids or their analogue derivatives (1 and 2). The reason for the poor kinetics may be due to some further step in the dye oxidation or the presence of other isomers in the sample.



1



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Natural colourants and stains are generally mixtures of compounds and are, as a result, less amenable to kinetic study than model organic dyes. Nonetheless, kinetics were obtained for some of these colourants. Tea and coffee proved difficult systems from which to obtain kinetic information,

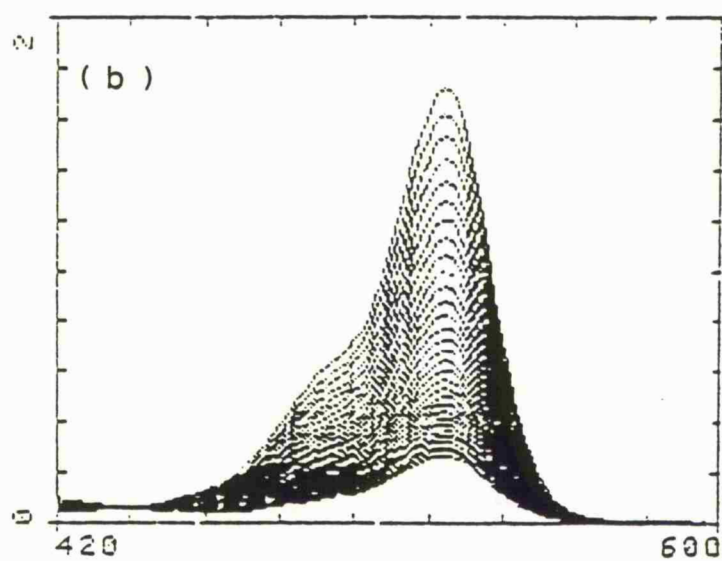
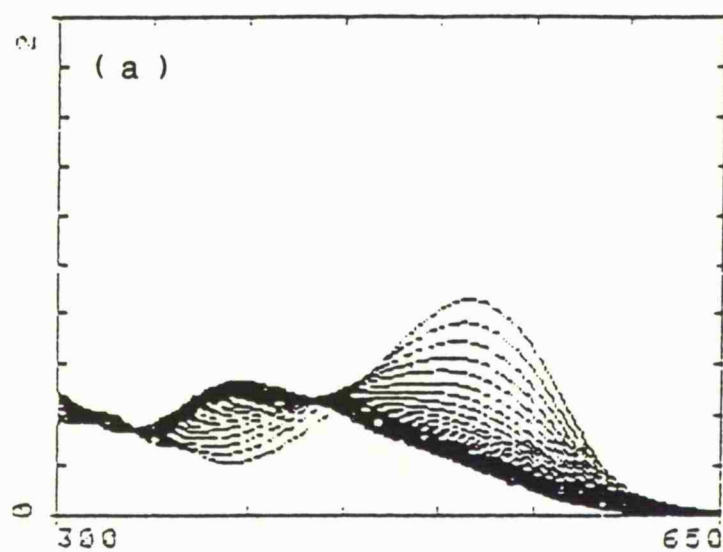
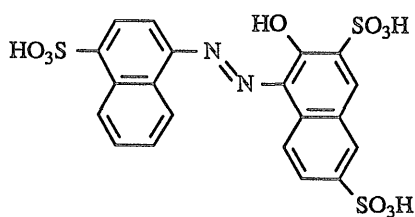
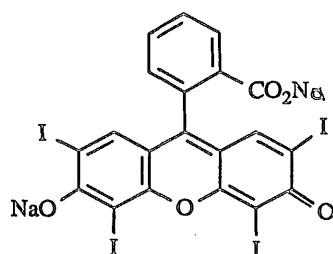


Figure 4.1: Repeat scan spectra for perborate oxidation of a) amaranth and b) erythrosin B.

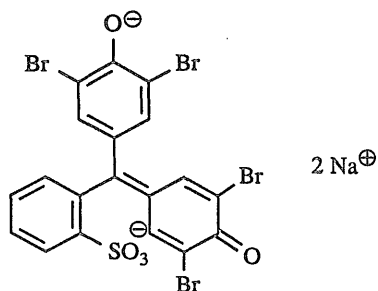
Figure 4.2: Structural formulae and λ_{max} of organic dyes used in peroxyanion kinetic study.



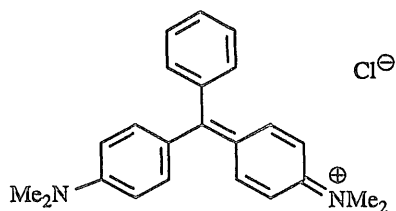
Amaranth ($\lambda_{\text{max}} = 522 \text{ nm}$)



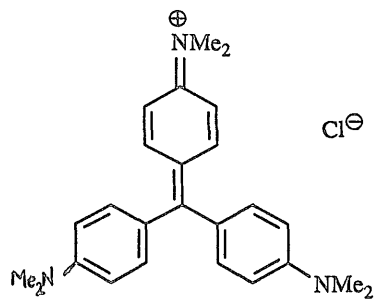
Erythrosin-B ($\lambda_{\text{max}} = 524 \text{ nm}$)



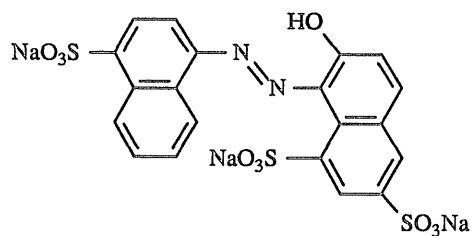
Bromophenol blue ($\lambda_{\text{max}} = 590 \text{ nm}$)



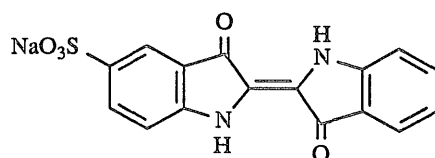
Malachite green ($\lambda_{\text{max}} = 617 \text{ nm}$)



Crystal violet ($\lambda_{\text{max}} = 588 \text{ nm}$)



New coccine ($\lambda_{\text{max}} = 506 \text{ nm}$)



Indigo carmine ($\lambda_{\text{max}} = 608 \text{ nm}$)

however some herbal teas proved suitable for limited study. Information is available on the compounds in red wine.^{4,5} The wine used in this study had an absorbance centred about $\lambda_{\max} = 516\text{nm}$ at pH 3.6 and $\lambda_{\max} = 582\text{nm}$ at pH 8.93. The red/purple constituents (anthocyanins) were bleached more rapidly by perborate than the brown (tannins). Blackcurrant juice ($\lambda_{\max} = 514\text{nm}$) gave surprisingly good kinetics in individual runs but suffers from the lack of reproducibility.

4.4 Perborate.

Table 4.1 compares observed rate constants, $k_{\text{obs}}/\text{s}^{-1}$, for the oxidation of dyes and stains by aqueous solutions of unbuffered sodium perborate, where $[\text{perborate}] = 0.01 \text{ mol dm}^{-3}$ and $\text{pH} \approx 10.1$. Table 4.2 reports the approximate time for 80% oxidation of the dye in aqueous solutions of 0.1 mol dm^{-3} sodium perborate, again $\text{pH} \approx 10.1$.

4.4(i) Order in substrate.

The perborate oxidations of organic dyes, with perborate present in excess, generally produced good first-order kinetics. Plots of $\ln\{(P_0 - P_\infty)/(P_t - P_\infty)\}$ vs. time/s yielded straight lines over 2.5 half-lives. Bromophenol blue and erythrosin-B exhibited good first order kinetics, readings for amaranth (especially at high pH) were slightly scattered. Oxidations of amaranth, red wine and blackcurrant juice show small but significant induction periods. It is interesting to note that in the repeat scan spectra for amaranth (figure 4.1a) the 'crossover point' covers a significant area rather than having a sharp isosbestic point. This observation is in contrast to the behaviour noted for percarboxylate oxidation of amaranth by Davies and Jones.³ No induction period was observed for bromophenol blue, crystal violet or malachite green. The fact that no induction period is present in the kinetics for these dyes indicates that this effect is probably not due to perborate. New coccine oxidations by sodium perborate showed two-stage kinetics. Whether this may have been due either to the presence of other isomers or some consecutive reaction involving impurities is undetermined at this stage.

Table 4.1: Rate constants, $k_{\text{obs}}/\text{s}^{-1}$, for the oxidation of real stains and model dyes in aqueous solutions of $0.010 \text{ mol dm}^{-3}$ perborate at various temperatures ($\text{pH}(298 \text{ K}) = 10.1$)

Substrate	$k_{\text{obs}}/\text{s}^{-1}$		
	298 K	303 K	318 K
Herbal Tea	$\sim 10^{-4}$	—	—
Red Wine	$5.6 \times 10^{-3\text{a}}$	$8.1 \times 10^{-3\text{a}}$	$2.2 \times 10^{-2\text{a}}$ 2.5×10^{-4}
Blackcurrant Juice	—	—	Too slow to measure
Bromophenol Blue	3.1×10^{-4}	—	—
Malachite Green Crystal Violet	$> 5 \times 10^{-2}$	—	—
Erythrosin-B ^b	1.1×10^{-4}	—	—

^a $[\text{Perborate}] = 0.067 \text{ mol dm}^{-3}$

^b $[\text{Perborate}] = 1.0 \text{ mol dm}^{-3}$

Table 4.2: Approximate time for 80% oxidation of real stains

by 0.1 mol dm^{-3} perborate (pH 10.1).

	298 K	303 K	318 K
Red Wine		2 hours ^a	
Blackcurrant		> 24 hours	20 mins
Herbal Tea	5 hours		

^a For first stage.

4.4(ii) Order in perborate.

Initial kinetic studies suggested that oxidation of amaranth is first-order in initial added perborate (Table 4.3). Erythrosin-B, at comparable concentrations ($0.01\text{--}0.04\text{ mol dm}^{-3}$), showed peculiar kinetics. This can be attributed to the time factor involved in monitoring the oxidation at these low concentrations. Even at a concentration of 0.04 mol dm^{-3} , a kinetic run spanned several hours. During this time, the perborate in solution decomposed to hydrogen peroxide, which is less reactive to erythrosin-B than perborate, making an assignment of order difficult at these concentrations. Erythrosin-B was oxidised at reasonable rates at $[\text{perborate}] > 0.1\text{ mol dm}^{-3}$. However, due to the presence of polynuclear borate species (section 3.6) and solubility problems above 0.1 mol dm^{-3} the study was limited to a perborate concentration of 0.1 mol dm^{-3} or less. Further experiments using 'fresh' perborate solutions and careful pH control indicated that the oxidation of bromophenol blue is essentially first-order in perborate. The dependence of $k_{\text{obs}}/\text{s}^{-1}$ on $[\text{perborate}]$ is illustrated in figure 4.3. Added chloride and sulphate were used to maintain ionic strength. These anions do not significantly affect the pH and are unlikely to affect the reactivity. Also included in figure 4.3 is the dependence of k_{obs} on $[\text{perborate}]$ in the absence of added salt; i.e. ionic strength increasing with increase in $[\text{perborate}]$.

4.4(iii) Effect of pH and added anions.

One might expect that the effect of pH and added anions would be difficult to quantify due to the fact that pH control is by virtue of adding co-solutes to the solution. Once added there are possible interactions with perborate, liberated hydrogen peroxide from initial perborate hydrolysis, or indeed the dye or stain. However, for perborate (as for hydrogen peroxide) pH effects are dominant, the nature of added anion having little or no effect. Hence it is possible to produce a pH/rate profile of the type illustrated in figure 4.4.

Table 4.3: Dependence of $k_{\text{obs}}/\text{s}^{-1}$ on $[\text{perborate}]/\text{mol dm}^{-3}$ for oxidation of amaranth in aqueous solution of pH 10 $\pm$ 0.1 at 298 K.

$[\text{Perborate}]^{\text{a}}/\text{mol dm}^{-3}$	$k_{\text{obs}}/\text{s}^{-1}$
0.010	4.45×10^{-4}
0.020	1.01×10^{-3}
0.040	2.28×10^{-3}

^a The value for perborate concentration corresponds to the amount of perborate weighed out initially. In solution the actual concentration of perborate will be less than this value due to the equilibrium with hydrogen peroxide (see chapter 3.6; figure 3.8)

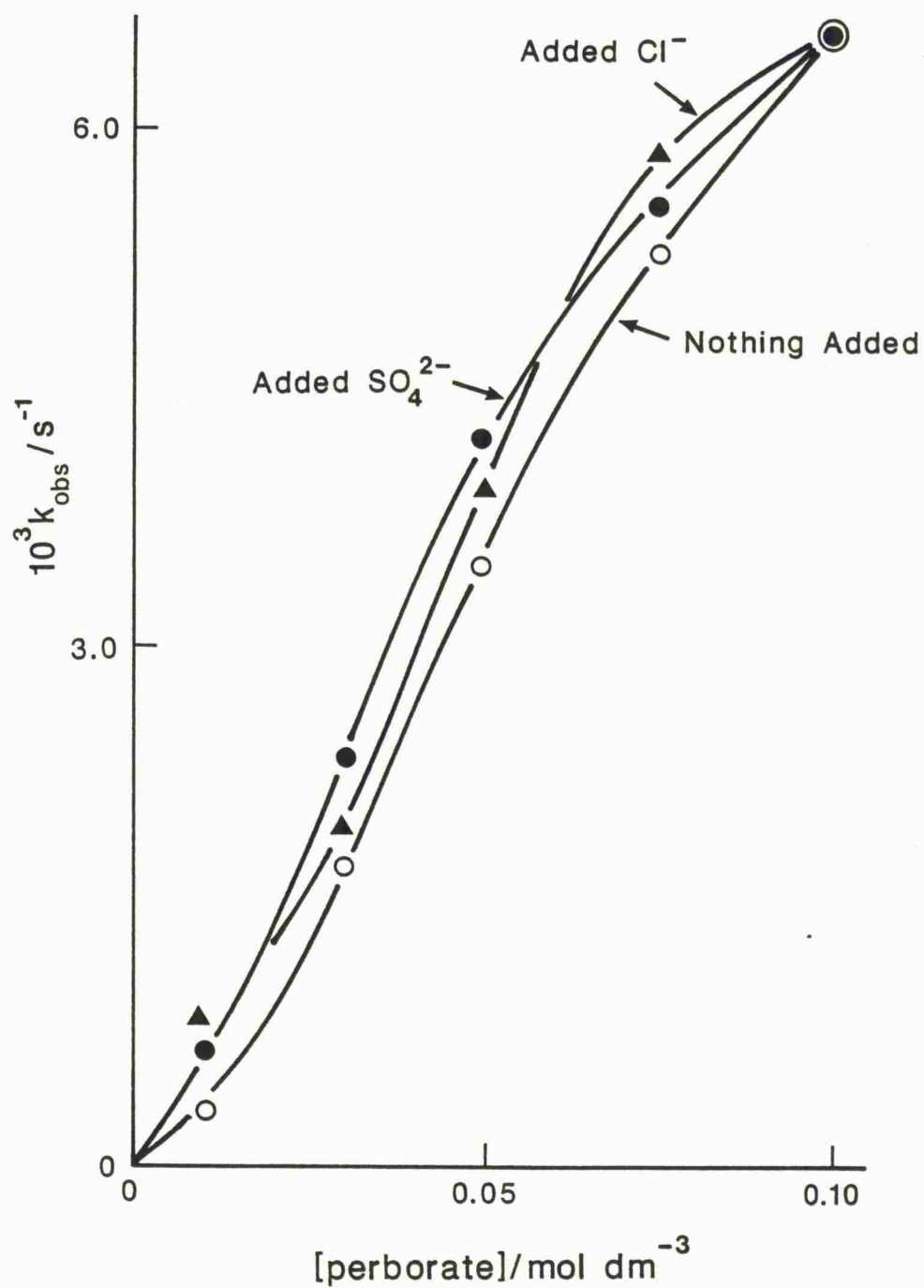
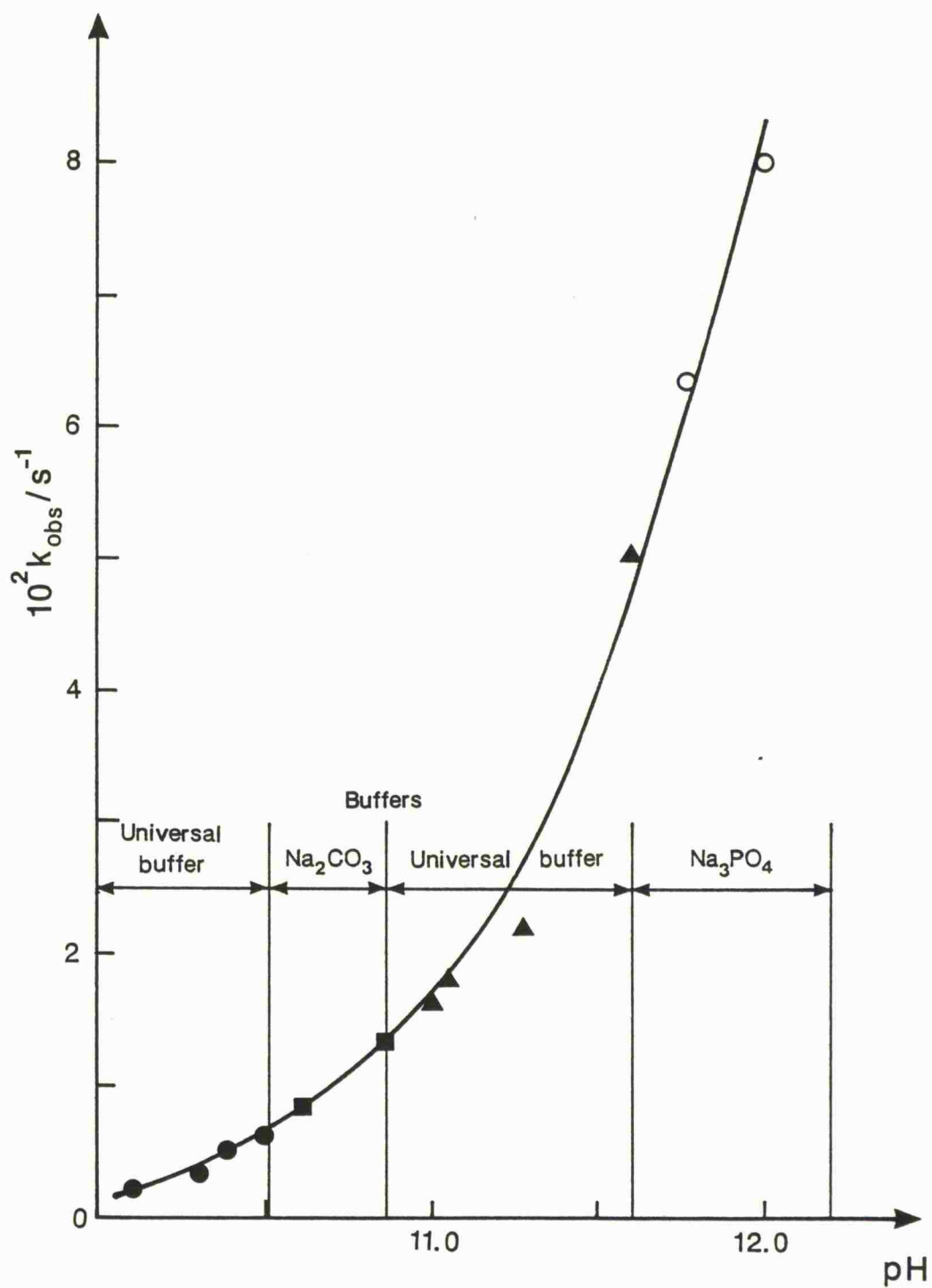


Figure 4.3: Dependence of observed rate constants for perborate oxidation of bromophenol blue on [perborate] at 298K and pH10; ● = added SO₄²⁻, ▲ = added Cl⁻, ○ = nothing added.



In the studies on the effect of added anions, the pH was carefully controlled, because the rate is subject to large variation with small variation in pH, especially at high pH values. Added sulphate and chloride have little effect on rate constant or pH; figure 4.3. Effects of added carbonate can be probed as the pH of a solution of perborate and 0.025 mol dm⁻³ sodium carbonate/ sodium bicarbonate has the same pH as an unbuffered solution of perborate. Table 4.4 shows that the carbonate/bicarbonate buffer has a small inhibiting effect on perborate oxidation of the dyes amaranth and erythrosin-B. Comparisons at higher concentrations of carbonate/bicarbonate were not possible due to the associated increase in pH. Comparable increases in pH were obtained when E100 silicate is added to solutions of perborate; Table 4.5 indicates that the effect of added carbonate and silicate are similar, the results for the silicate system further supporting the assignment of a first-order dependence on [perborate] for oxidation of bromophenol blue. Erratic increases in rate constant with increase in [perborate] may indicate some specific interaction or may have been the result of inadequate pH control. Isolated results on erythrosin-B and bromophenol blue indicate that added phosphate also has a small retarding effect.

4.4(iv) Effect of age of solution on rate of oxidation.

Studies on variation of rate constant with increase in age of solution showed an interesting trend.⁶ Rate constants for oxidation of bromophenol blue and new coccine decreased with increase in age of solution. The rate constant for oxidation of these dyes by a solution of perborate, several hours old, was normally in the region of 20% less except when silicate or phosphate buffers were added to the stock solution. This effect can be attributed to the decomposition of liberated hydrogen peroxide in the perborate solution. The half-life for decomposition of perborate at 298 K is approximately 32 hours (see figure 3.9). Hence the probable cause of this decomposition is the presence of trace metal ions, which are effectively sequestered when phosphate and silicate are added to the stock solution.

Table 4.4: Effect of added sodium carbonate/bicarbonate (0.025 mol dm⁻³ of each component) on the perborate oxidation of amaranth and erythrosin at 298 K ([perborate] = 0.1 mol dm⁻³, pH = 10)

substrate	$k_{\text{obs}}/\text{s}^{-1}$	
	No additive	added carbonate/ bicarbonate
Amaranth	4.5×10^{-3}	3.2×10^{-3}
Erythrosin-B	8.9×10^{-5}	6.8×10^{-5}

Table 4.5: Effect of added sodium carbonate/bicarbonate and silicate on perborate oxidation of bromophenol blue in aqueous solution at 298 K and pH 10.7 to 11.0.

[Perborate]/mol dm ⁻³	10 ³ k _{obs} /s ⁻¹	
	carbonate/bicarbonate ^a	Silicate ^b
0.010	7.0	5.3
0.025	11.0	11.0
0.050	13.0	17.0

^a Concentration of carbonate/bicarbonate buffer is such as to bring the total anion concentration to 0.1 mol dm⁻³.

^b 0.01 cm³ of E100 silicate per 25 cm³ of solution in each case.

4.4(v) Effect of added metal ions.

There has been much interest in the effects of added metal ions on perborate oxidation. Detailed kinetic investigation was not possible due to the nature of the effects of added metal ions. However, simple visual tests were carried out using a number of metal ions in both significant (0.01 mol dm^{-3}) and trace ($0.0001 \text{ mol dm}^{-3}$) amounts added to solutions containing perborate and bromophenol blue. At higher $[M^{n+}]$, all transition metal ions tested gave precipitates (probably the hydroxide), whilst Mg^{2+} and Zn^{2+} had no visible effect on reaction rate. In trace amounts, addition of metal ions to perborate solutions either had no visible effect, or retarded the oxidation (notably $Cu(II)$). Catalytic acceleration of perborate/hydrogen peroxide decomposition was observed in the solutions containing transition metal ions.

4.4(vi) Activation parameters.

Table 4.6 details rate constants as a function of temperature for the perborate oxidation of three dyes at various concentrations and pH. Included in the table are calculated activation parameters for the oxidations. Figure 4.5 is an example of an Arrhenius plot obtained from the kinetic data using second-order rate constants.

Closer examination of the temperature dependence reveals a general curvature, the value of k_{obs} showing less of an increase on successive increases in temperature. The rather large errors in $\Delta H^\ddagger$ make detailed comparisons of these values difficult as they are statistically similar. If one considers the change in composition of the perborate solution with temperature one realises that a solution of perborate at 298 K has a different perborate to free hydrogen peroxide ratio to a similar solution at, say, 338 K due to enhanced perborate hydrolysis. Changes in pH over the temperature range must also be considered. These factors render activation parameters obtained by this method of little informative value.

Studies to determine the activation volumes, $\Delta^\ddagger V$, for

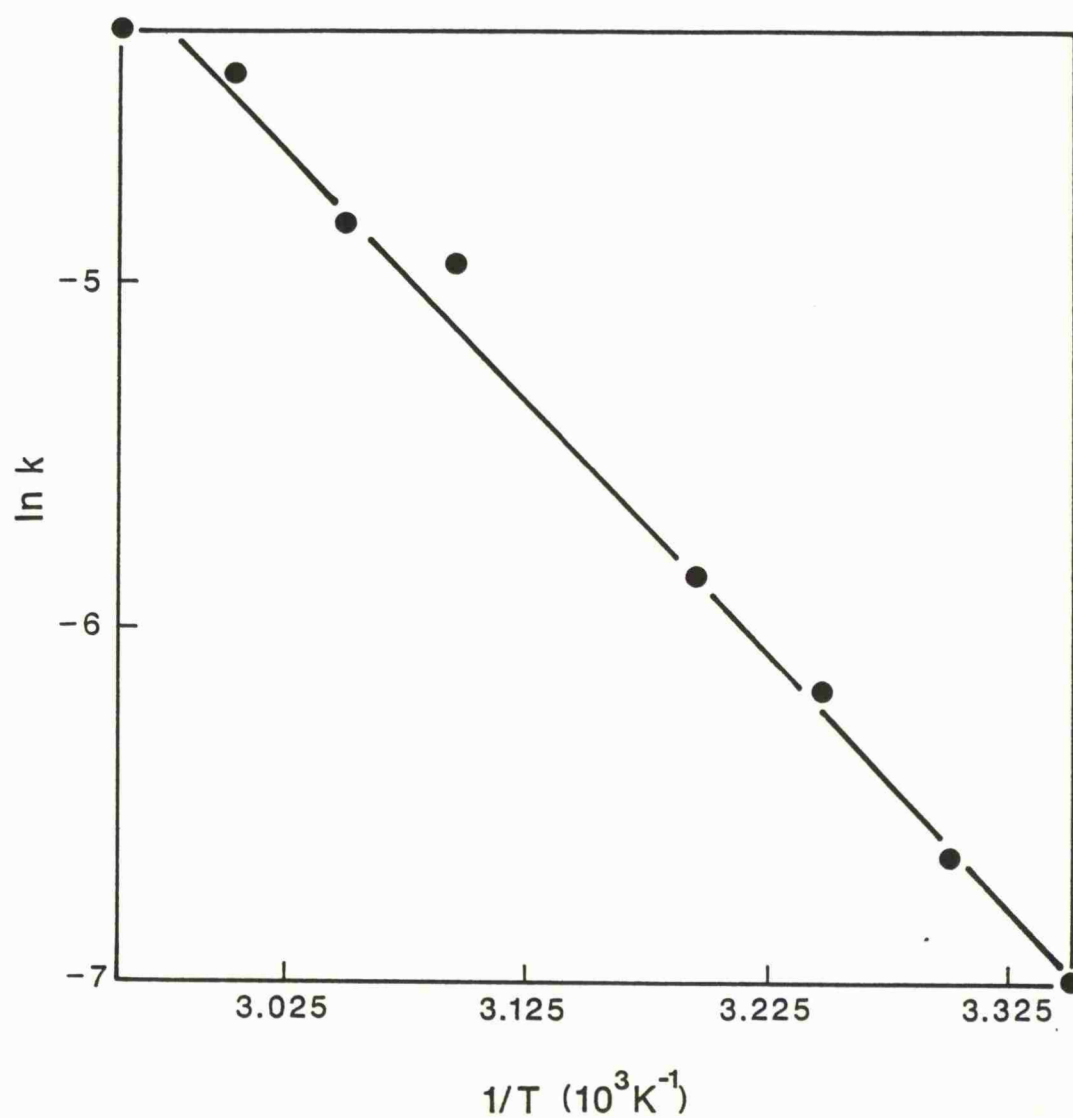


Figure 4.5: Arrhenius plot illustrating temperature dependence of perborate oxidation of erythrosin-B (*no added buffer*).

Table 4.6: Dependence of k_{obs} on temperature for oxidations of various dyes by perborate in aqueous solution. Also shown are calculated activation parameters.

	$10^3 k_{\text{obs}}/\text{s}^{-1}$				$\Delta^\ddagger H^a$	$\Delta^\ddagger S^b$
	298K	303K	308K	313K		
amaranth						
[pb] ^c =0.1; pH=10.1	4.50	6.20	8.30	10.9	40	-119
[pb]=0.1; pH=11.5 ^d	1.30	2.20	3.40	4.4	59	- 67
[pb]=0.01; pH=12.0 ^d	0.34	0.47	0.49	0.72	39	-144
erythrosin-B						
[pb]=0.1; pH=10.1	0.09	0.13	0.21	0.29	56	-101
[pb]=0.1; pH=11.5 ^d	1.05	1.49	2.06	3.10	50	- 98
[pb]=0.01; pH=12.0 ^d	0.20	0.38	0.49	0.54	44	-113
bromophenol blue						
[pb]=0.01; pH=12.0 ^d	13.4	20.8	25.2	28.8	34	-111

^a Values of $\Delta^\ddagger H$ are accurate to a σ of $\pm 5.0 \text{ kJ mol}^{-1}$ (i.e. a real error in the region of $\pm 15 \text{ kJ mol}^{-1}$)

^b Units $\text{J K}^{-1} \text{ mol}^{-1}$

^c Units mol dm^{-3}

^d Mixture of $\text{Na}_3\text{PO}_4 + \text{Na}_5\text{P}_3\text{O}_{10}$ added to solution

perborate oxidation of amaranth and erythrosin-B yielded values of +4 and 0 cm³ mol⁻¹ respectively.⁷ These values represent a balance between an intrinsic value of -10 cm³ mol⁻¹ for a bimolecular process⁸ and a positive contribution from the expansion of the solvent on forming the transition state, electrostricted solvent being released from the solvent shell into the bulk solvent. It is therefore surprising that values of $\Delta^\ddagger S$ are significantly negative, though correlations between $\Delta^\ddagger S$ and $\Delta^\ddagger V$ values in this instance are subject to similar problems as comparisons between values of $\Delta^\ddagger H$.

4.4(vii) Activators.

From a commercial point of view, it is desirable to improve the efficiency of perborate as a bleaching agent at temperatures below 338 K, especially in view of current trends towards low temperature domestic washes.

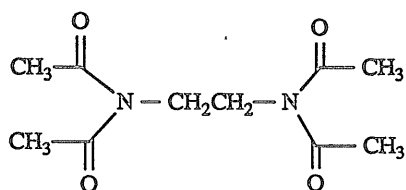
The effect of metal ions has already been discussed, although addition of a manganese complex is thought to have beneficial effects on perborate oxidation at lower temperatures.⁹ Section 3.7 has already mentioned that TAED (N,N,N',N'-tetraacetylenediamine) reacts with perborate in aqueous solution to produce peracetic acid which oxidises organic substrates at an enhanced rate. Oxidations of amaranth and erythrosin-B by solutions of 0.01 mol dm⁻³ perborate and 0.01 mol dm⁻³ TAED gave the following results;

$$\text{Amaranth: pH} = 8.9 \quad k_{\text{obs}} = 4.19 \times 10^{-3} \text{ s}^{-1}$$

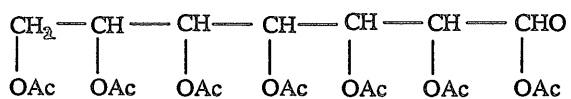
$$\text{Erythrosin-B: pH} = 8.9 \quad k_{\text{obs}} = 1.50 \times 10^{-3} \text{ s}^{-1}$$

If these results are compared to those in table 4.3 it can be seen that addition of an equimolar amount of TAED to aqueous solutions of perborate at 298 K greatly enhances the oxidation of amaranth and erythrosin-B. The rate enhancement of substrate oxidation by TAED and other so-called activators (figure 4.6) present interesting possibilities for in situ generation of organic peroxoanions by perborate-based

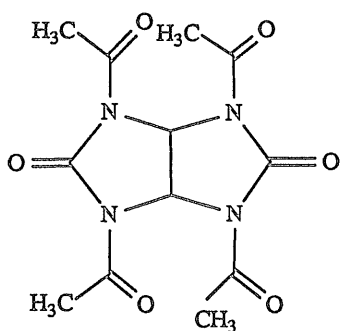
Figure 4.6: Sources of organic peroxides when reacted with aqueous solutions of perborate.



TAED



PAG



TAGU

domestic washing formulations, with a view to improving low temperature bleaching performance.¹⁰

4.5 Redox potentials.

Information on the redox potentials of organic substrates, in particular the dyes used in this study and perborate itself, is limited. However, redox potentials for some substrates that have marginal relevance in the present context are shown in table 4.7.^{11,12} It was possible to perform simple test tube experiments to establish whether or not the perborate oxidation of the organic substrates is reversible. The results are shown in table 4.8. The reversibility of the oxidation of amaranth by single oxygen atom transfer to give the azoxybenzene derivative is understandable in the light of previous work.³ The results for the other dyes are somewhat puzzling, especially for malachite green and crystal violet considering their structural similarity, making the establishment of a trend difficult.

4.6 Hydrogen peroxide.

In view of the fact that hydrogen peroxide exists in equilibrium with a perborate species on dissolution of solid sodium perborate, it is necessary to study selected oxidations of various dyes by hydrogen peroxide in order to draw a comparison.

4.6(i) Order in substrate.

As with perborate, the rates were first-order in substrate with some scatter observed for amaranth oxidations.

4.6(ii) Order in hydrogen peroxide.

Data for the dependence of k_{obs} on $[\text{H}_2\text{O}_2]$ for the oxidation of bromophenol blue in the absence of additives are summarised in table 4.9a. Bromophenol blue showed zero-order kinetics for the oxidation. This trend may be due to rate-limiting solvolysis of the dye in these slow oxidations at

Table 4.7: Redox potentials of some organic substrates (after refs. 13 and 14).

Substrate	E°/V (vs. NHE)
N-phenylanthranilic acid	1.08
Erioglaucine	1.00
Eriogreen	0.99
Variamine blue	0.73
Methylene blue	0.53

Table 4.8: Summary of reversibility of perborate oxidation of organic substrates in aqueous solutions; i = irreversible, r = reversible (reducing agent = ascorbic acid).

Substrate	
Amaranth	r
Bromophenol blue	i
Crystal violet	i
Erythrosin-B	i
Malachite green	r

Table 4.9a: First-order rate constants, k_{obs} , for oxidation of bromophenol blue by hydrogen peroxide in aqueous solution at 298 K (no additives).

$[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	pH	$10^4 k_{\text{obs}}/\text{s}^{-1}$
0.010	6.7	1.1
0.025	↓	1.5
0.050		1.4
0.075	5.2	1.6

Table 4.9b: First-order rate constants, k_{obs} , for oxidation of bromophenol blue by hydrogen peroxide at high pH and 298 K (sodium phosphate buffer).

$[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	pH	$10^2 k_{\text{obs}}/\text{s}^{-1}$
0.0125	11.8	1.8
0.025	11.9	2.7
0.050	11.4	2.4
0.075	11.7	3.8

low pH. Bromophenol blue exists in the protonated form in acid media, and this may also lead to complexities in the kinetics. The dependence of k_{obs} on $[\text{H}_2\text{O}_2]$ at higher pHs, where the predominant species is the perhydroxyl ion, are given in table 4.9b. Unfortunately inconsistencies in pH control prevent the assignment of a definite order of reaction. However, taking into account the magnitude of the differences in pH it can be seen that the oxidation of bromophenol blue at higher pH is approximately first-order in $[\text{H}_2\text{O}_2]$.

4.6(iii) Effect of pH and added anions.

As for perborate, hydrogen peroxide oxidations of organic substrates are dominated by pH effects. The dependence of k_{obs} , at constant $[\text{H}_2\text{O}_2]$, on pH for the oxidation of bromophenol blue is illustrated by figure 4.7. The plot has a similar curvature to that of the pH/rate profile of perborate.

Anions such as phosphate, carbonate, etc. have a significant effect on the pH of hydrogen peroxide solutions, making a quantitative assessment of interaction effects difficult. However, it was possible to assess the effect of added borate, BO_3^- , as pH of the solution is relatively unaffected by its addition over a range of concentrations (table 4.10). The decreases in rate constant on addition of increasing equivalent amounts of borate and hydrogen peroxide can be explained, to some degree, by the existence of a perborate species in equilibrium with the borate ($\text{B}(\text{OH})_3$) and hydrogen peroxide. The pH of these measurements is around that of the pK_a of borate ($\text{pK}_a = 9.5$) which leads to complications involving a competing acid base equilibria. The high value of k_{obs} at $[\text{H}_2\text{O}_2]/[\text{Borate}] = 0.01 \text{ mol dm}^{-3}$ may indicate incomplete oxidation, and the reaction mixture going to equilibrium as a result of these competing equilibrium. The values of k_{obs} as concentration of H_2O_2 and borate are increased become closer to that expected if only the perborate/ H_2O_2 + borate equilibrium was present. This is not inconsistent with the observations of Kern and Edwards.^{13,14} It is interesting to note that the scheme in chapter 5 would

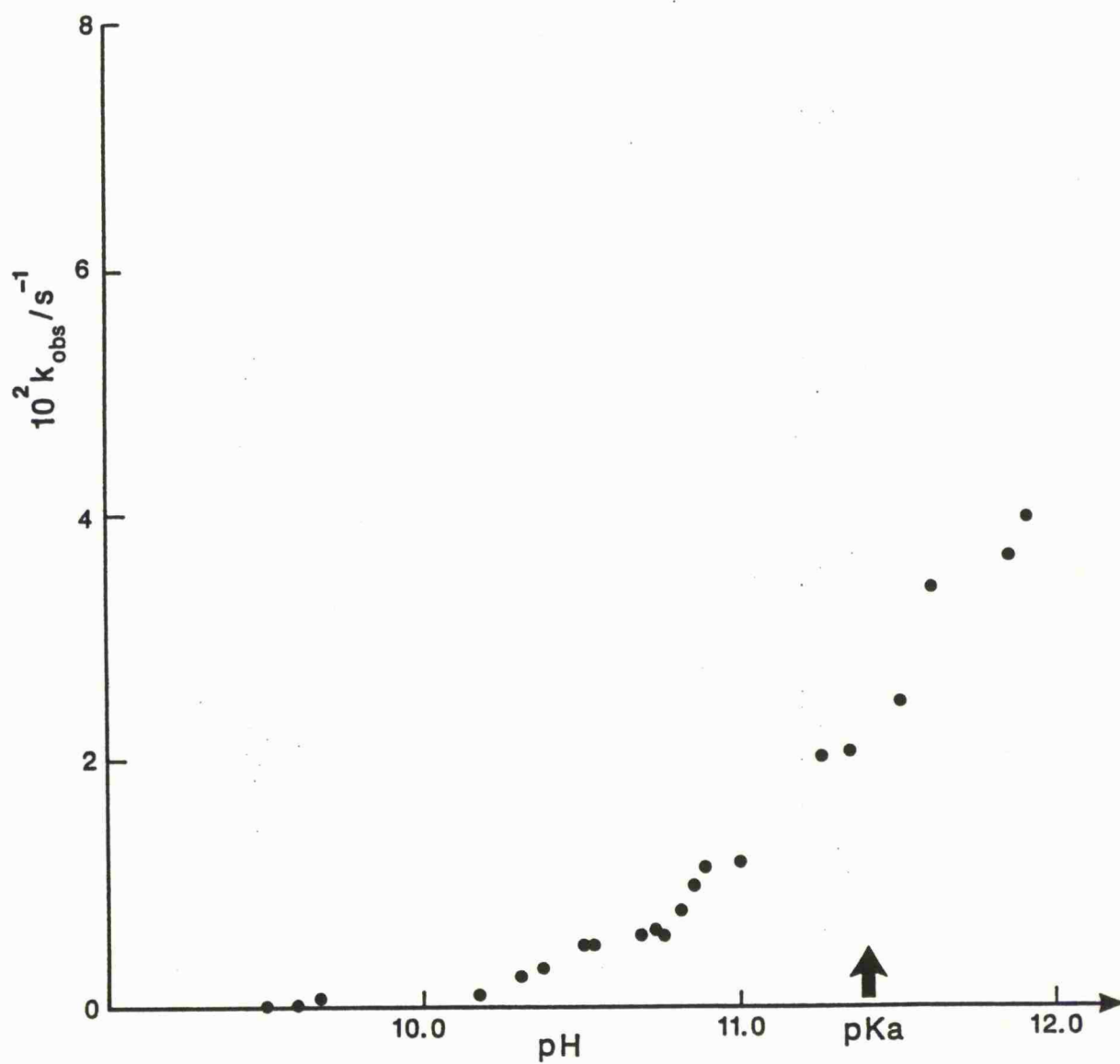


Figure 4.7: pH/rate profile for the hydrogen peroxide oxidation of bromophenol blue in aqueous solution at 298K. The arrow marks the pK_a of hydrogen peroxide.

Table 4.10: First-order rate constants for oxidation of bromophenol blue in aqueous solutions of hydrogen peroxide and sodium borate at 298 K.

$[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	$[\text{Borate}]/\text{mol dm}^{-3}$	pH	$10^4 k_{\text{obs}}/\text{s}^{-1}$
0.010	0.010	9.4	5.0
0.025	0.025	9.5	4.8
0.050	0.050	9.4	2.6
0.075	0.075	9.4	3.0

be able to investigate such interconnecting equilibria, but at present suffers from lack of available kinetic data.

4.7 Sodium percarbonate.

For the purposes of this kinetic study, sodium percarbonate may be considered as hydrogen peroxide and sodium carbonate in solution (section 3.5). The ratio of hydrogen peroxide to sodium carbonate in the Leicester University sample was determined, by iodometric titration, as 1.02 : 1. To confirm this, two oxidations of bromophenol blue were performed. The first by 0.01 mol dm^{-3} sodium percarbonate ($\text{pH} = 10.38$), yielded a rate constant of $2.69 \times 10^{-3} \text{ s}^{-1}$; and the second by a solution of 0.01 mol dm^{-3} sodium carbonate and $0.0102 \text{ mol dm}^{-3}$ hydrogen peroxide ($\text{pH} = 10.44$), yielded a rate constant of $3.38 \times 10^{-3} \text{ s}^{-1}$. These values, taking into account experimental error (section 2.5) and small variation in pH, confirm the titre result.

4.7(i) Order in substrate.

The oxidations of the organic substrates by sodium percarbonate were first-order in substrate. However, oxidations of amaranth exhibited characteristic scatter, as had been seen for amaranth oxidations by perborate and hydrogen peroxide.

4.7(ii) Order in sodium percarbonate.

Figure 4.8 summarises the dependence of k_{obs} on [percarbonate] for some organic substrates.⁶ The oxidations are first-order with respect to percarbonate, the notable exception being amaranth which shows significant curvature in the rate plot.

4.7(iii) Effect of pH.

Effects of pH on the percarbonate and perborate oxidation of indigo carmine have been studied kinetically,⁶ and the results summarised in figure 4.9. In contrast to the other substrates included in this study, indigo carmine was

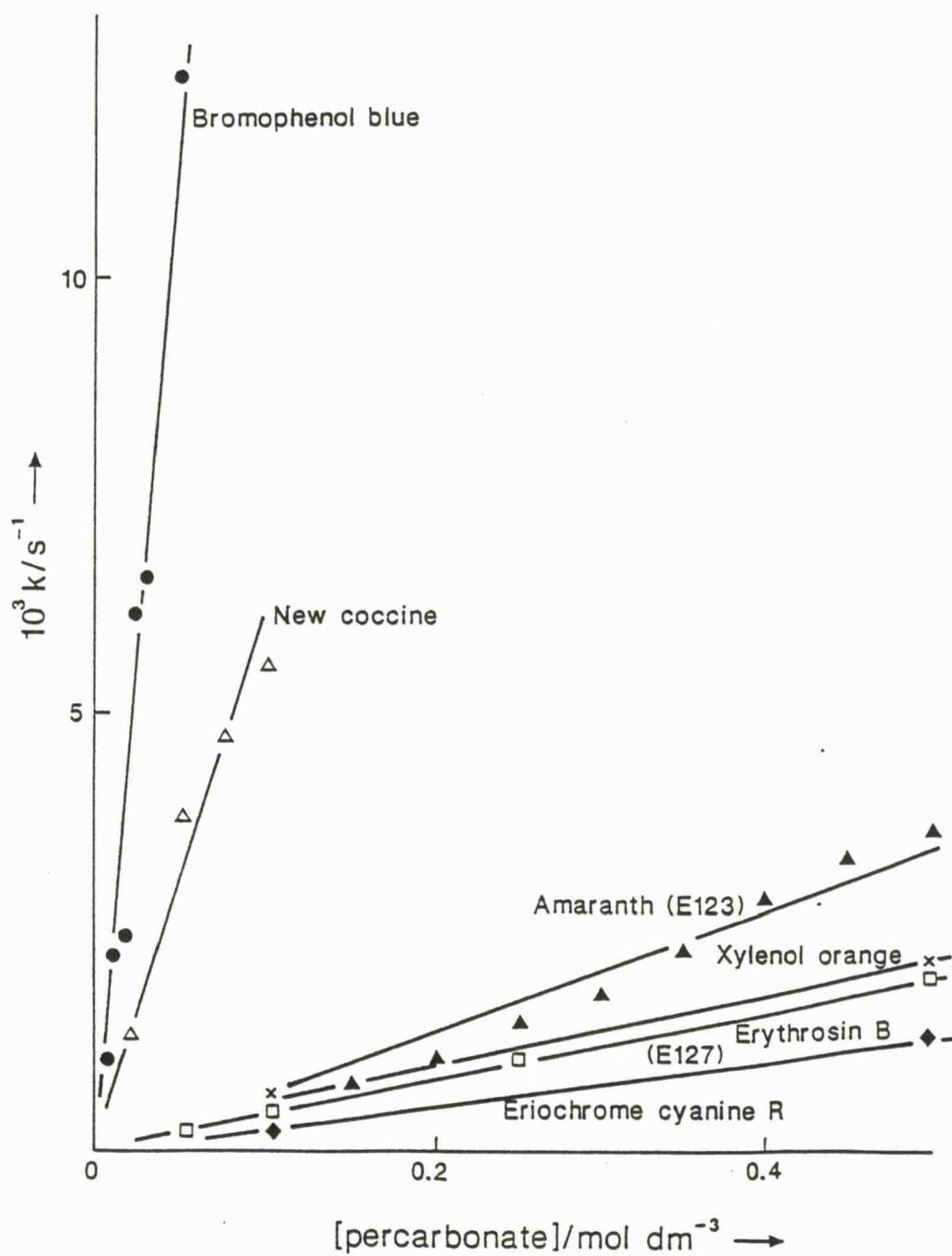


Figure 4.8: Dependence of k_{obs}/s^{-1} on $[percarbonate]/mol\ dm^{-3}$ for the oxidation of some organic substrates in aqueous solution at 298K.

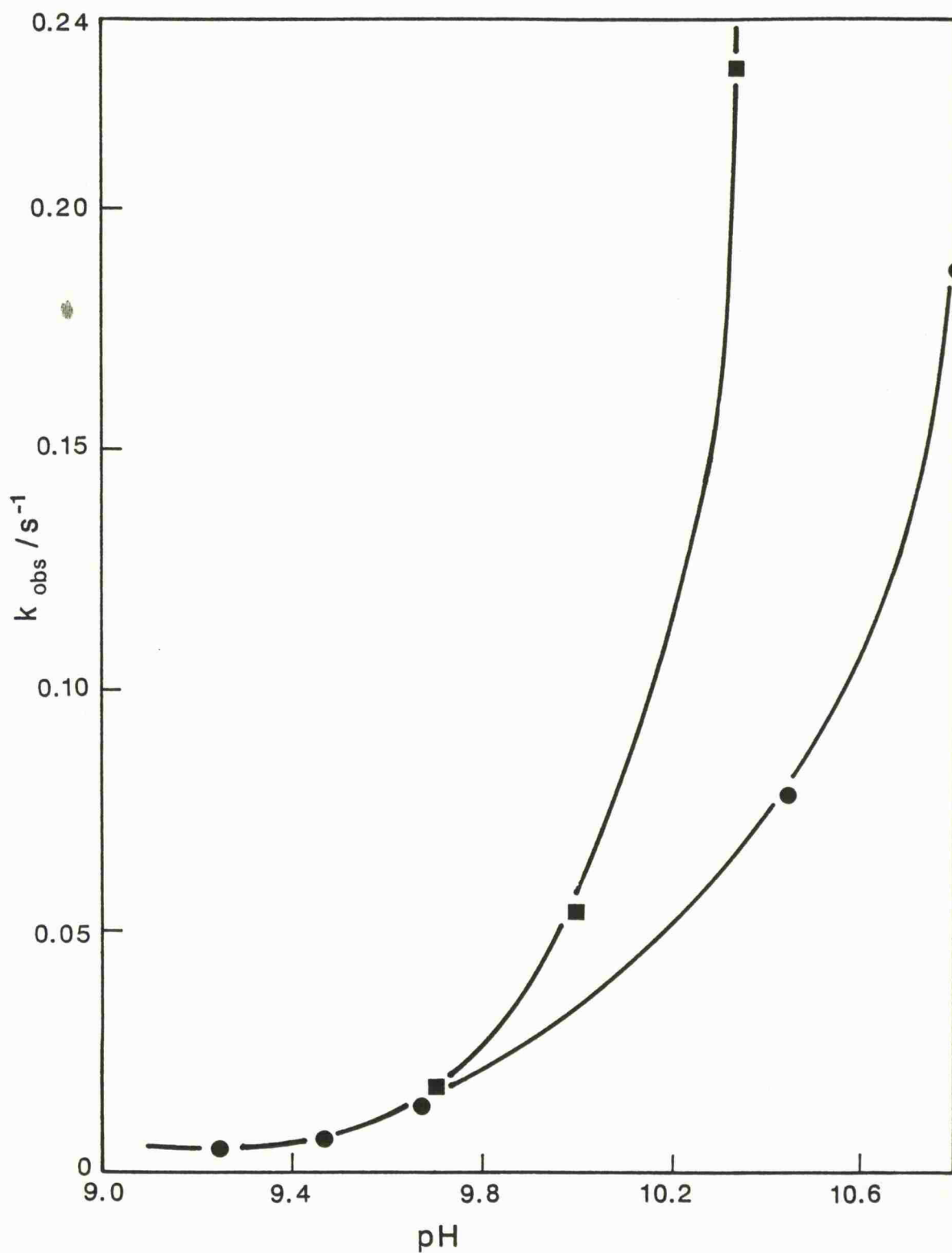


Figure 4.9: pH rate profile for oxidation of indigo carmine by 0.1 mol dm⁻³ perborate (●) and 0.1 mol dm⁻³ percarbonate (■) in aqueous solution at 298K (after ref. 6).

oxidised at a greater rate by percarbonate than perborate at comparable pH. This indicates that comparisons of the rate of oxidation of organic substrates by hydrogen peroxide and perborate are dye dependent, although indigo carmine is the only substrate in the current study to be oxidised faster by hydrogen peroxide than perborate under precise pH control.

4.8 Peroxodisulphate.

Few oxidations using peroxodisulphate, $S_2O_8^{2-}$, were performed in this present study. However, the effect of pH on the oxidation of bromophenol blue by PDS ($[PDS] = 0.1 \text{ mol dm}^{-3}$) has been briefly examined. The following results were obtained⁶

$$\begin{aligned} \text{pH} = 9.2 \quad k_{\text{obs}} &= 1.57 \times 10^{-4} \text{ s}^{-1} \\ \text{pH} = 11.8 \quad k_{\text{obs}} &= 1.52 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

These isolated results seem to indicate that a large change in pH has no effect on the rate constant for oxidation. This can be explained by the absence of a protonation equilibria involving the -O-O- bond in PDS.

4.9 Discussion.

The question raised in any study of perborate oxidation and a comparison with hydrogen peroxide is 'Is sodium perborate merely a passive carrier for hydrogen peroxide?'. The key to any answer to this question lies in the 'Pizer-Horvath' diagram (section 3.6). Table 4.11 details equilibrium proportions of free hydrogen peroxide and perborate in aqueous solutions at 298 K, as a function of pH and initial perborate concentration. If these values are now compared to values of k_{obs} for perborate/hydrogen peroxide oxidations in table 4.12 it can be seen that the rate constants for perborate are higher than would be expected than if oxidation were dependent on hydrogen peroxide alone. For example, bromophenol blue in aqueous solution, at $[\text{oxidant}] = 0.05 \text{ mol dm}^{-3}$, pH 10.54 and temperature 298 K, is oxidised at a greater rate by perborate than hydrogen peroxide. According to the 'Pizer-Horvath' diagram, a solution of perborate under these conditions contains approximately 50% hydrogen peroxide

Table 4.11: Equilibrium ratios of hydrogen peroxide and perborate in aqueous solution at 298 K, as a function of initial perborate concentration and pH (from the 'Pizer-Horvath' diagram).

[perborate] _{init.} mol dm ⁻³	pH	%perborate(eq)	%H ₂ O ₂ (eq)
0.05	10.54	42	58
0.1	10.20	57	43
0.1	10.78	c.60	c.40
0.1	11.50	60	40

Table 4.12: Comparison of rate constants, $k_{\text{obs}}/\text{s}^{-1}$, for dye oxidation by perborate and hydrogen peroxide in aqueous solution at 298 K.

Dye	$k_{\text{obs}}(\text{H}_2\text{O}_2)$ s^{-1}	$k_{\text{obs}}(\text{per})^{\text{a}}$ s^{-1}	pH	$[\text{Ox}]^{\text{b}}$	buffer
Bromophenol Blue	5.2×10^{-3}	9.29×10^{-3}	10.54	0.05	Phosphate
Bromophenol Blue	4.6×10^{-3}	1.05×10^{-2}	10.54	0.05	Carbonate
Bromophenol Blue	8.1×10^{-3}	1.7×10^{-2}	10.78	0.1	Phosphate
Amaranth	3.4×10^{-4}	1.3×10^{-3}	11.50	0.1	Phosphate
Indigo Carmine	1.3×10^{-1}	5.0×10^{-2}	10.20	0.1	———

^a perb = perborate

^b $[\text{Ox}] = [\text{Oxidant}]/\text{mol dm}^{-3}$

and 50% perborate. Perborate oxidation should therefore have a smaller value of k_{obs} (by c.50% assuming a first-order dependence) than that of hydrogen peroxide under similar conditions. This is clearly not the case, suggesting that a perborate moiety plays an active role in both the oxidations of bromophenol blue and amaranth. However, oxidation of indigo carmine in aqueous solution at 298 K exhibits a k_{obs} for perborate oxidation in the region of that predicted by the 'Pizer-Horvath' diagram if oxidation rate is independent of perborate present in the solution.

Having now identified a role for perborate in the oxidation of at least two dyes, the next task is to attempt to obtain a value of $k(\text{perborate})$. If we consider the pH/rate profiles for bromophenol blue oxidation by perborate and hydrogen peroxide (figures 4.4 and 4.7; overlayed in figure 4.10), it can be seen that there is a significant difference between the values of k_{obs} for the two oxidations above a pH of 10.50. The shape of the hydrogen peroxide profile is somewhat puzzling. One would expect the classical 's' shaped plot with a point of inflexion at the pK_a of the $\text{H}_2\text{O}_2/\text{HO}_2^-$ equilibrium. This is not observed as such on the plot, possibly due to inconsistencies in ionic strength. However, a general 'flattening' of the curve is hinted at at pH 11.6. It would be an advantage to have further values of k_{obs} at higher pHs but this would lead to problems with the alkaline hydrolysis of the dye becoming a competing process. Even so, it is possible to make an estimate as to the value of second order rate constant for bromophenol blue oxidation by hydrogen peroxide in aqueous solution at 298 K. From figure 4.10 we obtain a value of approx. $4.0 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Information on the pK_a of perborate is not available and cannot be estimated from the pH/rate profile obtained in this study. However, if we consider the following equation it is possible to make a 'ball-park' estimate.

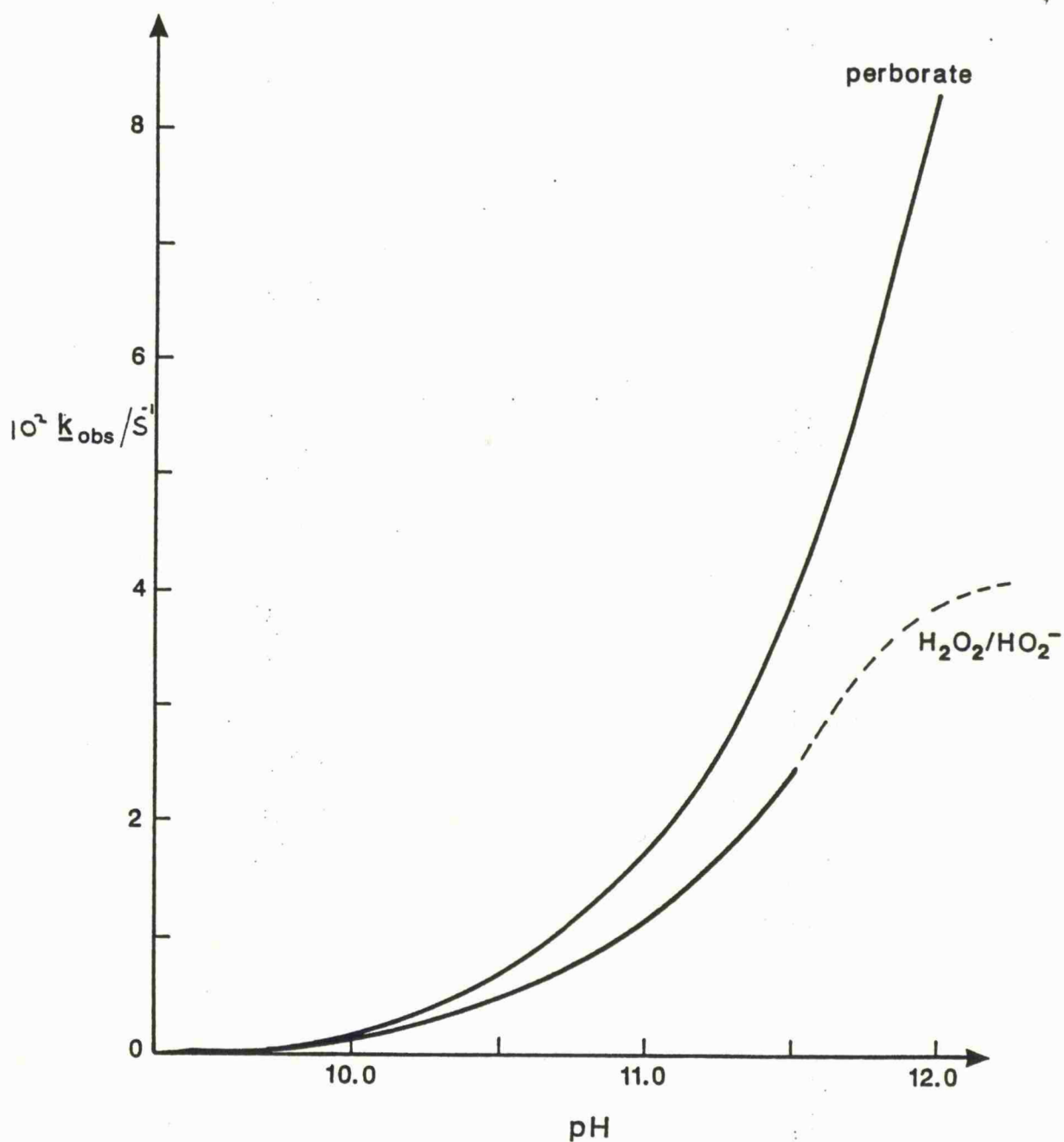


Figure 4.10: Overlay of the pH/rate profiles for bromophenol blue oxidation in aqueous solution at 298K by hydrogen peroxide and perborate.
 [----- = Estimated line of limiting rate constant $k(\bar{\text{O}}_2\text{H})$].

$$\begin{aligned}
 - \frac{d \ln[\text{dye}]}{dt} &= k_{\text{obs}}[\text{perborate}] \\
 &= k_{\text{pb}}[\text{perborate}]_{\text{eq}} + k_{\text{perox}}[\text{H}_2\text{O}_2]_{\text{eq}} \quad 4.1
 \end{aligned}$$

where k_{pb} and k_{perox} are the first-order rate constants for oxidation by perborate and hydrogen peroxide respectively, eq denotes equilibrium concentration.

In the case of indigo carmine, k_{pb} is approximately zero, but k_{pb} has a significant value for the oxidations of bromophenol blue and amaranth. For bromophenol blue oxidation in aqueous solution at 298 K, and pH 12 an estimated value of $k_{\text{pb}} = 2.40 \times 10^{-2} \text{ s}^{-1}$ is obtained ($[\text{perborate}] = 0.1 \text{ mol dm}^{-3}$; $[\text{Perborate}]_{\text{eq}} = 0.04 \text{ mol dm}^{-3}$; $[\text{H}_2\text{O}_2]_{\text{eq}} = 0.06 \text{ mol dm}^{-3}$; $k_{\text{perox}} = 5.6 \times 10^{-2} \text{ s}^{-1}$ from figure 4.10).

The studies of Pizer and Tihai,¹⁵ and Flanagan et al¹⁶ offer evidence that, under the conditions of this kinetic study, hydrogen peroxide and borate are in equilibrium with the tetrahedral perborate species $\text{B}(\text{OH})_3(\text{O}_2)^{-}/\text{B}(\text{OH})_3(\text{O}_2\text{H})$. As has already been mentioned, the lack of information on the pK_a of perborate makes it difficult to ascertain whether the species present at pH 12.0 is protonated or unprotonated perborate. However, as long as the initial perborate concentration remains $\leq 0.1 \text{ mol dm}^{-3}$ the presence of any polynuclear species, as described by Edwards,¹⁰ is unlikely.

At this stage of the study, detailed mechanistic information on perborate oxidation cannot be obtained. Indeed, due to changes in perborate/hydrogen peroxide ratios and further hydrolysis of the perborate, this information may prove to be elusive at best. For amaranth it may be reasonable to suggest that initial attack occurs at or near the azo bond, as has been postulated for oxidation of this dye by peroxobenzoates.³ A comprehensive study of oxidations of organic dyes of varying structural types by both perborate and hydrogen peroxide to build on this initial work would be advantageous, and may reveal some further mechanistic information.

The crucial finding from this study shows that, far from being a passive carrier of hydrogen peroxide, sodium perborate contains some active bleaching moiety in the oxidations of some organic dyes.

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Chapter 5

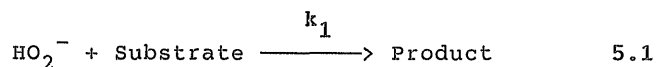
*Computer simulation of the perborate ion in aqueous
solution*

5.1 Introduction.

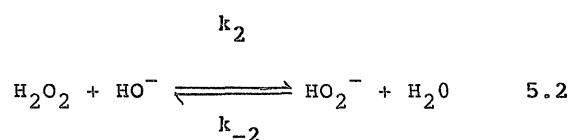
This chapter presents details of the development of a computer simulation (written in FORTRAN) of various equilibria relating to perborate in aqueous solution. This work has been somewhat overtaken by the findings of chapter 4, in as much as the scheme described here is not directly applicable to the kinetic study. In this simulation, account is taken of possible equilibria arising from the initial hydrolysis of perborate on dissolution and subsequent reactions of the peroxy species produced. In the kinetic study dye oxidation was completed before the following equilibria came 'into play'. However, should a suitable dye be found for this system which exhibits reasonable kinetics over the time period required for decomposition, this program will provide a basis for developing a full simulation of the interconnecting perborate equilibria in aqueous solution.

5.2 Reaction scheme.

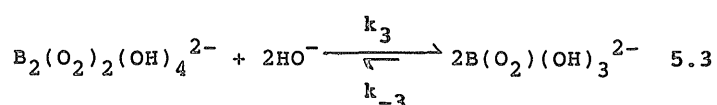
The FORTRAN simulation incorporates seven equilibria with associated forward and reverse rate constants. The equilibria are presented below along with the associated rate equation (N.B. The order of the reactions is that in the program not that which occurs in solution, see section 5.4):



$$\text{rate} = k_1[\text{HO}_2^-][\text{Substrate}]$$



$$\begin{aligned} \text{forward rate} &= k_2[\text{H}_2\text{O}_2][\text{HO}^-] \\ \text{back rate} &= k_{-2}[\text{HO}_2^-] \end{aligned}$$

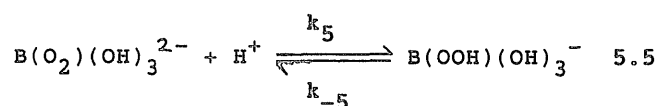


$$\begin{aligned} \text{forward rate} &= k_3[\text{B}_2(\text{O}_2)_2(\text{OH})_4^{2-}][\text{HO}^-]^2 \\ \text{reverse rate} &= k_{-3}[\text{B}(\text{O}_2)(\text{OH})_3^{2-}]^2 \end{aligned}$$

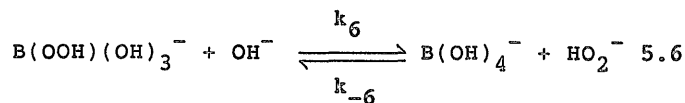
N.B. This equilibrium is assumed to be far to the right, hence the value of k_{-3} is small compared to k_3 . Therefore, it is further assumed that no oxidation of the substrate by the di-boron species occurs.



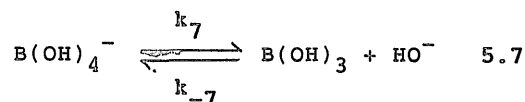
$$\text{rate} = k_4[\text{B}(\text{O}_2)(\text{OH})_3^{2-}][\text{Substrate}]$$



$$\begin{aligned} \text{forward rate} &= k_5[\text{B}(\text{O}_2)(\text{OH})_3^{2-}][\text{H}^+] \\ \text{back rate} &= k_{-5}[\text{B}(\text{OOH})(\text{OH})_3^-] \end{aligned}$$



$$\begin{aligned} \text{forward rate} &= k_6[\text{B}(\text{OOH})(\text{OH})_3^-][\text{HO}^-] \\ \text{back rate} &= k_{-6}[\text{B}(\text{OH})_4^-][\text{HO}_2^-] \end{aligned}$$



$$\begin{aligned} \text{forward rate} &= k_7[\text{B}(\text{OH})_4^-] \\ \text{back rate} &= k_{-7}[\text{B}(\text{OH})_3][\text{HO}^-] \end{aligned}$$

5.2(i) Estimates of rate constants.

Rate constants for the oxidations in reactions one and four have been measured experimentally; chapter 4. Rate constants for the other equilibria must be estimated from literature information. The rate constants for the equilibria in equation 5.2 are readily available.¹ Decomposition of the perborate dimer to the active monomeric species has been briefly examined by Griffith,² and although no rate constant is mentioned, it is implied that this equilibrium is rapidly established. Griffith also mentions that the equilibrium in equation 5.7 is fast on the NMR time scale. Lack of information on the rest of the equilibria requires the use of 'dummy' rate constants in the simulation.

5.3 Development of the simulation.

It has already been mentioned that the order of the reactions in the above scheme is that presented in the computer simulation rather than in a real solution. This is a consequence of the development of the simulation itself. Initially, the simulation contained only steps for substrate oxidation by hydrogen peroxide. Such an oxidation can be described by equations 5.1 and 5.2. Gradually, further steps were added to the simulation to describe perborate oxidation of substrate and hydrolysis into hydrogen peroxide, each successive development containing a more complex 'chemical network'. These original simulations were written in FORTRAN on a VAX main-frame computer and the final version in this format contained ten interconnecting equilibria. It was desirable, for reasons of enhanced presentation and ease of data transfer, to run the simulation on a personal computer (PC). Problems arose from the use of routines on the PC that

performed the numerical integration analysis on inputted data. The main-frame NAG version of the analysis was considerably more robust than that contained in the PC, which could not cope with the simulation version that was run on the main-frame. Fortunately, it was possible to remove three equilibria which were found to be negligible under the conditions applied in the program. The PC version, although being more fragile than the main-frame analogue, could perform the required calculations using these seven equilibria.

5.4 The FORTRAN computer simulation.

After establishing a theoretical 'chemical network', it was possible to write a program that used input values of rate constant to produce calculated values of concentration at a specific time after initiation of the scheme. The subroutines are outlined below.

5.4(i) Program ANALYSIS.

Figure 5.1 shows the main part of the program 'analysis.for'. The main comment block (lines 6-20) assigns a number to each species in the 'chemical network', each number being unique to that particular species. This part of the program calls the subroutines XRATE and ANALY, then transfers values of number of data points (jj), elapsed time, (tx(i)), and concentration, (x(j,i)), of each species at stated time to a file 'borate.dat'.

5.4(ii) Subroutine XRATE.

Subroutine XRATE (figure 5.2) sets initial values for pH (xph; line 52) from which are calculated $[\text{HO}^-]$ and $[\text{H}^+]$ (ohm and hp respectively). Rate constants are set in subroutine RATE, described in the next section, which is called in line 55 of this subroutine. Also set are the initial values of $[\text{B}_2(\text{O}_2)_2(\text{OH})_4^{2-}]$ and [Substrate] (x(5,1) and x(3,1) respectively). In this case initial perborate concentration (in moles of mononuclear boron) is 0.1 mol dm^{-3} and initial substrate concentration is $1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Figure 5.1: Program ANALYSIS.

```

1      program analysis
2      implicit double precision(a-h,o-z)
3      common/ian/tx(200),x(20,200),rk(7,2)
5      common/mike/hp,ohm,istep,tstep,xend
6  c
7  c      t          = time at predefined intervals
8  c
9  c      x(i,100) = array of concentrations
10 c
11 c      i = 1      OOH-
12 c
13 c      i = 2      Substrate
14 c
15 c      i = 3      Product
16 c
17 c      i = 4      H2O2
18 c
19 c      i = 5      B2(O2)2(OH)42-
20 c
21 c      i = 6      B(OH)4-
22 c
23 c      i = 7      B(O2)(OH)2-
24 c
25 c      i = 8      B(OOH)(OH)2
26 c
27 c      i = 9      B(OH)3
28 c
29 c      i = 19     OH-
30 c
31 c      i = 20     H+
32 c
33 write(6,10)
34 format(1h,30x,'Ian M. Horn')
35 write(6,20)
36 format(1h,20x,'Department of Chemistry')
37 call xrate
38 call analy
39 open(unit=8,file='BORATE.DAT')
40 write(8,100)
41 format(1h,'BORATE')
42 jj=int(tstep)
43 do 110 i=1,jj
44 write(8,120)i
45 format(1h,i3)
46 write(8,130)tx(i)
47 format(1h,1pe15.6)
48 do 140 j=1,9
49 write(8,130)x(j,i)
50 continue
51 140 continue
52 110 continue
53 close(unit=8)
54 write(6,11)
55 format(1h,10x,'that is all folks')
56 end

```

Figure 5.2: Subroutine XRATE.

```

44      subroutine xrate
45      implicit double precision(a-h,o-z)
46      common/ian/tx(200),x(20,200),rk(2,2)
47      common/mike/hp,ohm,istep,tstep,xend
48      c
49      c      xkw = kw for water, 10.0e-14
50      c      xph = pH for solution as set
51      c
52      xph=10.0
53      hp=10.0**(-xph)
54      ohm=1.0e-14/hp
55      call rate
56      c
57      c      Set initial conc. for h2o2 and substrate
58      c
59      x(5,1)=1.0e-1
60      x(2,1)=1.0e-3
61      write(6,200) x(5,1)
62      200 format(1h,10x,'perborate at time zero =',1pe15.6)
63      write(6,210)x(2,1)
64      210 format(1h,10x,'substrate at time zero = ',1pe15.6)
65      return
66      end

```

5.4(iii) Subroutine RATE.

Called in XRATE, subroutine RATE (figure 5.3) contains all forward and back rate constants, $x(i,j)$ where i is the number of the equilibrium in the scheme and $j = 1$ or 2 indicating forward or back reaction respectively. These values of individual rate constants are obtained from literature estimates or experimental data. Line 85 opens a file called 'input.dat', to which are written values of rate constants.

5.4(iv) Subroutine ANALY.

This subroutine (figure 5.4) defines the total time of the run ($xend$) and the time interval between successive calculations ($tstep$). An external NAG routine, D02CBF, is called at line 133, this is a standard numerical integration analysis routine stored in the NAG library of the PC. In order to call the NAG routine, certain associated variable must first be defined (lines 116 to 123);

XX: On entry to the subroutine, xx is set to the initial value of time. On exit, xx becomes $xend$, the total time for the calculation.

IFAIL: An error indicator. On entry to subroutine $ifail = 0$, if on exit from the subroutine the value of $ifail$ changes the program crashes, as can be seen from the stop statement on line 135.

N: The number of differential equations in calculation. N is an integer value and must be ≥ 1 .

IR: An integer number which determines the type of error control in the analysis. A value of 0 gives a mixture of error in terms of a set number of correct significant digits or decimal places (defined by tol).

Figure 5.3: Subroutine RATE.

```

67      subroutine rate
68      implicit double precision(a-h,o-z)
69      common/ian/tx(200),x(20,200),rk(7,2)
70      common/mike/hp,ohm,istep,tstep,xend
71      rk(1,2)=0.0
72      rk(1,1)=0.24
73      rk(2,1) = 4.9e-3
74      rk(2,2)= 1.0e-5
75      rk(3,1) = 1.0e-3
76      rk(3,2)= 1.0e-5
77      rk(4,1) = 1.0e-1
78      rk(4,2)= 0.0
79      rk(5,1) = 1.0e-3
80      rk(5,2)= 1.0e-5
81      rk(6,1) = 1.0e-7
82      rk(6,2)= 1.0e-5
83      rk(7,1) = 1.0e-1
84      rk(7,2)= 1.0e-2
85      open(unit=9,file='input.dat')
86      write(9,41)
87  41      format(1h,'RATE CONSTANTS')
88      do 42 i=1,7
89      do 43 j=1,2
90      write(9,44)i,j,rk(i,j)
91  44      format(1h,i3,2x,i3,2x,1pe15.6)
92  43      continue
93  42      continue
94      close(unit=9)
95      write(6,50)
96  50      format(1h,10x,'* RATE CONSTANTS *')
97      do 60 i=1,7
98      write(6,70)i,rk(i,1),rk(i,2)
99  70      format(1h,5x,i3,2(2x,1pe15.6))
100 60      continue
101      return
102      end

```


Figure 5.4: Subroutine ANALY.

```

103      subroutine analy
104      implicit double precision(a-h,o-z)
105      common/ian/tx(200),x(20,200),rk(7,2)
106      common/mike/hp,ohm,istep,tstep,xend
107      dimension y(9),w(1000)
108      external d02cbf,fcfn,output
109      xend=700.0
110      istep=9
111      kstep=1
112      tstep=xend/35.0
113      hstep=tstep
114      write(6,101) tstep
115 101    format(1h ,10x,'Time Step/s =',1pe15.6)
116      xx=0.0
117      ifail=0
118      n=9
119      mped=0
120      irelab=0
121      tol=0.0001
122      iw=1000
123      tx(1)=0.0
124      do 110 j=1,9
125      y(j)=x(j,1)
126      write(6,105)j,y(j)
127 105    format(1h ,2x,i3,2x,1pe15.6)
128 110    continue
129      ir=0
130c
131c      nag routine
132c
133      call d02cbf(xx,xend,n,y,tol,ir,fcfn,output,w,ifail)
134      if(ifail.eq.0) goto 120
135      if(ifail.ne.0) stop
136 120    continue
137      return
138      end

```

TOL: Defines the tolerance of the analysis as a function of the correct decimal digits defined in the solution.

5.4(v) Subroutine OUTPUT.

A 'counter' calculation is performed in this subroutine (figure 5.5). The integer quantity kstep (defined in subroutine ANALY, line 111) is increased by an increment of one each time the subroutine is called, and is then used as a flag for how many intervals of time have elapsed. Line 144 then resets the time to the previous time + successive time interval.

5.4(vi) Subroutine FCN.

This is the crucial subroutine in the computer simulation (figure 5.6). Lines 167 to 180 define the rate equations for the forward and back reactions of each of the equilibria in the scheme, xf(i) and xb(i) respectively (where i is the number of the equilibria). In this subroutine concentration of a species is given by y(i) where i = 1 to 9, redefined in subroutine OUTPUT, line 151. The quantities f(1) to f(9) are the differential equations of each species. This subroutine is called via the NAG routine D02CBF.

5.5 Graphical output.

Section 5.4(i) described how data produced by 'analysis.for' was written to a file 'borate.dat'. A further program was written to read the data contained therein, and produce graphical output on a roland plotter. The flow chart in figure 5.7 illustrates the main features of the program. Using this plotting program, it is possible to isolate a particular species in the scheme and obtain an illustration of the dependence of [species]/mol dm⁻³ on time/s. Figure 5.8 gives an example of such a plot for the depletion of substrate in the solution as a function of elapsed time.

Figure 5.5: Subroutine OUTPUT.

```
139      subroutine output(xx,y)
140      implicit double precision(a-h,o-z)
141      common/ian/tx(200),x(20,200),rk(7,2)
142      common/mike/hp,ohm,istep,tstep,xend
143      dimension y(9)
144      kstep=kstep+1
145      tx(kstep)=xx
146      write (6,153) xx
147 153   format(1h,4x,'time/s =',1pe15.6)
148      write (6,154) kstep
149 154   format(1h,4x,'kstep =',i3)
150      do 20 i=1,9
151      x(i,kstep)=y(i)
152      write(6,30) i,y(i)
153 30   format(1h,2x,i3,4x,1pe15.6)
156 20   continue
157      xx=xend-(istep*tstep)
158      istep=istep-1
159      return
160      end
```

Figure 5.6: Subroutine FCN.

```

161      subroutine fcn(tlum,y,f)
162      implicit double precision(a-h,o-z)
163      common/ian/tx(200),x(20,200),rk(7,2)
164      common/mike/hp,ohm,istep,tstep,xend
165      dimension xf(7),xb(7),f(9),y(10)
166      xf(1)=rk(1,1)*y(1)*y(2)
167      xb(1)=0.0
168      xf(2)=rk(2,1)*y(4)*ohm
169      xb(2)=rk(2,2)*y(1)
170      xf(3)=rk(3,1)*y(5)
171      xb(3)=rk(3,2)*y(7)*y(7)
172      xf(4)=rk(4,1)*y(7)*y(2)
173      xb(4)=0.0
174      xf(5)=rk(5,1)*y(7)*hp
175      xb(5)=rk(5,2)*y(8)
176      xf(6)=rk(6,1)*y(8)
177      xb(6)=rk(6,2)*y(9)*y(1)
178      xf(7)=rk(7,1)*y(9)*ohm
179      xb(7)=rk(7,2)*y(6)
180      f(1)=-xf(1)+xf(2)- xb(2)+xf(6)-xb(6)
181      f(2)=-xf(1)-xf(4)
182      f(3)=+xf(1)+xf(4)
183      f(4)=-xf(2)+xb(2)
184      f(5)=-xf(3)+xb(3)
185      f(6)=xf(7)-xb(7)
186      f(7)=xf(3)-xb(3)-xf(4)+xb(4)-xf(5)+xb(5)
187      f(8)=xf(5)-xb(5)-xf(6)+xb(6)
188      f(9)=xf(6)-xb(6)-xf(7)+xb(7)
189      return
190      end
191

```

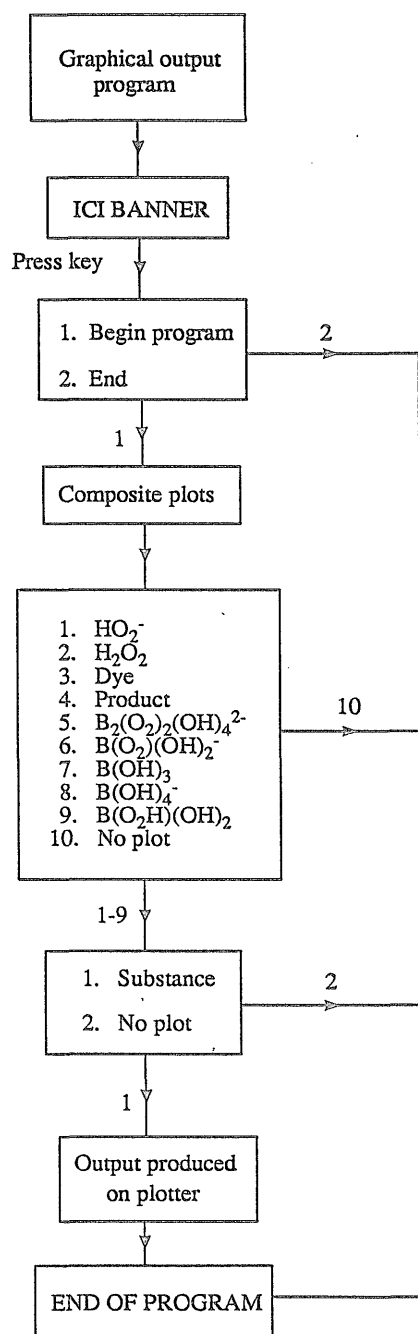


Figure 5.7: Flow diagram illustrating the essential features of the plotter program.

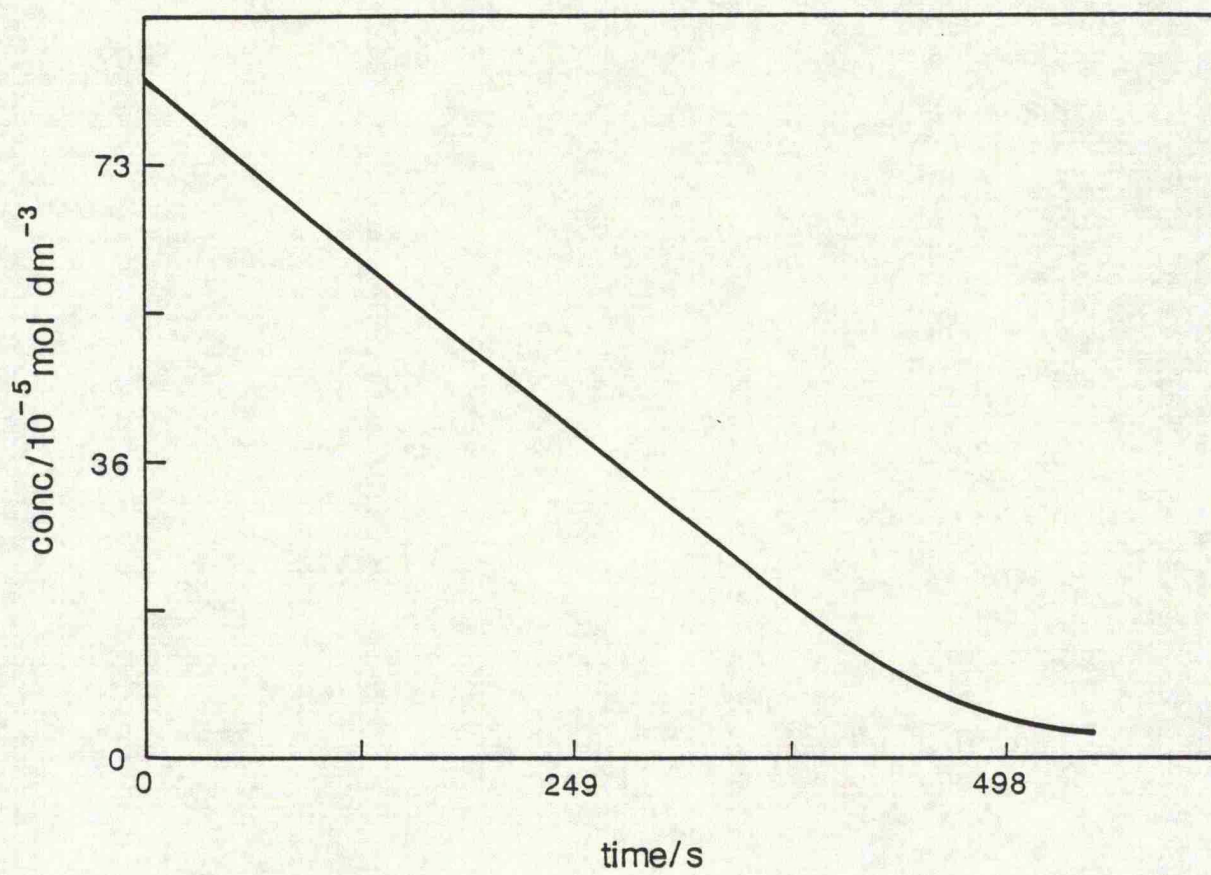


Figure 5.8: Example of output produced by the plotter program, showing calculated [DYE] as a function of time.

5.6 Discussion.

Here we have seen the initial basis for a computer simulation of the perborate oxidation/hydrolysis system in aqueous solution. Even at this early stage of development the main advantages of such an approach are clear. In principle it is possible to alter input variables to see how changes, subtle or otherwise, affect the overall reaction of the substrate under study. The fact that this program is written on a PC means that it can be stored on a portable disk for use with compatible machines at other sites. Use of the program requires little previous knowledge of the intricacies of programming, as all the user needs to vary are the input parameters. The graphical program is menu driven and presents the produced data in an appealing form. Clearly, this program is a versatile theoretical tool, which may also be used to simulate other systems by altering the equations contained in subroutine FCN and input values of the various variables. Figure 5.8 gives an example of the plots produced by this simulation, it is however somewhat unexciting and varies little from the rest of the plots produced. This is basically due to the time scale involved in the kinetic data obtained. More information could be gathered from a study using dyes with large second-order rate constants, such that the time scale for dye oxidation is of the order of the initial perborate hydrolysis equilibria. Measurements on this time scale require the use of stop-flow spectrophotometry, currently not available at Leicester University, to measure reactions of this type (the HP 8451A spectrophotometer could measure reactions with $t_{1/2}$ in the region of 12 seconds).

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Chapter 6

Kinetic salt effects

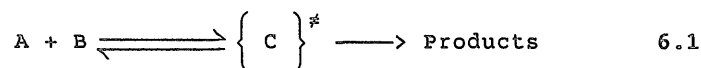
6.1 Introduction

When salts are added to an aqueous solution they often have a significant effect upon rates of chemical reaction.¹⁻⁴ Theories concerning kinetic salt effects have developed over the last seventy years from a simple consideration of ionic strength to descriptions of interaction between co-spheres surrounding added ions and substrates undergoing reaction.

The classic approach to understanding salt effects on rates of reactions involving ions uses the Debye-Hückel Theory of ion-ion interactions in conjunction with the Brønsted-Bjerrum treatment.

6.2 Classical approach.

According to the theory proposed by Brønsted, in a reaction between substrates A and B in solution a transition state, C, is formed. Thermodynamic equilibrium is established.



The Brønsted equation (6.2) relates the nature and concentration of ions present in aqueous solution to the rate constant, k , of a reaction at fixed T and P .

$$k = k_0 \cdot \frac{\gamma_A \gamma_B}{\gamma_C} \quad 6.2$$

where k_0 is the limiting rate constant for reaction at zero ionic strength; γ_A and γ_B are the activity coefficients of ions A and B respectively; γ_C is the activity coefficient of the solute species C, which has a charge number equal to the algebraic sum of the charge numbers on ions A and B such that $\lim(I \rightarrow 0) \gamma_A, \gamma_B, \gamma_C \rightarrow 1.0$ at all temperatures and pressures.

Although Bjerrum⁵ referred to C as a collision complex, it is usually described as the transition state following the development of Transition State Theory.⁶

In 1924 Debye and Hückel⁷ derived a relationship between the ionic activity coefficient of an ionic species, j , and ionic strength, I . For dilute solutions, the dependence of $\ln \gamma_j$ is given by the Limiting Law i.e. DHLL.

$$\ln \gamma_j = -A_\gamma \cdot z_j^2 \left(\frac{I}{m^\circ} \right)^{\frac{1}{2}} \quad 6.3$$

where $m^\circ = 1.0 \text{ mol kg}^{-1}$; A_γ depends on the temperature and relative permittivity of the solvent; $I(\text{mol kg}^{-1})$ is defined by equation 6.4.

$$I = \frac{1}{2} \sum_j m_j z_j^2 \quad 6.4$$

A key term in this theory is the quantity κ which is dependent on ionic strength, temperature and the relative permittivity of the solvent. The basis of the DHLL assumes that a given ion- j is surrounded, at a distance κ^{-1} (equal to $(B a_j)^{-1}$ in equation 6.6). The term κ can be understood by considering its reciprocal κ^{-1} , which is the distance between the centre of ion- j and the shell produced by all other ions having a charge equal in magnitude but opposite in sign to that on ion- j . With increase in I the intensity of ion-ion interactions increases. The ion-atmosphere represents the effect of all other ions in solution on ion- j . So the Debye length κ^{-1} decreases and the intensity of the interaction between ion- j and the ion atmosphere increases. Thus ion- j is stabilised by ion- $j \leftrightarrow$ ion atmosphere interactions. The DHLL assumes that the solution is dilute such that $\kappa^{-1} \gg r_j$ where r_j is the ionic radius.

Combination of equations 6.2 and 6.3 leads to the Brønsted-Bjerrum relationship for reaction in solutions having ionic strength I ;

$$\ln \left(\frac{k}{k^0} \right) = -2A_{\gamma} z_A z_B \left(\frac{I}{m^0} \right)^{1/2} \quad 6.5$$

$$\lim (I \rightarrow 0) k \rightarrow k^0$$

According to equation 6.5, a reaction of the type described in equation 6.1 should show a linear dependence of $\ln(k/k_0)$ upon $I^{1/2}$. Many experiments⁸ have tested the validity of the Brønsted-Bjerrum relationship. Equation 6.5 predicts a positive salt effect for reactions between ions of unlike charge, negative salt effect for reactions between ions of like charge and no salt effect for reactions involving neutral solute molecules. This prediction appears to have been confirmed by Livingston⁸ and was considered to be a validation of the Brønsted relationship.

With increase in ionic strength the treatment falls down when based on the DHLL. Hence the full Debye-Hückel equation is often used to relate $\ln \gamma_j$ to ionic strength; equation 6.6

$$\ln \gamma_j = -A_{\gamma} \frac{z_j^2 \left(\frac{I}{m^0} \right)}{1 + B a_j \left(\frac{I}{m^0} \right)} \quad 6.6$$

Here B depends on temperature and relative permittivity of the solvent; a_j reflects the distance of closest approach of other ions in solution.

For salt effects to be observed, the dependence of activity coefficients of initial and transition states upon ionic strength must differ. The full Debye-Hückel equation, incorporated into equation 6.2 makes it possible to examine

additional specific effects on the two states by ions in solution.⁹ If $a_i > a_‡$ the transition state will be stabilised relative to the initial state at constant I leading to an increase in rate constant. Conversely, if $a_‡ > a_i$ the opposite will be the case and a decrease in rate constant will be observed.

Using this approach Blandamer et al⁹ calculated some values for a_i and $a_‡$ for tetrabutylammonium, tetramethyl- ammonium and potassium bromides (see table 6.1). From these values, equation 6.2 would predict an increase in rate constant for the aquation of $[\text{Fe(II)(5-NO}_2\text{-phen)}_3]^{2+}$ when tetrabutylammonium bromide was added, indicating a greater stabilisation of the transition state, whilst added potassium and tetramethylammonium bromides destabilise the transition state relative to the initial state giving rise to an increase in rate constant. Figure 6.1 appears to confirm this.

With increase in ionic strength the Debye-Hückel treatment breaks down. This is primarily due to the assumptions upon which the theory is based. Three important assumptions are

- i) Ions are treated as solid charged spheres.
- ii) The dielectric properties of the solution are constant independent of ionic strength.
- iii) The Boltzmann distribution has been replaced by a linear expression in which e^{-x} is replaced by $(1 - x)$, where $x = (z_i e \psi_j) / kT$; z_i is the charge on ion-i and ψ_j is the charge density.

While these assumptions hold for dilute solutions they become unacceptable with increase in I. In an attempt to improve the fit to observed data, a term linear in molality is often added to equation 6.6.

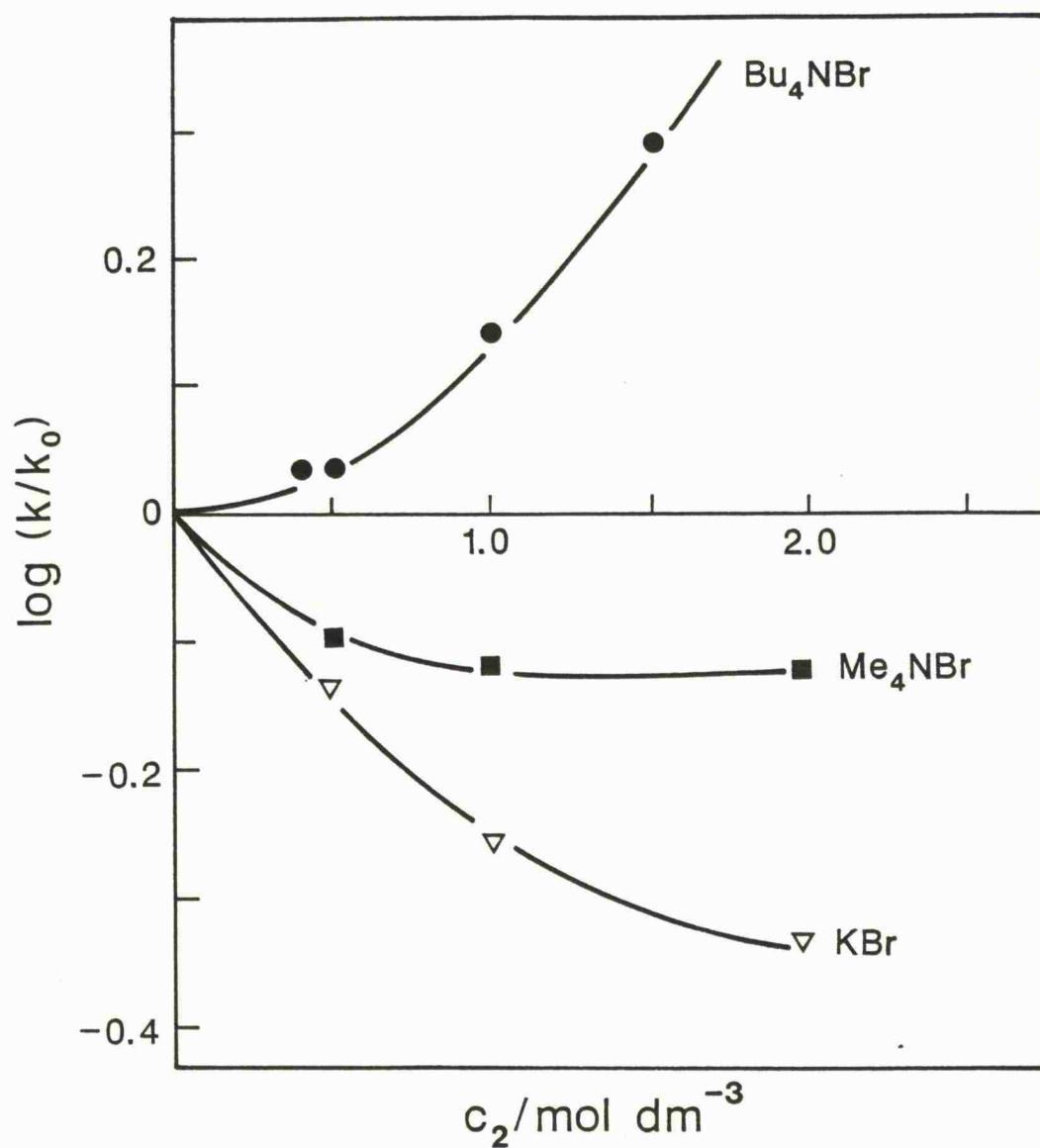


Figure 6.1: Comparison of observed dependencies of $\ln(k/k_0)$ on concentration of added salt for aquation of the ion $[\text{Fe}(\text{5-NO}_2\text{-phen})_3]^{2+}$ at 298.15K

Table 6.1: Calculated values of Debye-Hückel a_j parameters for some bromide salts (after ref. 9).

Salt	a_i/nm	a_{Br}/nm
KBr	5.2	11.0
Me_4NBr	4.9	6.6
Bu_4NBr	5.3	2.9

$$\ln \gamma_j = -A_\gamma \frac{z_j^2 \left(\frac{I}{m^\circ} \right)^{1/2}}{1 + B a_j \left(\frac{I}{m^\circ} \right)^{1/2}} + \sum_i C m_i \quad 6.7$$

The sum is taken over all ions in solution.

Guggenheim¹⁰ reported that dependence on ionic strength of ionic activity coefficients of ions in aqueous solution could be described by equation 6.8, where the term $B a_j$ is assumed to be close to unity.

$$\ln \gamma_j = -A_\gamma \frac{z_j^2 \left(\frac{I}{m^\circ} \right)^{1/2}}{1 + B a_j \left(\frac{I}{m^\circ} \right)^{1/2}} + C \left(\frac{I}{m^\circ} \right) \quad 6.8$$

However, Scatchard claimed that a better fit is obtained by setting $B a_j$ to 1.5.¹¹

Since,

$$\frac{1}{1 + \left(\frac{I}{m^\circ} \right)^{1/2}} = 1 - \left(\frac{I}{m^\circ} \right)^{1/2} + \left(\frac{I}{m^\circ} \right) - \left(\frac{I}{m^\circ} \right)^{3/2} \quad 6.9$$

with the condition $I^{1/2} < 1$, Guggenheim's equation becomes

$$\begin{aligned} \ln \gamma_j = & -A_\gamma z_j^2 \left(\frac{I}{m^\circ} \right)^{1/2} + (C + A_\gamma z_j^2) \left(\frac{I}{m^\circ} \right) \\ & - A_\gamma z_j^2 \left(\frac{I}{m^\circ} \right)^{3/2} \end{aligned} \quad 6.10$$

and Scatchard's

$$\ln \gamma_j = -A_\gamma z_j^2 \left(\frac{I}{m^\circ} \right)^{\frac{1}{2}} + \left(C + (3/2)A_\gamma z_j^2 \right) \left(\frac{I}{m^\circ} \right) - (3/2)A_\gamma z_j^2 \left(\frac{I}{m^\circ} \right)^{3/2} \quad 6.11$$

Describing the activity coefficient in terms of increasing powers of ionic strength is unsatisfactory¹² and these classical treatments failed to describe the effect of added ions on kinetic salt effects.

6.3 Solvent structure about solvated species.

Frank and Wen¹³ proposed a hydration model for the hydration of simple ions in aqueous solution. Around a given ion-j in an ideal aqueous solution, three zones of solvent are identified. Electrostricted water in zone A is the primary hydration shell. Water molecules in zone C are unaffected by the presence of the ion and may be considered bulk solvent. The size and nature of zone B is ion dependent and is defined as 'structure broken'. Zone B consists of water molecules where organisation is not compatible with zone A or zone C. For Li^+ and F^- zone B does not exist and these ions are called electrostrictive structure formers. Ions such as I^- and Br^- have large zones B and are termed electrostrictive structure breakers. Tetraalkylammonium ions (R_4N^+ where $\text{R} \geq \text{Et}$) fall into the category hydrophobic water structure formers, acting to enhance neighbouring water-water interactions whilst ion-water interactions are weak. X-ray diffraction data for tetrabutylammonium fluoride in aqueous solution at 298 K¹⁴ appear to confirm this model. The results of this X-ray study indicate that the butyl chains are located in cavities formed by hydrogen bonded water molecules. This model is further supported by comparisons of the physical properties of solutions containing the ions $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}^+(\text{aq})$ and $(\text{HOCH}_2\text{CH}_2)_4\text{N}^+(\text{aq})$, both ions being of similar size.¹⁵⁻¹⁷ Introduction of the hydrophilic OH groups into the alkyl chains provides a locations for direct water-water

interactions resulting in the loss of properties characteristic of $R_4N^+(aq)$ ions. The comparisons were made between the concentration dependence of partial molar volumes, enthalpies of dilution and viscosity for solutions containing both ions. Solutions containing the $(CH_3CH_2CH_2)_4N^+(aq)$ ion exhibited effects on these physical properties characteristic of enhanced water-water interactions around the inert alkyl chains. These effects were not seen for similar data for solutions containing $(HOCH_2CH_2)_4N^+(aq)$, indicating a disruption of the water structure enhancement observed around the alkyl analogue. The degree of water structure enhancement increases with the size of the alkyl chains.

For a real aqueous solution, an additional important feature are the ion-ion interactions. The chemical potential of a 1:1 salt-j is defined by;

$$\mu_j(aq;T;P) = \mu(aq;T;P;m_j=1;\gamma_{\pm}=1) + 2RT \ln \left(\frac{m_j}{m^\circ} \right) + 2RT \ln \gamma_{\pm} \quad 6.12$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient;
 $m^\circ = 1.0 \text{ mol kg}^{-1}$

Equation 6.12 can be divided into two parts. The first two terms describe the ideal contribution to the chemical potential. The third is the non-ideal contribution. In aqueous solution $\ln \gamma_{\pm}$ describes the effect of charge-charge interactions as described in the context of the Debye-Hückel equation (equation 6.5). However, an equally important contribution describes the impact of co-sphere interactions. Gurney defined a co-sphere in terms of the solvent around a given solute molecule where the organisation of the solvent differs from that of the pure solvent.¹⁸ In a real solution these co-spheres overlap and interact, hence contributing to $\ln \gamma_{\pm}$ for a salt in aqueous solution.

Desnoyers et al¹⁹ examined the dependence of $\ln \gamma_{\pm}$ on alkylammonium and alkali metal halides in aqueous solution

at 298.15 K and at constant ionic strength. They showed that co-sphere - co-sphere overlap is an important factor in determining $\ln \gamma_{\pm}$ and related thermodynamic properties of added salts in aqueous solutions. As has already been discussed, in a dilute solution, $\ln \gamma_{\pm}$ is adequately described by the Debye-Hückel treatment (equations 6.3 and 6.5). At low ionic strength, co-sphere - co-sphere overlap is negligible and $\ln \gamma_{\pm}$ is determined by charge-charge interactions alone. In summary,

$$\ln \gamma_{\pm} = f(\text{Debye - Hückel}) + f(\text{co-sphere - co-sphere}) \quad 6.13$$

Desnoyers developed the ideas proposed by Frank and Wen, who discussed the organisation of water in the hydration sphere around ions in solution, suggesting that this organisation played a role in ion-ion interactions. Indeed, Desnoyers indicated that the organisation of water molecules in the hydration sphere was a key factor in determining the contribution of co-sphere interactions to $\ln \gamma_{\pm}$ and the overall effect of co-sphere overlap on the structure of the overlapping shells of the bulk solvent. Using this model Desnoyers suggested that it was unimportant whether a hydrophilic ion was an overall structure maker or structure breaker, as long as the increase in ordering is different from that produced by hydrophobic ions. For example, interaction III in figure 6.2 between two structure breakers (Cs^+ and I^-) leads to the same effect on $\ln \gamma_{\pm}$ as that between two structure formers (Li^+ and F^-). In both cases sharing of co-spheres enhances water orientation or reduces structure breaking, which leads to the same overall effect on $\ln \gamma_{\pm}$.

6.4 Salt effects upon neutral species in aqueous solution.

Conventionally, kinetic salt effects have been studied using reactions between ions. Plots of $\ln(k/k_0)$ against $I^{1/2}$ are prepared as was discussed in 6.1. The results of studies involving neutral dipolar substrates, using salt effects are normally summarised using plots of $\ln(k/k_0)$ against [salt].²⁰

Effect of Overlap
& Resulting Force

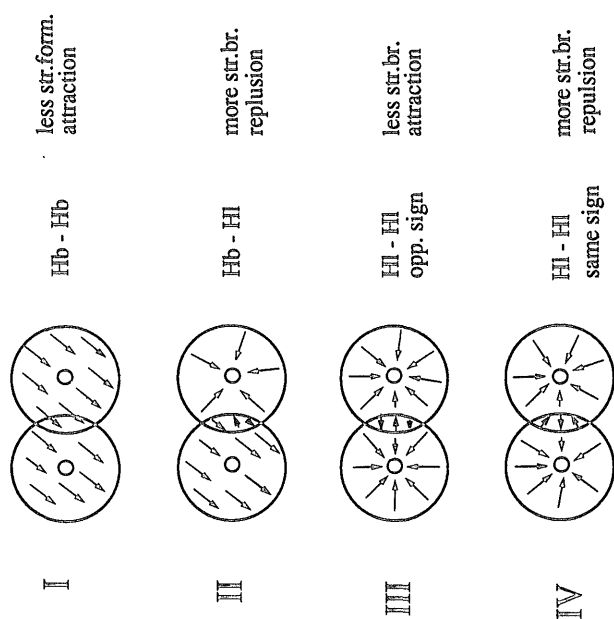
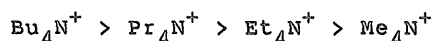


Figure 6.2: Structural hydration interaction model. Hb = hydrophobic ion; HI = hydrophilic ion; str. form = structure forming; str. br. = structure breaking.

Engberts et al²¹ studied salt effects in aqueous solution at fixed temperature and pressure on the kinetics of hydrolysis of two neutral dipolar compounds, phenyl and p-methoxyphenyl dichloroacetate. In figure 6.3 the dependence of $\ln\gamma_{\pm}$ on cation for a given anion in aqueous salt solutions at fixed ionic strength is summarised. The format of this figure follows the pattern suggested by Desnoyers and coworkers. The close similarity in the pattern formed by plots of $\ln\gamma_{\pm}$ and of $\ln(k/k_0)$ against anion (with common cation throughout the plot) highlights the importance of co-sphere overlap in aqueous solution.

Figure 6.3 shows some interesting trends. For tetrabutylammonium bromide, cation-cation co-sphere interactions dominate the properties of the solution. Tetrabutylammonium cations are strongly hydrophobic whereas bromide anions are less hydrophilic than chloride or fluoride anions. As can be seen from figure 6.3, there is a resulting attraction between hydrophobic co-spheres and a corresponding decrease in $\ln\gamma_{\pm}$ below that calculated by the DHLL. In other words cation $\leftrightarrow$ cation co-sphere overlap is a stabilising factor in these solutions. The hydrophobic nature of tetraalkylammonium cations decreases in the following order;



For the fluoride salts, co-sphere interactions appear to be dominated by repulsive co-sphere interactions, i.e. hydrophobic-hydrophilic for tetraalkylammonium fluorides and hydrophilic-hydrophilic (same sign) for alkali metal salts.

Engberts et al²¹ showed that the dependence of $\ln(k/k_0)$ for neutral hydrolysis of phenyldichloroacetate and its para-methoxy derivative on salts at fixed ionic strength followed the same pattern. In other words the kinetics of aquation were sensitive to the structure of the salt solution produced by the co-sphere overlap interactions.

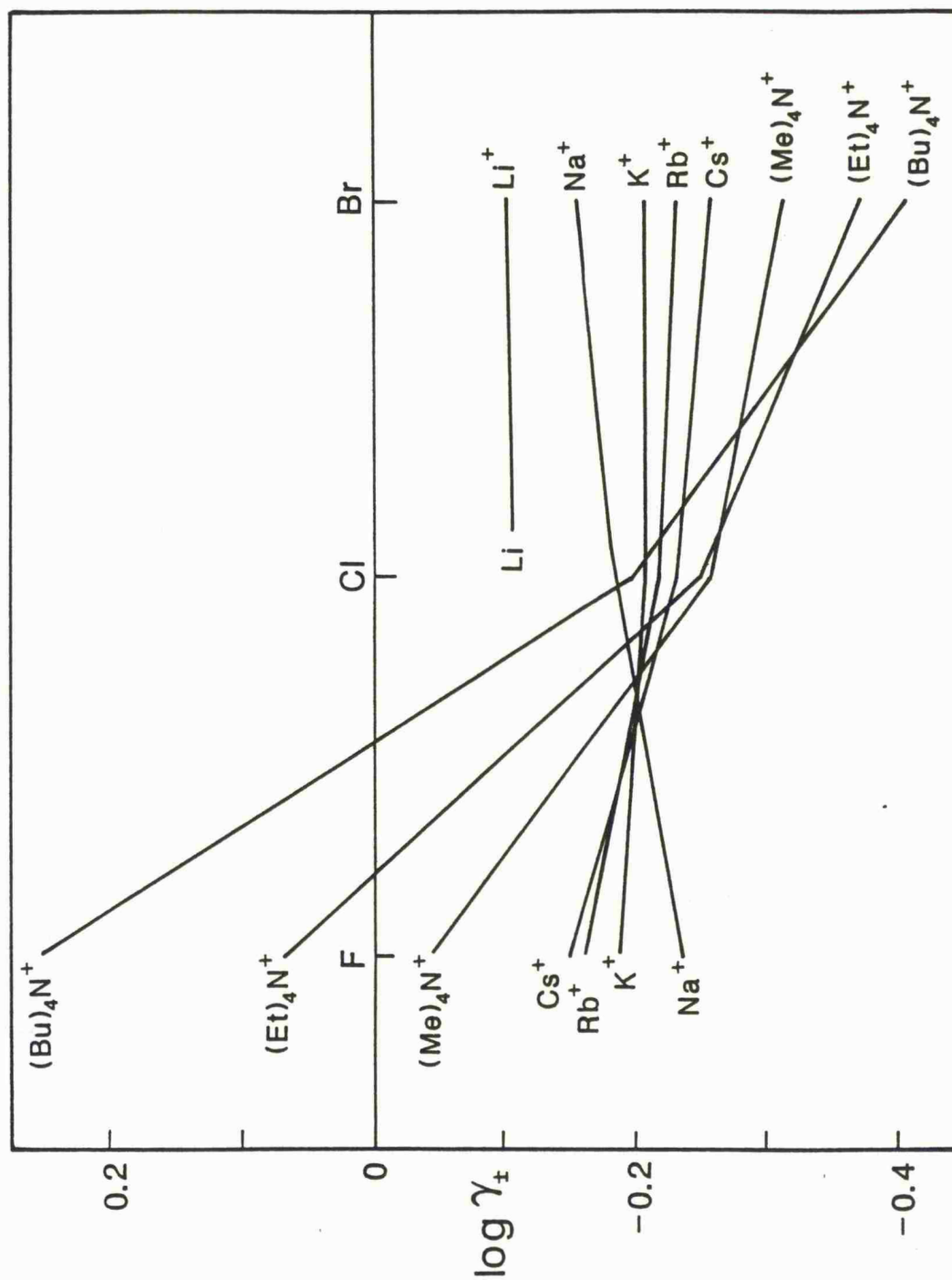


Figure 6.3: Dependence of mean ionic activity coefficient against anion for a given cation

6.5 Pitzer's equations.

Consider an aqueous solution containing ion-j at molality m_j , the chemical potential for ion-j is defined by equation 6.14.

$$\mu_j(\text{aq}; T; P) = \mu_j^\#(\text{aq}; T; P; m_j=1; \gamma_j=1) + RT \ln \left(\frac{m_j \gamma_j}{m^\circ} \right) \quad 6.14$$

where γ_j is the single ion activity coefficient of ion-j.

For an aqueous solution containing 1 mole of salt MX, the molality of cations and anions (assuming complete dissociation) being v_m and v_x respectively, the chemical potential of the salt in solution (see equation 6.12) is related to that of the single ions by equation 6.15.

$$\mu(\text{salt}; \text{aq}; T; P) = v_m \mu_m(\text{aq}; T; P) + v_x \mu_x(\text{aq}; T; P) \quad 6.15$$

In the Pitzer treatment^{4,22} the single ion activity coefficient, γ_j is described by successive terms which take into account both charge-charge interactions and co-sphere effects. Equations 6.16 and 6.17 relate the single ion activity coefficients of cationic and anionic species respectively (M and X) in aqueous solution to the ionic strength.

$$\begin{aligned} \ln \gamma_M = & z^2 M f_\gamma + 2 \sum_a m_a \left(2B_{Ma}^\gamma + zC_{Ma}^\gamma \right) \\ & + 2 \sum_c m_c \left(2\phi_{Mc} + \sum m_c \psi_{Mca} \right) \end{aligned} \quad 6.16$$

$$\ln \gamma_X = z^2 X f_Y + 2 \sum_c m_c \left(2B^Y_{cX} + zC^Y_{cX} \right) \quad 6.17$$

$$+ 2 \sum_a m_a \left(2\phi_{Xa} + \sum_c m_c \psi_{cXa} \right)$$

The leading terms of equations 6.16 and 6.17 are that part of $\ln \gamma_j$ which arise from charge-charge interactions between ion-j and other ions in solution. The quantity f^Y incorporates the Debye-Hückel term (see equation 6.6) and is defined by equation 6.18.

$$f_Y = -\frac{A_Y}{3} \left\{ \frac{\left(\frac{I}{m^0} \right)}{1 + b \left(\frac{I}{m^0} \right)} + \left(\frac{2}{b} \right) \ln \left[1 + b \left(\frac{I}{m^0} \right)^{1/2} \right] \right\} \quad 6.18$$

where A_Y is a function of solvent permittivity and density and b is a constant,⁵ $1.2 \text{ mol}^{1/2} \text{ kg}^{1/2}$.

The following terms of equations 6.16 and 6.17 describe the non-coulombic interactions of the ions in solution. The B^Y , C^Y and ϕ terms in equations 6.16 and 6.17 are characteristic of the pairwise non-coulombic interactions of the subscripted ions in aqueous solution. The ψ term is a composite cross term characteristic of the triplet non-coulombic interaction parameter. This brief outline forms the basis of the calculations in chapter 7.

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Chapter 7

Application of Pitzer's equations to the alkaline hydrolysis of bromophenol blue in aqueous salt solutions.

7.1 Introduction.

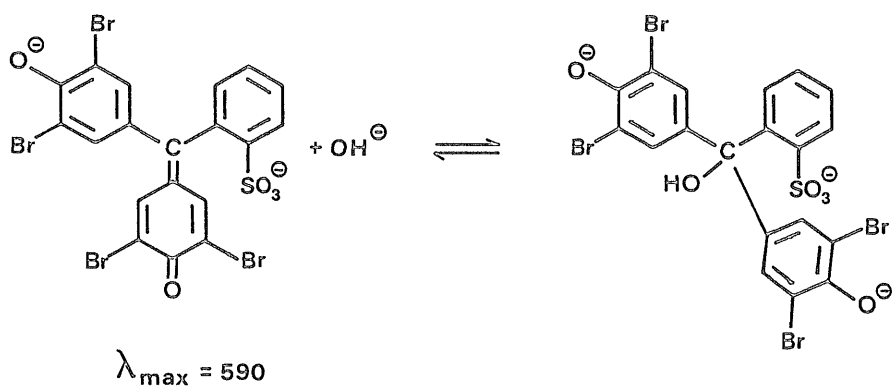
The alkaline hydrolysis of the intensely coloured dye bromophenol blue (tetrabromosulphonphthalein) involves the formation of the corresponding triphenyl carbinol derivative (colourless). The rate of hydrolysis is sensitive to the nature and concentration of added co-solute. Therefore this system offers a convenient testbed for theories concerning the effects of added salts upon rate constants for reactions in aqueous solutions. The reaction involves mono- (i.e. OH^-) and di-negative (i.e. BPB^{2-} ; formula shown in figure 7.1) ions, the transition state bearing a tri-negative charge. This reaction is a classic reaction of the type described in equation 6.1.

Previously reported second order rate constants for this base hydrolysis reaction^{1,2,3} in the presence of added tetraalkylammonium halides are analysed in the light of new data for reaction in the presence of alkali metal halides. The DHLL (see chapter 6) predicts that the second order rate constant will increase with ionic strength. This was not the observed effect of added Et_4N^+ halides. In the procedure described here we examine trends in $\ln(k_2/k_0)$ using Pitzer's equations,^{4,5} where k_2 is the rate constant for the hydrolysis reaction in aqueous salt solution of ionic strength I and k_0 is the rate constant for the reaction at zero ionic strength (introduced in chapter 6). Kinetic data are fitted to an equation for kinetic salt effects in a single step for added Me_4N^+ and alkali metal halides using a FORTRAN program. This produced a common set of specific ion-ion interaction parameters for the complete data set. These were incorporated into a separate fitting exercise necessary to analyse the effects of added Et_4N^+ halides.

7.2 Experimental.

A concentrated stock solution of the di-sodium salt of bromophenol blue (BPB) was prepared using a method documented by Amis and LaMer.⁶ The reaction between BPB ($\lambda_{\text{max}} = 590\text{nm}$) and hydroxide ions is illustrated in figure 7.1. The carbinol species is characterised by an intense

Figure 7.1: The alkaline hydrolysis of bromophenol blue.



absorption band centred at $\lambda_{\text{max}} = 510\text{nm}$, this corresponds to a $\pi \rightarrow \pi^*$ transition.

A cell of path length 1.0 cm containing a solution of added salts of ionic strength I ($0.0 \leq I/\text{mol kg}^{-1} \leq 2.0$) was placed in the cell holder of a computer controlled Pye-Unicam SP1800 spectrophotometer and allowed to attain thermal equilibrium over five minutes at 298.15K. To this solution was added one drop of concentrated BPB solution such that the initial absorbance was approximately 1.0. The reaction was monitored for 2.5 half-lives.

First order rate constants, $k(\text{obs})/\text{s}^{-1}$, were obtained for the alkaline fading of the dye in solutions where $[\text{OH}^-] = 0.1 \text{ mol dm}^{-3}$ and $[\text{OH}^-] \gg [\text{BPB}]$ i.e. $[\text{BPB}] \approx 10^{-5} \text{ mol dm}^{-3}$. Overall, the reaction is second order but, by having the concentration of hydroxide in vast excess to that of the dye first-order rate constants were obtained. Given that P is the absorbance

$$\frac{dP}{dt} = k(\text{obs}) \cdot [\text{BPB}] \quad 7.1$$

Hence, under these conditions

$$k(\text{obs}) = k_2 \cdot [\text{NaOH}] \quad 7.2$$

where $k_2/\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ is the second order rate constant.

Absorbance time data were analysed as outlined in chapter 2.

7.3 Results.

Second order rate constants for the effect of added tetraalkylammonium salts given here agree with those reported previously¹. The range of dependence of rate constants on ionic strength is extended for tetraalkylammonium halides and the data set now also incorporates data for alkali metal halides (tables 7.1-7.3). With increase in ionic strength, I , of added tetramethylammonium and alkali metal halides there was a corresponding increase

Table 7.1 Second order rate constants for the alkaline hydrolysis of bromophenol blue in aqueous salt solutions containing alkali metal halides at 298.15 K and ambient pressure.

I/mol kg ⁻¹	k ₂ /10 ⁻⁴ dm ³ mol ⁻¹ s ⁻¹				
	KBr	KI	KCl	NaI	NaCl
0.25	8.99	8.42	9.41	10.30	9.73
0.50	9.65	8.56	10.60	9.41	10.70
0.75	10.10	8.76	11.50	9.17	11.30
1.00	10.31	8.61	12.10	8.64	11.70
1.25			12.20	7.36	11.80
1.50	10.56	8.05	12.50		11.90
1.75				7.26	12.20
2.00	10.85	7.55		6.95	12.50
	LiCl	LiBr			
0.25	9.39	9.44			
0.50	9.96	9.70			
0.75	10.00	9.79			
1.00	10.20	9.58			
1.25	10.30	9.26			
1.50	9.98	8.89			
1.75		8.36			
2.00	9.71	7.78			

Table 7.2 Second order rate constants for the alkaline hydrolysis of bromophenol blue in aqueous salt solutions containing tetramethylammonium halides at 298.15 K and ambient pressure.

I/mol kg ⁻¹	k ₂ /10 ⁻⁴ dm ³ mol ⁻¹ s ⁻¹		
	Me ₄ NF	Me ₄ NCl	Me ₄ NBr
0.25	10.9	10.1	9.43
0.50	13.3	11.3	10.0
0.75	15.3	12.3	10.1
1.00	16.8	13.1	10.3
1.50	21.0	14.4	10.6
2.00	25.3	10.6	10.8

Table 7.3 Second order rate constants for the alkaline hydrolysis of bromophenol blue in aqueous salt solutions containing tetraethylammonium halides at 298.15K and ambient pressure.

	$k_2/10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		
$I/\text{mol kg}^{-1}$	Et_4NF	Et_4NBr	Et_4NI
0.10	6.41	—	—
0.25	5.34	6.36	6.98
0.40	4.21	—	—
0.50	3.76	5.76	6.90
0.60	3.18	—	—
0.75	2.68	5.19	6.81
1.00	—	4.49	6.81
1.50	—	3.97	—
2.00	—	3.53	—

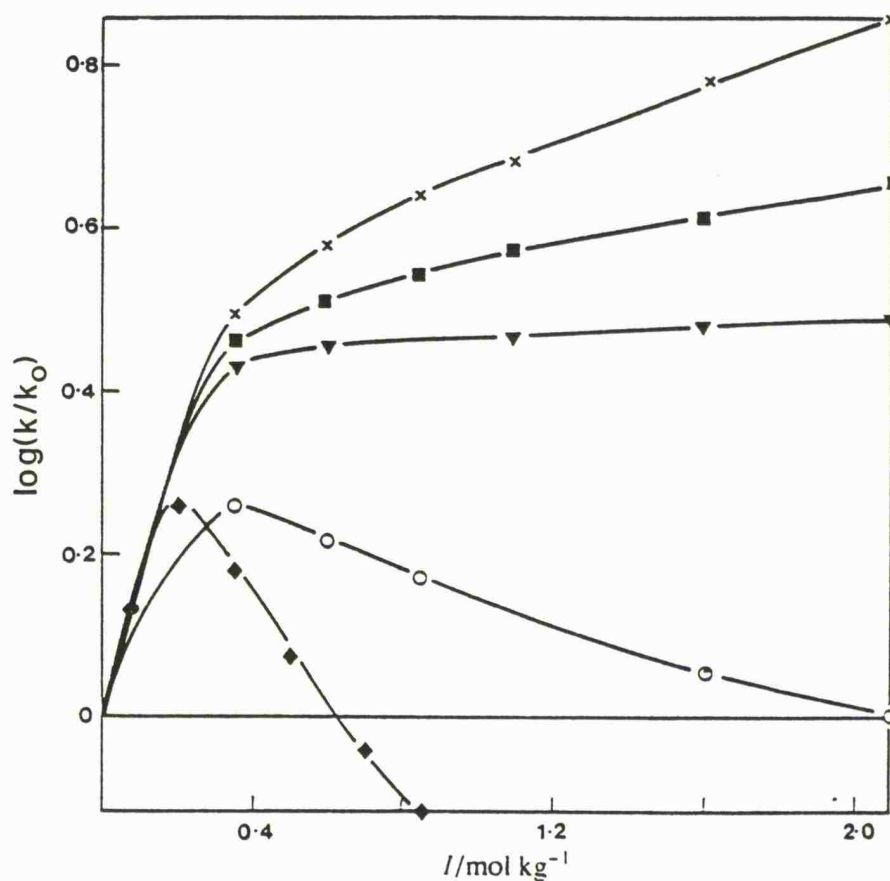


Figure 7.2: Dependence of $\log(k_2/k_0)$ on ionic strength of added tetramethyl- and tetraethyl ammonium halides for alkaline hydrolysis of bromophenol blue at 298.15K and ambient pressure; TMAF (x); TMACl (■); TMABr (▼); TEABr (○); TEAl (♦).

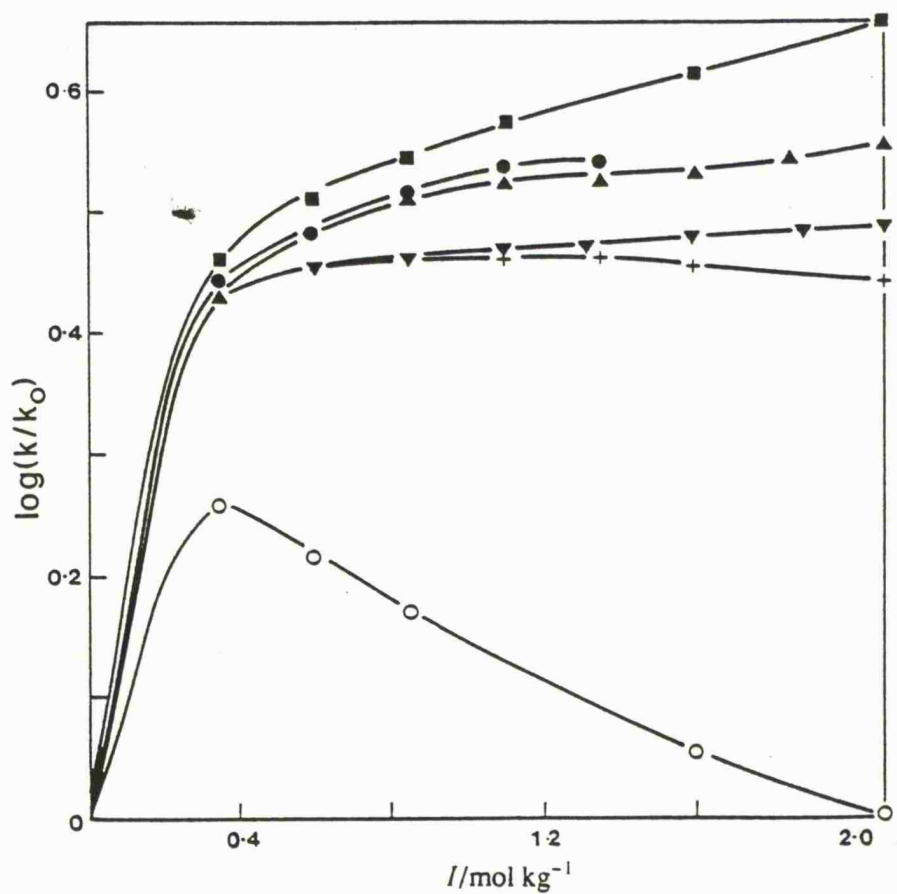
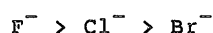


Figure 7.3: Dependence of $\log(k/k_0)$ on ionic strength of added salt for alkaline hydrolysis of bromophenol blue at 298.15K and ambient pressure showing the effects of added chloride salts of: Me_4N^+ ($\blacksquare$); K^+ ($\bullet$); Na^+ ($\blacktriangle$); Li^+ ($+$); and bromide salts of: Me_4N^+ ($\blacktriangledown$); Et_4N^+ ($\circ$).

in the second order rate constant for the alkaline hydrolysis of BPB with respect to k_0 (the rate constant at zero ionic strength, $k_0 = 3.507 \times 10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$).⁶ A specific anion effect was observed for salts with a common cation (figure 7.2), the rate increases being in the order



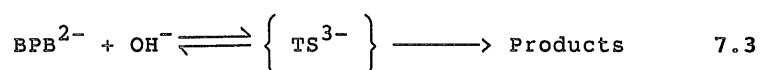
When salts with a common anion were added to an alkaline solution containing the BPB(2-) anion, rate constants were cation dependent (figure 7.3).

In the case of added tetramethylammonium iodide, the rate constant was found to increase initially with respect to k_0 but fall below k_0 with increase in I . The fall in rate constant was less marked with added bromide and, in the case of the fluoride, there was a slight initial increase with the rate constant remaining unchanged in the region $0.25 \leq I/\text{mol kg}^{-1} \leq 1.0$. Problems involving the 'salting-out' of Bu_4N^+ halides during kinetic runs excluded them from this preliminary analysis.

Analysis of data.

7.4 Description of systems.

According to the Brønsted-Bjerrum approach (section 6.1) the dependence of second order rate constant on ionic strength, I , is related to the ionic activity coefficients of transition and initial states.⁷



For this reaction

$$\ln \left(\frac{k_2}{k_0} \right) = \ln \gamma(\text{TS}; z = -3) + \ln \gamma(\text{BPB}^{2-}; z = -2) \quad 7.4$$

$$+ \ln \gamma(\text{OH}^-; z = -1)$$

where $\lim(I \rightarrow 0), k_2 \rightarrow k_0$

and

$$\ln \gamma(\text{OH}^-) = -A^\gamma z(\text{OH}^-)^2 \left(\frac{I}{m^\circ} \right) \quad 7.5$$

$$\ln \gamma(\text{BPB}^{2-}) = -A^\gamma z(\text{BPB}^{2-})^2 \left(\frac{I}{m^\circ} \right) \quad 7.6$$

$$\ln \gamma(\text{TS}^{3-}) = -A^\gamma z(\text{TS}^{3-})^2 \left(\frac{I}{m^\circ} \right) \quad 7.7$$

where $A^\gamma = 1.1763$, z is the charge number of the ion and $m^\circ = 1.0 \text{ mol kg}^{-1}$.

According to Transition State Theory,⁸ in the presence of NaOH (aq; 0.1 mol dm^{-3}) and added salt MX, the molalities of $\text{BPB}^{2-}(\text{aq})$ ions and their counter ions, $\text{Na}^+(\text{aq})$, are negligible and can be ignored for the purposes of calculating ionic strength.

Hence, at time, t , ionic strength, I , is given by equation 7.8.

$$I = \frac{1}{2} \left[m(\text{BPB}^{2-}) \cdot z(\text{BPB}^{2-})^2 + m(\text{Na}^+) \cdot z(\text{Na}^+)^2 \right. \\ \left. + m(\text{OH}^-) \cdot z(\text{OH}^-)^2 + m_M \cdot z(M)^2 + m_X \cdot z(X)^2 \right] \quad 7.8$$

where m_M and m_X are the molalities of cation and anion respectively, assuming complete dissociation and BPB is the di-negative initial state of bromophenol blue.

According to the DHLL, the activity coefficient of an ion in dilute aqueous salt solution at 298 K can be related to ionic strength using equation 6.3. The DHLL predicts a linear dependence of $\ln(k_2/k_0)$ upon $(I/m^\circ)^{1/2}$ and, for this reaction, charge numbers would operate to give a positive salt effect. Figure 7.4 shows the predicted relative

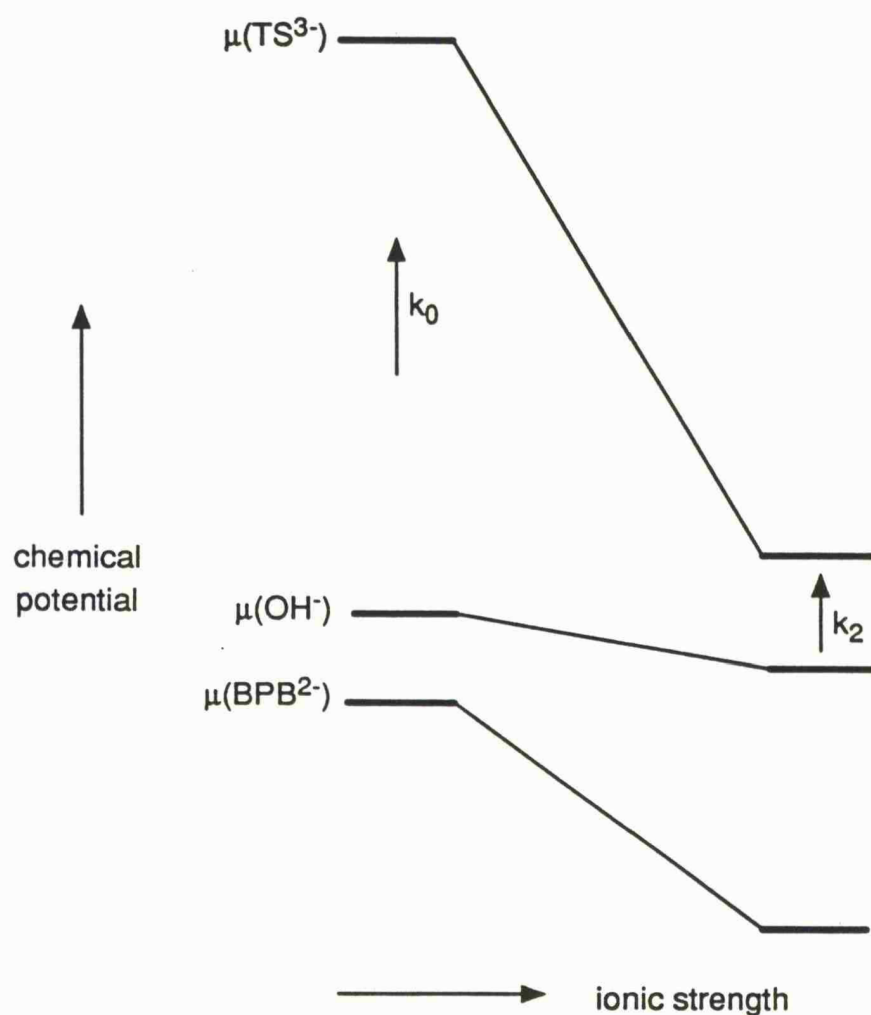


Figure 7.4: Illustration of relative stability of solute species in solution, showing effect of increase in ionic strength on rate constant. The transition state is stabilised to a greater extent by added salt than either component of the initial state.

stability of the ions involved with increase in ionic strength. The transition state is predicted to be stabilised to a greater extent with increase in ionic strength than either component of the initial state producing an increase in rate constant.

7.5 Pitzer's equations.

Pitzer's treatment of the properties of salt solutions^{4,5} is based on a statistical thermodynamic treatment of solutions in which osmotic and activity coefficients are related to pair correlation functions for solute molecules.

In an ideal solution there are no interactions between solute molecules. However, in a real solution interactions occur and contribute to the overall Gibbs energy of the system. A convenient measure of solute-solute interaction in solution is the excess Gibbs energy. Pitzer describes the latter property in terms of a virial expansion. For a solution containing n_W kg of solvent and species $i, j, k, \dots$ at molalities of $m_i, m_j, m_k, \dots$ respectively, the total excess Gibbs energy is given by;

$$\frac{G^E}{n_W RT} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} \quad 7.9$$

The first term includes the DHLL; $\lambda_{ij}(I)$ is the second virial coefficient (pairwise) which depends on ionic strength, I , where

$$I = \frac{1}{2} \sum m_i z_i^2 \quad 7.10$$

The third virial coefficient (triplet) has, in principle, a dependence on ionic strength, but this is small and usually ignored. The λ - and μ -terms depend on temperature and pressure, and on composition through ionic strength. Pitzer defines the term $f(I)$, a function of ionic strength;

$$f(I) = - \frac{4A^\phi \left(\frac{I}{m^\circ} \right)}{b} \cdot \ln \left[1 + b \left(\frac{I}{m^\circ} \right) \right] \quad 7.11$$

where b is a constant, $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$. A^ϕ is the Debye-Hückel parameter given by equation 7.12;

$$A^\phi = \frac{1}{3} \left(\frac{2\pi N_O d_W}{1000} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_O \epsilon kT} \right) \quad 7.12$$

with ϵ the relative permittivity and d_W the density of the solvent.

In the application discussed below, the required quantity is the single ion activity coefficient for an anionic species in aqueous solution. Pitzer shows that $\ln \gamma_X$, where X is an anionic species, is given by

$$\begin{aligned} \ln \gamma_X = & z^2_X f^Y + \sum_c m_c \left(2B^Y_{cX} + zC^Y_{cX} \right) \\ & + \sum_a m_a \left(2\phi_{Xa} + \sum_c m_c \psi_{cXa} \right) \end{aligned} \quad 7.13$$

Here the first term is analogous to the quantity described in the Debye-Hückel approach

$$f^Y = -3A^\phi \left[\frac{\left(\frac{I}{m^\circ} \right)^{1/2}}{1 + b \left(\frac{I}{m^\circ} \right)^{1/2}} + \left(\frac{2}{b} \right) \ln \left\{ 1 + b \left(\frac{I}{m^\circ} \right) \right\} \right] \quad 7.14$$

$$z = \sum_i m_i |z_i| \quad 7.15$$

The terms in B^Y , C^Y , ϕ and ψ describe specific ion-ion interactions.

$$E_{ij} = \beta^{\circ}_{ij} + \beta^1_{ij} g \left\{ -\alpha \left(\frac{I}{m^{\circ}} \right) \right\} \quad 7.16$$

$$\Phi_{ij} = \Theta_{ij} + E_{\Theta ij} \quad 7.17$$

In terms of the analysis of kinetic data discussed below the C term and the $E_{\Theta ij}$ term, incorporated into Φ_{ij} are negligible. Hence for the three anionic reacting species in a solution containing 1:1 salt completely dissociating to produce anions a and cations c, the specific ionic activity coefficients are given by the following equations

For the BFB^{2-} anion,

$$\begin{aligned} \ln \gamma_{\text{BFB}^{2-}} = & -4f^{\gamma} + 2 \sum_a m_a \Theta_{\text{BFB}^{2-};a} + 2 \sum_c m_c \beta^{\circ}_{\text{BFB}^{2-};c} \\ & + 2 \sum_c m_c \beta^1_{\text{BFB}^{2-};c} g \left\{ -\alpha \left(\frac{I}{m^{\circ}} \right) \right\} \end{aligned} \quad 7.18$$

For the hydroxide anion,

$$\begin{aligned} \ln \gamma_{\text{OH}^-} = & -f^{\gamma} + 2 \sum_a m_a \Theta_{\text{OH}^-;a} + 2 \sum_c m_c \beta^{\circ}_{\text{OH}^-;c} \\ & + 2 \sum_c m_c \beta^1_{\text{OH}^-;c} g \left\{ -\alpha \left(\frac{I}{m^{\circ}} \right) \right\} \end{aligned} \quad 7.19$$

For the transition state,

$$\begin{aligned} \ln \gamma_{\ddagger} = & -9f^{\gamma} + 2 \sum_a m_a \Theta_{\ddagger;a} + 2 \sum_c m_c \beta^{\circ}_{\ddagger;c} \\ & + 2 \sum_c m_c \beta^1_{\ddagger;c} g \left\{ -\alpha \left(\frac{I}{m^{\circ}} \right) \right\} \end{aligned} \quad 7.20$$

The leading terms of the above equations define that part of γ_j , the ionic activity coefficient of an ion-j in aqueous solution, which is due to charge-charge interactions between ion-j and all other ions in solution. This term is γ_j^{elect} ;

$$\ln \gamma_j^{\text{elect}} = (z_j)^2 \cdot f^{\gamma} \quad 7.21$$

It is now possible to calculate the contribution of charge-charge interactions to $\ln(k_2/k_0)$ as required by $\ln \gamma_j^{\text{elect}}$. With $z(\text{B}^2)^2 - z(\text{OH}^-)^2 - z(\text{BFB})^2 = 4$, and F being the algebraic sum of the f^{γ} terms we can write

$$\ln \left(\frac{k_2}{k_0} \right) = -4 \cdot F \quad 7.22$$

If charge-charge interactions alone were responsible for observed kinetic salt effects the quantity γ^{elect} , as defined by equation 7.11, should be equal to zero.

$$\gamma^{\text{elect}} = \ln k_2 - \ln k_0 + 4F \quad 7.23$$

In practice γ^{elect} is not equal to zero and the magnitude of the measured rate constant is less than predicted by equation 7.22

7.6 Tetramethylammonium and alkali metal halides.

For this group of added salts in aqueous solution, the ionic activity coefficient of ion-j, γ_j , was expressed using equations 7.24-7.26. Considering activity coefficients for BFB^{2-} , OH^- , TS^{3-} , added anion X^- , added cation M^+ and also the Na^+ counter ion to OH^- , $\ln(k_2/k_0)$ was related to ionic strength, I .

A curve fitting exercise was performed by virtue of defining several Δ quantities, which are characteristic of a given ion in solution and its interactions with the BFB^{2-} , OH^- and TS^{3-} ions. Thus a quantity $\Delta\theta(\text{X}^-)$ is defined for added anion X^- , such that;

$$\Delta\theta(\text{X}^-) = \theta_{\text{X}^-} - \theta_{\text{BFB}^{2-};\text{X}^-} - \theta_{\text{OH}^-;\text{X}^-} \quad 7.24$$

Similarly for reactant anion, OH^- ,

$$\Delta\theta(\text{OH}^-) = \theta_{\text{OH}^-} - \theta_{\text{BFB}^{2-};\text{OH}^-} - \theta_{\text{OH}^-;\text{OH}^-} \quad 7.25$$

Similar Δ quantities are defined for β^0 and β^1 terms.

For example;

$$\Delta\beta^{\circ}(M^{+}) = \beta^{\circ}_{\neq;M^{+}} - \beta^{\circ}_{BFB2-;M^{+}} - \beta^{\circ}_{OH-;M^{+}} \quad 7.26$$

If a quantity Y is defined such that;

$$Y = \ln\left(\frac{k_2}{k_0}\right) + F \quad 7.27$$

These Δ quantities are related to the rate constant, k_2 , using equation 7.28.

$$\begin{aligned} Y = & -2\Delta\theta(OH^{-})m(OH^{-}) - 2\Delta\theta(X^{-})m(X^{-}) \\ & - 2\Delta\beta^{\circ}(Na^{+})m(Na^{+}) - 2\Delta\beta^{\circ}(M^{+})m(M^{+}) \\ & - 2\Delta\beta^1(Na^{+})g\left[\alpha\left(\frac{I}{m^{\circ}}\right)^{\frac{1}{2}}\right]m(Na^{+}) \\ & - 2\Delta\beta^1(M^{+})g\left[\alpha\left(\frac{I}{m^{\circ}}\right)^{\frac{1}{2}}\right]m(M^{+}) \end{aligned} \quad 7.28$$

In the event of the dependence of $\ln(k_2/k_0)$ being determined by charge-charge interactions alone, the quantity Y would be zero. The results of the calculations presented here indicate that this is not the case for this system. The curve fitting exercise was performed for the whole of the tetramethylammonium and alkali metal data set producing a set of common interaction parameters, i.e. in analysing the effects of added potassium bromide and tetramethylammonium bromide the parameter $\Delta\theta(Br^{-})$ is common to both salt effects.

In the original calculations, kinetic data for reactions in solutions containing tetraethylammonium halides were included in this analysis. It was found, however, that the data set for the hydrophobic tetraethylammonium cation stood apart from the other systems requiring a modified analysis. The interaction parameters were calculated using a least-squares analysis incorporated into a FORTRAN program using progressive interaction terms for each added ion.

The analysis showed that observed kinetic salt effects of added MX (where M = tetramethylammonium or alkali metal

cation) could be satisfactorily accounted for using terms up to β^0 ; β^1 parameters were negligible (figure 7.5).

7.7 Tetraethylammonium halides.

Interaction parameters for characterising the data for tetramethylammonium and alkali metal halides were inadequate when applied to the data for tetraethylammonium halides. This indicated that the observed kinetic salt effect for tetraethylammonium halides involved a more complex explanation than one based on simple pairwise additivity.

In order to analyse the effects of added tetraethylammonium halides a separate fitting exercise was applied. Calculations involved the inclusion of not only the β^1 term, but also a cross term of the type described by Pitzer.⁵ Hence equation 7.24 can be modified in the following way;

$$\ln \gamma_{\text{BPB}^{2-}} = [\text{Eq}^{\text{N}} 7.24] + |z_j| \sum_c \sum_a m_c m_a \psi_{m;\text{BPB}^{2-}}; x \quad 7.35$$

X = F⁻, Br⁻ and I⁻ in this case. Similar equations can be written for the other reacting species in solution, with a $\Delta\psi$ quantity being defined as shown in equations 7.30-7.34.

A further quantity, γ^{ET} , was defined such that;

$$\begin{aligned} \gamma^{\text{ET}} = \ln \left(\frac{k_2}{k_0} \right) + 4F + 2\Delta\theta(\text{OH}^-)m(\text{OH}^-) \\ + 2\Delta\theta(\text{X}^-)m(\text{X}^-) + 2\Delta\beta^0(\text{Na}^+)m(\text{Na}^+) \end{aligned} \quad 7.36$$

Equation 7.18 incorporates previously derived estimates for $\Delta\theta(\text{OH}^-)$, $\Delta\theta(\text{X}^-)$, $\Delta\beta^0(\text{Na}^+)$. Using this equation, the FORTRAN program was modified to fit the dependence of γ^{ET} upon ionic strength of added tetraethylammonium cation and halide anions. Equation 7.38 was used to evaluate the terms characteristic of the tetraethylammonium cation.

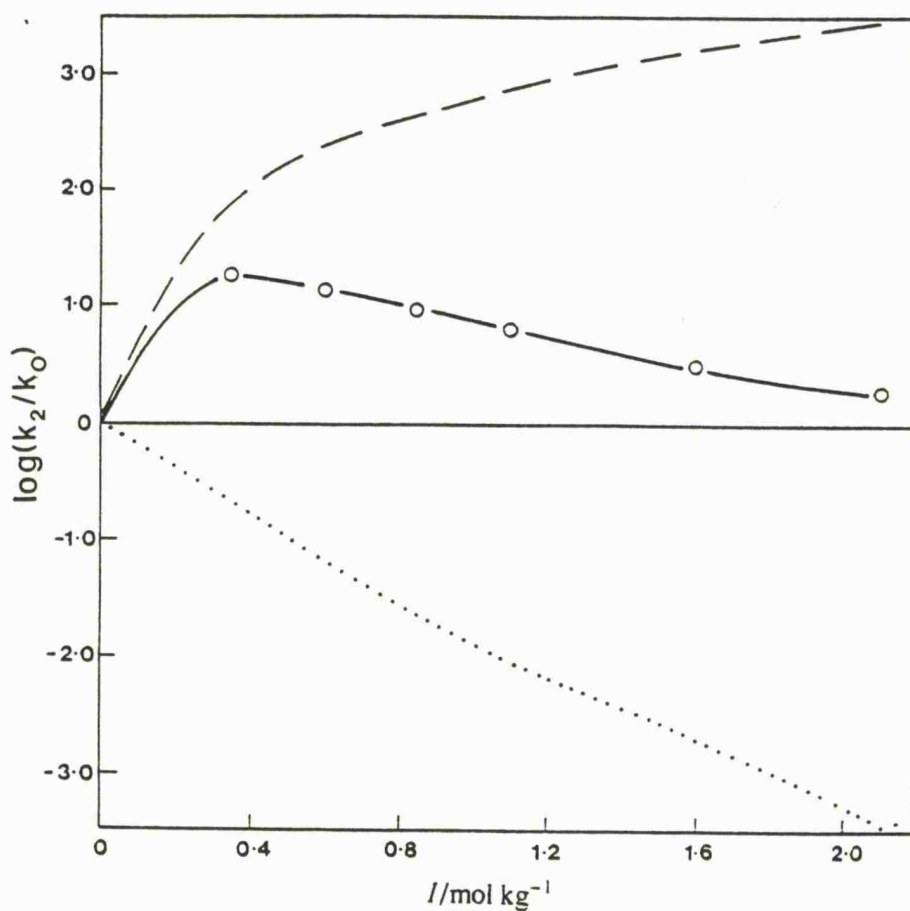


Figure 7.5: Dependence of $\ln(k_2/k_0)$ on ionic strength $I(\circ)$ for aqueous $\text{Me}_4\text{N}^+\text{Br}$ solutions; (— — — —) indicates the dependence predicted by Charge-Charge interactions (the F - term) and (.....) by $\Delta\Theta$ and $\Delta\beta^0$ terms in equation 7.16.

$$\begin{aligned}
y^{ET} = & -2\Delta\beta^0(Et_4N^+)m(Et_4N^+) - 2\Delta\beta^1(Et_4N^+)g\left\{\alpha\left(\frac{I}{m^0}\right)\right\} \\
& - \Delta\psi(Et_4N^+; j; X^-)m(Et_4N^+)m(X^-)
\end{aligned}
\tag{7.37}$$

The contribution of the component terms of y^{ET} , as described in equation 7.37, to the magnitude of $\ln(k_2/k_0)$ are illustrated in figure 7.6 and the calculated parameters produced by both analyses are summarised in tables 7.4 and 7.5.

7.8 Discussion.

The work outlined in this chapter describes the the first application of Pitzer's equations to kinetic salt effects. The Pitzer theory^{4,5} links the Debye-Hückel approach, involving charge-charge interactions, with that of Desnoyers, who developed the concept of co-sphere - co-sphere overlap between solvated ions; chapter 6. Classical descriptions of kinetic salt effects take into account the effect of added salt rather than added ion, as in the Pitzer approach. Furthermore, Pitzer's theory offers an opportunity to quantify the effect of charge-charge and co-sphere - co-sphere interactions. The application presented here develops Pitzer's original equations defining several Δ quantities (section 7.6), making it possible to apply the theory to a reaction in aqueous solution.

The defined Δ parameters make it possible to assess the effect of a specific added ion upon the rate constant of a specific reaction. For example, the $\Delta\theta(Cl^-)$ term is common to the observed kinetic salt effect produced by the addition of potassium chloride and sodium chloride and is independent of associated cation. Similarly, the $\Delta\beta^0$ terms are common to salts with common cations and independent of associated anion.

For the alkaline hydrolysis of bromophenol blue charge-charge interactions, as described by the F-term (equation 7.22), enhance the rate constant significantly. In contrast

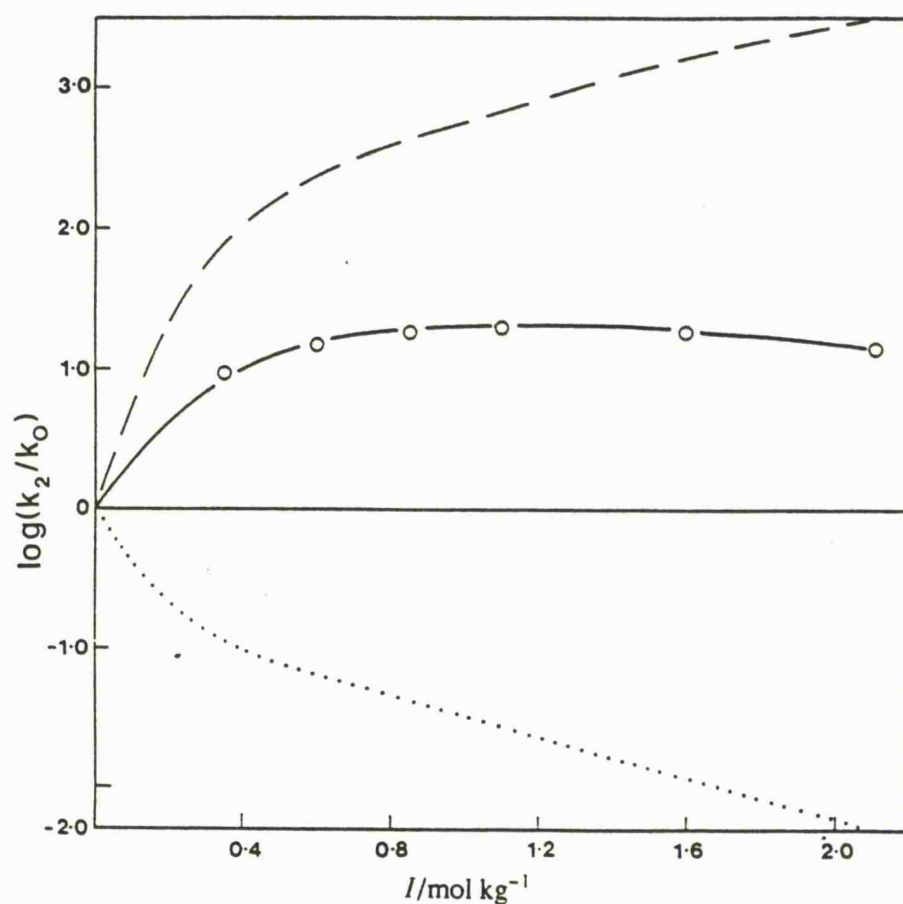


Figure 7.6: Dependence of $\ln(k_2/k_0)$ on ionic strength I ($\circ$) for aqueous $\text{Et}_4\text{N}^+\text{I}^-$ solutions; (.....) indicates the dependence predicted by Charge-Charge interactions (the F-term) and (.....) by $\Delta\beta^0\Delta\beta^1$ and $\Delta\psi$ terms.

Table 7.4 Calculated interaction parameters for alkali metal and tetramethylammonium halides.

Ion	$\Delta\theta(\text{ion})$	ion	$\Delta\beta^0(\text{ion})$
F^-	-0.23 ± 0.04	Li^+	0.65 ± 0.03
Cl^-	-0.24 ± 0.03	Na^+	0.68 ± 0.02
Br^-	-0.14 ± 0.04	K^+	0.65 ± 0.04
I^-	-0.18 ± 0.05	Me_4N^+	0.51 ± 0.02
OH^-	3.29 ± 1.70		

Table 7.5 Calculated interaction parameters for tetraethylammonium halides.

Parameter	Et_4N^+
$\Delta\beta^0$	0.82 ± 0.03
$\Delta\beta^1$	2.27 ± 1.20
$\Delta\psi(\text{Et}_4\text{N}^+; j; \text{F}^-)$	1.25 ± 0.20
$\Delta\psi(\text{Et}_4\text{N}^+; j; \text{Br}^-)$	-0.24 ± 0.16
$\Delta\psi(\text{Et}_4\text{N}^+; j; \text{I}^-)$	-0.46 ± 0.20

the terms characteristic of co-sphere - co-sphere overlap ($\Delta\theta$, $\Delta\beta^\circ$) reduce the rate constant relative to k_0 . The HO^- ions differ from the other ions in solution in that they are both reactants and contribute to the overall salt effect. Therefore a direct comparison between $\Delta\theta(\text{HO}^-)$ and the $\Delta\theta$ values characteristic of other added anions is difficult at this early stage. Added cations retard the rate constant for this reaction, the $\Delta\beta^\circ$ terms being approximately double the magnitude of the $\Delta\theta$ terms. The Olson-Simonson rule^{9,10} states that in a reaction involving ions of the same sign of charge (in this case BPB^{2-} and HO^-), the rate in an aqueous solution at ionic strengths in the region of 0.01 - 0.1 mol dm^{-3} is independent of the charge of the added ions of the same sign as the reactants. This effect can be explained if one considers the compatible orientation of water molecules in the co-spheres around reactant anion and added cation (see figure 6.2). This has a stabilising effect on the initial states. However, for the alkaline hydrolysis studied here a specific anion effect is observed but the effect of the anions is less than that of added cations. This is in general agreement with the Olson-Simonson rule.

For added anions, the effects are dominated by charge density and hydration intensity of the halide ions. It can be seen from the trend in section 7.3 that strong anion-water interactions appear to stabilise the transition state to a greater extent than the initial states of HO^- or bromophenol blue.

There is a marked increase in the magnitude of the $\Delta\beta^\circ$ parameter on going from Me_4N^+ to Et_4N^+ . This is probably due to the increase in hydrophobic character. On going from Me_4N^+ to Et_4N^+ the hydration character becomes dominated by weak water-ion and strong, local water-water interactions. The inclusion of not only the $\Delta\beta^1$ term, but also a cross term of the type described by Pitzer indicates that the effects of added tetraethylammonium cations are dependent on associated anion. It can be seen that the kinetic salt effect of Et_4N^+ is different when the counter-ion is strongly electrostrictive fluoride to that when the

counter-ion is weakly electrostrictive iodide. The observed trend here is similar to those reported previously.¹¹

The analysis outlined here takes a very general approach which we have then applied to one reaction. The lack of comparable parameters for other reactions and the difficulty in obtaining reaction parameters for higher alkylammonium salts (due to lack of solubility) made it difficult to establish the significance of the magnitude and signs of the interaction parameters. Any future development of the approach described here should aim to extend the range of reactions studied and hydration characteristics of the salts used therein. However, the Pitzer analysis will prove to an important step forward in examining the effects of added salts on rate constants and understanding the role of specific interactions in aqueous solutions.

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Chapter 8

Kirkwood-Buff description of interactions in aqueous mixtures

8.1 Introduction.

Previous chapters have described procedures to evaluate thermodynamic variables of systems using long-range intermolecular forces, i.e. charge-charge interactions. An alternative, proposed by Kirkwood and Buff,¹ involves a more localised approach. The Kirkwood-Buff theory of solutions provides relations between thermodynamic quantities and molecular distribution functions.

A canonical ensemble² is used in a description of the thermodynamic properties of a multi-system ensemble. Each system in the ensemble is in contact and can exchange energy but not particles. The systems can be macroscopic. However, a grand canonical ensemble is more general and can be used to describe systems that exchange both energy and particles. Kirkwood and Buff¹ used the theory of the grand canonical ensemble to relate composition fluctuations to both radial distribution functions of the numerous chemical pairs present in the system, and chemical potentials of the systems components.

The Kirkwood-Buff integral (equation 8.1) is a powerful tool in determining the thermodynamic properties of solutions from localised composition fluctuations. Furthermore, Ben-Naim^{3,4,5} and Hall⁶ have shown that this treatment can be successfully applied to aqueous solutions.

$$G_{\alpha\beta} = \int_0^{\infty} [g_{\alpha\beta}(R) - 1] 4\pi R^2 dR \quad 8.1$$

Here $g_{\alpha\beta}(R)$ is the angle-averaged pair correlation function between α -molecules and β -molecules.

8.2 Theoretical background.

8.2(i) Configuration.

In an assembly of molecules, the relative position of each molecule can be written as Cartesian co-ordinates (x,y,z) or $\underline{R}$, representing the vector co-ordinate. This co-ordinate indicates the centre of the molecule.

If we now consider an infinitesimal element of volume, , the volume element can be expressed by equation 8.2.

$$dV = dx \cdot dy \cdot dz \quad 8.2$$

or more conveniently, for a spherical shell of radius r and width dr , the volume element is given by,

$$dV = 4\pi r^2 dr \quad 8.3$$

For a rigid, non-spherical molecule- i the configuration X_i is written,

$$X_i = (V_i, \Omega_i) \quad 8.4$$

and for a system containing N -molecules, the total configuration can be expressed by,

$$X^N = X_1, X_2, \dots, X_N \quad 8.5$$

also an infinitesimal element of configuration dX_i is given by equation 8.6.

$$dX_i = dV_i \cdot d\Omega_i \quad 8.6$$

8.2(ii) The pair correlation function.

The quantity dX_i is an effective element of volume. We consider two such volume elements dX_i' and dX_i'' and the

probability of a particle occupying both i.e.

$$\left\{ \text{Particle in } dx_{i'} \right\} \cap \left\{ \text{Particle in } dx_{i''} \right\}$$

Hence we can define two possible cases;

(i) The separation of the volume elements $V = |V'' - V'|$ is small. Hence a particle present in $dx_{i'}$ reduces the chance of finding a particle in $dx_{i''}$.

(ii) V is large. The probability of finding a particle in both elements is the product of the individual probabilities.

$$\rho^{(2)}(x', x'') dx_{i'} dx_{i''} = \rho^{(1)}(x') dx_{i'} \cdot \rho^{(1)}(x'') dx_{i''} \quad 8.7$$

where $\rho^{(1)}(x')$ and $\rho^{(1)}(x'')$ are the probabilities of finding a particle in elements $dx_{i'}$ and $dx_{i''}$ respectively and $\rho^{(2)}(x', x'')$ is the probability of finding a particle in both elements. Hence

$$\begin{aligned} \rho^{(2)}(x', x'') &= \rho^{(1)}(x') \cdot \rho^{(1)}(x'') \\ &= \left(\frac{\rho}{8\pi^2} \right)^2 \quad \lim R \rightarrow \infty \end{aligned} \quad 8.8$$

This limiting case describes a fine structureless continuum. The pair correlation function $g(x', x'')$ measures deviations from this limiting case. Hence

$$\rho^{(2)}(x', x'') = \rho^{(1)}(x') \cdot \rho^{(1)}(x'') \cdot g(x', x'')$$

and,

$$\rho^{(2)}(x', x'') = \left(\frac{\rho}{8\pi^2} \right)^2 g(x', x'') \quad 8.9$$

The quantity $g(x', x'')$ is written $g(R)$ being a locational pair correlation function.

For an ideal gas, where intermolecular forces are absent, $g(R) = 1.0$ so that $\rho^{(2)}(x', x'')$ is given by equation

8.8. Figures 8.1a and 8.1b illustrate the variation of $g(R)$ with R for low density systems. For a gas, where atoms are treated as hard spheres; $R < \sigma$, $g(R) = 0$ (σ being the particle diameter), and when $R > \sigma$, $g(R) = 1.0$. For real, simple, spherical particles, such as argon, repulsive forces act at $R < \sigma$ therefore $g(R) = 0$. At a distance slightly greater than σ attractive forces contribute to $g(R)$ leading to the 'bump' in figure 8.1b.

For a simple liquid system, at large distances from the reference molecule the local density is that of the bulk solvent. However, near the reference molecule there will be significant fluctuations in composition (Figure 8.2). These localised composition fluctuations are short range and only occur within a few molecular diameters of the reference.

The pair correlation function $g(R)$ is linked to the isothermal compressibility of a solution using equation 8.10.

$$\begin{aligned} \kappa_T &= \frac{1}{kT\rho} + \frac{1}{kT} \int_0^\infty g(R) 4\pi R^2 dR \\ &= - \frac{1}{V} \left(\frac{dV}{dP} \right)_T \quad \text{by definition} \end{aligned} \quad 8.10$$

The first term on the right of equation 8.10 is the compressibility of an ideal gas, and the second measures the interaction between molecules. The quantity $g(R)$ has been calculated for ions in homogeneous solutions (typically H_2O or D_2O) or dilute simple aqueous mixtures using X-ray or neutron diffraction methods.^{7,8,9} However, for binary liquid mixtures, containing alcohols as co-solvent, insufficient data are available on the higher alcohols (beyond ethanol/water mixtures) at reasonable concentrations. The next section deals with the application of inverse Kirkwood-Buff (IKB) to such mixtures.

8.3 Binary liquid mixtures.

Previous sections have concentrated on a single component homogeneous system. We expand this description to encompass

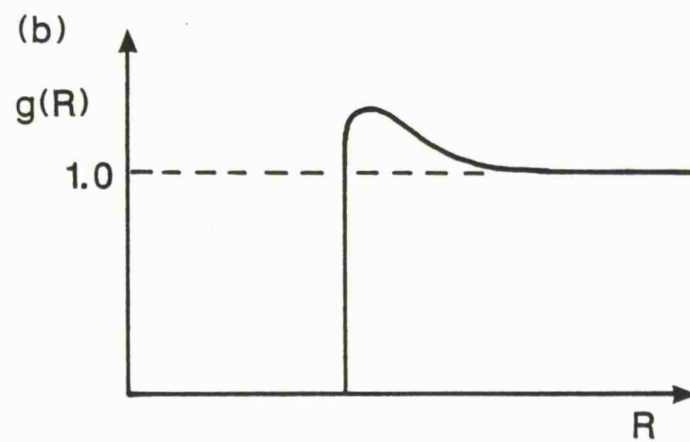
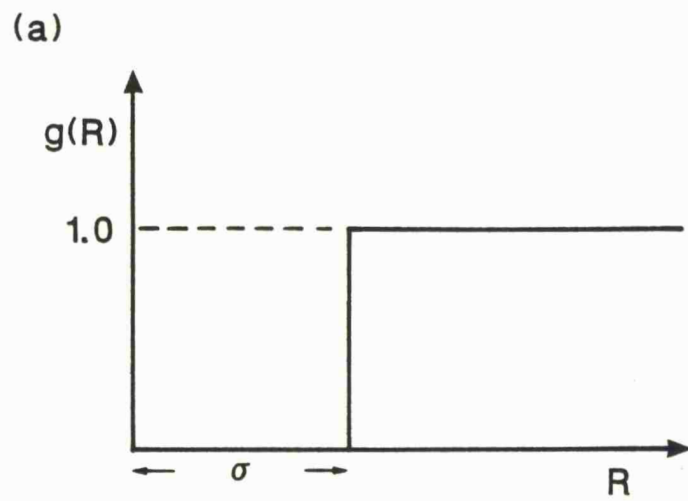


Figure 8.1: (a) Variation of the pair correlation function with distance R for hard spheres of disc diameter σ .

(b) Variations of the pair correlation function with distance R for real, simple, spherical particles.

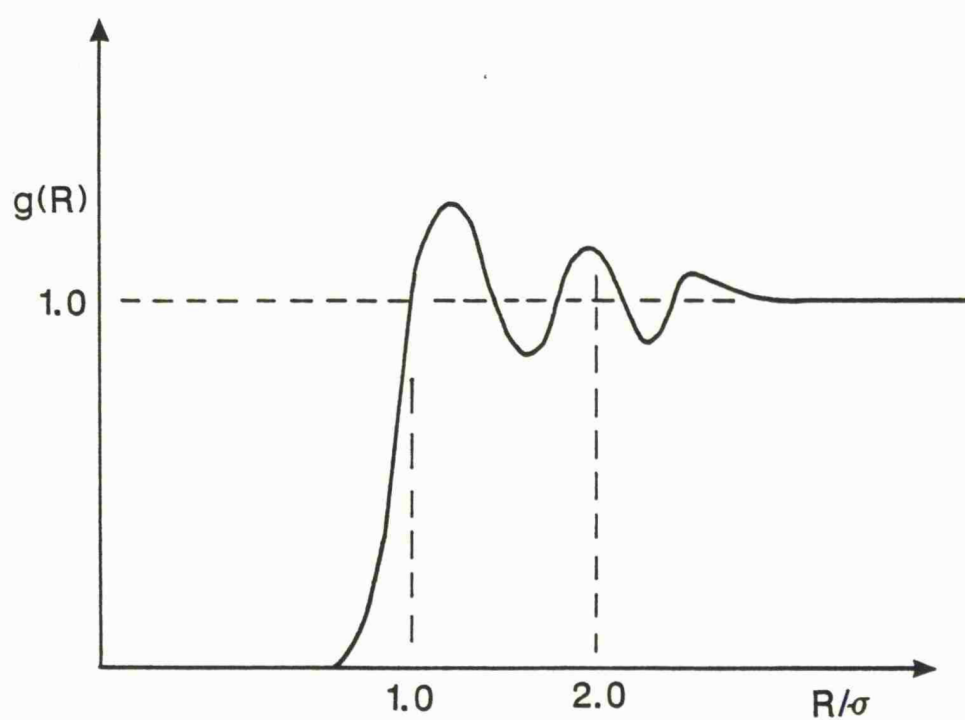


Figure 8.2: Variation of pair correlation function with distance (measured as a ratio of distance to molecular diameter) for a simple liquid system.

more complex systems. Consider a system comprising molecules α and β . One can imagine descriptions of the system using various correlation functions which determine the extent of correlation of position and orientation of all molecules in the system, e.g. $g(X', X'')$. However, these quantities are usually not available from experimental data. In practice it is possible to consider the locational (or averaged angle) pair correlation function $g_{\alpha\beta}(R)$. This approach is limited to the number of systems for which $g_{\alpha\beta}(R)$ can be evaluated, and therefore the more general Kirkwood-Buff integral is employed (equation 8.1). It can be argued that at low R , $G_{\alpha\beta}$ is dominated by $[g_{\alpha\beta}(R) - 1]$ and therefore yields the tendency of α -molecules to be in close proximity to β -molecules.

If we now consider a binary liquid mixture, composed of liquid-1 and liquid-2 the Kirkwood-Buff integral becomes

$$G_{12} = \int_0^{\infty} [g_{12}(R) - 1] 4\pi R^2 dR \quad 8.11$$

where $g_{12}(R)$ is the averaged pair correlation function between molecules of liquid-1 and liquid-2.

Similar expressions can be written for G_{11} and G_{22} . It is possible to calculate these parameters using the IKB approach, which calculates the integral functions from thermodynamic parameters.

8.4 Inverse Kirkwood-Buff treatment of liquid mixtures.

The basis of the IKB treatment is an expression for the thermodynamic properties of a liquid mixture. Information required for IKB calculations are the dependencies on mole fraction x_2 of G_m^E (or vapour pressures), v_m^E (or densities, or partial molar volumes) and isothermal compressibilities κ_T . Crucial to this approach is the evaluation of the derivative $(d\mu_2/dx_2)$ as a function of mole fraction of added organic co-solvent x_2 . This quantity can be derived by differentiation of G_m^E with respect to x_2 (appendix 1, section I) giving equation 8.12.

$$\frac{1}{R \cdot T} \left(\frac{dG_m^E}{dx_2} \right) = \ln f_2 - \ln f_1 \quad 8.12$$

Here the Gibbs-Duhem equation has been used in the following form.

$$x_1 \cdot \frac{d \ln f_1}{dx_2} + x_2 \cdot \frac{d \ln f_2}{dx_2} = 0 \quad 8.13$$

We write the excess molar Gibbs energy

$$G_m^E = x_1 RT \ln f_1 + x_2 RT \ln f_2 \quad 8.14$$

Substitution of equation 8.12 into equation 8.14 yields an expression for $\ln f_2$.

$$\frac{G_m^E}{R \cdot T} = \ln f_2 - \frac{x_1}{R \cdot T} \left(\frac{dG_m^E}{dx_2} \right) \quad 8.15$$

Therefore,

$$\ln f_2 = \frac{1}{R \cdot T} \left[G_m^E + (1 - x_2) \left(\frac{dG_m^E}{dx_2} \right) \right] \quad 8.16$$

Hence, given that we can calculate G_m^E and its dependence on x_2 , we can evaluate $\ln f_2$. We now derive an expression for the dependence of the chemical potential of liquid-2 $\mu_2(\text{mix}; T; P)$ upon mole fraction x_2 (appendix 1, section II)

$$\left(\frac{d\mu_2}{dx_2} \right) = \frac{R \cdot T}{x_2} + (1 - x_2) \left(\frac{d \ln f_2}{dx_2} \right) \quad 8.17$$

Therefore,

$$\left(\frac{d\mu_2}{dx_2} \right) = \frac{R \cdot T}{x_2} + (1 - x_2) \left(\frac{d^2 G_m^E}{dx_2^2} \right) \quad 8.18$$

Here $d\mu_2/dx_2$ is expressed in $J \text{ mol}^{-1}$.

In the next step of the IKB calculations involves

expressions for the volumetric parameters of the system. The molar volume V_m of a mixture formed by n_1 moles of liquid-1 and n_2 moles of liquid-2, at constant temperature and pressure, is related to the partial molar volumes, $V_1(\text{mix}; T; P)$ and $V_2(\text{mix}; T; P)$, of the components using equation 8.19.

$$V_m = x_1 V_1(\text{mix}; T; P) + x_2 V_2(\text{mix}; T; P) \quad 8.19$$

Hence, using the Gibbs-Duhem equation (appendix 1, section III),

$$V_2(\text{mix}; T; P) = V_m - (1 - x_2) \left(\frac{dV_m}{dx_2} \right)_{T, P} \quad 8.20$$

or, in terms of the excess volume,

$$V_2(\text{mix}; T; P) = V_2^*(\text{liq}; T; P) + V_m^E + (1 - x_2) \left(\frac{dV_m^E}{dx_2} \right)_{T, P} \quad 8.21$$

For a mixture of volume V containing n_1 moles liquid-1

$$\rho_1 = \frac{n_1}{V} = \frac{x_1}{V_m} = \frac{(1 - x_2)}{V_m} \quad 8.22$$

similarly,

$$\rho_2 = \frac{(1 - x_1)}{V_m} \quad 8.23$$

and

$$\rho = \frac{(n_1 + n_2)}{V} = \frac{1}{V_m} \quad 8.24$$

hence,

$$\rho_1 V_1(\text{mix}; T; P) + \rho_2 V_2(\text{mix}; T; P) = 1.0 \quad 8.25$$

The final parameter to consider in the IKB calculations is the isothermal compressibility, already introduced in equation 8.10, in terms of the molar volume of the system.

$$\kappa_T = - \frac{1}{V} \left(\frac{dV}{dP} \right)_T = - \frac{1}{V_m} \left(\frac{dV_m}{dP} \right)_T \quad 8.26$$

8.5 Ben-Naim's equations.

Having derived expressions for V_m , $V_1(\text{mix}; T; P)$, $V_2(\text{mix}; T; P)$, $(d\mu_2/dx_2)$, ρ_1 , ρ_2 , ρ and κ_T above, we can now link these parameters to the Kirkwood-Buff integral functions G_{11} , G_{22} and G_{22} using equations described^{2,4,5} by Ben-Naim. The calculation proceeds in four stages.

Stage I: The properties ρ_1 , ρ_2 , ρ and $(d\mu_2/dx_2)$ are used to calculate a quantity η (mol m^{-3}) as a function of x_2 .

$$\eta = R \cdot T \frac{\rho^2}{\rho_2} \left(\frac{d\mu_2}{dx_2} \right) \quad 8.27$$

Stage II: The quantity η and the isothermal compressibility are then used to calculate a dimensionless quantity ξ .

$$\xi = \frac{\kappa_T \eta}{R \cdot T} \quad 8.28$$

Stage III: A combination of volumetric data and parameters η and ξ yield an expression for the integral G_{12} .

$$V_1(\text{mix}; T; P) \cdot V_2(\text{mix}; T; P) = \frac{[\xi - \eta G_{12}]}{\eta^2} \quad 8.29$$

Stage IV: The remaining two integral functions are obtained from volumetric data and the quantity η .

$$V_1(\text{mix}; T; P) = \frac{[1 + \rho_2(G_{22} - G_{12})]}{\eta} \quad 8.30$$

$$V_2(\text{mix}; T; P) = \frac{[1 + \rho_1(G_{11} - G_{12})]}{\eta} \quad 8.31$$

We can now apply these calculations to aqueous mixtures, linking the Kirkwood-Buff integral functions with thermodynamic quantities using the method described here. These calculations will provide a quantitative link between rate constants for reactions in aqueous mixtures and the thermodynamic properties of the solvent media.

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Chapter 9

*Role of preferential solvation in the hydrolysis of an
Iron(II) complex and 4-methoxyphenyl-2,2-
dichloropropionate*

9.1 Introduction.

The nature and mole fraction of added co-solvent often have a significant impact upon the rate constant for reactions in aqueous solutions.^{1,2} This variation in rate constant is an indication of the effect of added co-solvent on initial and transition states. The Kirkwood-Buff theory of interactions in solution is applied to examples of data describing these effects on rate constants. The thermodynamic properties of a binary aqueous solvent mixture are briefly examined, and a procedure is outlined for combining thermodynamic properties with kinetic data. This procedure in turn yields parameters characterising interactions between solutes (i.e. initial and transition states) and components of the binary solvent media. These parameters offer information on the affinities of solutes for components of the solvent mixture, giving an indication of the role of preferential solvation in the reaction mechanism. Examples using kinetic data describing an inorganic and organic reaction are quoted.

9.2 Analysis of dependence of excess Gibbs energy on mole fraction of added co-solvent.

The calculations outlined in chapter 8 incorporate the second differential of the excess Gibbs energy with respect to mole fraction of added co-solvent (equation 8.18) to calculate $d\mu_2/dx_2$. An approach involving second differentials places severe demands on any analysis and the experimental data therein. Excess molar properties can be fitted³ using the Redlich-Kister (or Guggenheim-Scatchard) equation written in the following form;

$$\frac{1}{R \cdot T} G_m^E = x_2(1 - x_2)Q_g \quad 9.1$$

where

$$Q_g = \sum_{j=1}^{j=i} a_j(G)(1 - 2x_2)^{j-1} \quad 9.2$$

or

$$Q_g = a_1 + a_2(1 - 2x_2) + a_3(1 - 2x_2)^2 + \dots \quad 9.3$$

Hence

$$\begin{aligned} \frac{dQ_g}{dx_2} &= -2a_2 - 4a_3(1 - x_2) - 6a_4(1 - 2x_2) + \dots \\ &= - \sum_{j=2}^{j=i} 2a_j(j-1)(1-2x_2)^{j-2} \end{aligned} \quad 9.4$$

And

$$\begin{aligned} \frac{d^2Q_g}{dx_2^2} &= -8a_3 - 24a_4(1 - 2x_2) \\ &= - \sum_{j=3}^{j=i} 4a_j(j-1)(j-2)(1-2x_2)^{j-3} \end{aligned} \quad 9.5$$

Then

$$\frac{1}{R \cdot T} \left(\frac{dG_m^E}{dx_2} \right) = (1 - x_2)Q - x_2Q + x_2(1 - x_2) \left(\frac{dQ}{dx_2} \right) \quad 9.6$$

or

$$\frac{1}{R \cdot T} \left(\frac{dG_m^E}{dx_2} \right) = (1 - 2x_2)Q + x_2(1 - x_2) \left(\frac{dQ}{dx_2} \right) \quad 9.7$$

$$\begin{aligned} \frac{1}{R \cdot T} \left(\frac{d^2G_m^E}{dx_2^2} \right) &= -2Q + 2(1 - 2x_2) \left(\frac{dQ}{dx_2} \right) \\ &\quad + x_2(1 - x_2) \left(\frac{d^2Q}{dx_2^2} \right) \end{aligned} \quad 9.8$$

Estimates of the coefficient $a_j(G)$ were calculated using a least squares analysis, ensuring that the derived parameters were statistically significant with respect to their standard errors.

In certain cases the Redlich-Kister approach proved inadequate. Closer numerical investigation uncovered a fundamental flaw in the analysis when applied to certain systems. We recall that for immiscible liquids $(d\mu_2/dx_2) < \text{zero}$. In the fitting procedures based on equation 9.1 the leading term is given by $(1/RT)G_m^E$ at $x_2 = 0.5$. Consequently if a_1 is close to 2.0, there is a chance that the calculated term $(d\mu_2/dx_2)$ is driven negative in the numerical analysis, even though the mixture exists as a homogeneous liquid. The condition $(G_m^E/RT) > 0.5$ is linked with a tendency to partial miscibility (appendix 2). For those systems where $G_m^E < \text{zero}$ (e.g. DMSO + water mixtures) the Redlich-Kister analysis proved to be adequate. However for those systems where G_m^E is large and positive (e.g. ethanol + water mixtures) an orthogonal polynomial was applied (equation 9.9)

$$\frac{1}{R \cdot T} G_m^E = \sum_{j=2}^N a_j P_j(x_1; x_2) \quad 9.9$$

where $P_2 = x_1 x_2$

$$P_3 = x_1 x_2 (1 - 2x_2)$$

$$P_4 = x_1 x_2 \left[1 - \left(\frac{14x_2}{3} \right) + \left(\frac{14x_2^2}{3} \right) \right]$$

$$P_5 = x_1 x_2 (1 - 8x_2 + 18x_2^2 - 12x_2^3)$$

or for the N^{th} term

$$P_N = \frac{[(2N - 1)(1 - x_2)P_{N-1} - (N - 3)P_{N-2}]}{(N + 2)} \quad 9.10$$

9.3 Water + ethanol mixtures.

9.3(i) Kirkwood-Buff calculations.

Calculations based on the Kirkwood-Buff theory of interactions in solution were incorporated into a FORTRAN program. Thermodynamic parameters were calculated for water + ethanol mixtures which were then used to calculate the Kirkwood-Buff integral functions G_{11} , G_{22} and G_{12} , as outlined in chapter 8. G_m^E as a function of x_2 at 298.15 K was calculated from data published by Pemberton and Marsh,⁶ reporting G_m^E as a function of x_2 at 303.15, 323.15, 343.15 and 363.15K, via the Gibbs-Helmholtz equation (equation 9.11). C_{pm}^E was assumed to be small such that H_m^E is temperature independent over the range $298.15 \leq T/K \leq 363.15$. The dependence of G_m^E on x_2 required the use of five terms in the orthogonal polynomial (equation 9.9), these parameters are summarised in table 9.1. The required volumetric data were calculated from data reported by Benson and Kiyohara.⁷ Dependencies of compressions on mixture composition given by Moriyoshi et al⁸ were used to calculate compressibilities. Figure 9.1 summarises the calculated thermodynamic excess properties for water + ethanol mixtures, and figure 9.2 shows the variation of Kirkwood-Buff integral functions with x_2 .

$$\Delta H_m^E = \left\{ \frac{d \left(\frac{\Delta G_m^E}{T} \right)}{d \left(\frac{1}{T} \right)} \right\} \quad 9.11$$

The trends shown in figure 9.2 for the dependencies of G_{11} , G_{22} and G_{12} on x_2 for water + ethanol mixtures conform broadly to those reported by Ben-Naim.⁹ It is clear from the figure that water-water interactions are dominant in water + ethanol mixtures, being a maximum at $x_2 = 0.4$. At high mole fraction of water, ethanol-ethanol interactions are more significant than water-ethanol interactions.

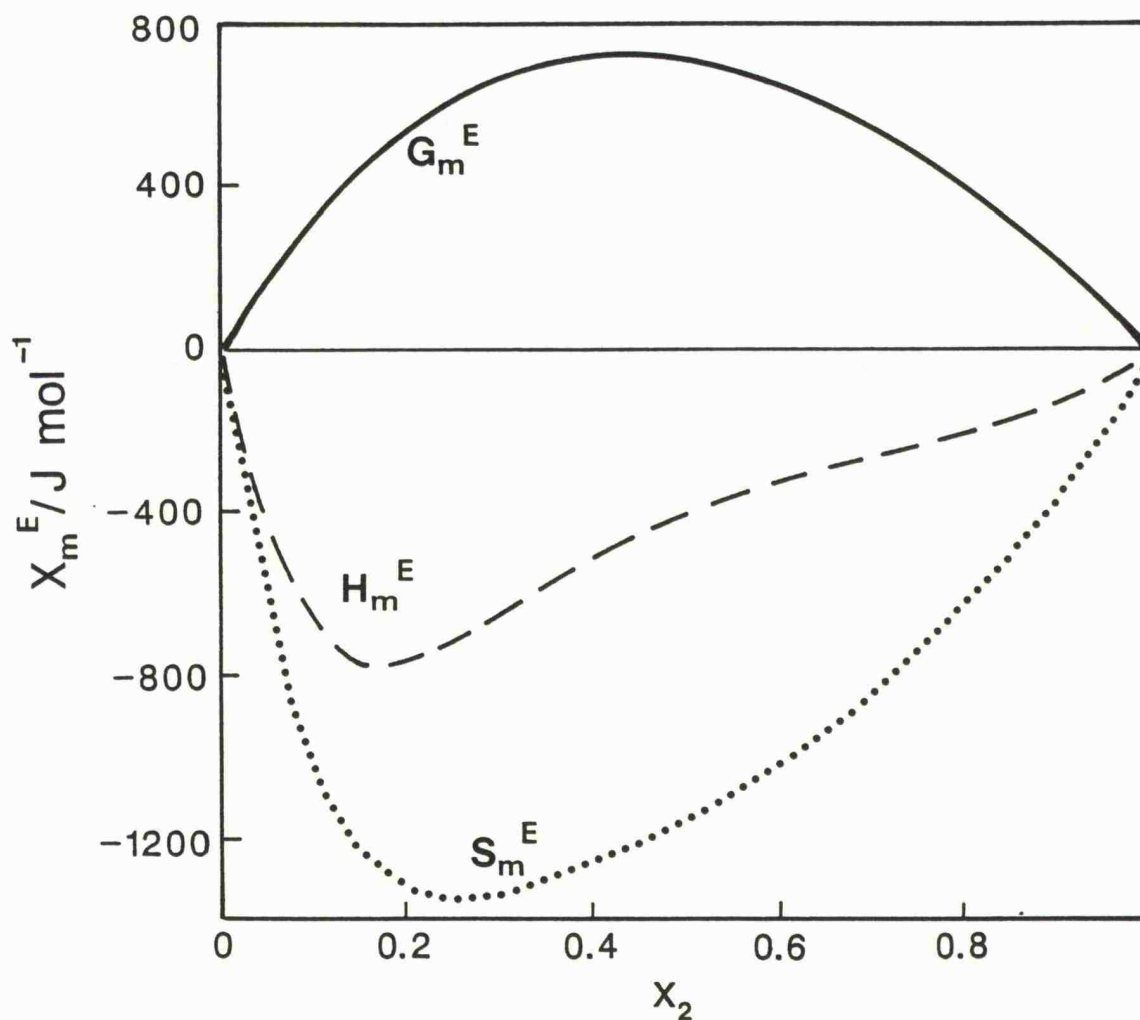


Figure 9.1: Calculated excess molar Gibbs energies G_m^E , molar enthalpies H_m^E and entropies S_m^E and mixing for ethanol + water mixtures at 298K as a function of mole fraction x_2 .

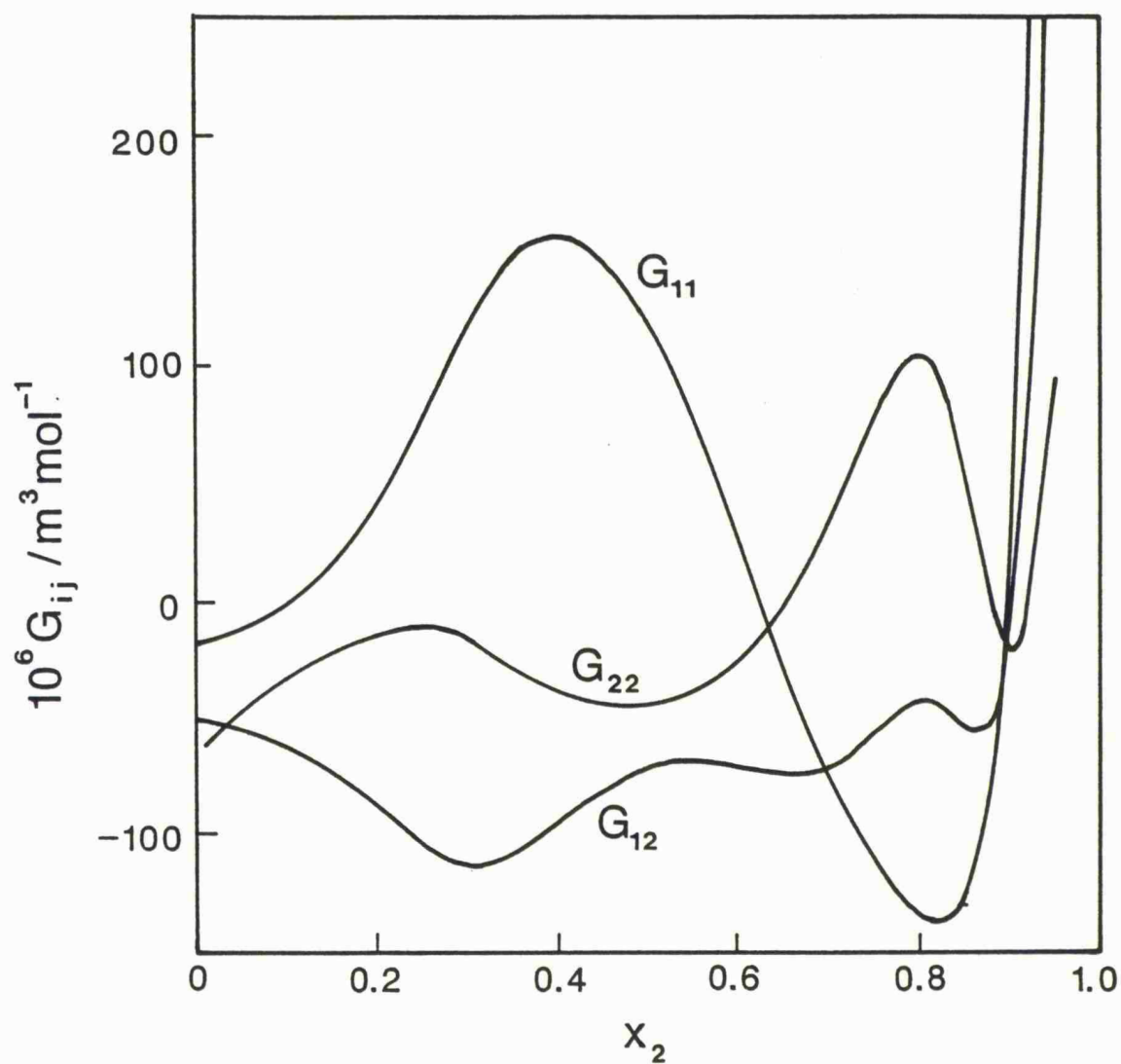


Figure 9.2: Inverse Kirkwood-Buff integral functions $G_{\alpha\beta}$ for ethanol + water mixtures at 298K as a function of mole fraction x_2 .

Table 9.1: Calculated orthogonal parameters for the dependence of G_m^E on x_2 for ethanol + water mixtures at 298.15K.

Parameter	Value
P_1	$(1\ 190.0 \pm 3.66) \times 10^{-4}$
P_2	$(2\ 815.0 \pm 9.93) \times 10^{-4}$
P_3	$(-41.66 \pm 1.87) \times 10^{-3}$
P_4	$(-45.71 \pm 3.14) \times 10^{-3}$
P_5	$(-60.82 \pm 5.05) \times 10^{-3}$

9.3(ii) Franks classification of aqueous mixtures.

A useful classification for aqueous mixtures was proposed by Franks,^{10,11} and is based on the thermodynamic properties of these mixtures,¹² particularly excess Gibbs energies G_m^E , enthalpies H_m^E , entropies S_m^E , volumes V_m^E and isobaric heat capacities C_{pm}^E . Franks identified two broad classes of aqueous mixture;

- (i) Typically aqueous, for which $G_m^E > \text{zero}$ and $|T.S_m^E| > |H_m^E|$.
- (ii) Typically non-aqueous, for which $|T.S_m^E| < |H_m^E|$; the sign of G_m^E is undefined.

One can clearly see from figure 9.2 that the thermodynamic properties of water + ethanol mixtures fall into the typically aqueous class.

Having given an example of the application of the Kirkwood-Buff theory to a binary aqueous liquid system, we now examine the properties of a solute-j in a similar binary aqueous mixture. The concept of solvent co-spheres around a solute-j, introduced in chapter 6, is used to illustrate the model proposed by Hall,¹³ Covington¹⁴ and Newman.^{14,15}

Consider a solute molecule-j in a mixture of liquid-1 and liquid-2. We imagine a solvation sphere of solvent molecules around the solute (figure 9.3) whose volume is defined by the radius R in equation 9.11.

$$\text{Total volume of sphere} = \frac{4}{3} \pi R^3 \quad 9.11$$

In the absence of the solute molecule-j the sphere would contain N_1 moles of liquid-1 and N_2 moles of liquid-2. Hence, we can define the excess quantities N_{1j} and N_{2j} .

$$N_{1j} = N_{1j}' - N_1$$

$$N_{2j} = N_{2j}' - N_2$$

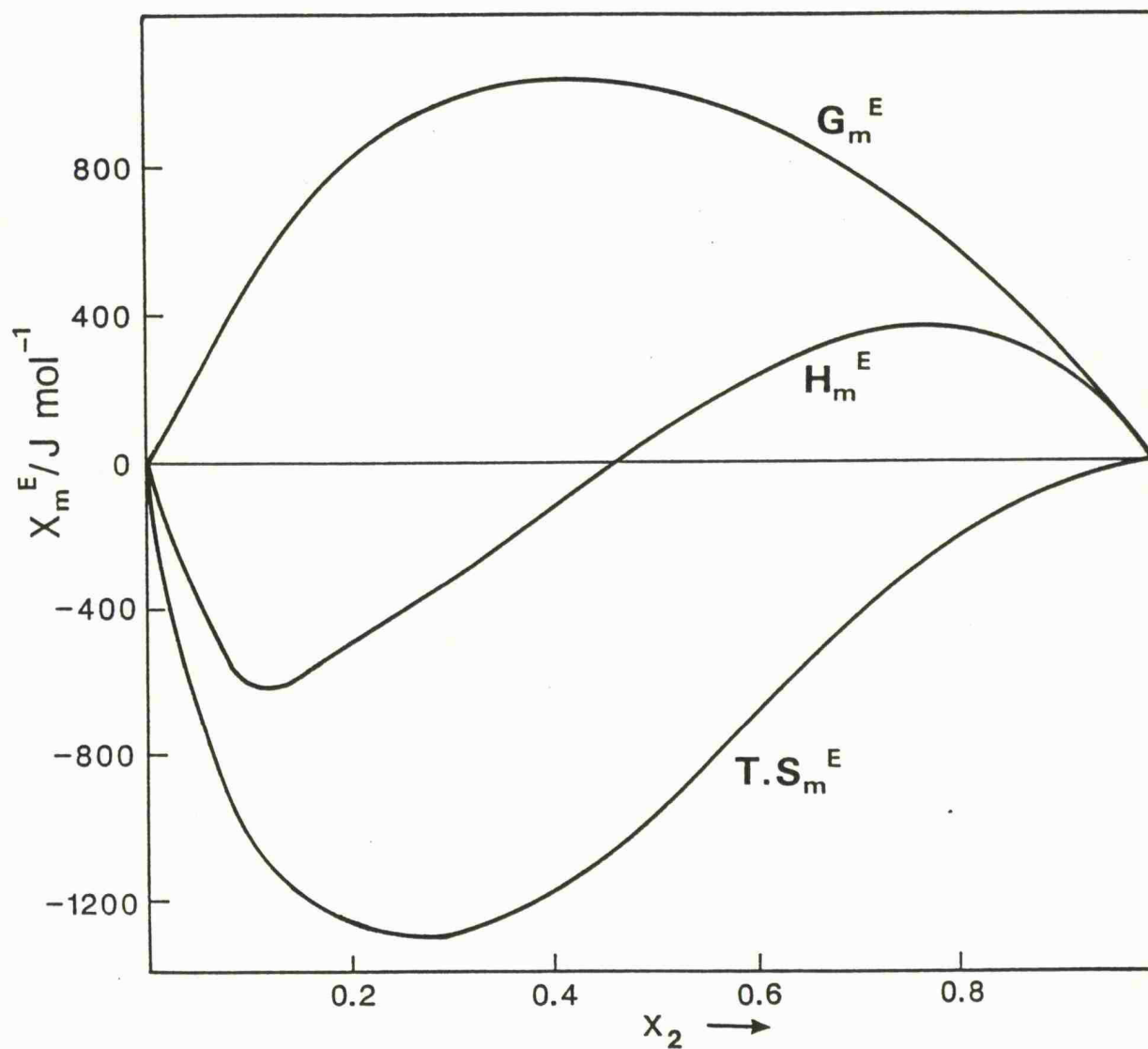


Figure 9.3: Calculated molar Gibbs energies G_m^E , molar enthalpies H_m^E , and entropies S_m^E of mixing for t-Butanol + water mixtures at 298K as a function of mole fraction x_2 .

If ρ_1 and ρ_2 are the number densities of liquid-1 and liquid-2 respectively, we can relate each N_{ij} quantity to the appropriate Kirkwood-Buff integral function G_{ij} using equation 9.13.

$$N_{1j} = \rho_1 \int_0^{\infty} [g_{1j}(R) - 1] 4\pi R^2 dR = \rho_1 G_{1j} \quad 9.13$$

$$N_{2j} = \rho_2 \int_0^{\infty} [g_{2j}(R) - 1] 4\pi R^2 dR = \rho_2 G_{2j} \quad 9.14$$

An important equation linking the quantities defined in equations 9.13 and 9.14 to $d\mu_j^\circ$ was derived by Hall.¹³

$$d\mu_j^\circ(\text{mix}) = - \sum_{i=2}^{i=1} N_{ij} d\mu_2(\text{mix}) \quad 9.15$$

Therefore, using equation 9.13 and 9.14

$$\left(\frac{d\mu_j^\circ(\text{mix})}{dx_2} \right) = [G_{1j} - G_{2j}] \rho_2 \left(\frac{d\mu_2}{dx_2} \right) \quad 9.16$$

Equation 8.18 states

$$\left(\frac{d\mu_2}{dx_2} \right) = \frac{R \cdot T}{x_2} + (1 - x_2) \left(\frac{d^2 G_m^E}{dx_2^2} \right) \quad 9.17$$

But

$$\rho_2 = \frac{N_2}{V} = \frac{N_2}{N_1 + N_2} \cdot \frac{N_1 + N_2}{V} = \frac{x_2}{V_m} \quad 9.18$$

Therefore

$$\left(\frac{d\mu_j^\circ(\text{mix})}{dx_2} \right) = [G_{1j} - G_{2j}] \frac{R \cdot T}{V_m} \left\{ 1 + \frac{1}{R \cdot T} x_2 (1 - x_2) \left(\frac{d^2 G_m^E}{dx_2^2} \right) \right\} \quad 9.19$$

Hence

$$[G_{1j} - G_{2j}] = \left(\frac{d\mu_j^o(\text{mix})}{dx_2} \right) \left(\frac{V_m}{F(x_2)} \right) \quad 9.20$$

where

$$F(x_2) = R \cdot T \left[1 + \frac{1}{R \cdot T} x_2 (1 - x_2) \left(\frac{d^2 G_m^E}{dx_2^2} \right) \right] \quad 9.21$$

Thus the difference in affinities of solute-j for liquid-1 and liquid-2 (i.e. the preferential solvation) can be calculated, from the dependence of standard chemical potential of solute-j on mole fraction composition, providing the thermodynamic properties of the mixture are known. Newman also showed¹⁵ that estimates of the separate G_{ij} terms are obtained from a knowledge of the dependence on x_2 of the limiting partial molar volume V_j^∞ as follows;

$$V_j^\infty(x_2) = \rho_2 V_2(\text{mix}; T; P) [G_{1j} - G_{2j}] - G_{1j} + \kappa_T RT \quad 9.22$$

where $V_j^\infty(x_2)$ = limiting partial molar volume of solute-j in liquid mixture,

$V_2(\text{mix}; T; P)$ = partial molar volume of liquid-2 in mixture.

Hence

$$G_{1j} = \frac{x_2 V_2(\text{mix}; T; P)}{V_m} [G_{1j} - G_{2j}] + \kappa_T RT - V_j^\infty \quad 9.23$$

So the transfer chemical potentials have been re-expressed in terms of the Kirkwood-Buff parameters G_{1j} and G_{2j} .

9.4 Kinetics of reaction in binary solvent mixtures.

We are now in a position to combine the above analysis with a description of chemical reactions in aqueous solutions using transition state theory.¹⁶ The treatment can be divided into two stages. Stage I uses kinetic data describing the dependence of rate constant on mole fraction x_2 , stage II develops equation 9.23 for those cases where volumes of activation are included in the kinetic data.

9.4(i) First-order kinetics.

The Gibbs energy of activation $\Delta G^\ddagger(x_2)$ for a first-order reaction in a binary aqueous solvent medium, having co-solvent mole fraction x_2 , is related to the difference between standard chemical potentials of initial $\mu^\circ(is;x_2)$ and transition $\mu^\circ(\ddagger;x_2)$ states at fixed temperature and pressure using transition state theory.

$$\Delta G^\ddagger(x_2) = \mu^\circ(\ddagger;x_2) - \mu^\circ(is;x_2) \quad 9.24$$

Then the change in Gibbs energy of activation between that of an aqueous solution (aq) and that of a solvent mixture having co-solvent mole fraction x_2 is given by;¹⁷

$$\begin{aligned} \Delta(aq \rightarrow x_2)\Delta G^\ddagger &= \Delta(aq \rightarrow x_2)\mu^\circ(\ddagger) - \Delta(aq \rightarrow x_2)\mu^\circ(is) \\ &= -R \cdot T \ln \left(\frac{k(x_2)}{k(aq)} \right) \end{aligned} \quad 9.25$$

where $k(aq)$ and $k(x_2)$ are the first order rate constants for reaction in solution with no added co-solvent and added co-solvent of mole fraction x_2 respectively.

STAGE I: The differential $d\Delta(aq \rightarrow x_2)\Delta G^\ddagger/dx_2$ is employed to describe the dependence of rate constant on mole fraction x_2 . Combination of equations 9.20 and 9.25 yields equation 9.26.

$$\begin{aligned} [G_{1\ddagger} - G_{2\ddagger}] - [G_{1is} - G_{2is}] &= [G_{1\ddagger} - G_{1is}] - [G_{2\ddagger} - G_{2is}] \\ &= V_m \frac{\left[\frac{d\Delta(aq \rightarrow x_2)\Delta G^\ddagger}{dx_2} \right]}{RTF} \\ &= g_k \text{ (by definition)} \end{aligned} \quad 9.26$$

Hence g_k is the change in relative affinities of the substrate for liquid-1 (water) and liquid-2 (co-solvent) on going from initial state to transition state.

STAGE II: According to equation 9.23, the affinity for the initial state is given by equation 9.27.

$$G_{1is} = x_2 \left(\frac{V_2}{V_m} \right) [G_{1is} - G_{2is}] + \kappa_T RT - V_{is}^\infty(x_2) \quad 9.27$$

Similarly for the transition state

$$G_{1\ddagger} = x_2 \left(\frac{V_2}{V_m} \right) [G_{1\ddagger} - G_{2\ddagger}] + \kappa_T RT - V_{\ddagger}^\infty(x_2) \quad 9.28$$

By substituting into equation 9.26, we define a quantity g_{k1} .

$$\begin{aligned} [G_{1\ddagger} - G_{1is}] &= V_m \frac{\left\{ \frac{\Delta(aq \rightarrow x_2) \Delta G^\ddagger}{dx_2} \right\}}{RTF} \\ &= g_{k1} \end{aligned} \quad 9.29$$

Here $[G_{1\ddagger} - G_{1is}]$ is the change in affinity of the substrate on activation for liquid-1. Having calculated this quantity we obtain, using g_k , the corresponding affinity for the liquid-2 measured by $[G_{2\ddagger} - G_{2is}]$ as defined by g_{k2} .

9.4(ii) Second-order kinetics.

The initial state consisting of components isA and isB exist for this type of reaction which combine to form a single transition state $\ddagger$. Equation 9.25 is rewritten;

$$\begin{aligned} \Delta(aq \rightarrow x_2) \Delta G^\ddagger &= \Delta(aq \rightarrow x_2) \mu^\circ(\ddagger) - \Delta(aq \rightarrow x_2) \mu^\circ(isA) \\ &\quad - \Delta(aq \rightarrow x_2) \mu^\circ(isB) \\ &= - R \cdot T \ln \left(\frac{k_2(x_2)}{k_2(aq)} \right) \end{aligned} \quad 9.30$$

$\ln(k_2(x_2)/k_2(aq))$ is the logarithm of the ratio of second order rate constants.

STAGE I: The analogue of equation 9.20 for a second order reaction incorporates parameters describing the affinities for the two transition states.

$$\left\{ \begin{array}{l} [G_{1\ddagger} - G_{2\ddagger}] - \\ [G_{1isA} - G_{2isA}] - \\ [G_{1isB} - G_{2isB}] \end{array} \right\} = V_m \frac{\left[\frac{d\Delta(aq \rightarrow x_2)\Delta G^\ddagger}{dx_2} \right]}{RTF} = g_k \text{ (by definition)} \quad 9.31$$

STAGE II: Expressions analogous to equation 9.29 are used to obtain $[G_{1\ddagger} - G_{1isA} - G_{1isB}]$ and $[G_{2\ddagger} - G_{2isA} - G_{2isB}]$.

9.5 Water + t-butanol mixtures.

Kirkwood-Buff integral functions for water + t-butanol mixtures were calculated as described earlier. Excess Gibbs energies of mixing were taken from data given by Kenttamaa et al.¹⁸ As can be seen from figure 9.3, G_m^E is large and positive. Therefore the dependence of G_m^E on x_2 was fitted using an orthogonal polynomial^{4,5} as described in section 9.2. Figure 9.3 also shows the dependence on x_2 of the excess molar enthalpy of mixing^{18,19} indicating that the mixing is exothermic at low x_2 and endothermic at high x_2 . However, across the whole mole fraction range $|T.S_m^E| > |H_m^E|$ placing this mixture in the typically aqueous class of the Franks classification.^{10,11}

Density data reported by Sakurai²⁰ were used to calculate volumetric parameters and compressibilities were obtained from data reported by Moriyishi et al.⁸ The pattern observed in figure 9.4, summarising the dependence of the Kirkwood-Buff integral functions on x_2 , is similar to that reported by Lepori and Matteoli.²¹ Maxima in G_{11} and G_{22} along with a sharp minimum in G_{12} at x_2 approximately equal to 0.2 can be explained in terms of microheterogeneities,^{12,22} which exist as short lived water-rich and alcohol-rich domains having mole fractions $0.05 \leq x_2 \leq 0.25$.

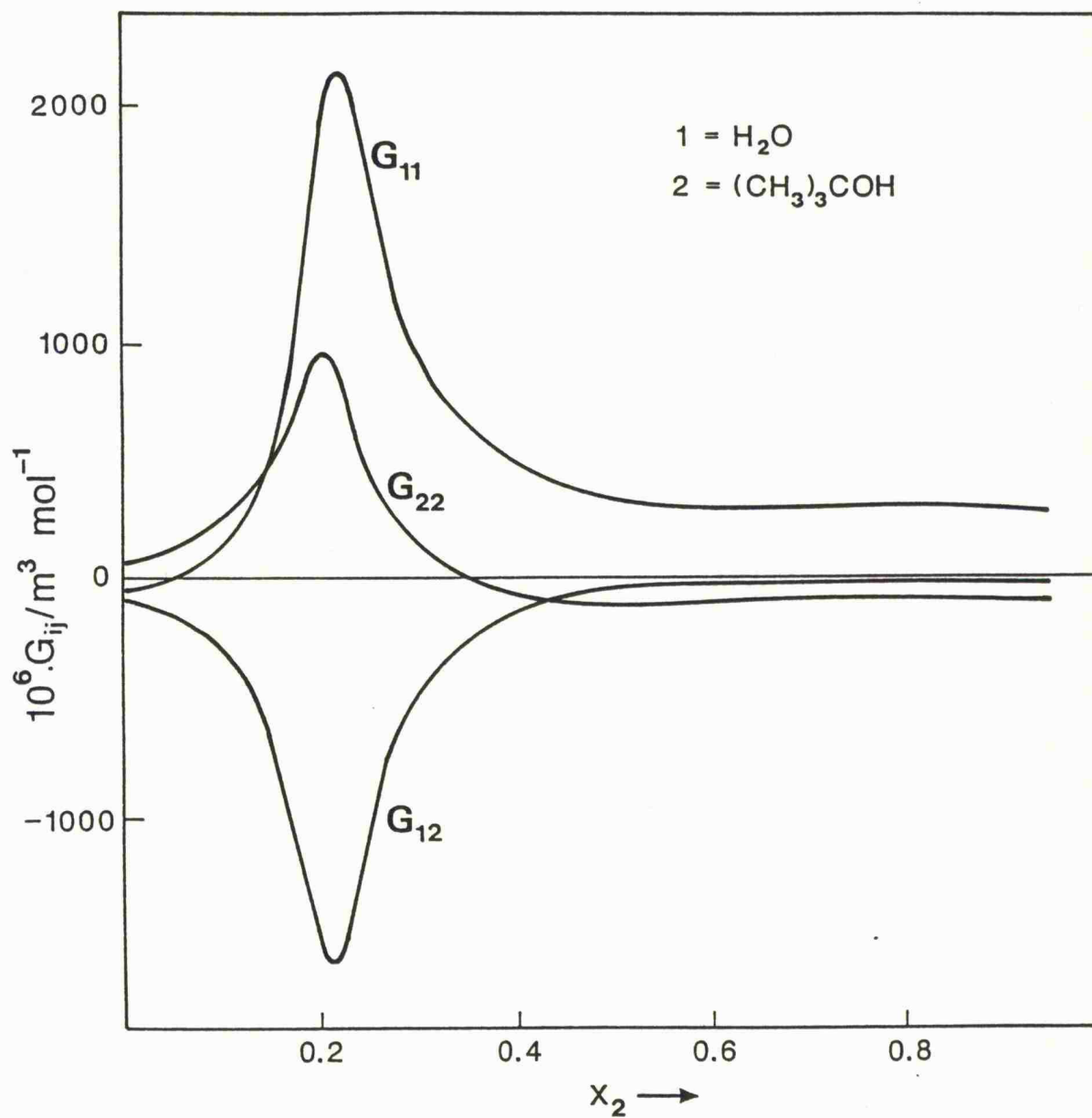


Figure 9.4: Inverse Kirkwood-Buff integral functions $G_{\alpha\beta}$ for t-Butanol water mixtures at 298K as a function of mole fraction x_2 .

9.5(i) Kinetics of hydrolysis of 4-methoxyphenyl-2,2-dichloropropionate.

At 298.15K the first order rate constant for the spontaneous hydrolysis of 4-methoxy-2,2-dichloropropionate (figure 9.5) is $1.15 \times 10^{-5} \text{ s}^{-1}$. This rate constant shows a dramatic increase with increasing mole fraction of co-solvent. The volume of activation for this reaction is $32.0 \text{ cm}^3 \text{ mol}^{-1}$, decreasing on addition of alcohol.²³ The dependencies of Gibbs energies $\Delta G^\ddagger(x_2)$ and volumes of activation $\Delta V^\ddagger(x_2)$ were fitted to polynomials in x_2 . These polynomials yielded $d\Delta(\text{aq} \rightarrow x_2)\Delta G^\ddagger(x_2)/dx_2$ and $\Delta V^\ddagger(x_2)$ as a function of x_2 . A combination of these parameters and the properties of the solvent mixture yielded g_k as defined in stage I. Dependences of both g_{k1} and g_{k2} as defined by equations 9.27-9.29 were obtained by incorporating data on volumes of activation with equation 9.29. Values of g_k , g_{k1} and g_{k2} are summarised in figure 9.6.

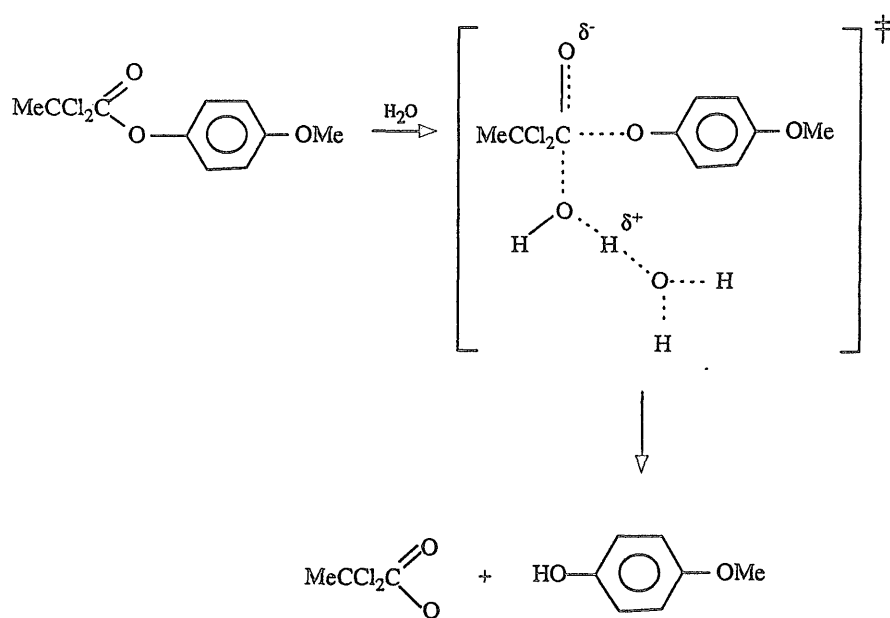
9.5(ii) Alkaline hydrolysis of an iron(II) complex.

The second order rate constant for the alkaline hydrolysis of the iron(II) complex $[\text{Fe}(\text{gmi})_3]^{2+}$ (figure 9.7) increases with increase in mole fraction of added alcohol at 298.15K, whereas the volume of activation ($16.7 \text{ cm}^3 \text{ mol}^{-1}$)²⁴ exhibits a decrease with increase in x_2 . The analysis was repeated to yield the parameters summarised in figure 9.8.

9.6 Discussion.

Patterns of kinetic and thermodynamic properties of reactions in binary aqueous mixtures are understood in terms of preferential solvation of both initial and transition states by either component of the solvent media. The term 'preferential solvation' indicates that the composition of the co-sphere around a solute (initial or transition state for the above example) differs from that of the bulk solvent. The basis of the argument is that the Kirkwood-Buff integral functions for solute-j, G_{1j} and G_{2j} , are dominated

Figure 9.5: Mechanism for spontaneous hydrolysis of 4-methoxyphenyl-2,2-dichloropropionate (*after ref. 23*) involving water catalysed nucleophilic attack of water on the ester carbonyl.



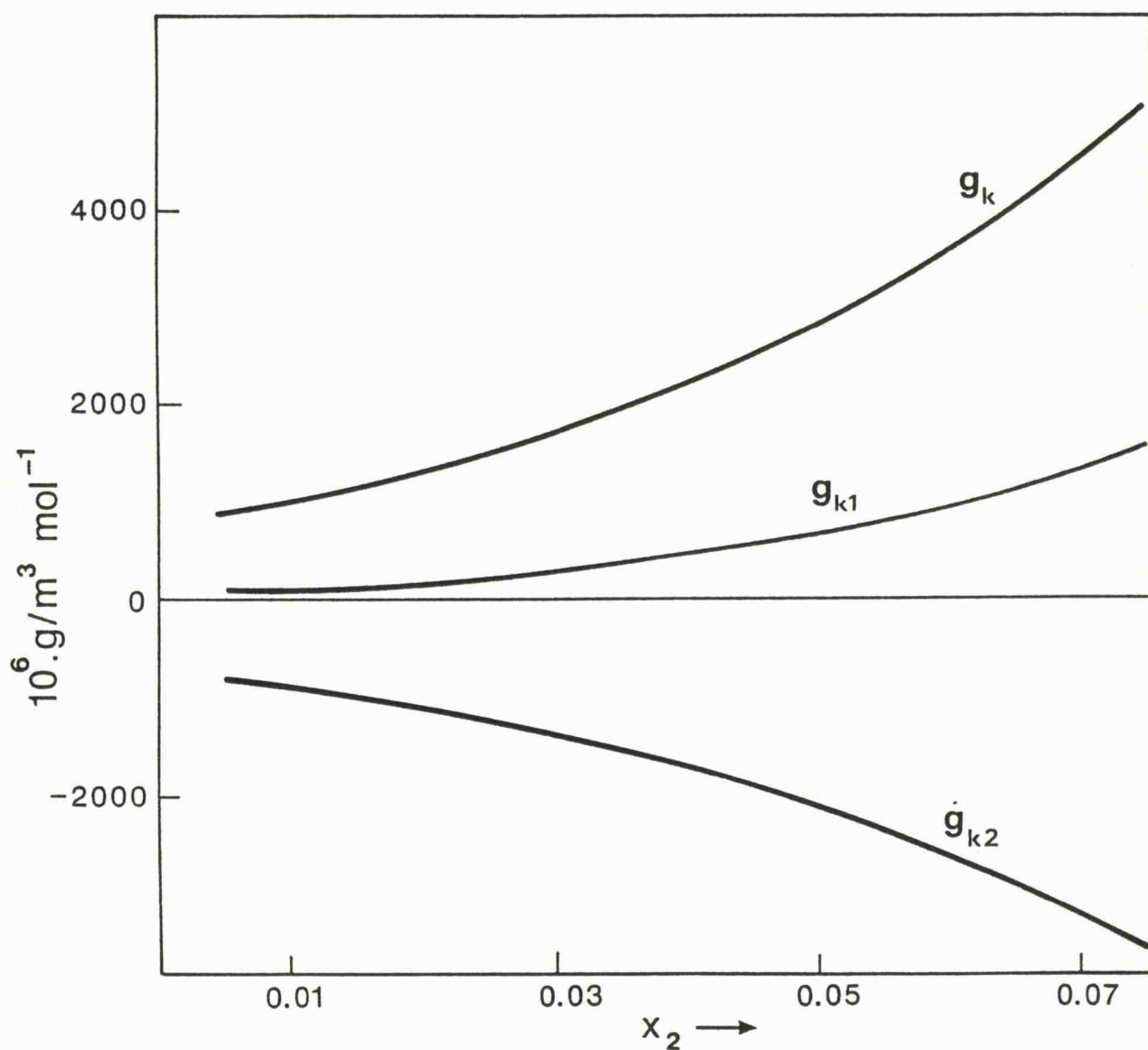


Figure 9.6: Dependence of the preferential solvation parameters, g_k , g_{k1} , g_{k2} , on mole fraction x_2 for the spontaneous hydrolysis of 4-methoxyphenyl-2,2-dichloropropionate.

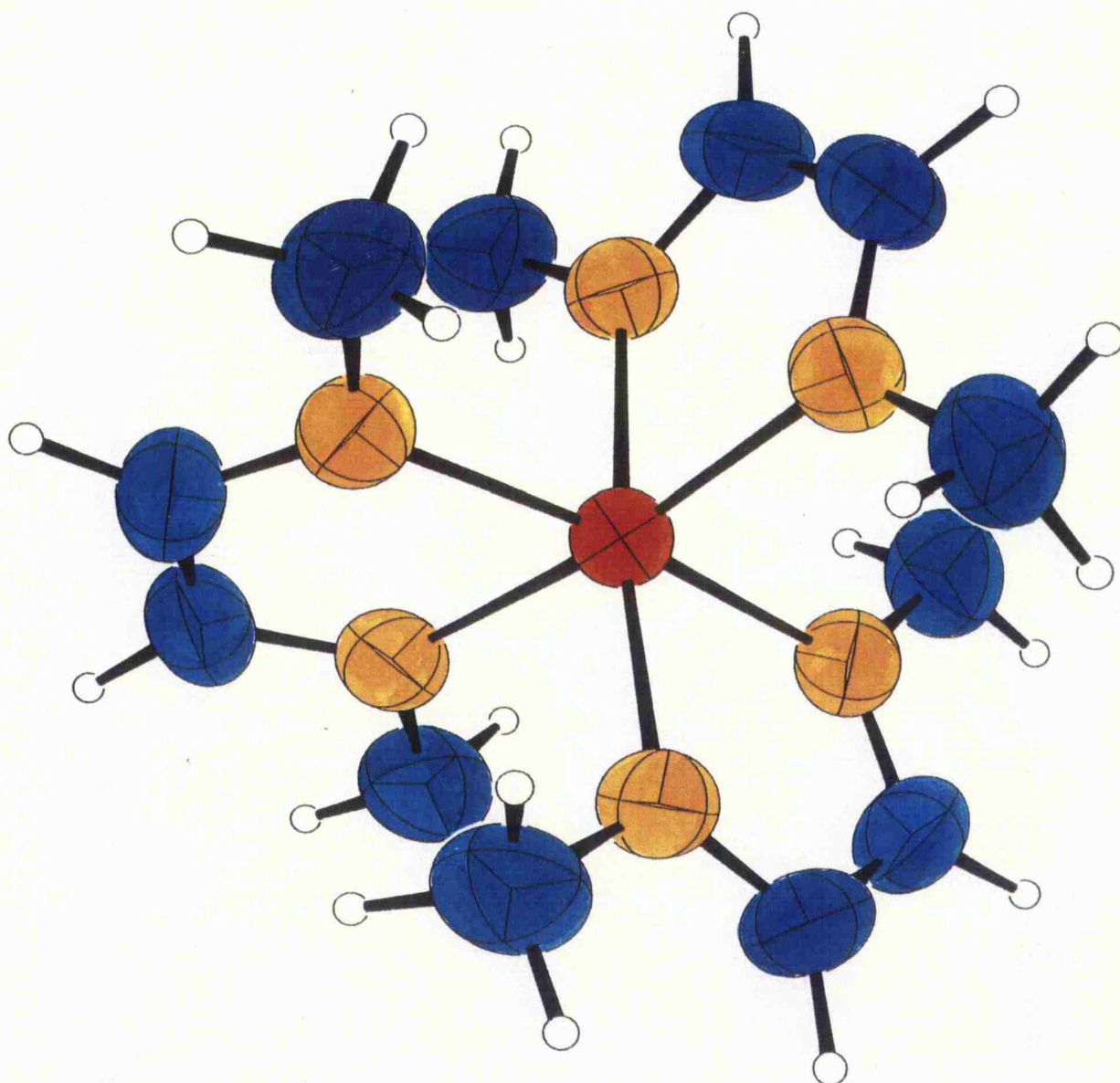


Figure 9.7: Structure of the iron(II) complex $[\text{Fe}(\text{gmi})_3]^{2+}(\text{BF}_4)_2^-$ (after ref. 27).

● = Iron ● = Nitrogen ● = Carbon ○ = Hydrogen

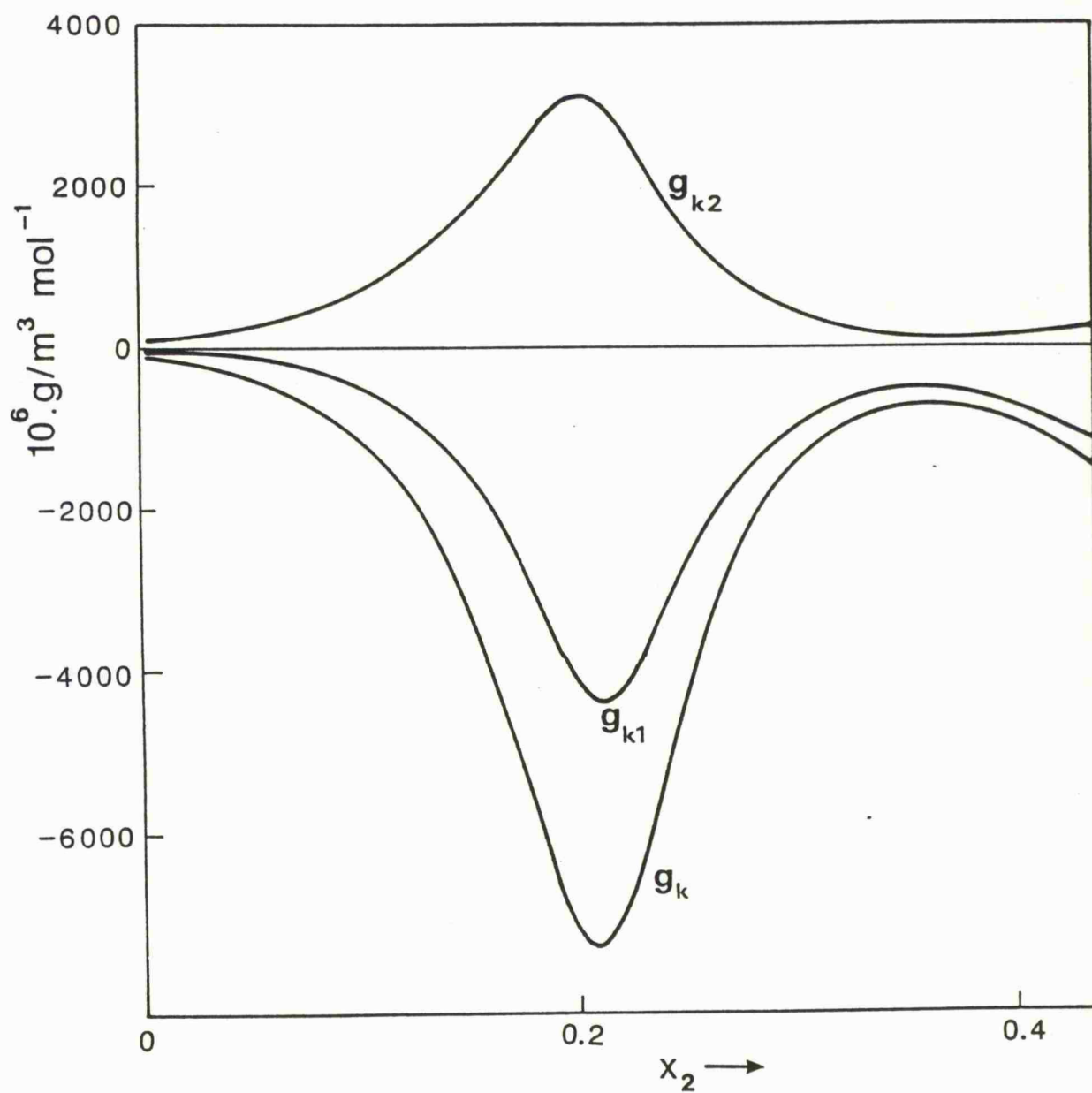


Figure 9.8: Dependence of the preferential solvation parameters, g_k , g_{k1} , g_{k2} , on mole fraction x_2 for the alkaline hydrolysis $[Fe(gmi)_3]^{2+}$.

by composition fluctuations in the locality of solute-j. Therefore, the defined g_k quantities g_{k1} and g_{k2} offer information about such localised composition fluctuations around solutes during the activation process. The two systems described above were chosen to illustrate processes where there is a change of hydrophobic/hydrophilic character on activation.¹

For the hydrolysis reaction in 9.5(i), the hydrophobic character of the initial state decreases during activation leading to a corresponding increase in hydrophilicity. The parameter g_k exhibits a marked increase with increase in x_2 indicating a significant difference between the composition of the co-spheres and the bulk solvent. We recall that g_k is given by $\{[G_{1*} - G_{1is}] - [G_{2*} - G_{2is}]\}$. Any one of these four terms cannot immediately identify this phenomenon. One possibility would be to approximate $[G_{2*} - G_{1is}]$ to zero, and $G_{1*} > G_{1is}$ so that the preferential solvation of the polar transition state by water dominates the pattern in g_k . Another approach discussed by Robertson²⁵ might propose that G_{1*} approximates to G_{2*} , and that $|G_{2is}| > |G_{2*}|$. For such a case the dominant feature would be the hydrophobic bonding between initial state and added alcohol. On examining the separate dependencies of g_{k1} and g_{k2} on x_2 we observe that the magnitude of g_{k2} is at least twice that of g_{k1} . This indicates that the trend in g_k and hence the dependence of rate constant on x_2 is dominated by hydrophobic interaction between substrate and added alcohol. This conclusion supports that proposed by Engberts.²⁶

The treatment of the organic substrate is hindered by the lack of data on the volumes of activation. In contrast, kinetic data for the alkaline hydrolysis of $[\text{Fe}(\text{gmi})_3]^{2+}$ exist for a broader range of mole fractions. One might expect that the preferential hydration of the hydroxide ions is the dominant factor in this case, leading to G_{1*} approximating to zero with $G_{1is} > \text{zero}$ (the initial state being those of the complex and OH^-). By means of the data describing volumes of activation, the obtained g_k parameters show that $|g_{k1}| < |g_{k2}|$ which we associate with the

preferential solvation of hydroxide ions in the mixture by water (figure 9.8). Figures 9.6 and 9.8 show clearly that in a liquid mixture there is little preferential solvation above $x_2 = 0.3$, the co-sphere composition being similar to that of the bulk solvent. If we also consider trends in transfer chemical potentials, i.e. $\delta\mu^\ominus$, we find that from mole fraction of added alcohol, x_2 , = 0 to 0.4 the change in $\delta\mu^\ominus$ is small (of the order of 3 kJ mol^{-1}).²⁹ From this it is possible to conclude that the change in solvation of the iron complex changes little on going from initial to transition state, with water molecules being able to solvate the nitrogen atoms in the ligand (coloured yellow in figure 9.7), by virtue of the lack of hindrance from the hydrogen atoms, and the alcohol solvating the $=\text{CH}-\text{CH}=$ part of the ligand. Hence, we can conclude that the decrease in overall hydrophilic character is due to the incorporation of the hydroxide ions into the inorganic cation, with a slight contribution from the extension of Fe-N bonds, leading to the hydrophobic ligands being forced out into the solvent. Here g_k exhibits a large initial decrease on addition of alcohol to the reacting solution.

The Kirkwood-Buff treatment is an important development in the investigations on solvent effects on kinetics of reactions in binary aqueous mixtures and indeed provides a basis for a quantitative probe of the role of preferential solvation in reaction kinetics.

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Appendix 1

Section I

Consider a mixture containing n_1 moles of liquid-1 and n_2 moles of liquid-2, at constant temperature and pressure. The chemical potential of the components can be written,

$$\mu_1(\text{mix}; T; P) = \mu_1^*(\text{liq}; T; P) + RT \ln(x_1 f_1) \quad [1]$$

$$\lim (x_1 \rightarrow 1), f_1 = 1.0$$

$$\mu_2(\text{mix}; T; P) = \mu_2^*(\text{liq}; T; P) + RT \ln(x_2 f_2) \quad [2]$$

$$\lim (x_2 \rightarrow 1), f_2 = 1.0$$

The total Gibbs energy of the mixture is given by equation 3.

$$\begin{aligned} G(\text{Total}; T; P) = n_1 \left[\mu_1^*(\text{liq}; T; P) + RT \ln(x_1 f_1) \right] \\ + n_2 \left[\mu_2^*(\text{liq}; T; P) + RT \ln(x_2 f_2) \right] \end{aligned} \quad [3]$$

or, for an ideal case,

$$\begin{aligned} G(\text{Total}; \text{id}; T; P) = n_1 \left[\mu_1^*(\text{liq}; T; P) + RT \ln(x_1) \right] \\ + n_2 \left[\mu_2^*(\text{liq}; T; P) + RT \ln(x_2) \right] \end{aligned} \quad [4]$$

But,

$$G_m^E = \frac{G(\text{Total}; T; P) - G(\text{Total}; \text{id}; T; P)}{n_1 + n_2} \quad [5]$$

therefore,

$$G_m^E = x_1 RT \ln f_1 + x_2 RT \ln f_2 \quad [6]$$

According to the Gibbs-Duhem equation, at fixed temperature and pressure,

$$\sum_i n_i d\mu_i = 0 \quad [7]$$

Then

$$n_1 \left(\frac{d\mu_1}{dx_2} \right) + n_2 \left(\frac{d\mu_2}{dx_2} \right) = 0 \quad [8]$$

and

$$x_1 \frac{d}{dx_2} \left[\mu_1^*(\text{liq}; T; P) + RT \ln(x_1) + RT \ln(f_1) \right] \quad [9]$$

$$+ x_2 \frac{d}{dx_2} \left[\mu_2^*(\text{liq}; T; P) + RT \ln(x_2) + RT \ln(f_2) \right] = 0$$

but

$$\left(\frac{d \ln x_2}{dx_2} \right) = \frac{1}{x_1} \left(\frac{dx_1}{dx_2} \right) = - \frac{1}{x_1} \quad [10]$$

Hence

$$-1 + x_1 \left(\frac{d \ln f_1}{dx_2} \right) + 1 + x_2 \left(\frac{d \ln f_2}{dx_2} \right) = 0 \quad [11]$$

thus

$$x_1 \left(\frac{d \ln f_1}{dx_2} \right) + x_2 \left(\frac{d \ln f_2}{dx_2} \right) = 0 \quad [12]$$

We now differentiate equation 6 with respect to x_2 to obtain equation 13.

$$\begin{aligned} \frac{1}{R \cdot T} \left(\frac{dG_m^E}{dx_2} \right)_{T;P} &= x_1 \left(\frac{d \ln f_1}{dx_2} \right)_{T;P} - \ln f_1 + \ln f_2 \\ &+ x_2 \left(\frac{d \ln f_2}{dx_2} \right)_{T;P} \end{aligned} \quad [13]$$

Substituting equation 12 into equation 13 gives,

$$\frac{1}{R \cdot T} \left(\frac{dG_m^E}{dx_2} \right)_{T;P} = \ln f_2 - \ln f_1 \quad [14]$$

Section II

Dependence of $\mu_2(\text{mix}; T; P)$ on x_2 .

As shown in the previous section, for a mixture containing n_1 moles of liquid-1 and n_2 moles of liquid-2 at constant temperature and pressure,

$$\mu_2(\text{mix}; T; P) = \mu_2^*(\text{liq}; T; P) + RT \ln(x_2) + RT \ln f_2 \quad [15]$$

then

$$\left(\frac{d\mu_2}{dx_2} \right) = RT \left[\frac{1}{x_2} + \left(\frac{d \ln f_2}{dx_2} \right)_{T;P} \right] \quad [16]$$

But

$$\ln f_2 = \frac{1}{R \cdot T} \left[G_m^E + (1 - x_2) \left(\frac{dG_m^E}{dx_2} \right)_{T;P} \right] \quad [17]$$

Hence

$$\begin{aligned} RT \left(\frac{d \ln f_2}{dx_2} \right)_{T;P} &= \left(\frac{dG_m^E}{dx_2} \right)_{T;P} + (1 - x_2) \left(\frac{d^2 G_m^E}{dx_2^2} \right)_{T;P} \\ &\quad - \left(\frac{dG_m^E}{dx_2} \right)_{T;P} \end{aligned} \quad [18]$$

Hence

$$\left(\frac{d \ln f_2}{dx_2} \right)_{T;P} = \frac{(1 - x_2)}{R \cdot T} \left(\frac{d^2 G_m^E}{dx_2^2} \right)_{T;P} \quad [19]$$

Therefore

$$\left(\frac{d\mu_2}{dx_2} \right)_{T;P} = \frac{RT}{x_2} + (1 - x_2) \left(\frac{d^2 G_m^E}{dx_2^2} \right)_{T;P} \quad [20]$$

Section III

Volumetric parameters.

For a liquid consisting of n_1 moles liquid-1 and n_2 moles liquid-2, at constant temperature and pressure, the molar volume V_m of the system can be written,

$$V_m = x_1 V_1(\text{mix}; T; P) + x_2 V_2(\text{mix}; T; P) \quad [21]$$

where $V_1(\text{mix}; T; P)$ and $V_2(\text{mix}; T; P)$ are the partial molar volumes of liquid-1 and liquid-2 respectively.

Therefore

$$\begin{aligned} \left(\frac{dV_m}{dx_2} \right)_{T,P} &= -V_1(\text{mix}; T; P) + x_1 \left(\frac{dV_1}{dx_2} \right)_{T,P} \\ &\quad + V_2(\text{mix}; T; P) + x_2 \left(\frac{dV_2}{dx_2} \right)_{T,P} \end{aligned} \quad [22]$$

But, according to the Gibbs-Duhem equation,

$$x_1 \left(\frac{dV_1}{dx_2} \right)_{T,P} + x_2 \left(\frac{dV_2}{dx_2} \right)_{T,P} = 0 \quad [23]$$

hence

$$V_1(\text{mix}; T; P) = V_2(\text{mix}; T; P) - \left(\frac{dV_m}{dx_2} \right)_{T,P} \quad [24]$$

To obtain an expression in terms of liquid-2 we substitute equation 24 into equation 21.

$$V_m = x_1 V_2(\text{mix}; T; P) - x_1 \left(\frac{dV_m}{dx_2} \right)_{T,P} + x_2 V_2(\text{mix}; T; P) \quad [25]$$

$$V_m = V_2(\text{mix}; T; P) - x_1 \left(\frac{dV_m}{dx_2} \right)_{T,P} \quad [26]$$

hence

$$V_2(\text{mix}; T; P) = V_m + (1 - x_2) \left(\frac{dV_m}{dx_2} \right)_{T,P} \quad [27]$$

By definition, the excess molar volume V_m^E of a system is written,

$$V_m^E = x_1 \left\{ V_1(\text{mix}; T; P) - V_1^*(\text{liq}; T; P) \right\} + x_2 \left\{ V_2(\text{mix}; T; P) - V_2^*(\text{liq}; T; P) \right\} \quad [28]$$

then

$$\left(\frac{dV_m^E}{dx_2} \right) = - \left\{ V_1(\text{mix}; T; P) - V_1^*(\text{liq}; T; P) \right\} + x_1 \left(\frac{dV_1}{dx_2} \right)_{T;P} + x_2 \left\{ V_2(\text{mix}; T; P) - V_2^*(\text{liq}; T; P) \right\} + \left(\frac{dV_2}{dx_2} \right)_{T;P} \quad [29]$$

Hence

$$\left\{ \frac{V_1(\text{mix}; T; P) - V_1^*(\text{liq}; T; P)}{V_1^*(\text{liq}; T; P)} \right\} = \left\{ \frac{V_2(\text{mix}; T; P) - V_2^*(\text{liq}; T; P)}{V_2^*(\text{liq}; T; P)} \right\} - \left(\frac{dV_m^E}{dx_2} \right)_{T;P} \quad [30]$$

Substituting into equation 28,

$$V_m^E = x_1 \left\{ \frac{V_2(\text{mix}; T; P) - V_2^*(\text{liq}; T; P)}{V_2^*(\text{liq}; T; P)} \right\} + x_1 \left(\frac{dV_m^E}{dx_2} \right)_{T;P} + x_2 \left\{ \frac{V_2(\text{mix}; T; P) - V_2^*(\text{liq}; T; P)}{V_2^*(\text{liq}; T; P)} \right\} \quad [29]$$

Then,

$$\left\{ \frac{V_2(\text{mix}; T; P) - V_2^*(\text{liq}; T; P)}{V_2^*(\text{liq}; T; P)} \right\} = V_m^E + (1 - x_2) \left(\frac{dV_m^E}{dx_2} \right)_{T;P} \quad [30]$$

Appendix 2

Phase Separation.

Consider a liquid mixture composed of liquid-1 and liquid-2 at constant temperature and pressure. It has already been shown (appendix 2, section I) that the excess Gibbs function of the mixture can be described in terms of the activity of both liquids;

$$G_m^E = R \cdot T \left\{ x_1 \ln f_1 + x_2 \ln f_2 \right\} \quad [1]$$

and

$$\left(\frac{dG_m^E}{dx_2} \right)_{T,P} = R \cdot T \left(\ln f_2 - \ln f_1 \right) \quad [2]$$

A plot of G_m^E as a function of x_2 for a simple (or regular) solution is illustrated in figure 1. The curve is described by the parabolic equation below and has a slope of (dG_m^E/dx_2) .

$$G_m^E = x_1 x_2 \omega \quad [3]$$

where $\omega = R \cdot T \ln \left(\frac{f_1}{x_2^2} \right)$

If we now consider an increment in G_m^E , δG_m^E , at mole fraction x_2 , illustrated by the region XY on figure 1; such that

$$\delta G_m^E = x_2 \left(\frac{dG_m^E}{dx_2} \right)_{T,P} \quad [4]$$

Then

$$\begin{aligned} G_m^E - \delta G_m^E &= RT \left\{ x_1 \ln f_1 + x_2 \ln f_2 - x_2 \ln f_2 + x_2 \ln f_1 \right\} \quad [5] \\ &= R \cdot T \ln f_1 \end{aligned}$$

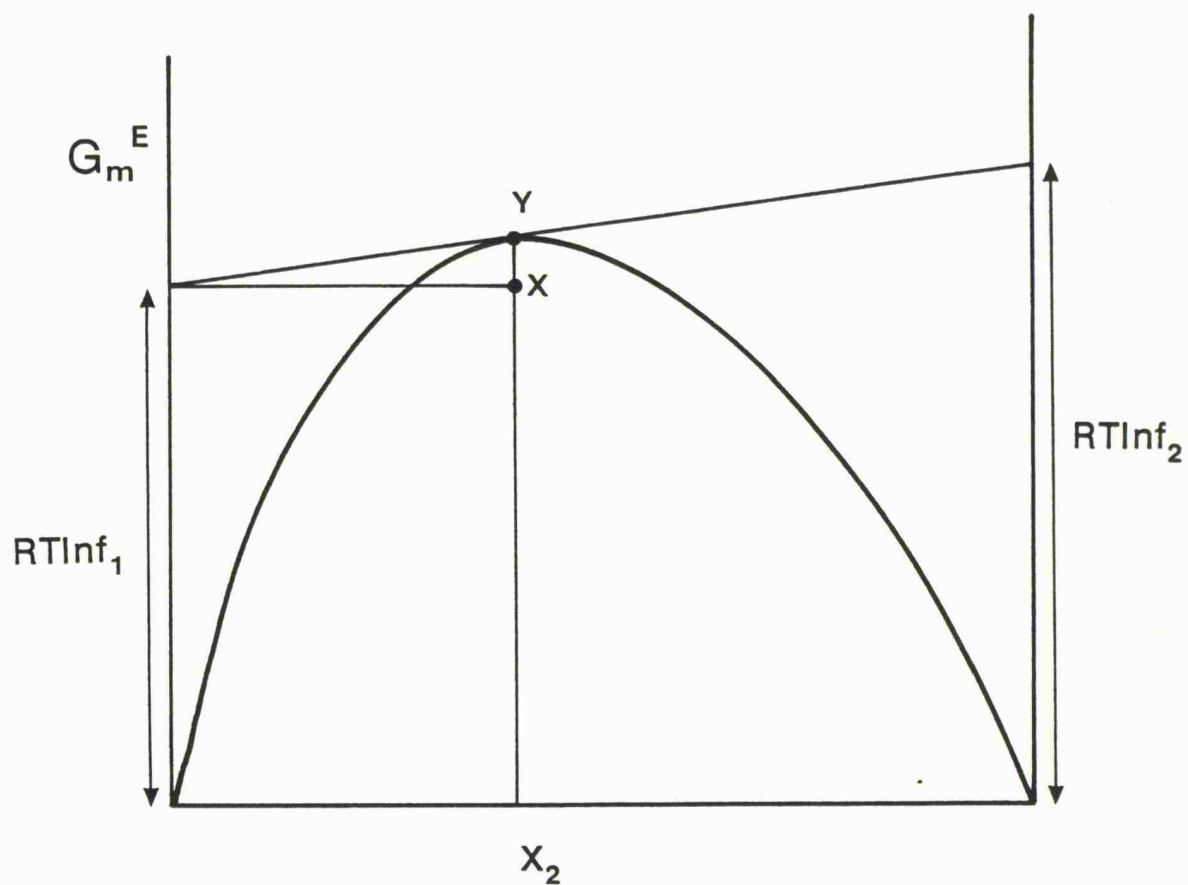


Figure 1: Excess Gibbs energy as a function of mole fraction, x_2 , at constant temperature and pressure for a regular solution.

but

$$\begin{aligned} G_m^E - \delta G_m^E &= x_1 x_2 \omega - x_2 \{x_1 \omega - x_2 \omega\} \\ &= x_2^2 \omega \end{aligned} \quad [6]$$

Therefore

$$R \cdot T \ln f_1 = x_2^2 \omega \quad [7]$$

and

$$R \cdot T \ln f_2 = x_1^2 \omega \quad [8]$$

Hence

$$f_1 = \exp \left(\frac{x_2^2 \omega}{R \cdot T} \right) \quad [9]$$

$$f_2 = \exp \left(\frac{x_1^2 \omega}{R \cdot T} \right) \quad [10]$$

By definition

$$\frac{P_2}{P_2^*} = x_2 f_2 \quad [11]$$

where P_2 is the molar pressure of liquid-2 in the mixture.
Hence

$$\frac{P_2}{P_2^*} = x_2 \exp \left(\frac{x_2^2 \omega}{R \cdot T} \right) \quad [12]$$

The criterion for phase separation is

$$\frac{d \left(\frac{P_2}{P_2^*} \right)}{dx_2} = 0 \quad [13]$$

Then

$$\frac{d \left(\frac{P_2}{P_2^*} \right)}{dx_2} = x_2 \exp \left(\frac{x_1^2 \omega}{R \cdot T} \right) \left(\frac{-2x_1 \omega}{R \cdot T} \right) + \exp \left(\frac{x_1^2 \omega}{R \cdot T} \right) \quad [14]$$

$$= \exp \left(\frac{x_1^2 \omega}{R \cdot T} \right) \left\{ - \left(\frac{2x_1 x_2 \omega}{R \cdot T} \right) + 1 \right\} \quad [15]$$

Hence

$$\left(\frac{2x_1 x_2 \omega}{R \cdot T} \right) = 1 \quad [16]$$

Therefore

$$\frac{G_m^E}{R \cdot T} = \frac{1}{2} \quad [17]$$