KINETICS AND THERMODYNAMICS OF CHEMICAL REACTIONS IN AQUEOUS SOLUTIONS

Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester

by

Heather Jane Cowles B.Sc. (Leicester) Department of Chemistry University of Leicester

July 1990

UMI Number: U030816

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U030816 Published by ProQuest LLC 2015. Copyright in the Dissertation held by the Author. Microform Edition © ProQuest LLC. All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code.



ProQuest LLC 789 East Eisenhower Parkway P.O. Box 1346 Ann Arbor, MI 48106-1346



I dedicate this thesis to my parents for their love and support

and

to the memory of my grandparents

<u>Kinetics and Thermodynamics of Chemical Reactions</u> <u>in Binary Aqueous Mixtures</u>

Heather Jane Cowles

<u>ABSTRACT</u>

The kinetics of reaction and solvation properties of binary aqueous mixtures are discussed from different theoretical standpoints. Kinetic data are reported for reactions involving several Iron(II) complex cations in binary aqueous mixtures.

The Savage-Wood Additivity Group Scheme (SWAG) is applied to kinetic data for the aquation of [Fe(5-nitro-1,10-phenanthroline)3]²⁺ in binary aqueous mixtures. Limitations of the theory are examined. The theory works well for reactions in alcohol-water and some carboxylic acid-water mixtures but not for reactions in urea-water and cyclic ether-water mixtures. The conclusion is reached that this theory can only be applied to relatively simple solutions. Otherwise, the assumptions made in the theory are not valid.

Attention is then turned to the Kirkwood-Buff theory which can be applied to reactions in mixtures containing significant amounts of the cosolvent. Few assumptions are made in its derivation. This theory is used to probe the properties of a wide range of binary aqueous mixtures. Kinetic data describing reactions in these binary mixtures are then examined, leading to a consideration of preferential solvation.

Finally, the possibility of monitoring chemical reactions under isochoric conditions is considered. A meaningful isochoric volume is defined. Kinetic and equilibrium reaction data are then analysed under these isochoric conditions.

PUBLICATIONS

 M. J. Blandamer, J. Burgess, H. J. Cowles, A. J. De Young, J. B. F. N. Engberts, S. A. Galema, S. J. Hill and I. M. Horn, J. Chem. Soc., Chem. Comm., 1988, 1141.
 M. J. Blandamer, J. Burgess, H. J. Cowles, I. M. Horn, J. B. F. N. Engberts, S. A. Galema and C. D. Hubbard, J. Chem. Soc., Faraday Trans. I, 1989, <u>85</u>, 3733.

3. M. J. Blandamer, J. Burgess, H. J. Cowles, I. M. Horn, N. J. Blundell and J. B. F. N. Engberts, J. Chem. Soc., Chem. Comm., 1989, 1233.

4. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn, J. Chem. Soc., Faraday Trans., 1990, 86, 277.

5. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn, J. Chem. Soc., Faraday Trans., 1990, <u>86</u>, 283.

6. J. B. F. N. Engberts, J. Haak, M. J. Blandamer, J. Burgess and H. J. Cowles, J. Chem. Soc., Perkin Trans. II, 1990, 1059.

7.M. J. Blandamer, J. Burgess, A. Cooney, H. J. Cowles, I. M. Horn, K. J. Martin, K. W. Morcom and P. Warrick Jr., J. Chem. Soc., Faraday Trans., 1990, <u>86</u>, 2209. 8. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles, J. B. F. N. Engberts, I. M. Horn and P. Warrick Jr., J. Am. Chem. Soc., 1990, in press.

ACKNOWLEDGMENTS

I would like to take the opportunity to thank the people who have helped and supported me throughout this work.

Firstly I am very grateful to my supervisors, Drs. Mike Blandamer and John Burgess for their expert guidance and approachability at all times. It has been a great pleasure to work with them. Thanks are also due to Mr. Phil Acton for prompt and efficient maintenance of the spectrophotometers.

I would also like to thank my brother, Steven, for providing the word processor on which the bulk of this thesis was produced.

Finally I am extremely grateful to Paul Ratcliff for producing the equations and some of the diagrams.

I acknowledge the Science and Engineering Research Council for their provision of a grant.

CONTENTS

Abstract		
Publications		
Acknowledgments		
Contents		
<u>CHAPTER ONE - Introduction</u>		
1.1 - References	6	
<u> CHAPTER TWO - A Study of the Savage-Wood Additivity Group</u>		
Scheme and its Application to an Inorganic Reaction		
2.1 - Introduction	8	
2.2 - Theoretical Background	9	
2.3 - Results(I)	18	
2.4 - Discussion(I)	28	
2.5 - Results(II)	32	
2.6 - Discussion(II)	43	
2.7 - Conclusions	47	
2.8 - References	49	

.

CHAPTER THREE - An Outline of the Development of the Kirkwood

-Buff Theory of Solutions

3.1	-	Introduction	51
3.2		Theoretical Background	53
3.3	-	Discussion	62

3.4 - References

CHAPTER FOUR - Application of the Inverse Kirkwood-Buff Procedure to a Range of Binary Aqueous Mixtures 4.1 - Introduction

4.2 - Typically Aqueous Mixtures(TA)	67
4.3 - Typically Non-Aqueous Mixtures(TNA)	91
4.4 - Complex Mixtures	110
4.5 - Conclusions	119
4.6 - References	122

CHAPTER FIVE - Application of the Inverse Kirkwood-Buff

Procedure to Kinetic Reactions in Binary Aqueous Mixtures

5.1 - Introduction	126
5.2 - Theoretical Outline	126
5.3 - Analysis of an Iron(II) complex	134
5.4 - Analysis of an inorganic compound	138
5.5 - Summary	142
5.6 - References	144

CHAPTER SIX - A Theoretical Outline of Isochoric

Thermodynamic Parameters for Reactions in Aqueous Solutions

6.1	-	Introduction			146
6.2	-	Conventional	isobaric/isothermal	conditions	147

64

6.3 - Intensive and extensive variables	149
6.4 - Some approaches to constant volume parameters	151
6.5 - Constant molar volume of pure solvent	162
6.6 - Discussion	169
6.7 - References	171

CHAPTER SEVEN - An Isochoric Study of Equilibrium and

<u>Kinetic Data</u>

74
79
87
89
91

APPENDIX TWO - Flow Diagrams

.

201

.

CHAPTER ONE

Introduction

The study of kinetic reactions in aqueous mixtures has attracted interest for many years 1-4 Much of the more recent study has been directed towards binary aqueous mixtures 1, 5, 6 with a view to obtaining a deeper understanding of reaction mechanisms and the solvation properties of the mixture.

The dictionary⁷ defines kinetics as, "those aspects of a particular process that relate to the rate at which it occurs; the details of the way a process occurs, especially as regards its rate".

As stated above, many kinetic studies have been carried out in aqueous or binary aqueous solutions, a theme continued in this thesis. The study of water has always promoted a lot of interest², chiefly because it is intrinsic to the vast majority of life forms. Figure 1.1 shows a hydrological cycle showing the constant cycling and usage of water.



Figure 1.1 - A hydrological cycle²

A knowledge of some of the properties of water is necessary to allow study of its role as a solvent. Important properties of water include an unusually high molar heat capacity and a decrease in the molar volume on melting with a maximum density at 277K. These properties can be explained by considering the strong intermolecular forces which operate in liquid water; namely hydrogen bonds. Many structures have been proposed⁸⁻¹³ for liquid water but no one structure has been shown to be totally correct. It is accepted that any model that will describe the structure of water adequately must consider water as a "structured" or associated liquid to take account of the extensive hydrogen bonding.

The aim of this thesis is to probe the role of the solvent in chemical kinetics and hence understand more about the structure of binary aqueous mixtures and the reaction mechanisms. This is done using a number of different theories.

The Savage-Wood Additivity Group Scheme (SWAG)¹⁴ attempts to quantify solute-solute interactions and, if carefully applied, may lead to a situation whereby the effects of solute-solute interactions can be predicted. This study of solute-solute interactions is then extended to consider group pairwise interactions between molecules. This theory is studied in Chapter Two where the solutes under consideration are alcohols, carboxylic acids, ureas and cyclic ethers.

The SWAG¹⁴ scheme describes the properties of dilute aqueous systems only. If more concentrated solutions are used, higher order interactions would become important making the theory too complex for ready analysis.

This concentration limitation led to a study of the Kirkwood-Buff¹⁵ theory. This theory allows for the study of the microscopic structure of binary solutions over the entire mole fraction range. Ben-Naim¹⁶ adapted this theory and his method is used here. Kirkwood-Buff integral functions are determined which provide information about the local composition of the medium surrounding the component which make up the binary liquid mixture. This theory is outlined in Chapter Three. In Chapter Four the theory is applied to a wide range of binary aqueous mixtures and in Chapter Five it is developed and applied to kinetic reactions in binary aqueous mixtures.

Finally, reaction conditions are compared in Chapters Six and Seven. Conventional reaction conditions are isobaric/isothermal, but it was proposed¹⁷ by Evans and Polanyi that isochoric (constant volume) reaction conditions may be more fundamental. Which volume should be held constant is considered in Chapter Six. Having determined the volume to be held constant, the treatment is applied to kinetic and equilibrium reactions in Chapter Seven.

.

.

REFERENCES

M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A. W.
 Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C.
 Hubbard and E.-E. A. Abu-Gharib, J. Chem. Soc., Faraday
 Trans. I, 1986, <u>82</u>, 1471.

2. "Water- A Comprehensive Treatise", ed. F. Franks, Plenum Press, New York, 1972.

3. K. J. Laidler, "Reaction Kinetics: Volume 2 - Reactions in Solutions", Pergamon Press, 1963.

4. E. A. Moelwyn Hughes, "The Chemical Statics and Kinetics of Solutions", Academic Press, London, 1971.

5. M. J. Blandamer, J. Burgess and J. B. F. N. Engberts, Chem. Soc. Rev., 1985, <u>14</u>, 237.

6. M. J. Blandamer, J. Burgess, J. B. F. N. Engberts and F. Sanchez, Faraday Disc. Chem. Soc., 1988, <u>85</u>, 309.

7. "The Oxford English Dictionary", 2nd. ed., Clarendon Press, Oxford, 1989.

J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1933, <u>1</u>,
 515.

9. G. Némethy and H. A. Scheraga, J. Chem. Phys., 1962, <u>36</u>, 3382.

10. L. Pauling, "The Nature of the Chemical Bond", Cornell University.Press, New York, 1960.

(London), 1951, <u>A205</u>, 155.
12. H. S. Frank and W.-Y. Wen, Disc. Faraday Soc., 1957, <u>24</u>, 133.
13. H. S. Frank and A. S. Quist, J. Chem. Soc., 1961, <u>34</u>, 604.
14. J. J. Savage and R. H. Wood, J. Sol. Chem., 1976, <u>5</u>, 733.
15. J. G. Kirkwood and F. P. Buff, J. Chem. Phys., 1951, <u>19</u>, 774.
16. A. Ben-Naim, J. Chem. Phys., 1977, <u>67</u>, 4884.
17. M. G. Evans and M. Polanyi, Trans. Faraday Soc., 1935, <u>31</u>,875.

7

11. Sir J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc.

CHAPTER TWO

A Study of the Savage-Wood Additivity Group Scheme and its Application to an Inorganic Reaction

,

2.1 - INTRODUCTION

When considering both the thermodynamic properties of a dilute aqueous solution and the rate of a chemical reaction in such a solution, it is constructive to look at the types of interactions which are present in that solution.

In the case of a simple solution comprising a single solute and a single solvent we can consider three types of interactions, solvent-solvent interactions, solvent-solute interactions and solute-solute interactions. For aqueous solutions where the added solute is a hydrocarbon, or contains a hydrocarbon-like group, an interaction of considerable interest is the solute-solute interaction known as the hydrophobic interaction¹.

The Savage-Wood Additivity Group Scheme (SWAG) was proposed by Savage and Wood² as a method by which these solute-solute interactions could be measured, perhaps leading to a situation whereby the information gained by this treatment could be used to predict solute-solute interactions. These ideas of Savage and Wood have been both developed and criticised by a number of workers³⁻⁶. This Savage-Wood treatment has been extended to consider kinetic data⁷⁻⁹.

This chapter reviews the SWAG analysis with reference to an inorganic hydrolysis reaction. The aim was to extend the application of SWAG to include kinetic data for this class of reaction and hence to probe the limitations of the method.

2.2 - THEORETICAL BACKGROUND

2.2.1 - Savage-Wood Additivity Group Scheme (SWAG)

Savage-Wood Additivity Group Scheme The (SWAG) was developed 2 to describe the role of pairwise solute-solute interactions which, by are definition, present in dilute, real solutions. Savage and Wood used enthalpy of dilution measurements to calculate pairwise enthalpic interaction parameters for organic solutes. They then attempted to take their calculations to the next level of detail by determining pairwise interaction parameters between the groups in solute molecules. To do simple additivity and Wood developed a this Savage principle in which each molecule is considered as a number of independent functional groups. The principle assumes that every functional group on one molecule interacts with every functional group on the other molecule and that each of these interactions has a characteristic effect on the particular thermodynamic parameter under consideration, this effect being independent of the positions of the

functional groups on the two molecules. The thermodynamic parameters which have been calculated are enthalpies and Gibbs energies. SWAG states that the total pairwise molecular interaction is equal to the sum of all the possible individual pairwise functional group interactions.

The experimental enthalpy of dilution data were fitted³ to a series of equations leading to a consideration of pairwise interactions. Equation (2.2.1) is used to determine the change in the enthalpy of dilution Δ_{di1} H,

$$\Delta_{dil}H = nH_{sol}^{E}(m_{i}) - nH_{sol}^{E}(m_{f})$$

$$= n[H_{sol}^{E}(m_{i}) - H_{sol}^{E}(m_{f})]$$
(2.2.1)

where n is the total number of moles of solute, m_i is the initial molality before dilution with water and m_f is the final molality. $H_{sol}^{E}(m)$ is the excess enthalpy of solution per mole of solute at molality m. H_{sol}^{E} can be represented by,

$$H_{sol}^{E}(m) = h_{2}m + h_{3}m^{2} + h_{4}m^{3} + \dots$$
 (2.2.2)

and substitution of (2.2.2) into (2.2.1) leads to,

$$\Delta_{dil}H/n = h_2(m_i - m_f) + h_3(m_i^2 - m_f^2) + \dots \quad (2.2.3)$$

As we are only considering dilute solutions and therefore only concerned with pairwise interactions between solutes, we only need to look at coefficient h_2 in equation (2.2.3) and this provides information about pairwise interactions between the solute molecules A and B.

$$h_2 = h_{AA}x_A^2 + h_{BB}x_B^2 + 2h_{AB}x_Ax_B$$
 (2.2.4)

where x_A and x_B are the mole fractions of solutes A and B respectively. Applying SWAG leads to,

$$h_{AB} = \sum_{i} \sum_{j} n_{A}^{i} n_{B}^{j} H_{ij}$$
 (2.2.5)

where n_A^i and n_B^j are the number of i-functional groups on molecule A and j-functional groups on molecule B. H_{ij} is the enthalpy of an i-j interaction and h_{AB} represents the pairwise interaction of molecule A with molecule B.

A similar summation can be derived for the Gibbs energy of an i-j interaction. Calculations of such Gibbs energies of interaction have been made by Wood and coworkers10 using freezing temperature measurements. Conversion of equation (2.2.5) to yield the Gibbs energy

of the functional group interaction gives,

$$g_{AB} = \sum_{i} \sum_{j} n_A^{i} n_B^{j} G_{ij} - M_S RT/2$$
 (2.2.6)

where G_{ij} is the Gibbs energy of an i-j interaction, M_s is the molar mass of the solvent, R is the gas constant and T is the temperature.

Savage and Wood² acknowledged from the outset that this additivity principle was only approximate in nature. Despite this they considered that the results were meaningful and of use. They realised that the requirement that each functional group should interact with all other functional groups independent of positions was simplistic as steric effects and nearest-neighbour effects would also play an important role. The nature of the solvation shells around the functional groups might also present problems. Other authors 3-6,11 have also highlighted these limitations. These problems are discussed further later in the light of the results presented here. Despite these problems the Savage-Wood Additivity Group Scheme provides a method by which the sign and magnitude of a variety of interactions can be predicted.

$2.2.2 - Fe(5-nitro-1, 10-phenanthroline)_3^{2+}$ complexes

The Iron(II) complex used in this study of the Savage-Wood Additivity Group Scheme (SWAG) was $Fe(5-NO_2-phen)_3^{2+}$. Unlike the majority of Iron(II) complexes, Fe(5-NO2-phen)32+ is a low spin complex to the large crystal field effect of due the ligands. These low substituted phenanthroline spin di-imine complexes are relatively inert. In aqueous solution, $Fe(5-NO_2-phen)_3^{2+}$ has an intense dark red colour due to the back-bonding between the filled t2g orbitals of the Fe²⁺ and the π^* orbitals of the phenanthroline ligands; Figure 2.1.



Figure 2.1 - Back bonding in a low spin Fe(II) complex 1?

2.2.3 - Kinetics

The aquation of $Fe(5-NO_2-phen)_3^{2+}$ is a first order reaction of the type ,

^k1 A -----> [TS]≠ ----> PRODUCTS (2.2.7)

Transition State Theory¹³ states that the rate constant for a chemical reaction measures the difference between the chemical potentials of the initial state (IS) and the transition state (TS). The rate of formation of the products is given by,

$$-d[A]/dt = k_1[A]$$
 (2.2.8)

2.2.4 - Application of SWAG to Kinetics

The original applications of the Savage-Wood Additivity Group Scheme (SWAG) used measurements of enthalpies of dilution and other related experimental data. More recently**7-9,14** the SWAG procedure has been studied using kinetic data. These measurements have been used to probe the reaction mechanisms and also the SWAG procedure itself.

Consider an aqueous solution containing substrate S, and added solute A. We know that,

$$\mu_{s} = \mu_{s}^{\circ} + RTln(m_{s}\gamma_{s}/m^{\circ})$$
 (2.2.9)

where μ_s is the chemical potential of substrate S undergoing chemical reaction, m_s and γ_s are the molality and activity coefficient of substrate S respectively, and $m^\circ = 1.0 \text{ mol } \text{kg}^{-1}$. μ_s° is the standard chemical potential of substrate S in an ideal aqueous solution where $m_s = 1.0 \text{ mol } \text{kg}^{-1}$. μ_s° is determined by substratewater interactions. By definition,

lim
$$(m_s \longrightarrow 0; m_A \longrightarrow 0) \gamma_s = 1.0$$
 (2.2.10)

and this holds for all temperatures and pressures. In a real aqueous solution, $\gamma_s \neq 1.0$ as a result of S<->S, S<->A and A<->A interactions. In a very dilute solution, substrate S will only be present in trace amounts so we need only be concerned with S<->A interactions. A similar argument is valid for the situation where the substrate is the transition state TS.

Considering the reaction of substrate S in a real, dilute aqueous solution containing an added solute A, and applying Transition State Theory¹³, we have,

$$\gamma_{s} \neq \gamma_{T_{s}} \neq 1.0$$
 (2.2.11)

where γ_s is the activity coefficient of substrate S at the start of the reaction (initial state, IS) and γ_{TS} is the activity coefficient for the transition state (TS). This leads us to a rate equation,

$$\ln[k(m_{A})/k(m_{A}=0)] = \ln\gamma_{S} - \ln\gamma_{TS} - n\Phi m_{A}M_{W}$$
 (2.2.12)

where $k(m_A)$ is the observed rate constant for the reaction in the presence of added solute A, of molality m_A , and $k(m_A=0)$ is the observed rate constant for the same reaction in aqueous solution. M_W is the molar mass of water, Φ is the practical osmotic coefficient for the solution $(\lim(m->0)\Phi = 1.0)$ and n is the order of the reaction with respect to water.

For real, dilute solutions, the excess Gibbs energy G^E , is determined by the pairwise interactions S<->S, S<->A and A<->A, giving us,

$$G^{E}(aq;T;p) = g_{SS}(m_{S}/mo)^{2} + 2g_{AS}m_{S}m_{A}/(m^{o})^{2}$$

$$+ g_{AA}(m_{A}/mo)^{2}$$
(2.2.13)

where g_{AA} , g_{AS} and g_{SS} represent the pairwise interactions. At constant T, p, m_A ,

$$\ln \gamma_{\rm s} = (1/RT) (\partial G^{\rm E}/\partial m_{\rm s}) \qquad (2.2.14)$$

thus, differentiating (2.2.13) gives,

$$RTln\gamma_{s} = 2g_{ss}m_{s}/(m^{\circ})^{2} + 2g_{As}m_{A}/(m^{\circ})^{2}$$
 (2.2.15)

As substrate S is only present in trace amounts, we need only consider the cross-term g_{AS} , simplifying equation (2.2.15) to,

$$RTln\gamma_{s} = 2g_{As}m_{A}/(m^{\circ})^{2}$$
 (2.2.16)

An analogous equation applies for the case where the substrate is the transition state.

Savage and Wood² took these interactions

one step further to consider interactions between functional groups X and Y on the solute molecules A and B. Returning to equation (2.2.12) and substituting equation (2.2.16) leads to a rate equation which now includes Savage-Wood interaction parameters,

$$\ln(k(m_{A})/k(m_{A}=0)) = (2/RT)(1/m^{0})^{2}[g_{AS}-g_{A\neq}]m_{A}$$
(2.2.17)
$$-n\Phi m_{A}M_{w}$$

For dilute solutions, the term $n \Phi m_{\text{A}} M_{\text{w}}$ is negligibly small. Hence,

$$\ln(k(m_A)/k(m_A=0)) = (2/RT)[g_{AS}-g_{A\neq}]m_A/(m^{\circ})2$$
 (2.2.18)

which is the working equation for SWAG kinetic analyses.

2.3 - RESULTS(I)

The $Fe(5-nitro-1,10-phenanthroline)_3^{2+}$ complex was prepared using stoichiometric quantities of Fe(II) ammonium sulphate and (5-N02-phen) ligand.

each kinetic run the cells contained For 3 cm³ of an aqueous acidic solution of the appropriate cosolvent, to which was added 2 x 10^{-5} cm³ of the stock solution ($\simeq 0.01 \text{ mol } dm^{-3}$) of the Fe(5-NO₂-phen)₃ complex. the solution was rendered acidic using sulphuric acid, the final concentration within the cell being $0.10 \text{ mol} \text{ dm}^{-3}$. Acid required was to scavenge the substituted ligand after being released from the phenanthroline Fe(II) centre, thus inhibiting the reverse reaction. The kinetic runs were carried out using Pye Unicam SP1800 and Hewlett-Packard HP8451A spectrophotometers, the results being analysed as described in Appendix 1. The aquation reaction was monitored by recording the decrease in absorbance of the band at λ_{max} = 510 nm original to the complex. The initial absorbance reading was approximately 1.0 and the reaction was followed until the intense dark red colour had essentially completely disappeared, the time taken for the colour to disappear being equal to at least $2\frac{1}{2}$ half lives. All reactions were carried out at 298.2 K and atmospheric pressure.

The kinetics of reaction for the Fe(II) complex under consideration have been extensively studied 15-18 both for the aquation reaction and attack by different nucleophiles, all in a range of different solvents. The reaction for the aquation of this complex

under acid conditions can be given by,

$$H_20$$

Fe(5-N0₂-phen)₃²⁺(aq) + 3H⁺(aq) ---->
(2.3.1)
Fe²⁺(aq)+35Nophen.H⁺(aq)

The rate of reaction was known to be independent of the acid strength. In the activation step the Fe-N bonds within the complex cation stretch, reaching a limit where one of the substituted phenanthroline ligands is released into the solvent surrounding the complex cation. This is shown in Figure 2.2. This scheme implies that the transition state will be more hydrophobic than the initial state.

The rate constant for the reaction with no added solute was measured.

$$k_{obs} = 5.57 \times 10^{-4} s^{-1}$$

The kinetic results for reactions in a series of aqueous solutions containing added alcohols and carboxylic acids are shown in the Tables below.



Figure 2.2 - First step in the aquation reaction of the complex.

Table 2.1 - Alcohols

.

2.1.1 - METHANOL

m _A / mol kg ⁻¹	ln (k _{obs} /ko _{obs})
0	0
0.31	0.022
0.59	0.036
0.88	0.066
1.17	0.083
1.49	0.110

2.1.2 - ETHANOL

^m A / mol kg ⁻¹	ln (k _{obs} /k ^o obs)
0	0
0.30	0.030
0.64	0.045
0.93	0.095
1.20	0.117
1.50	0.132

$m_A / mol kg^{-1}$	$\ln (k_{obs}/k_{obs}^{o})$
0	0
0.33	0.037
0.66	0.080
1.07	0.110
1.40	0.136
1.70	0.179
2.15	0.253

2.1.3 - i-PROPANOL

2.1.4 - t-BUTANOL

m_A / mol kg-1

 $\ln (k_{obs}/k_{obs}^{o})$

0	0
0.32	0.039
0.62	0.079
0.74	0.103
1.11	0.134
Table 2.2 - Carboxylic Acids

2.2.1 - METHANOIC ACID

m _A / mol kg ⁻¹	ln (k _{obs/k} o _{obs})
0	0
1.56	-0.086
2.06	-0.128
2.61	-0.173
3.15	-0.211

2.2.2 - ETHANOIC ACID

m_A / mol kg⁻¹

ln (k_{obs}/ko_{obs})

0	0
1.00	-0.052
1.48	-0.078
2.03	-0.104
2.56	-0.122

2.2.3 - PROPANOIC ACID

 m_A / mol kg⁻¹In (k_{obs}/k^o_{obs}) 000.54-0.0801.08-0.1431.62-0.1752.16-0.0982.70-0.118

2.2.4 - BUTANOIC ACID

m_A / mol kg⁻¹

 $\ln (k_{obs}/k_{obs})$

0	0
0.47	-0.110
0.92	-0.116
1.27	-0.075
1.69	-0.055
2.10	+0.081

These results are summarised in Figure 2.3 and 2.4 where ln (k_{obs}/k_{obs}^{o}) is plotted against the molality of the added cosolvent, m_A . The slopes obtained from these graphs are substituted into equation (2.2.18) to give the Savage-Wood interaction parameters; Table 2.3.





Table 2.3 - Slopes and Savage-Wood Parameters

cosolvent	slope/kg mol-1	$[G(i < >IS)-G(i < >TS)]/J kg^{-1}$
methanol	0.073	90.5
ethanol	0.091	111.8
i-propanol	0.111	137.6
t-butanol	0.129	160.0
methanoic	-0.064	-79.3
ethanoic	-0.050	-62.0
(propanoic)		
(butanoic)		
	.	

(Lines forced through origin)

2.4 - DISCUSSION(I)

Consider first the alcohols and the first two acids. The values for the Savage-Wood interaction parameters shown in Table 2.3 show a constant increment of +21(±4) J kg⁻¹. In each case the chain length of the added solute under consideration has been incremented by one -CH₂- group. Applying the Savage-Wood Additivity Group Scheme, the calculated increment in the interaction parameters is close to the value of $-34(\pm 5)$ J kg⁻¹ obtained by Wood¹⁰ for the G(CH₂<->CH₂) pairwise

group interaction parameter. From this we concluded that as we move from the initial state (IS) to the transition state (TS) for the aquation reaction of $Fe(5-NO_2-phen)_3^{2+}$ acidic conditions, there increase under is an in hydrophobicity (as indicated by the positive value obtained for $G(CH_2 \langle - \rangle CH_2)$ of slightly less than one methylene group. From a mechanistic viewpoint we would expect that the increase in exposure of the substituted phenanthroline ring to the solvent medium as the Fe-N bond is stretched would lead to an increase in the hydrophobic character of the substrate during the activation process. These results showed that there was no change in the reaction mechanism as either the molality or composition of the added solute was changed.

We now turn our attention to propanoic and butanoic acid. According to Figure 2.4 the kinetic results produce a non-linear plot which means that Savage-Wood interaction parameters cannot be calculated from the slope. It would seem unlikely that this change in behaviour on moving down the homologous series from ethanoic acid to propanoic acid is caused by a change in the reaction mechanism. Therefore, we must look for other explanations.

It is important to remember throughout this discussion that we are concerned with reactions in aqueous solution and that we must consider therefore the effects of solvation. In addition to the interactions of the acid molecules with each other, the acid molecules will hydrogen bond with the water cosolvent molecules. The level of this hydrogen bonding is not simply dependent on the molality of the added solute as is the case with the other cosolvents studied; here we must consider the decrease in acid strength as we move down the series. As with all acids, the carboxylic acids will be subject to ionisation and will be at least partially dissociated in these aqueous solutions. This means that the balance between solvated acid molecules and solvated acid ions should be allowed for. The SWAG procedure as it stands treats the acid molecules as undissociated molecules.

Wood and coworkers19 have applied the SWAG the same carboxylic acid series using treatment to enthalpy of dilution measurements. They state that their results for the full series of aliphatic, straight-chain acids right through to butanoic acid, show good correlation with other results obtained using SWAG. This is in apparent contradiction to the results reported here. However, in applying the SWAG treatment they took into account ionisation of the acid molecules and also triplet interactions between acid molecules. They consider that

clustering of acid molecules into trimers or even larger species, particularly for propanoic and butanoic acids, is very important and increases with chain length as the hydrophobic group on the acid exerts a greater effect. For acids. propanoic and butanoic trimers can have а significant effect on results, even when the acid molality is low. To allow for both triplet interactions and the dissociation of some of the acid molecules, Wood fitted the data to activity expansion equations which had been developed previously 20. This activity expansion theory uses the same equation for weak or strong electrolytes making no distinction between them. The theory represents the activity of the i-th component both as a function of the stoichiometric molality of each component (in the case of the acids there are two components, H^+ and A^-) and as "sociation" constants denoting the interactions of the component species.

is clear therefore, that It the highercarboxylic acids do fit the Savage-Wood order not Additivity Group Scheme in its original form, even at low molalities as the first two acids do. This is because the SWAG procedure does not allow for two very important properties of the acids, namely their tendency to cluster and their ability to dissociate. However, the SWAG method of analysis does work well for the homologous series of alcohols.

2.5 - RESULTS(II)

The aquation reaction of $Fe(5-NO_2-phen)_3$ was studied in a variety of aqueous solutions where the added solute was one of a series of alkyl-substituted ureas or cyclic and related ethers. Reactions involving all of these solutes were carried out under acidic conditions as in Section 2.3. Measurements involving some of the ureas as added solutes were repeated using 0.01 mol dm^{-3} EDTA (present as the disodium salt) instead of 0.10 moldm-3 sulphuric acid. A11 other reaction conditions remained unchanged. The EDTA scavenges the Fe(II) itself, instead of the substituted phenanthroline ligands as is the case with added acid. As with added sulphuric acid the purpose of the EDTA is to stop the reverse reaction.

The kinetic results for these solutes are given in the Tables below.

N.B.
$$k_{obs}^{o} = 5.57 \times 10^{-4} s^{-1}$$

Table 2.4 - Ureas (+ H^+)

 m_A / mol kg⁻¹In (k_{obs}/k^o_{obs}) 000.250.1540.500.2140.750.3151.000.4171.500.662

2.4.2 - METHYLUREA

m _A / mol kg ⁻¹	ln (k _{obs} /ko _{obs})
0	0

0.10	0.059
0.30	0.191
0.50	0.276
0.80	0.471
1.00	0.529

.

2.4.3 - ETHYLUREA

 m_A / mol kg⁻¹In (k_{obs}/k^o_{obs}) 000.200.0970.400.1890.500.2430.800.3341.000.382

2.4.4 - 1,3-DIMETHYLUREA

m_A / mol kg⁻¹ ln (k_{obs}/k^oobs) 0 0 0.20 0.127 0.40 0.217 0.60 0.300

> 0.75 0.365 1.00 0.468

2.4.5 - 1,1,3,3-TETRAMETHYLUREA

m _A / mol kg ⁻¹	ln (k _{obs} /ko _{obs})
0	0 .
0.20	0.080
0.40	0.129
0.60	0.160
0.80	0.214
1.00	0.250
1.20	0.307

.

Table 2.5 - Ethers $(+ H^+)$

2.5.1 - TETRAHYDROFURAN (THF)

m _A / mol kg ⁻¹	ln (k _{obs} /k ^o obs)
0	0
0.20	0.011
0.40	0.034
0.60	0.052
0.70	0.054
1.00	0.079
1.50	0.158

2.5.2 - 1,4-DIOXANE

 m_A / mol kg⁻¹In (k_{obs}/k^o_{obs}) 000.200.0250.400.0540.800.0811.000.0981.500.157

2.5.3 - 1,2-DIMETHOXYETHANE (DME)

$m_A / mol kg^{-1}$ ln	(k _{obs} /k ^o obs)
------------------------	--

0
0.070
0.112
0.154
0.197
0.283

Table 2.6 - Ureas (+ EDTA)

2.6.1 - UREA (+ EDTA)

 m_A / mol kg⁻¹

ln (k_{obs}/k^oobs)

0	0
0.30	0.150
0.50	0.226
0.80	0.324
1.20	0.419

2.6.2 - METHYLUREA (+ EDTA)

$m_A / mol kg^{-1}$	ln (k _{obs} /k ^o obs)
0	0
0.20	0.154
0.73	0.321
1.00	0.411
1.20	0.513

2.6.3 - ETHYLUREA (+ EDTA)

$m_A / mol kg^{-1}$	ln (k _{obs} /k ^o obs)
0	0
0.20	0.140
0.50	0.273
0.70	0.332
0.90	0.367
1.20	0.463

These results are shown in Figures 2.5 - 2.7 where ln (k_{obs}/k_{obs}^{o}) is plotted against the molality of the added solute, m_A. The slopes obtained from these plots are substituted into equation (2.2.18) to give the interaction parameters; Tables 2.7 and 2.8.



 $\begin{array}{l} \hline \mbox{Figure 2.5} & - \mbox{ Dependence on molarity of organic solute } m_A \mbox{ for } \\ & \ln\left(k, /k^\circ\right) \mbox{ describing rate}_A^{\mbox{ of aquation of iron(II)}} \\ & \mbox{ complex [Fe(5 - NO_2 - phen)_3]}^{2+} \mbox{ in aqueous acidic solutions at 298.2K. Solutions are (---) urea; (---) \\ & \mbox{ methylurea; (---) thylurea; (---) 1,3-dimethylurea; \\ & \mbox{ and (---) 1,1,3,3-tetramethylurea.} \end{array}$



Figure 2.6- Dependence on molarity of organic solute m_A for $\ln(k_*/k_{ots}^{\circ})$ describing rate of aquation of iron(II)complex [Fe(5 - NO2 - phen)]²⁺ in aqueous acidicsolutions at 298.2K. Solutions are (---) THF; (---)dioxane; and (----) DME.



 $\begin{array}{l} \underline{Figure \ 2.7} & - \ Dependence \ on \ molarity \ of \ organic \ solute \ m_A \ for \\ & \ln\left(k_{\bullet,\bullet}^{\prime}/k_{\bullet,\bullet}^{\circ}\right) \ describing \ rate_A \ of \ aquation \ of \ iron(II) \\ & complex \ [Fe(5 - NO_2 - phen)_3]^{2+} \ in \ aqueous \ solutions \\ & (EDTA) \ at \ 298.2K. \ Solutions \ are \ (---) \ urea; \ (---) \\ & methylurea; \ and \ (---) \ ethylurea. \end{array}$

Table 2.7 - Interaction Parameters (UREAS)

cosolvent	slope kg mol ⁻¹	no.CH ₂ grps	[G(i<->IS)-G(i<->TS)] J kg ⁻¹	
urea(H ⁺)	0.438	0	543.0	
meth(H ⁺)	0.559	1.5	692.9	
eth(H ⁺)	0.448	2.5	555.3	
dime(H ⁺)	0.495	3.0	613.6	
tetra(H ⁺)	0.271	6.0	335.9	
ur(EDTA)	0.414	0	513.2	
me(EDTA)	0.466	1.5	577.7	
et(EDTA)	0.448	2.5	555.3	

Table 2.8 - Interaction Parameters (ETHERS)

cosolvent	slope kg mol ⁻¹	Сн ₂	+	0	[G(i<->IS)-g(i<->TS)] J kg ⁻¹
THF(H ⁺)	0.087	4	+	1	107.8
diox(H ⁺)	0.104	4	+	2	128.9
DME(H ⁺)	0.276	5	+	2	342.1

2.6 - DISCUSSION(II)

The results in **Tables 2.7 and 2.8** and **Figures 2.5** - **2.7** show that neither the ureas nor the cyclic and related ethers fit the Savage-Wood Additivity Scheme² in the expected way. The ureas follow no clear pattern based on the number of $-CH_2$ - groups (N.B. 1 x CH_3 = 1.5 x CH_2) and for the ethers the value obtained for a CH_2 - group interaction parameter is unacceptably large. Obviously the chemical nature of these added solutes needs to be considered to explain these results.

Looking first at the ureas, we can see that there appears to be a complete change in the nature of the solute-water solvent medium between methylurea and ethylurea as we go through the series. There is another such change before 1,3-dimethylurea. Clearly the continued alkyl-substitution of urea leads to far more dramatic changes in the properties of the added solute than is the case for the alcohols.

Urea itself is a polyfunctional molecule and is very soluble in water. This high solubility is due to the formation of hydrogen bonds between water and urea via the -NH and -C=O groups on the urea molecules. These hydrogen bonds are short-term interactions and do not form an extensive network. Urea is considered to be a "structure-breaker" as it breaks up the hydrogen bonded network of water molecules when it forms an aqueous solution. Let us consider the equilibrium,

1

$$(H_20)_b <===> (H_20)_d$$
 (2.6.1)

where $(H_20)_b$ is "bulk" water and is an extensively hydrogen bonded network, and $(H_20)_d$ is "dense" water and is composed of non-bonded groups. Urea molecules do not have the correct geometry to bond well with "bulk" water but do bond well with "dense" water, thus lowering the chemical potential of $(H_20)_d$. This is turn moves the equilibrium in favour of $(H_20)_d$, so "breaking" the water structure.

As hydrophobic alkyl groups are added to the urea molecule we see a change in behaviour. This change has been observed by several authors²¹⁻²⁴. As the alkyl-substituted molecules become more hydrophobic in nature they develop a "structure making" character and enhance the ordering of water molecules within the aqueous solution. Clearly the effect of the added hydrophobic groups outweighs the "structure breaking" effect of the -NH and -C=0 groups. Perron et al.²¹ split the effect of

methyl-substitution into three groups; (i) an intrinsic hydrophobic contribution of the methyl group; (ii) a hindrance of hydrogen bonding ability of the amino group; and (iii) a decrease in the level of hydrogen bonding of the carbonyl group.

The results in Tables 2.7 - 2.8 show that we must consider not only the change in character of the "structure-breakers" alky1-substituted ureas from to "structure-makers", but also we must look at where exactly the substitution takes place, i.e. whether the alkyl groups are positioned on one or both ends of the basic al.²³ looked at this problem and urea unit. Barone et concluded that the ordering for ethylurea and 1.3dimethylurea may not be as expected. To study this we need to look at the hydrophobic interactions which are taking the place within the aqueous solution. In case of ethylurea there will be ethyl-ethyl interactions while for 1,3-dimethylurea these interactions will only be between methyl groups although there will be many more of these. This means that the balance between quantity and strength of interactions must be carefully considered.

The results for the first three ureas were

repeated using EDTA to inhibit the reverse reaction instead of sulphuric acid. The results in **Table 2.7** and **Figure 2.7** show that the overall trend remained the same indicating that the presence of acid was not the cause of the unexpected pattern.

We now turn our attention to the ethers. Here the trend is essentially as expected but the values obtained for the Savage-Wood parameter for the interaction of one $-CH_2$ - group with another were extremely large.

An explanation for the ether results (and other results which do not appear to fit the theory) may lie within the "rules" of the Savage-Wood Additivity Group Scheme. These state that the interactions of the various groups within a molecule are independent of their position within molecule. Clearly that this is an oversimplification. In the case of the ethers studied, a cyclic ether is going to have tighter steric restrictions on its interactions with other similar molecules than will be the case for a straight-chain ether. Another limitation SWAG relates to the nature of groups within the of molecule other than the particular group under investigation; namely near-neighbour effects. If there is an electron-withdrawing or -donating group next to, or sufficiently close to, the group whose interaction is being monitored, then the presence of such a group will

affect the results obtained. The SWAG theory does not allow for this although Savage and Wood did acknowledge these difficulties. The compatibility of the hydration spheres around the functional groups of the interacting molecules must also be considered, as, if these are incompatible then the interactions between molecules will be affected. These problems have been considered by a number of authors^{2-5,11}.

In conclusion we can say that the results in Section 2.5 highlight a number of the limitations of the Savage-Wood Additivity Group Scheme.

2.7 - CONCLUSIONS

The aim of this chapter has been to study the Savage-Wood Additivity Group Scheme (SWAG) and its application to an inorganic reaction. Four types of added solutes were studied; alcohols, carboxylic acids, alkyl-substituted ureas and cyclic and related ethers. The results obtained for the alcohols and the first two acids fitted the theory well and gave a value for the $G(CH_2\langle -\rangle CH_2)$ interaction parameter of $+21(\pm 4)$ J kg⁻¹. This was in good agreement with values obtained elsewhere. However, the ureas and cyclic ethers gave results which were far from those expected, and these results led to a consideration of the limitations of the procedure. In the case of the ureas, although the solvent (water) is not considered in the SWAG procedure, clearly the solvent is of major importance due to the relatively dramatic changes which take place in its character as we see changes in the properties of the alkyl-substituted ureas.

The data reported in this chapter, in consideration alongside work reported elsewhere, could be said to show that the values obtained for the Savage-Wood interaction parameters (in this case $G(CH_2 \langle -\rangle CH_2)$) will vary considerably with the particular solutes used. This may mean that it is not completely meaningful to give the parameters absolute numerical values.

2.8 - REFERENCES

1) C. Tanford, "The Hydrophobic Effect", John Wiley and Sons, New York, 1973. 2) J. J. Savage and R. H. Wood, J. Sol. Chem., 1976, 5, 733. 3) I. R. Tasker and R. H. Wood, J. Phys. Chem., 1982, <u>86</u>, 4040. 4) H. E. Kent, T. H. Lilley, P. J. Milburn, M. Bloemendal and G. Somsen, J. Sol. Chem., 1985, 14, 101. 5) S. K. Suri, J. J. Spitzer, R. H. Wood, E. G. Abel and P. T. Thompson, J. Sol. Chem., 1985, 14, 781. 6) G. M. Blackburn, T. H. Lilley and P. J. Milburn, J. Chem. Soc., Faraday Trans. I, 1986, 82, 2965. 7) W. Blokzijl, J. B. F. N. Engberts, J. Jager and M. J. Blandamer, J. Phys. Chem., 1987, <u>91</u>, 6022. 8) M. J. Blandamer, J. Burgess, H. J. Cowles, A. J. De Young, J. B. F. N. Engberts, S. A. Galema, S. J. Hill and I. M. Horn, J. Chem. Soc., Chem. Commun., 1988, 1141. 9) S. A. Galema, M. J. Blandamer and J. B. F. N. Engberts, J. Org. Chem., 1989, <u>54</u>, 1227. 10) J. J. Spitzer, S. K. Suri and R. H. Wood, J. Sol. Chem., 1985, <u>14</u>, 561. 11) I. R. Tasker and R. H. Wood, J. Sol. Chem., 1982, <u>11</u>, 729.

12) B. Briggs, Ph.D. Thesis, University of Leicester,1985.

13) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941. 14) W. Blokzijl, J. Jager, J. B. F. N. Engberts and M. J. Blandamer, J. Am. Chem. Soc., 1986, 108, 6411. 15) J.-M. Lucie, D. R. Stranks and J. Burgess, J. Chem. Soc., Dalton Trans., 1975, 245. 16) J. Burgess, J. Chem. Soc. (A), 1969, 1899. 17) J. Burgess and R. H. Prince, J. Chem. Soc., 1965, 4697. 18) J. Burgess, F. M. Mekhail and E. R. Gardner, J. Chem. Soc., Dalton Trans., 1973, 1335. 19) A. L. Harris, P. T. Thompson and R. H. Wood, J. Sol. Chem., 1980, 9, 305. 20) R. H. Wood, T. H. Lilley and P. T. Thompson, J. Chem. Soc., Faraday Trans. I, 1978, 74, 1301. 21) P. R. Philip, G. Perron and J. E. Desnoyers, Can. J. Chem., 1974, 52, 1709. 22) M. Roseman and W. P. Jencks, J. Am. Chem. Soc., 1975, **97**, 631. 23) G. Barone, G. Castronuovo, V. Crescenzi, V. Elia and E. Rizzo, J. Sol. Chem., 1978, 7, 179. 24) R. H. Wood and L. H. Hiltzik, J. Sol. Chem., 1980, <u>9</u>,

50

45.

CHAPTER THREE

,

An Outline of the Development of the Kirkwood-Buff Theory of Solutions

•

3.1 - INTRODUCTION

the previous chapter the Savage-Wood In Additivity Group Scheme was described. This scheme allows the interactions between solute molecules to be studied by calculating the pairwise interaction parameters and the group pairwise interaction parameters. This theory is limited in application to dilute solutions where higher order interactions are unimportant. The equations which would be generated if concentrated solutions were studied would be extremely complex to take account of these higher order interactions. Therefore, if we wish to study the interactions of the different types of molecules within a binary mixture over the entire mole fraction range a new approach is required.

The solution theory devised by Kirkwood and Buff¹ and subsequently adapted by Ben-Naim²⁻⁴ and others⁵⁻⁶ provides us with a procedure for examining the role of molecular interactions involving solutes in binary solvent systems over the complete mole fraction range.

The Kirkwood-Buff theory¹ uses several thermodynamic properties of a multicomponent liquid system obtain the corresponding radial distribution functions. These radial distribution functions provide information about the local composition of the medium surrounding the components which make up the liquid system. The Kirkwood-Buff theory can

be said to relate macroscopic properties of the system to its microscopic, or molecular, structure. Taking this one step further, the Kirkwood-Buff theory enables us to monitor the relative attraction (or repulsion) that one component of the system may have for another component. This means that the local nature of the theory makes it ideal for monitoring preferential solvation.

The reason that this theory is so useful stems from the lack of restrictions placed on its application. Ben-Naim² listed three points emphasising this usefulness.

1) The theory is valid for any kind of particle, not necessarily spherical.

2) Only the spatial pair correlation functions appear in the relations, even when the particles are not spherical. (This is as opposed to angular-dependent pair correlation functions).

3) No assumption of additivity of the total potential energy is made. Often, expressions involving thermodynamic parameters assume that there is total pairwise additivity for the components within the system. This is clearly not valid for complex concentrated solutions.

Considering the many advantages of the Kirkwood-Buff theory 1 it is surprising perhaps that it took twenty years for its potential to be realised⁵. One reason for this may be that as written by Kirkwood and Buff, the theory required the Kirkwood-Buff parameters Gii, and then used these parameters to calculate thermodynamic quantities. The radial distribution functions necessary for the calculation of G_{ij} can only be determined readily for very simple systems. When Ben-Naim $^{2-4}$ developed his inversion procedure, making it possible to calculate G_{ij} from thermodynamic data, he opened the way towards wider use of the Kirkwood-Buff theory of solutions.

3.2 - THEORETICAL OUTLINE

3.2.1 - The Kirkwood-Buff Theory of Solutions

The Kirkwood-Buff Theory¹ is a statistical mechanics theory which is applied to solutions. The theory shows that by using (a) derivatives of the chemical potential, (b) partial molar volumes, and (c) compressibilities, parameters can be determined which involve integrals of radial distribution functions for the molecular pairs present in the solution under consideration. These parameters are known as Kirkwood-Buff integrals. This theory was seldom used to probe the molecular structure of solvent mixtures until Ben-Naim^2 showed its potential for just such an investigation. A summary of his work is given in Section 3.2.2.

Let us consider an assembly of molecules. The position of any such molecule can be given by the cartesian coordinates (x,y,z) or by vector R. The volume will be given by (dx,dy,dz) or by dR. This volume dR, for a shell surrounding the molecule could be expressed as,

$$dR = 4\pi r^2 dr$$
 (3.1.1)

Returning to our assembly of molecules we identify two infinitesimal volume elements of configuration dX' and dX", these being separated by a distance R. The probability of finding a molecule in dX' is $\rho^{(1)}(X').dX'$ and the probability of finding a molecule in dX" is $\rho^{(1)}(X').dX'$. The probability of finding a molecule in dX' and dX" simultaneously is given by $\rho^{(2)}(X',X'')dX'.dX''$. <u>i.e.</u> we are considering an intersection of two events,

$$\{\text{molecule in } dX'\} \bigcap \{\text{molecule in } dX''\} \qquad (3.1.2)$$

We can look at the two limiting cases. (1) The separation R is so small that putting a molecule in dX' will drastically reduce the probability of finding a molecule in dX". This probability can be adjudged to be negligibly small. (2) The separation R is so large that the probability of finding a molecule in dX' and a molecule in dX" simultaneously is given by the sum of the individual probabilities,

$$\rho^{(2)}(X',X'') = \rho^{(1)}(X')dX' \cdot \rho^{(1)}(X'')dX''$$
(3.1.3)

giving us,

$$\rho^{(2)}(X',X'') = \rho^{(1)}(X') \cdot \rho^{(1)}(X'')$$
 (3.1.4)

Equation (3.1.4) shows that the local densities at X' and X" are not correlated. Equation (3.1.4) is valid for a structureless continuum. If we wish to apply this theory to real solutions, then we must consider real molecules of real size and remember that these molecules will interact with one another. This means that for real systems the local densities will be correlated. This correlation, or deviation from the ideal case, is accounted for by introducing a pair correlation function into equation (3.1.4),

$$\rho^{(2)}(X',X'') = \rho^{(1)}(X')\rho^{(1)}(X'')g(R)$$
 (3.1.5)

where g(R) is the pair correlation function. Considering the limiting system where we have an ideal gas, the particles will have zero size and will not interact. This means that equation (3.1.4) is valid and g(R)=1.0. Figure 3.1 shows the relationship between g(R) and R for a system composed of hard

spheres at low density. For a simple liquid system (which is nearer to our real system under consideration) we observe deviations from the value of g(R)=1.0 found for ideal systems; Figure 3.2.



Figure 3.1 - Pair correlation function g(R) for a hard sphere system at low density.



Figure 3.2 - Pair correlation function g(R) for a simple pure liquid

As R/σ (where σ is the molecular diameter) becomes larger the deviations decrease until we reach unity indicating that the molecules are no linger correlated. The deviations from ideality can be expressed in terms of the difference, g(R) - 1. The vital link between the molecular information given by g(R) and the thermodynamic properties of the system is given by the exact expression for the compressibility,

$$\kappa_{\rm T} = [1/kT\rho] + (1/kT) \int_{0}^{\infty} [g(R)-1] 4\pi R^2 dR$$
 (3.1.6)

where $\kappa_{\rm T}$ is the isothermal compressibility. This is close to the key Kirkwood-Buff equation¹.

If we now look at a system, which is made up of two components, component-1 and component-2, then we have a number of correlation functions which describe the correlation of position and mutual orientation for these component molecules. These correlation functions are angleaveraged, orientation-averaged pair correlation functions and are given by $g_{11}(R)$, $g_{22}(R)$ and $g_{12}(R)$. This leads us to the Kirkwood-Buff integral¹, <u>e.g.</u> G_{12} ,

$$G_{12} = \int_{0}^{\infty} [g_{12}(R) - 1] 4\pi R^{2} dR \qquad (3.1.7)$$

Looking at this Kirkwood-Buff equation we would like to obtain information on the pair correlation function $g_{12}(X',X'')$, giving us details of the correlation between the positions and orientations of the molecules of the system. Currently this cannot be obtained. However, we can study the locational (or angle-averaged) correlation function $g_{12}(R)$. If ρ is the number density of component-1, then we can explain the physical model represented by equation (3.1.7). $\rho_1 g_{12}(R) 4\pi R^2 dR$ is a measure of the average number of molecules of component-1 in a spherical shell of thickness dR which are at a distance R from the centre of a molecule of component-2. $\rho_1 4\pi R^2 dR$ provides a measure of the average number of molecules of component-1 in the same spherical shell, the origin of this shell being chosen at random. Thus the composite quantity $\rho_1[g_{12}(R)-1]4\pi R^2 dR$ is a measure of the excess (or deficiency) in the average number of molecules of component-1 in a spherical shell of thickness dR at a distance R from a component-2 molecule relative to the number obtained by eliminating the condition that a component-2 molecule be at the origin. This gives us the condition that $\rho_1 G_{12}$ is equal to the total average excess (or deficiency) of component-1 molecules in the complete surroundings of a component-2 molecule. This means that $G_{1,2}$ is a measure of this excess (or deficiency) per unit density. This quantity is symmetrical, <u>i.e.</u> $G_{12} = G_{21}$.

Ben-Naim²⁻⁴ derived the Inverse Kirkwood-Buff treatment (IKB) to simplify the use of the Kirkwood-Buff theory and so obtain information on the microscopic behaviour of a solvent system. This IKB procedure is described in the next section.
3.2.2 - Inverse Kirkwood-Buff Procedure (IKB)

This Inverse Kirkwood-Buff procedure developed²⁻⁴ by Ben-Naim gives us access to Kirkwood-Buff parameters for a mixed solvent system, and hence information on its microscopic properties,via calculations involving thermodynamic data on that system. The IKB procedure is explained in detail in Ref. 3; a brief outline is given below.

There are five important quantities in the inversion procedure :-

(a)
$$\eta = \rho_1 + \rho_2 + \rho_1 \rho_2 (G_{11} + G_{22} - 2G_{12})$$
 (3.2.1)

(b)
$$\xi = 1 + \rho_1 G_{11} + \rho_2 G_{22} + \rho_1 \rho_2 (G_{11} \cdot G_{22} - G_{12}^2) \quad (3.2.2)$$

(c)
$$\kappa_{\rm T} = \xi / k_{\rm B} T \eta$$
 (3.2.3)

where $\kappa_{\rm T}$ is the isothermal compressibility, $k_{\rm B}$ is the Boltzmann constant, and T is the absolute temperature.

(d)
$$V_1 = [1 + \rho_2 (G_{22} - G_{12})]/\eta$$
 (3.2.4)

$$V_2 = [1 + \rho_1 (G_{11} - G_{12})]/\eta \qquad (3.2.5)$$

 $v_1 v_2 = [\xi - \eta G_{12}] / \eta^2$ (3.2.6)

(e)
$$\mu_{11} = \rho_2 RT / \rho_1 \eta V$$
 (3.2.7)

$$\mu_{22} = \rho_1 RT / \rho_2 \eta V$$
 (3.2.8)

$$\mu_{12} = \mu_{21} = -RT/\eta V$$
 (3.2.9)

The above equations are then used in conjunction with thermodynamic relations and data to obtain the Kirkwood-Buff integrals G_{11} , G_{22} and G_{12} . These calculations can be divided into six stages.

STAGE 1 - Calculation of $(d\mu_2/dx_2)_{T,p}$. This can be done using vapour pressure or partial pressure data.

STAGE 2 - Analysis of the volumetric data to obtain the number densities ρ_1 and ρ_2 .

STAGE 3 - Determination of the molar quantity η using the quantities $(d\mu_2/dx_2)_{T,p}$ and ρ_1 and ρ_2 as determined in the first two stages.

STAGE 4 - Compressibility data $\kappa_{_T}$, and the quantity η are used to determine a dimensionless quantity ξ .

STAGE 5 - Quantities η and ξ are combined with the volumetric data to obtain G₁₂.

STAGE 6 -The volumetric data is combined with $\eta~$ and G_{12} to obtain G_{11} and $G_{22}.$

By combining all of the Kirkwood-Buff parameters we obtain,

$$\Delta_{12} = G_{11} + G_{22} - 2G_{12}$$
 (3.2.10)

For a symmetrically ideal solution, $\Delta_{12} = 0$. This means that Δ_{12} can be used to monitor deviations from ideality.

Returning to the Kirkwood-Buff equation¹,

$$G_{12} = \int_{0}^{\infty} [g_{12}(R) - 1] 4\pi R^{2} dR \qquad (3.2.11)$$

Ben-Naim split this into two regions,

$$G_{12} = \int_{0}^{\sigma_{12}} (-4\pi R^2 dR) + \int_{\sigma_{12}}^{n\sigma_{12}} [g(R) - 1] 4\pi R^2 dR \qquad (3.2.12)$$

where σ_{12} is the distance of closest approach between molecule-1 and molecule-2. $n\sigma_{12}$ represents a number of molecular diameters such that $g(R) \rightarrow 1.0$. Equation (3.1.12) can be written as,

 $G_{12} = -V_{12} + I_{12}$ (3.2.13)

 V_{12} is a volume term and can be treated as being composition independent. The second term, I_{12} , could be considered to be an "interaction" term, as it provides a measure of the attraction (or repulsion) between molecule-1 and molecule-1 Thus it can be seen that by employing Ben-Naim's Inverse Kirkwood-Buff Procedure³ we can analyse the microscopic behaviour of solvent systems as intended by Kirkwood and Buff¹.

3.3 - DISCUSSION

In more recent years the Kirkwood-Buff theory of Solutions¹ has been applied to a variety of systems by a number of workers^{3,5-15}. The theory has been applied to a number of important issues. Ben-Naim has applied the theory to the problem of preferential solvation⁴, monitoring this over the complete mole fraction range providing useful information on the limits of preferential solvation in binary mixtures. Ben-Naim also applied the IKB theory³ to hydrophobic interactions¹⁶ by studying the G_{22} parameter in binary aqueous systems which contain an organic cosolvent as component-2.

As is often the case when applying theories to practical measurements, the limitations of the theory must be realised and allowed for. In the case of the Kirkwood-Buff theory there are few limitations to consider as very few made in derivation. Instead, assumptions are its the limitations may be in the data used. The measurements may have been made by a number of different research groups who may have all reported their results using different limits and symbols may also have used different accuracy limits. Kato $^{f 8}$ and

suggested that the determination of the concentration derivative of the chemical potential using thermodynamic measurements may be the "weak link" in the accuracy of the Kirkwood-Buff parameters obtained. Kato used concentration fluctuation measurements determined via small-angle x-ray scattering data instead, maintaining that the accuracy was greater this way. Other authors¹⁴ have also followed this approach.

In conclusion it can be said that this theory¹ appears valuable, especially for binary aqueous mixtures where it provides a measure of the probability of finding a cosolvent molecule in close proximity to either another cosolvent molecule or a water molecule over the entire mole fraction range. Taking the case of the water molecule, the Kirkwood-Buff Theory of Solutions provides vital clues as to the degree of solvation. This work is developed in the next two chapters. In Chapter 4 the theory is applied to a number of binary aqueous mixtures, and in chapter 5 the work is extended using kinetic measurements to consider added solutes in these binary mixtures.

3.4 - REFERENCES

1) J. G. Kirkwood and F. P. Buff, J. Chem. Phys., 1951, 19, 774. 2) A. Ben-Naim, "Water and Aqueous Solutions", Chpt. 4, Plenum Press, New York, 1974. 3) A. Ben-Naim, J. Chem. Phys., 1977, 67, 4884. 4) A. Ben-Naim, Cell Biophys., 1988, 12, 255. 5) D. G. Hall, Trans. Faraday Soc., 1971, <u>67</u>, 2516. 6) K. E. Newman, J. Chem. Soc., Faraday Trans. I, 1988, 84, 1387. 7) M. C. A. Donkersloot, J. Sol. Chem., 1979, 8, 293. 8) T. Kato, T. Fujiyama and H. Nomura, Bull. Chem. Soc. Japan, 1982, <u>55</u>, 3368. 9) E. Matteoli and L. Lepori, J. Chem. Phys., 1984, 80, 2856. 10) M. Žólkiewski, J. Sol. Chem., 1987, <u>16</u>, 1025. 11) R. G. Rubio, M. G. Prolongo, M. D. Pena and J. A. R. Renuncio, J. Phys. Chem., 1987, 91, 1177. 12) P. G. Kusalik and G. N. Patey, J. Chem. Phys., 1987, <u>86</u>, 5110. 13) J.-Y. Huot, E. Battistel, R. Lumry, G. Villeneuve, J.-F. Lavallee, A. Anusiem and C, Jolicoeur, J. Sol. Chem., 1988, 17, 601.

14) K. Nishikawa, H. Hayashi and T. Iijima, J. Phys. Chem., 1989, <u>93</u>, 6559.

15) M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn, J. Chem. Soc., Faraday Trans., 1990, <u>86</u>, 277; 283.

16) A. Ben-Naim, Far. Symp. Chem. Soc., 1982, 17, 121.

CHAPTER FOUR

Application of the Inverse Kirkwood-Buff Procedure to a Range of Binary Aqueous Mixtures

4.1 - INTRODUCTION

In Chapter Three an outline of the Kirkwood-Buff Theory of Solutions¹ was given, together with Ben-Naim's adaptation 2,3 of this theory leading to the Inverse Kirkwood-Buff (IKB) Procedure. This procedure produces IKB integral functions, and these functions provide information about the three types of long-term, space-averaged interactions which occur between the molecules within an aqueous binary system over the entire mole fraction range. These interactions are water-water interactions, solute-solute interactions and solute-water interactions. In this chapter the IKB procedure will be applied to a range of binary aqueous mixtures and the integral functions obtained will be considered in terms of the properties of these mixtures. First mixtures which fall into the "typically aqueous"^{4,5} class will be considered. These can be split into two groups, (1) the alcohols, and (2) the ketones and cyclic ethers. Then, "typically non-aqueous" mixtures will be studied. These also can be split into two groups. The first group contains those mixtures for which G_m^E is negative and the examples used in this chapter are hydrogen peroxide-water mixtures and dimethyl sulphoxide-water mixtures. 0ne example of the second group is the cyanomethane-water

system, this being a mixture for which G_m^E is positive. Finally, the complex behaviour displayed by the fluoroalcohol + water mixtures will be discussed.

4.2 - TYPICALLY AQUEOUS MIXTURES (TA)

Typically Aqueous (TA) mixtures^{4,5} compose a class of cosolvents who all display the following excess thermodynamic properties when added to water; $G_m^E > 0$ and $|T.S_m^E| > |H_m^E|$. This class includes alcohols, ketones and ethers. Figure 4.1 shows the excess thermodynamic functions of mixing for ethanol and 2-methyl propan-2-ol, both typically TA mixtures.

The S-shaped H_m^E curve for 2-methyl propan-2-ol - water mixtures marks a change from exothermic mixing in the water-rich regions to endothermic mixing in the cosolventrich regions. Many TA mixtures display this pattern. e.g. THF + water.

Before we move on to consider the individual TA mixtures, there are a number of general points which need to be considered.

As explained in Chapter Three, the IKB procedure requires thermodynamic data in order to calculate the integral functions. The data required are



Figure 4.1 – Excess molar thermodynamic functions of mixing⁵ as a function of x_2 for (a) water(1)-ethanol(2) at 298.15K; and (b) water(1)-2-methyl propan-2-ol(2) at 299.15K.

(1) excess molar Gibbs energies G_m^E , to yield derivatives of the chemical potential; (2) partial molar volumes; and (3) isothermal compressibilities. All data must be calculated as a function of x_2 . The starting data for any one binary aqueous mixture may come from several different research groups. In this chapter all the analyses and calculations were carried out using FORTRAN programs.

One of the most important steps in the IKB analysis is the determination of $d\mu_2/dx_2$ as a function of x_2 from the G_m^E data. The total free energy of solution is given by,

$$G_{sol} = \sum_{i} \mu_{i} n_{i}$$
 (4.2.1)

If we consider an ideal binary solution then,

. . .

$$\mu_2(\text{mix}; T; p) = {\mu_2}^*(1) + RTlnx_2$$
 (4.2.2)

where μ_2 is the chemical potential of component-2 in the solution, ${\mu_2}^*$ is the chemical potential of pure liquid-2 and x_2 is the mole fraction of component-2. A similar equation applies for component-1. For a real binary solution (i.e. non-ideal), equation (4.2.2) becomes,

$$\mu_2(\text{mix};T;p) = \mu_2^*(1) + \text{RTln}(x_2f_2)$$
 (4.2.3)

where f_2 is the activity coefficient for component-2. Again, a similar equation holds for component-1. Returning to equation (4.2.1), for an ideal solution we can write,

$$G_{tot}(id;mix;T;p) = n_1(\mu_1^*+RTlnx_1) + n_2(\mu_2^*+RTlnx_2)$$
 (4.2.4)

where n_1 is the number of moles of component-1 and n_2 is the number of moles of component-2. For a non-ideal solution,

$$G_{tot}(mix;T;p) = n_1(\mu_1^* + RTlnx_1f_1) + n_2(\mu_2^* + RTlnx_2f_2)$$
 (4.2.5)

Given that,

$$G^{E}(mix;T;p) = G_{tot}(mix;T;p) - G_{tot}(id;mix;T;p) \quad (4.2.6)$$

it follows that,

$$(1/kT)G_m^E(mix;T;p) = x_1 lnf_1 + x_2 lnf_2$$
 (4.2.7)

as $x_1 = n_1/(n_1 + n_2)$ and $x_2 = n_2/(n_1 + n_2)$. Using the form of the Gibbs-Duhem equation where,

$$x_1(dlnf_1/dx_2) + x_2(dlnf_2/dx_2) = 0$$
 (4.2.8)

we differentiate equation (4.2.7) with respect to x_2 to give,

$$(1/kT) (dG_m^E/dx_2) = lnf_2 - lnf_1$$
 (4.2.9)

We wish to obtain an equation in terms of lnf_2 . Therefore by rearranging equation (4.2.9) and substituting into (4.2.7) gives,

$$(1/kT)G_{m}^{E} = lnf_{2} - (x_{1}/kT)(dG_{m}^{E}/dx_{2})$$
 (4.2.10)

and rearranging equation (4.2.10) gives,

$$\ln f_{2} = (1/kT) [G_{m}^{E} + (1-x_{2}) (dG_{m}^{E}/dx_{2})]$$
 (4.2.11)

Our aim here is to obtain $d\mu_2/dx_2$ in terms of G_m^E or its derivatives. Therefore if we differentiate equation (4.2.3) with respect to x_2 we obtain,

$$d\mu_2/dx_2 = RT[(1/x_2) + (dlnf_2/dx_2)]$$
 (4.2.12)

Now, if we differentiate (4.2.11) with respect to \mathbf{x}_2 we obtain,

$$dlnf_2/dx_2 = [(1-x_2)/kT][d^2G_m^E/dx_2^2]$$
 (4.2.13)

We can substitute equation (4.2.13) into equation (4.2.12) to produce an equation for $d\mu_2/dx_2$ in terms of the second derivative of G_m^E ,

$$d\mu_2/dx_2 = RT\{(1/x_2) + [(1-x_2)/RT](d^2G_m^E/dx_2^2)\}$$
 (4.2.14)

The units of $d\mu_2/dx_2$ are J mol⁻¹.

The volumetric data required for the IKB analysis are partial molar volumes. However, the input data are usually either molar volumes or excess molar volumes. We know that,

$$V_{M} = x_{1}V_{1}(sln) + x_{2}V_{2}(sln)$$
 (4.2.15)

where V_m is the molar volume and V_1 and V_2 are the partial molar volumes. The excess molar volume is given by,

$$V_{M}^{E} = x_{1}[V_{1}(sln) - V_{1}^{*}(l)] + x_{2}[V_{2}(sln) - V_{2}^{*}(l)]$$
 (4.2.16)

Using the Gibbs-Duhem equation (at fixed T and p),

$$x_1 (dV_1/dx_2) + x_2 (dV_2/dx_2) = 0$$
 (4.2.17)

we differentiate equation (4.2.15) with respect to x_2 to obtain,

$$dV_M/dx_2 = V_2(sln) - V_1(sln)$$
 (4.2.18)

As with the Gibbs energies, we rearrange equation (4.2.18)and substitute back into equation (4.2.15) to produce an expression for the partial molar volume V_2 ,

$$V_2(sln) = V_M + (1-x_2) (dV_M/dx_2)$$
 (4.2.19)

An analogous treatment can be applied to excess volumes to give,

$$V_{2}(sln) = V_{2}^{*}(l) + V_{M}^{E} + (l-x_{2}) (dV_{M}^{E}/dx_{2})$$
 (4.2.20)

As stated earlier, a FORTRAN program converted the raw data to the required form and calculated the IKB functions. This program included a linear least squares routine to analyse the dependence of variables calculated from the input data on mole fraction. The

equation used was the Redlich-Kister (Guggenheim-Scatchard) equation⁶,

$$Y = qx_2(1-x_2) \sum_{j=1}^{j=i} b_j(1-2x_2)^{(j-1)}$$
(4.2.21)

where Y is the particular variable under consideration, q is a constant peculiar to the particular variable, x_2 is the mole fraction of component-2 and b_j is the derived parameter. The number of parameters required was determined using a student-t test.

Now that some of the general points connected with the IKB procedure have been considered, we are in a position to study the TA mixtures in more detail.

4.2.1 - The Alcohols

The first class of TA cosolvents to be considered is the monohydric alcohol series. These alcohols have always been favoured as cosolvents for thermodynamic^{7,8} and kinetic⁹ studies and therefore not surprisingly these were the first solutes to be studied^{2,10,11} using the Inverse Kirkwood-Buff (IKB) procedure.

4.2.1.1 - METHANOL

Methanol is the first of the monohydric alcohol series. It is only marginally hydrophobic and therefore does not always display typical alcohol behaviour. The IKB calculations for methanol are outlined below.

In the first step the IKB analysis requires G_m^E data. These are then used to calculate the dependence of $d\mu_2/dx_2$ on x_2 as outlined in the previous section. Excess molar Gibbs energies of mixing reported by Simonson et al.¹² were fitted to the Redlich-Kister equation⁶ where $Y = G_m^E$ and q = RT.

The next set of measurements used for the analysis was volumetric data, molar volumes V_m , reported by Patel and Sandler¹³. These results were analysed using the Redlich-Kister equation where $Y = V_m$ and q = 1.0. The results obtained were then converted to partial molar volumes using equation (4.2.19).

The final data required are isothermal compressibilities. Here, results published by Easteal and Woolf¹⁴ were used.

Once the above results had been obtained as functions of x_2 , they were substituted into Ben-Naim's^{2,3} IKB analysis to yield the IKB integral functions G_{11} , G_{22} and G_{12} . These are shown in **Figure 4.2**.

Figure 4.2 shows that there are no real peaks present for methanol-water mixtures. G_{12} remains relatively constant throughout and this, combined with the lack of peaks, implies that methanol has no strong affinity for water, but also does not reject water as a near neighbour. G_{11} represents water-water interactions and this function steadily increases as the proportion of water within the solution decreases indicating a tendency for the water molecules to cluster together, but as this increase in G_{11} is very gradual and does not reach a maximum, this tendency is very weak.

4.2.1.2 - ETHANOL

Figure 4.1(a) shows the excess thermodynamic functions for water-ethanol mixtures. Pemberton and Marsh¹⁵ reported G_m^E data as a function of x_2 at four different temperatures and these data were used to calculate¹⁶ the dependence of G_m^E on x_2 at 298.15K. These data were fitted to the orthogonal equation⁶ (see Section 4.3).



<u>Figure 4.2</u> - Inverse Kirkwood-Buff integral functions for water(1)-methanol(2) mixtures as a function of x_2 at 298.2K.

Partial molar volumes were calculated¹⁶ from parameters reported by Benson and Kiyohara¹⁷. The isothermal compressibilities were determined from compressions reported by Moriyoshi¹⁸.

The IKB integral functions calculated from these data are shown in Figure 4.3.

Figure 4.3 shows a number of definite peaks and shoulders. G_{11} shows a broad peak at $x_2 \simeq 0.4$ indicating that at this point the water molecules are tending to cluster together. This gradually drops off as the mole fraction of water molecules decreases. G_{22} shows a distinct shoulder at $x_2 \simeq 0.25$ and then a definite peak at $x_2 \simeq 0.8$. G_{12} is the minor feature throughout the main mole fraction range indicating that intracomponent bonding is preferred to intercomponent bonding.

4.2.1.3 - i - PROPANOL

The G_m^E data used for the analysis were those reported by Sada and Morisue¹⁹. These results were analysed using the orthogonal equation⁶. The volumetric data used were reported by Sakurai²⁰ and the compressions used were reported by Moriyoshi¹⁸.



<u>Figure 4.3</u> - Inverse Kirkwood-Buff integral functions for water(1)-ethanol(2) as a function of x_2 at 298.2K16.



<u>Figure 4.4</u> - Inverse Kirkwood-Buff integral functions for water(1)-i-propenol(2) mixtures as a function of x_2 at 298.2K.

These data were analysed using the IKB procedure and the integral functions obtained are shown in Figure 4.4.

Figure 4.4 shows that the G_{22} integral function peaks quite sharply in the water-rich region indicating the formation of clusters of alcohol molecules. G_{12} shows a minimum at approximately the same mole fraction signifying that the possibility of finding a molecule of water in close proximity to a molecule of alcohol is at its lowest. G_{11} shows a broad peak over the range $x_2 = 0.2$ to $x_2 = 0.4$. G_{11} is also the dominant term over the bulk of the mole fraction range. G_{12} and G_{22} both show shallow peaks at $x_2 \simeq 0.7$

4.2.1.4 - 2-METHYL PROPAN-2-OL

The final alcohol-water system studied was 2-methyl propan-2-ol-water. The G_m^E data used were reported by Tommila and coworkers²¹. Figure 4.1(b) shows the excess thermodynamic functions for this mixture. Near $x_2 = 0.5 \ G_m^E$ is large and positive. In the analysis it proved necessary to use the orthogonal equation⁶ to analyse the G_m^E data in order to obtain $d\mu_2/dx_2$ (see Section 4.3). Volumetric data used were recorded by Sakurai²² and compressions by Moriyoshi¹⁸.



<u>Figure 4.5</u> - Inverse Kirkwood-Buff integral functions for water(1)-2-methyl propan-2-ol (2) as a function of x_2 at 298.2K.

The IKB integral functions were calculated¹⁶ from these data and the results are shown in Figure 4.5.

Figure 4.5 shows the most striking features observed yet for an alcohol. G_{11} shows a very sharp maximum at $x_2 \simeq 0.25$. G_{22} shows a slightly less dramatic maximum at the same mole fraction and G_{12} shows a sharp minimum at this mole fraction. These results indicate that in the " $x_2 = 0.25$ " region the water molecules cluster together and the alcohol molecules cluster together to form water-rich and alcohol-rich microdomains.

4.2.1.5 - DISCUSSION

As mentioned earlier a number of these alcohol-water mixtures were among the first mixtures to be analysed^{2,10,11} using the IKB procedure. Matteoli and Lepori²³ have also studied these alcohols using the same procedure.

Considering methanol first, Figure 4.2 shows that no distinct features are observed for any of the integral functions. This was considered to be due mainly to the small hydrophobic character of these molecules. The general pattern observed here for methanol

is similar to that shown by Donkersloot¹⁰ and Matteoli²³ although G_{11} does not reach a maximum at very high mole fraction as observed by Donkersloot and Matteoli.

The next alcohol in the series is ethanol and the integral functions for ethanol-water are shown in Figure 4.3. Ethanol-water was the system used by Ben-Naim^2 to explain his IKB procedure. Figure 4.3 shows definite features for all three integral functions although none are particularly sharp. Matteoli's²³ results for ethanolwater are similar to those shown here for all three integral functions up to $x_2 = 0.6$. Then, while Matteoli's results continue on smoothly, here we see a minimum in G_{11} and for G_{22} we observe a sharp peak at $x_2 = 0.8$. Ben-Naim's results are also similar. Variations in the different results could be due to the different method of analysis for the G_m^E data. Here, the data was fitted to an orthogonal polynomial equation⁶ whilst other authors have used a Redlich-Kister type of analysis⁶. The advantage that the orthogonal equation has over the Redlich-Kister equation is that at $x_2 = 0.5$ several parameters contribute to the analysis, whilst for the Redlich-Kister equation only the first parameter contributes. This can be very important in the analysis as for most of these mixtures the maximum in G_m^E comes at $x_2 \simeq 0.5$. (For further details on the orthogonal analysis see Section 4.3).

Iso-propanol was the next alcohol studied. Figure 4.4 shows the results obtained here for this alcohol. It can be seen that the peaks in the integral functions for i-propanol are sharper than those obtained for ethanol and also that they occur at lower mole fractions of added alcohol.

The final alcohol studied was 2-methyl propan-2-ol. This alcohol has been studied using the IKB procedure by a number of authors 11, 23, 24. The results reported in Figure 4.5 are in broad agreement with those reported by Matteoli²³ except for G_{22} , although the results reported here show much sharper features. The results reported by Patil¹¹ disagree strongly with these results and those reported by Matteoli. Nishikawa et al.²⁴ obtain results which are in greater agreement with those reported here. Interestingly, they are concerned that the greatest error in the IKB functions derives from $d\mu_2/dx_2$. This opinion was also voiced here, and so the orthogonal equation was used for some systems in preference to the Redlich-Kister equation in an attempt to obtain more accurate values for $d\mu_2/dx_2$ as a function of x2. Nishikawa approaches this problem in a totally different way and uses small-angle x-ray scattering results instead of derivatives of the chemical potentials. (See Chapter Three also).

In summary it can be seen that as we move through the alcohol series the features in the integral functions become more and more pronounced. Gradually a situation is reached whereby at low mole fractions of added alcohol the hydrophobic groups on the alcohol molecules cluster together to form alcohol-rich microdomains; these microdomains being shown by G_{22} . These hydrophobic groups also enhance the water structure and so G₁₁ shows that water-rich microdomains are also formed. $G_{1,2}$ tends to a minimum indicating that alcohol-water interactions are rare. A final point worthy of note is that these maxima and minima occur at lower mole fractions of added alcohol as we move down the alcohol series.

4.2.2 - The Ketones

Ketones form the second class of Typically Aqueous (TA) mixtures to be considered here. The example studied was propanone.

The first quantity necessary for the IKB analysis is $d\mu_2/dx_2$ as a function of x_2 . This was calculated from equation (4.2.14) and requires G_m^E data. The parametric equation reported by Villamanan and Van Ness²⁵ was used to determine the dependence of G_m^E on x_2 . The G_m^E data were fitted to the orthogonal polynomial equation⁶.

The volumetric data used in the analysis were molar volumes measured by Boje and Hvidt²⁶. These were fitted to the Redlich-Kister equation⁶.

The compressions reported by Moriyoshi and Uosaki²⁷ were used and from these $\kappa_{\rm T}$ was calculated as a function of x_2 .

From the above results the IKB integral functions were determined; Figure 4.6.

Figure 4.6 shows that G_{11} is the dominant term throughout and shows a minor peak at $x_2 \simeq 0.65$. G_{12} shows a slight dip at $x_2 \simeq 0.3$ and G_{22} remains essentially constant throughout. These results are very similar to those obtained by Matteoli²³. Clearly, whilst there is a tendency for the alcohol molecules to repel the water molecules, this is not as strong as in the higher alcohols. G_{11} shows that the water structure is enhanced by the alkyl-groups on the ketone molecules.

4.2.3 - The Cyclic Ethers

The final group of TA mixtures to be studied here is the cyclic ether group. The example used here is 1,4 - dioxane.



<u>Figure 4.6</u> - Inverse Kirkwood-Buff integral functions for water(1)-propanone(2) mixtures as a function of x_2 at 298.2K²⁸.



Figure 4.7 - Inverse Kirkwood-Buff integral functions for water(1)-1,4-dioxane(2) mixtures as a function of x_2 at 298.2K.

The G_m^E data used here were reported by Kortum et.al.²⁹. These data were reported at several temperatures and, from these, G_m^E was calculated¹⁶ at the required temperature. The volumetric data were reported by Griffiths³⁰ and the compressibility data by Nakagawa et al.³¹.

The results were combined to obtain the IKB integral functions shown in Figure 4.7.

Figure 4.7 shows a major peak in G_{11} , a shallow minimum in G_{12} and a very slight shoulder in G_{22} . The ring oxygens on the dioxane molecules will hydrogen bond with the water molecules, thus reducing the magnitude of G_{22} . These results are in close agreement with Matteoli²³.

4.2.4 - Summary

Essentially all of the TA mixtures display the same pattern. This pattern is typified by maxima in G_{11} and G_{22} , usually at fairly low mole fractions of added solute, and a minimum in G_{12} at a similar mole fraction. These trends in the integral functions signify clustering of like-molecules. In addition, we are also observing enhancement of the water structure, explaining why G_{11} is

often the dominant term for these TA mixtures. By looking at the alcohols, it can be seen that the development of these features increases with the size of the hydrophobic group.

4.3 - TYPICALLY NON-AQUEOUS MIXTURES (TNA)

The class of cosolvents known as "typically non-aqueous"^{4,5} can be divided into two sub-classes. For all TNA cosolvents the condition $|H_m^E| > |T.S_m^E|$ applies, but G_m^E can be greater than, or less than, zero. The first class, where G_m^E is negative (TNAN), includes hydrogen peroxide and dimethyl sulphoxide (DMSO) and plots of the excess thermodynamic functions of mixing for these two cosolvents are shown in **Figure 4.8**.

The second class of TNA mixtures, where G_m^E is positive (TNAP) has cyanomethane as its most popular example; Figure 4.9.

In order to understand the nature of these TNA mixtures more clearly, especially with respect to the interactions between the water and cosolvent molecules, three such mixtures were chosen for study^{28,32} using the Inverse Kirkwood-Buff (IKB) Procedure^{2,3}. The first two mixtures belong to the TNAN class and are hydrogen peroxide + water and DMSO + water. The third mixture,



<u>Figure 4.8</u> - Excess thermodynamic functions of mixing⁵ for (a) hydrogen peroxide-water and (b) DMSO-water at 298.2K as a function of x_2 .



<u>Figure 4.9</u> - Excess molar thermodynamic functions of mixing for water(1)-cyanomethane(2)32 as a function of x_2 at 298.2K.
cyanomethane + water, is a TNAP mixture. The IKB procedure was applied to these mixtures using a FORTRAN program (see Section 4.2 also).

4.3.1 - Hydrogen Peroxide

The G_m^E data for hydrogen peroxide-water mixtures were calculated from the parameters and equation reported by Scatchard³³. First G_m^E was calculated as a function of x_2 , then, the data were fitted to a linear least squares routine as explained in the previous section.

The volumetric data were based on densities reported by Wynne-Jones³⁴. Excess molar volumes V_m^E , were determined as a function of mole fraction x_2 , and fitted to the Redlich-Kister equation⁶. These calculations led to the determination of the partial molar volumes as a function of x_2 .

Relevant isothermal compressibility data were not available and therefore an assumption was needed, namely that the isothermal compressibilities for the hydrogen peroxide-water mixtures equals the value for water at 298.2K. This assumption was made on the grounds that the formulae for the two liquids are similar. It should also be borne in mind here that the isothermal

compressibility data play a very small role in the final Kirkwood-Buff integral functions as the magnitude of these compressibilities is so low. Matteoli and Lepori²³ calculate that the term $RT\kappa_T$ contributes 1 - 3 cm³ mol⁻¹ to a G_{ij} function, this being small relative to the total value of a G_{ij} parameter which may be several hundred cm³ mol⁻¹.

The thermodynamic data determined above yielded G_{11} , G_{22} and the cross-term G_{12} for hydrogen peroxide + water; Figure 4.10.

The two most outstanding features to be seen in Figure 4.10, especially when compared to the alcohols and other TA mixtures, are (1) the lack of any peaks or prominent features; and (2) the fact that G_{12} is the most important of the integral functions over essentially the entire mole fraction range. Clearly hydrogen peroxide behaves in a very different fashion when added to water to that shown by the alcohols. The structure of hydrogen peroxide makes it ideal for involvement in hydrogen-bonded networks and the lack of any hydrophobic alkyl groups (as with the alcohols) facilitates the formation of an intercomponent hydrogenbonded network between hydrogen peroxide and water molecules. This is shown by the dimant G_{12} term. The G_{11} and G₂₂ terms gradually decreas ' increase respectively



Figure 4.10 – Inverse Kirkwood-Buff integral functions for water(1) + hydrogen peroxide(2) as a function of x_2 at 298.2K.

as x_2 increases consistent with the respective decrease and increase in the number of molecules of water and hydrogen peroxide present in the aqueous solution. The fact that these terms show such gradual changes with no peaks indicates that there is no clustering of likemolecules into local water-rich or cosolvent-rich domains. Clearly, in hydrogen peroxide-water mixtures the most important and overriding interaction is the intercomponent interaction characterised by the G₁₂ Kirkwood-Buff integral function.

4.3.2 - Dimethyl Sulphoxide (DMSO)

 G_m^E data reported by Kenttamaa and Lindberg³⁵ were fitted to the Redlich Kister equation⁶ where Y = G_m^E and q = RT.

Several authors have reported volumetric data for DMSO-water mixtures. The data chosen here³⁶ were the most recently recorded. Here, the authors had already fitted the data to the Redlich-Kister equation and so their reported parameters were used to determine V_m^E for the entire mole fraction range. Hence the partial molar volumes were obtained.

From above, dV_m/dT was calculated using the molar volumes of water³⁷ and DMSO³⁸ and then used to calculated the isothermal expansivity α for the DMSO-water mixtures. Excess internal pressures Π_1^E , calculated from reported data³⁸, were then fitted to the Redlich-Kister equation to yield Π_i for the full mole fraction range. These estimates were combined with isothermal expansivities α to yield the isothermal compressibilities using equation (4.3.1),

$$\kappa_{\rm T} = \alpha T / (\Pi_1 + p)$$
 (4.3.1)

The pattern in G_{ij} integral functions (Figure 4.11) for DMSO-water mixtures is essentially the same as that observed for hydrogen peroxide-water mixtures. As with hydrogen peroxide, $G_{1,2}$ is the dominant term for the bulk of the mole fraction range and there are no peaks or major features found in any of the integral functions. For DMSO + water mixtures, H_m^{E} < O indicating that the intercomponent interaction is important and this is borne out by the $G_{1,2}$ term which represents the affinity of water molecules for hydrogen peroxide molecules. DMSO as a pure liquid has an ordered structure 39 but when added to water this structure breaks down and, due to its strong hydrogen-acceptor properties, forms hydrogen bonds with water as shown in Figure 4.12.



<u>Figure 4.11</u> - Inverse Kirkwood-Buff integral functions for water(1)-IMSO(2) as a function of x_2 at 298.2K.



Figure 4.12 - Hydrogen bonded structure formed in IMSO-water mixtures³⁹.

4.3.3 - Cyanomethane (MeCN)

Water + MeCN is a TNA mixture but differs from hydrogen peroxide and DMSO in that G_m^E is positive. Although MeCN is aprotic, the properties of an aqueous solution of MeCN are very different from those for hydrogen peroxide-water and DMSO-water mixtures.

Excess functions for MeCN-water mixtures as a function of x_2 (Figure 4.9) show that G_m^E is large and positive over the entire mole fraction range and is parabolic in shape with the maximum value at $x_2 \simeq 0.5$.

Thus, if we differentiate this curve to obtain dG_m^E/dx_2 we have a plot that is positive at low x_2 , passes through zero at the peak value and then becomes negative. If we then differentiate again to obtain $d^2G_m^{\ E}/dx_2^{\ 2}$ we will have a plot that is negative over the complete mole fraction range. In the IKB analysis used here to determine the G_{ij} integral functions, $d^2G_m^E/dx_2^2$ is used to obtain $d\mu_2/dx_2$ as required for the analysis. Therefore if the term $d^2G_m^E/dx_2^2$ is the dominant term in equation (4.2.14) used to determine $\text{d}\mu_2/\text{d}\textbf{x}_2$ then this will force $d\mu_2/dx_2$ negative. If $d\mu_2/dx_2$ is negative then this signifies a mixture which is only partially miscible⁶. Clearly this point must be considered when analysing mixtures for which G_m^E is large and positive.

The problems outlined above can be further highlighted by considering the Redlich-Kister equation⁶,

$$Y = qx_2(1-x_2) \sum_{j=1}^{j=i} b_j(1-2x_2)^{(j-1)}$$
(4.3.2)

If there is only one term in this equation, then,

$$G_{m}^{E} = RTx_{2}(1-x_{2})b_{1}$$
 (4.3.3)

where $Y = G_m^E$ and q = RT.

Differentiating twice with respect to mole fraction x_2 gives,

$$d^{2}G_{m}^{E}/dx_{2}^{2} = -2RTb_{1}$$
 (4.3.4)

If we now consider the situation where $G_m^E > RT/2$ then $b_1 > 2$ and so substituting into equation (4.2.14) means that $d\mu_2/dx_2$ will be negative⁴⁰. Concern over the magnitude of G_m^E is very important when using the Redlich-Kister equation to analyse data because at $x_2 = 0.5$ only the first term (i.e. j = 1) is involved. Therefore if $G_m^E > RT/2$ at $x_2 = 0.5$ then $d\mu_2/dx_2$ will be negative indicating that the system is only partially miscible when in fact it is probably completely miscible throughout.

Returning to the case of MeCN, we can check G_m^E to see whether it is greater than RT/2. At T = 298.2K, RT/2 = 1.240 kJ mol⁻¹. Reported values⁴¹ for G_m^E show that at $x_2 = 0.40096$, $G_m^E = 1.308$ (i.e. $G_m^E > RT/2$) and at $x_2 = 0.61102$, $G_m^E = 1.257$ (i.e. $G_m^E > RT/2$). Hence using the Redlich-Kister equation for MeCN-water mixtures will lead to negative values for $d\mu_2/dx_2$ even though the system is completely miscible.

The problems associated with applying the Redlich-Kister equation to MeCN-water mixtures were such that an alternative method of analysis was used to determine $d\mu_2/dx_2$ as a function of x_2 . Analysis of the data used an orthogonal equation⁶,

$$G_m^E = RT \sum_{i=2}^N a_{(i-1)} P_i(x_1, x_2)$$
 (4.3.5)

where,

$$P_2 = x_1 x_2$$
 (4.3.6)

$$P_{3} = x_{1}x_{2}(1-2x_{2})$$
 (4.3.7)

$$P_{4} = x_{1}x_{2}[1 - (14x_{2}/3) + (14x_{2}^{2}/3)]$$
 (4.3.8)

$$P_5 = x_1 x_2 [1 - 8x_2 + 18x_2^2 - 12x_2^3]$$
 (4.3.9)

the general expression being,

$$P_{N} = [(2N-1)(1-2x_{2})p_{N-1} - (N-3)p_{N-2}]/(N+2)$$
 (4.3.10)

(N.B. - the term orthogonal means that as more terms are added the previous terms do not change). If we now consider the situation where $x_2 = 0.5$, we find that P_3 , P_5 ,.... are equal to zero but the even terms P_2 , P_4 ,.... are non-zero meaning that more than one term can contribute to the analysis of G_m^E for MeCN-water mixtures at the critical point. The importance of this can be seen in Figures 4.13 and 4.14.



Figure 4.13 - $d\mu_2/dx_2$ values calculated using four parameters for (a) the Redlich-Kister equation; and (b) the orthogonal equation.



<u>Figure 4.14</u> - $d\mu_2/dx_2$ values calculated using the orthogonal equation with (a) 2 parameters; (b) 3 parameters; and (c) 4 parameters.

Figure 4.13 shows how the Redlich-Kister over the equation gives negative values for $d\mu_2/dx_2$ critical range while the orthogonal equation gives rise to values over the entire mole fraction positive $d\mu_2/dx_2$ range. Figure 4.14 examines the results obtained from the orthogonal equation in more detail. If only two parameters are used in the equation then $d\mu_2/dx_2$ is negative over a very wide range. This is because with only two parameters the equation is identical to equation (4.3.3). If we add a third parameter, Figure 4.14 shows that $d\mu_2/dx_2$ is still negative over a small range. When a further parameter is added to the orthogonal equation, $d\mu_2/dx_2$ becomes positive throughout. It is clear from Figures 4.13 and 4.14 that the critical point for MeCN-water mixtures is at $x_2 \simeq 0.35$. In all cases the analysis is finely balanced.

The data used in the orthogonal analysis to obtain $d\mu_2/dx_2$ were G_m^E dependences on x_2 reported by French⁴¹.

The dependences of excess molar volumes V_m^E on mole fraction x_2 reported by Blandamer et al.⁴² were used in this analysis. These data were analysed using the Redlich-Kister equation.

The molar volume data calculated above were combined with sound velocity data⁴³ to give isentropic compressibilities. These results were analysed using the Redlich-Kister equation. The approximation $\kappa_s = \kappa_T$ was used as the compressibility data only contribute a very small numerical value to the final IKB integral functions (see earlier).

The IKB integral functions calculated from the data outlined above are shown in Figure 4.15. These results are very different from those obtained for the TNAN mixtures, hydrogen peroxide-water and DMSO-water. Figure 4.15 shows sharp maxima in G_{11} and G_{22} at $x_2 \simeq 0.35$ and a sharp minimum in G_{12} at the same mole fraction. This mole fraction corresponds to the critical region observed for $d\mu_2/dx_2$.

The G_{11} , G_{22} and G_{12} functions can be interpreted giving details on the as long-term interactions within a liquid mixture. The sharp peaks in G_{11} and G_{22} indicate that there is a strong tendency for like-molecules to gather together forming water-rich and MeCN-rich microdomains. This tendency towards microheterogeneity ties in exactly with the mole fraction at which $d\mu_2/dx_2$ tended towards a negative value. This is further emphasised by the sharp minimum in G_{12} at the same mole fraction, this minimum indicating that the



<u>Figure 4.15</u> - Inverse Kirkwood-Buff integral functions for water(1)-MeON(2) mixtures as a function of x_2 at 298.2K.

probability of finding water and MeCN molecules in close proximity to one another is unlikely and at its lowest. From these results it can be seen that MeCN-water mixtures behave in a very different fashion from the TNAN mixtures studied.

From Typically Non-Aqueous the (TNA) mixtures studied here it can be seen that they fall into two very different and distinct groups. The TNAN mixtures show smooth curves throughout with no peaks. These curves indicate that the cosolvent molecules readily form hydrogen bonds with water molecules even in the highly water-rich regions. This is shown by the dominance of G_{12} for essentially the complete mole fraction range. On the other hand, the TNAP mixture studied shows sharp peaks with maxima in G_{11} and G_{22} and a sharp minimum in G_{12} this indicating that mixture tends towards microheterogeneity. The results obtained here show a degree of agreement with Matteoli and Lepori 23 although the features they observed are less marked than those reported here.

In summary it can be said that unlike the bulk of the Typically Aqueous (TA) mixtures which all show similar behaviour, the TNA mixtures show very different behaviour depending on the sign of G_m^E .

4.4 - COMPLEX MIXTURES

The final type of mixtures to be studied here using the Inverse Kirkwood-Buff^{2,3} (IKB) Procedure are those whose behaviour pattern changes as they move from a water-rich mixture to a cosolvent-rich mixture. The two systems which will be used as examples here are 2,2,2trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol.

Before analysing the properties of these mixtures using the IKB procedure, some properties of fluoroalcohols relevant to this discussion should be outlined.

If we consider size only first, then as a CF3-group is larger than a CH3-group it would be expected that replacing a CH3-group with a CF3-group would increase the hydrophobic nature of the organic cosolvent. This however neglects possible changes in the water-cosolvent interactions. In fact, these water-cosolvent interactions become far more complex when the CH3-group on an alcohol molecule is replaced by a CF_3 -group⁴⁴. The fact that fluorine is far more electronegative than hydrogen plays a role fluoroalcohol-water interactions. vital in the Firstly, the electronegativity of fluorine will increase the strength of intercomponent hydrogen bonds of TYPE A (see Figure 4.16). This change will be counterbalanced, at

least in part, by the fact that the strength of the alternative type of intercomponent hydrogen bonding, TYPE B, will probably be diminished. Secondly, by introducing fluorine atoms into the solvent mixture, an additional type of intercomponent hydrogen bonding is now possible; TYPE C. This third type of intercomponent hydrogen bonding is weak in nature, but evidence for its existence is shown by IR spectra of pure fluoroalcohols^{45,46}.

 $R-(H)O\cdots H-OH$ TYPE B

 $C-F \cdot \cdot \cdot H-OH$ TYPE C

Ň

<u>Figure 4.16</u> – The three major types of intercomponent hydrogen bonds present in fluoroalcohol-water mixtures.



Figure 4.17 - Excess molar thermodynamic functions of mixing for an aqueous mixture of 2,2,2-trifluoroethanol (TFE) as a function of x_2 at 298.2K⁴⁷.

4.4.1 - 2,2,2-Trifluoroethanol (TFE)

Figure 4.17 shows the excess thermodynamic functions of mixing for TFE.

The excess molar Gibbs energies G_m^E used in the IKB calculations are^{48,49} plotted in Figure 4.17. These data points were fitted to the orthogonal equation⁶. The volumetric data were reported by Rochester and Symonds⁵⁰. Isentropic compressibilities used were reported by Patil and Ali⁵¹. These were all substituted into the IKB procedure using a FORTRAN program, the results being given in Figure 4.18.

Figure 4.18 shows that G_{11} and G_{22} have maxima in the water-rich region while G_{12} has a minimum in the same region. These peaks are not particularly sharp however. The presence of these peaks indicates that likemolecules tend to cluster together in this region.

4.4.2 - 1,1,1,3,3,3-Hexafluoropropan-2-o1 (HFP)

Figure 4.19 shows the excess functions for this fluoroalcohol-water mixture.



Figure 4.18 - Inverse Kirkwood-Buff integral functions for water(1)-2,2,2-trifluoroethanol(2) mixtures as a function of x_2 at 298.2K.



<u>Figure 4.19</u> – Excess molar thermodynamic functions of mixing for water(1)-1,1,1,3,3,3hexafluoropropan-2-ol(2) as a function of x_2 at 298.2K⁴⁷.

The G_m^E results were calculated from measured vapour pressure data⁴⁷ using the Barker⁵² procedure. The dependence of G_m^E on mole fraction was fitted to the orthogonal equation⁶. Figure 4.19 shows that G_m^E has an S-shaped curve, positive at low x_2 , passing through zero and negative at high x_2 . The volumetric data^{50,53} were fitted to the Redlich-Kister equation⁶. Isentropic compressibilities were calculated from plots reported by Patil and Ali⁵¹. These data were all substituted into a FORTRAN program to generate the IKB integral functions shown in Figure 4.20.

Figure 4.20 shows that G_{11} and G_{22} have sharp maxima in the highly water-rich region while G_{12} has a sharp minimum in the same region. At high mole fractions of added cosolvent the peaks drop very rapidly and the mixture now resembles e.g. MeCN-water. This is in contrast to the behaviour of the comparable alcohol i-propanol.

4.4.3 - Discussion

The behaviour of the two fluoroalcohols studied here can be compared to that observed for the corresponding alkyl-substituted alcohols (see Section 4.2). The behaviour of the typically non-aqueous mixture MeCN-water should also be considered here.



<u>Figure 4.20</u> - Inverse Kirkwood-Buff integral functions for water(1)-1,1,1,3,3,3-hexafluoropropen-2-ol(2) as a function of x_2 at 298.2K⁴⁷.

Both of the fluoroalcohols behave as typically aqueous mixtures in the water-rich regions. The CF_3 -group is hydrophobic and thus enhances the water-water interactions around a fluoroalcohol molecule. This pattern of behaviour is identical to that of a CH_3 -group on an alkyl-alcohol. This behaviour is clearly indicated by the maxima in G_{11} and G_{22} and the minimum in G_{12} . The maxima are greater for the fluoroalcohols than for the alkylalcohols as CF_3 -groups are larger than CH_3 -groups making them more hydrophobic.

As more cosolvent is added to the mixture and we move away from the water-rich mole fraction region, we find that the behaviour of the fluoroalcohols, especially HFP, changes. Figure 4.20 shows that the peaks G₂₂ which indicate the water-rich and G₁₁ and in fluoroalcohol-rich domains drop away sharply as x2 increases. The mixture can no longer be said to resemble a typically aqueous mixture, but is now more like the typically non-aqueous mixture MeCN-water (see Figure 4.15). This rapid dropping off of the maxima is not shown comparable alkyl-alcohols. Clearly, by the in the fluoroalcohol-rich regions we are seeing the effects of intercomponent hydrogen bonding involving both the -OH and the -CF, groups of the fluoroalcohol molecules. As stated earlier, the interactions of the -OH groups with water molecules are likely to be stronger than the comparable

interactions in the alkyl-alcohols. The $-CF_3$ group interactions with water molecules give rise to the observed negative G_m^E in the fluoroalcohol-rich regions.

In conclusion, the CF₃-groups on fluoroalcohols appear to behave in a hydrophobic fashion in water-rich regions and a hydrophilic fashion in fluoroalcohol regions. Clearly, the fluoroalcohols are far more complex in behaviour than either the TA mixtures or the TNA mixtures.

4.5 - CONCLUSIONS

In this chapter the Inverse Kirkwood-Buff^{2,3} (IKB) Procedure has been applied to Typically Aqueous (TA), Typically Non-Aqueous (TNA) and complex mixtures.

For the TA mixtures we saw maxima and minima in the integral functions which indicated that in water-rich mixtures the like-molecules tended to cluster together to exclude molecules of the other component. As would be expected for such systems, these effects were enhanced as the size of the alkyl-substituent on the solute molecules increased. There was also evidence of enhancement of the water structure when the mole fraction of added solute was low.

The TNA mixtures need to be separated into those where G_m^E is negative (TNAN) and those where G_m^E is positive (TNAP). The TNAN showed no major features in the integral functions but G_{12} was the dominant term over essentially the entire mole fraction range showing that these solutes readily interact with water molecules. MeCN was the TNAP mixture studied and showed very different behaviour from the TNAN mixtures. The integral functions observed here were very similar to those seen for 2-methyl propan-2-ol + water, a TA mixture. The presence of the sharp maxima and minimum for MeCN-water add weight to the idea that this mixture tends towards microheterogeneity.

Finally the fluoroalcohols were analysed using the IKB procedure. These behaved like TA mixtures at low mole fractions of added cosolvent and like TNAP mixtures at high mole fractions.

Another major point discussed in this chapter was the relative merit of using the orthogonal equation⁶ instead of the Redlich-Kister equation⁶. In this chapter it has been shown that if the Redlich-Kister equation is used for mixtures where G_m^E is large and positive, then results may be obtained which indicate that the mixtures are only partially miscible, even though this is not the case.

The results in this chapter clearly show that the IKB^{2,3} procedure is a powerful tool for probing binary aqueous mixtures as long as the starting data are analysed carefully.

,

4.6 - REFERENCES

1. J. G. Kirkwood and F. P. Buff, J. Chem. Phys., 1951, <u>19</u>, 774.

2. A. Ben-Naim, J. Chem. Phys., 1977, <u>67</u>, 4884.

3. A. Ben-Naim, Cell Biophys., 1988, 12,255.

4. F. Franks, "Hydrogen-Bonded Solvent Systems", ed. A. K. Covington and P. Jones, Taylor and Francis Ltd., London, 1968.

 M. J. Blandamer, Adv. Phys. Org. Chem., 1977, <u>14</u>, 203.
 J. S. Rowlinson and F. L. Swinton, "Liquids and Liquid Mixtures", 3rd ed., Butterworth and Co. Ltd., London, 1982.

7. F. Franks and D. J. G. Ives, Quart. Revs., 1966, <u>20</u>,1.
8. "Water - A Comprehensive Treatise", Vol. 2, ed. F.
Franks, Plenum Press, New York, 1973.

9. e.g. M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A. W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C. D. Hubbard and E.-E. A. Abu-Gharib, J. Chem. Soc., Faraday Trans. I, 1986, <u>82</u>, 1471.

10. M. C. A. Donkersloot, J. Sol. Chem., 1979, <u>8</u>, 293.

11. K. J. Patil, J. Sol. Chem., 1981, 10, 315.

12. J. M. Simonson, D. J. Bradley and R. H. Busey, J. Chem. Therm., 1987, <u>19</u>, 479.

13. N. C. Patel and S. I. Sandler, J. Chem. Eng. Data, 1985, <u>30</u>, 218.

14. A. J. Easteal and L. A. Woolf, J. Chem. Therm., 1985, <u>17</u>, 49. 15. R. C. Pemberton and C. J. Marsh, J. Chem. Therm., 1978, 10, 867. 16. work carried out within research group. 17. G. C. Benson and O. Kiyohara, J. Sol. Chem., 1980, <u>9</u>, 791. 18. T. Moriyoshi, Y. Morishita and H. Inubushi, J. Chem. Therm., 1977, <u>9</u>, 577. 19. E. Sada and T. Morisue, J. Chem. Eng. Japan, 1975, 8, 191. 20. M. Sakurai, J. Sol. Chem., 1988, 17, 267. 21. J. Kenttamaa, E. Tommila and M. Marti, Ann. Acad. Sci. Fenn., 1959, AII, 932. 22. M. Sakurai, unpublished results. 23. E. Matteoli and L. Lepori, J. Chem. Phys., 1984, 80, 2856. 24. K. Nishikawa, Y. Kodera and T. Iijima, J. Phys. Chem., 1987, **91**, 3694. 25. M. A. Villamanan and H. C. Van Ness, J. Chem. Eng. Data, 1984, 29, 429. 26. L. Boje and A. Hvidt, J. Chem. Therm., 1971, 3, 663. 27. T. Moriyoshi and Y. Uosaki, J. Soc. Mater. Sci. Japan, 1984, <u>33</u>, 127. 28. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn, J. Chem. Soc., Faraday Trans., 1990, 86, 283.

29. G. Kortum and V. Valent, Ber. Bung. Phys. Chem., 1977, <u>81</u>, 752. 30. V. S. Griffiths, J. Chem. Soc., 1952, 1326. 31. M. Nakagawa, Y. Miyamoto and T. Moriyoshi, J. Chem. Therm., 1983, 15, 15. 32. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn. J. Chem. Soc., Faraday Trans., 1990, 86, 277. 33. G. Scatchard, G. M. Kavanagh and L. B. Ticknor, J. Am. Chem. Soc., 1952, 74, 3715. 34. M. F. Easton, A. G. Mitchell and W. F. K. Wynne-Jones, Trans. Faraday Soc., 1952, 48, 796. 35. J. Kenttamaa and J. Lindberg, Suomen Kemi., 1960, B33, 98. 36. T. Kimura and S. Takagi, J. Chem. Therm., 1986, 18, 447. 37. R. A. Fine and F. J. Millero, J. Chem. Phys., 1973, **59**, 5529. 38. D. D. MacDonald and J. B. Hyne, Can. J. Chem., 1971, **49**, 711. 39. A. J. Parker, Quart. Rev., 1962, 16, 163. 40. J. L. Copp and D. H. Everett, Disc. Faraday Soc., 1953, 15,174. 41. H. F. French, J. Chem. Therm., 1987, 19, 1155. 42. D. A. Armitage, M. J. Blandamer, M. J. Foster, N. J. Hidden, K. W. Morcom, M. C. R. Symons and M. J. Wootten, Trans. Faraday Soc., 1968, 64, 1193.

G. C. Benson, P. J. D'Arcy and Y. P. Thermochim. Acta, 1981, 46, 295. 44. K. Kinugawa and K. Nakanishi, J. Chem Phys., 1988, 89, 5834. 45. M. Oxi and H. Iwamura, Bull. Chem. Soc. Japan, 1962, 35, 1744. 46. P. Kreuger and H. D. Mettee, Can. J. Chem., 1964, 42, 340. 47. M. J. Blandamer, J. Burgess, A. Cooney, H. J. Cowles, I. M. Horn, K. J. Martin, K. W. Morcom and P. Warrick Jr., J. Chem Soc., Faraday Trans., 1990, 86, 2209. 48. A. Cooney and K. W. Morcom, J. Chem. Therm., 1988, 20, 735. 49. A. Cooney, Ph.D. Thesis, University of Leicester, 1988. 50. C. H. Rochester and J. R. Symonds, J. Fluor. Chem., 1974, <u>4</u>, 141. 51. K. J. Patil and S. I. Ali, Ind. J. Pure Appl. Chem., 1981, 19, 617. 52. J. A. Barker, Aust. J. Chem., 1953, 6, 207. 53. J. Murto, A. Kivinen, S. Kivimaa and R. Laakso, Suomen Kemi., 1967, **<u>B40</u>**, 250.

Handa,

43.

CHAPTER FIVE

Application of the Inverse Kirkwood-Buff Procedure to Kinetic Reactions in Binary Aqueous Mixtures

5.1 - INTRODUCTION

The usefulness of the Inverse Kirkwood-Buff (IKB) Theory^{1,2} in probing³⁻⁵ the solvation properties of binary aqueous mixtures was discussed in the previous chapter. In this chapter the IKB analysis is extended to consider the preferential solvation of ions in binary aqueous mixtures^{6,7}. The method was developed by Hall⁸ and by Newman⁹ and uses kinetic data to obtain information concerning the solvation of initial and transition states¹⁰.

Two classes of compounds which behave in totally different ways are discussed. First the properties of a low spin Iron(II) complex in methanol - water solvent mixtures are considered and then the behaviour of an organic solute in 2-methyl propan-2-ol - water is discussed.

5.2 - THEORETICAL OUTLINE

The theory proposed¹¹ by Kirkwood and Buff and developed^{1,2} by Ben-Naim allows for the study of molecular interactions between the components in a mixed solvent system over the entire mole fraction range. Hall⁸ and Newman⁹ extended this theory to consider the relative

solvation of solute molecules by the solvent molecules in binary solvent mixtures. In most cases these mixtures are binary aqueous mixtures.

The Kirkwood-Buff integral functions $G_{\alpha\beta}$ (where α and β =1,2) are described by equation (5.2.1) below,

$$G_{\alpha\beta} = \int_{0}^{\infty} [g_{\alpha\beta}(R) - 1] 4\pi R^{2} dR$$
 (5.2.1)

where $g_{\alpha\beta}$ is the angle-averaged, orientation-averaged pair correlation function and R is the intermolecular separation. $G_{\alpha\beta}$ is a measure of the local arrangement of α -molecules around β -molecules, thus showing the affinity of α -molecules for β -molecules. Chapters Three and Four show how these Inverse Kirkwood-Buff integral functions are determined for binary solvent mixtures. Here, the analysis is extended to consider the situation where a solute molecule-j is added to the binary solvent system. The method developed by Newman⁹ to explain such a situation is outlined below.

Consider a solute molecule-j in a binary solvent system; cosolvent-1 + cosolvent-2. The solute molecule-j will be surrounded by a solvation sphere composed of molecules of colvent-1 and/or cosolvent-2. The IKB theory is used to ______ on the composition of

this solvation sphere. A volume of solvent can be defined by a sphere of radius R centred on the solute molecule-j. If solute-j was not present in the solution then there would be N_1 moles of cosolvent-1 in the defined volume sphere and N_2 moles of cosolvent-2. If solute-j is now added to the binary system we have N_{1j} ' and N_{2j} ' moles in the sphere. Excess quantities are defined,

$$N_{1j} = N_{1j}' - N_1$$
; $N_{2j} = N_{2j}' - N_2$ (5.2.2)

If n_1 and n_2 are the number densities of cosolvent-1 and cosolvent-2, then,

$$N_{1j} = n_1 \int_0^{\infty} [g_{1j}(R) - 1] 4\pi R^2 dR = n_1 G_{1j}$$
 (5.2.3)

and similarly,

$$N_{2j} = n_2 \int_{0}^{\infty} [g_{2j}(R) - 1] 4\pi R^2 dR = n_2 G_{2j}$$
 (5.2.4)

Hall⁸ showed that,

$$d\mu_{j}^{o}(mix) = -\sum_{i=1}^{1-2} N_{ij} d\mu_{i}(mix)$$
 (5.2.5)

Therefore,

$$d\mu_{j}^{\circ}(mix) = -N_{1j}d\mu_{1}(mix) - N_{2j}d\mu_{2}(mix)$$
(5.2.6)
Substituting equations (5.2.3) and (5.2.4) into (5.2.6) gives,

$$d\mu_{j}^{\circ}(mix) = -n_{1}G_{1j}d\mu_{1}(mix) - n_{2}G_{2j}d\mu_{2}(mix)$$
 (5.2.7)

Given the Gibbs-Duhem equation,

$$n_1 d\mu_1 (mix) + n_2 d\mu_2 (mix) = 0$$
 (5.2.8)

then,

$$d\mu_{j}^{\circ}(mix) = (G_{1j}-G_{2j})n_{2}d\mu_{2}(mix)$$
 (5.2.9)

Differentiating equation (5.2.9) with respect to x_2 yields equation (5.2.10),

$$[d\mu_{j}^{o}(mix)/dx_{2}] = (G_{1j}-G_{2j})n_{2}(d\mu_{2}/dx_{2})$$
 (5.2.10)

In Chapter Four it is shown that the derivative of the chemical potential is one of the thermodynamic quantities necessary for the calculation of the IKB integral functions. Thus, an equation for the derivative of the chemical potential was obtained,

$$(d\mu_2/dx_2) = RT\{(1/x_2) + [(1-x_2)/RT](d^2G_m^E/dx_2^2)\}$$
 (5.2.11)

substituting equation (5.2.11) into (5.2.10),

$$[d\mu_{j}^{\circ}(mix)/dx_{2}] = (G_{1j}-G_{2j})n_{2}RT\{(1/x_{2}) + [(1-x_{2})/RT](d^{2}G_{m}^{E}/dx_{2}^{2})\}$$
(5.2.12)

given that,

$$n_2 = N_2/V = [N_2/(N_1+N_2)][(N_1+N_2)/V] = x_2/V_m$$
 (5.2.13)

where V_m is the molar volume of the binary mixture. Using equation (5.2.13) and rearranging (5.2.12) leads to,

$$(G_{1j}-G_{2j}) = \{ [d\mu_j^{\circ}(mix)/dx_2]V_m \} RT \cdot F$$
 (5.2.14)

where,

$$F = 1 + [x_2(1-x_2)/RT] (d^2G_m^E/dx_2)$$
 (5.2.15)

The term $(G_{1j} - G_{2j})$ measures the preference of solute-j for solvation by cosolvent-1 over cosolvent-2. If the separate terms G_{1j} and G_{2j} are required then the procedure described by Newman⁹ must be followed. Newman showed that,

$$G_{1j} = x_2 [V_2(mix)/V_m] (G_{1j}-G_{2j}) + \kappa_T RT - V_j^{\infty}(x_2)$$
 (5.2.16)

where $V_j^{\infty}(x_2)$ is the limiting partial molar volume of solute-j in the mixture, κ_T is the isothermal

compressibility and $V_2(mix)$ is the partial molar volume of cosolvent-2.

In this chapter kinetic results and solubility measurements are used 6,7 to determine the IKB integral functions for a solute in a binary aqueous system.

If solute-j is sparingly soluble in water and in a binary aqueous mixture, then the transfer parameter can be determined from solubility measurements,

$$\Delta(aq - x_2)\mu_j^{\circ} = \mu_j^{\circ}(mix; x_2) - \mu_j^{\circ}(aq)$$
 (5.2.17)

5.2.1 - First-Order Reactions

Using the Transition State Theory¹⁰, the Gibbs energy of activation for reaction in a binary aqueous mixture is related to the standard chemical potentials for the initial and transition states,

$$\Delta G^{\neq}(x_2) = \mu^{\circ}(\neq; x_2) - \mu^{\circ}(is; x_2)$$
 (5.2.18)

Therefore, it follows that the change in Gibbs energy of activation on going from an aqueous solution to a binary aqueous solution of mole fraction x_2 is given by,

$$\Delta(aq \rightarrow x_2) \Delta G^{\neq} = \Delta(aq \rightarrow x_2) \mu^{\circ}(\neq) - \Delta(aq \rightarrow x_2) \mu^{\circ}(is)$$

$$= - \operatorname{RTln}[k(x_2)/k(aq)]$$
(5.2.19)

Returning to equation (5.2.14) and considering equation (5.2.19) we have,

$$[G_{1\neq}-G_{2\neq}] - [G_{1is}-G_{2is}] \equiv [G_{1\neq}-G_{1is}] - [G_{2\neq}-G_{2is}]$$
 (5.2.20)

and,

$$[G_{1\neq}-G_{1is}] - [G_{2\neq}-G_{2is}] = V_m[d\Delta(aq-x_2)\Delta G^{\neq}/x_2]/RTF$$
 (5.2.21)

Here a term ${\boldsymbol{g}}_k$ can be introduced where,

$$g_k = [G_{1\neq} - G_{1is}] - [G_{2\neq} - G_{2is}]$$
 (5.2.22)

 g_k measures the changes in the relative affinities of the substrate for cosolvents-1 and -2 on passing from the initial state to the transition state.

5.2.2 - Second-Order Reactions

The procedure for analysis of a secondorder reaction is essentially as described above. However, there are two initial states, is A and is B, which react to form a single transition state \ddagger .

Equation (5.2.19) is rewritten as,

$$\Delta(aq - x_2) \Delta G^{\neq} = \Delta(aq - x_2) \mu^{\circ}(\neq) - \Delta(aq - x_2) \mu^{\circ}(isA)$$

-
$$\Delta(aq - x_2) \mu^{\circ}(isB)$$
 (5.2.23)

$$\approx$$
 - RTln[k(x₂)/k(aq)]

Here, $ln[k(x_2)/k(aq)]$ is the ratio of second-order rate constants. Similarly,

$$[G_{1\neq}-G_{2\neq}] - [G_{1isA}-G_{2isA}] - [G_{1isB}-G_{2isB}]$$

= $V_m[d\Delta(aq->x_2)\Delta G^{\neq}/x_2]/RTF$
(5.2.24)
= g_k

This time g_k measures the change in relative affinities for three solutes.

Now that IKB integral functions have been derived for solute-j undergoing chemical reactions in binary solutions, this theory can be applied to some practical measurements.

5.3 - ANALYSIS OF AN IRON(II) COMPLEX

The alkaline hydrolysis of a low-spin Iron(II) complex in a binary aqueous mixture is studied here; namely the alkaline hydrolysis of $[Fe(phen)_3]^{2+}$ in methanol-water (where phen = 1,10-phenanthroline).

When hydroxide ions are added to $[Fe(phen)_3]^{2+}$ in a binary mixture of methanol + water, the methanol will stabilise both the initial state and the transition state¹². Figure 5.1 shows the structure of $[Fe(phen)_3]^{2+}$. The rate-determining step for this reaction is bimolecular with hydroxide attack on the complex.



Figure 5.1 - The structure of $[Fe(1, 10-phenenthroline)_3]^{2+}$.

Determination of the IKB integral functions for methanol-water mixtures was discussed in detail in Chapter Four. The molar Gibbs energies¹³, G_m^E , molar volumes¹⁴, V_m , and isothermal compressibilities¹⁵, were used. All parameters were calculated for solutions at 298.2K using a FORTRAN program.

Transfer parameters for the $[Fe(phen)_3]^{2+}$ calculated using solubility data¹⁶ for were the thiocyanate salt using the $TATB^{12}$ assumption. From these results, transfer parameters for the initial state $\Delta(aq-x_2)\mu^{\circ}(cation+OH^{-})$, were calculated¹² and these data were combined with kinetic measurements for the alkaline hydrolysis to give the transfer parameters for the transition state, $\Delta(aq - x_2) \mu^{\circ}$ (TS)¹². From these transfer parameters the dependence of $d\mu^{\circ}/dx_2$ on x_2 was determined. Partial molar volume data¹⁷ were used to calculate estimates of $V_i^{\infty}(x_2)$ for the initial and transition states. These results were used to obtain G_{1i} and G_{2i} (where j = IS and TS). These calculations were carried out using a FORTRAN program. The results are shown in Figure 5.2.

As stated earlier, for this reaction, added methanol stabilises both the initial state and the transition state. This trend is attributed to the large hydrophobic phen ligands. In the transition state, the



Figure 5.2 - Dependence of Inverse Kirkwood-Buff integral functions on x_2 for water(1) + methanol(2) at 298.2K. G_{11} and G_{12} are the integral functions for the initial state $([Fe(phen)_3]^{2+} + 0H^-)$ and $G_{\pm 1}$ and $G_{\pm 2}$ are the corresponding functions for the transition state⁶.

hydroxide ions attack the Fe^{2+} centre and so force the phen ligands out into the surrounding solvent medium. The resultant stretching of the Fe-N bonds means that the transition state is more hydrophobic than the initial state. Therefore added methanol stabilises the transition state more than the initial state¹². Looking at Figure 5.2, and considering the composite term $(G_{i2} - G_{i1})$, it can be seen that this term remains positive throughout but decreases as the mole fraction of added methanol, x_2 , increases. This positive term indicates preferential solvation of the initial state by methanol. At high x_2 the magnitude of $(G_{i2} - G_{i1})$ becomes less due to the strong preferential solvation of the hydroxide ions by water. However, the fact that this term remains positive for the entire mole fraction range shows that hydrophobic solvation is a major consideration for the initial state.

For the transition state, $(G_{\neq 2}-G_{\neq 1})$ is also positive and is greater in magnitude than (G $_{12}$ - G_{i1}). Also, the tapering off of (G_{i2} - G_{i1}) at high mole fractions of added alcohol is less apparent for the transition state term. Two factors lead to this increase in magnitude. Firstly, as the Fe-N bonds stretch, the phen groups are pushed further out into the surrounding solvent medium making the transition state more hydrophobic than the initial state. This means that the hydrophobic stabilisation by the methanol is greater for the transition state than for the initial state. Secondly, the hydroxide ions attacking the complex cation centres become buried in these cations and so become less susceptible to

preferential solvation by water. This feature also contributes to the increase in magnitude of $(G_{\neq 2}-G_{\neq 1})$ over $(G_{i2} - G_{i1})$.

For this low-spin Iron(II) complex, the IKB integral functions bear out previously reported¹² conclusions which state that the transition state for this reaction is stabilised by the added alcohol to a greater extent than the initial state is.

5.4 - ANALYSIS OF AN ORGANIC COMPOUND

The organic reaction under consideration here is the spontaneous hydrolysis of 4-methoxyphenyl 2,2dichloropropionate in 2-methyl propan-2-ol - water mixtures. The hydrolysis reaction is carried out in mildly acidic solutions and is first-order with respect to the ester¹⁸. The reaction involves water-catalysed nucleophilic attack by water on the ester. Figure 5.3 shows the reaction scheme.

The IKB integral functions for 2-methyl propan-2-ol - water were determined in Chapter Four. The data used were excess molar Gibbs energies¹⁹, volumetric data²⁰ and isothermal compressibilities²¹. All results were calculated at 298.2K.



<u>Figure 5.3</u> - Reaction mechanism for the water-catalysed hydrolysis of 4-methoxyphenyl 2,2-dichloropropionate⁷.

For some kinetic reactions in binary aqueous mixtures, volumes of activation are measured. These measurements can be used in the IKB analysis of these systems.

For a first-order reaction, equation (5.2.16) leads to,

 $G_{1is} = x_2 (V_2/V_m) [G_{1is}-G_{2is}] + \kappa_T RT - V_{is}^{\infty}(x_2)$ (5.4.1)

and for the transition state,

$$G_{1\neq} = x_2 (V_2/V_m) [G_{1\neq} - G_{2\neq}] + \kappa_T RT - V_{\neq}^{\infty} (x_2)$$
 (5.4.2)

Considering equations (5.2.21) and (5.2.22) a new quantity g_{k1} can be defined,

$$[G_{1\neq}-G_{1is}] = V_m[d\Delta(aq->x_2)\Delta G^{\neq}/x_2]/RTF$$

$$= g_{k1}$$
(5.4.3)

Here, g_{k1} monitors the change in affinity of the substrate for cosolvent-1 on activation. The corresponding quantity g_{k2} can also be determined. A similar principle holds for second-order reactions.

Returning to the spontaneous hydrolysis of the acyl ester, the first-order rate constant decreases dramatically as the mole fraction of added alcohol increases^{18,22,23}. The volume of activation also decreases as alcohol is added^{22,23}. From these results and those for the alcohol-water mixtures, g_k , g_{k1} and g_{k2} were determined. The results are shown in **Figure 5.4**.



<u>Figure 5.4</u> - Dependence on mole fraction x_2 of Inverse Kirkwood-Buff parameters g_k , g_{kl} and g_{k2} for the spontaneous hydrolysis of 4-methoxyphenyl 2,2-dichloropropionate in water(1)-2-methyl propan-2-ol(2) at 298.2K.

According to Figure 5.3 the transition state is more hydrophilic than the initial state. Figure 5.4 bears this out in that g_k increases sharply with x_2 indicating that the solvent cosphere is very different from the bulk solvent. However, gk is a composite term and so, to gain insight into the preferential solvation by the two individual cosolvents, g_{k1} and g_{k2} must be studied. The magnitude of g_{k2} is approximately twice that of g_{k1} indicating that preferential solvation by 2-methyl propan-2-ol dominates over solvation by water. This shows that despite the increase in hydrophilic character on activation, hydrophobic bonding of the initial state is still the major feature.

5.5 - SUMMARY

The two substrates studied here behave very differently on activation for their reactions in alcoholwater mixtures. The alkaline hydrolysis of $[Fe(phen)_3]^{2+}$ shows an increase in hydrophobicity on going from the initial state to the transition state. For the spontaneous hydrolysis of 4-methoxyphenyl 2,2-dichloropropionate, the substrate becomes more hydrophilic on activation. Applying the Kirkwood-Buff theory to these reactions gives another

valuable method for probing preferential solvation of substrates in binary aqueous mixtures. A major advantage of this method is that it enables study of the microscopic structure of the local solvent cosphere over a wide range of mole fractions.

5.6 - REFERENCES

1. A. Ben-Naim, J. Chem. Phys., 1977, 67, 4884. 2. A. Ben-Naim, Cell Biophys., 1988, 12, 255. 3. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn, J. Chem. Soc., Faraday Trans., 1990, 86, 277; 283. 4. M. J. Blandamer, J. Burgess, A. Cooney, H. J. Cowles, I. M. Horn, K. J. Martin, K. W. Morcom and P. Warrick Jr., J. Chem. Soc., Faraday Trans., 1990, 86, 2209. 5. E. Matteoli and L. Lepori, J. Chem. Phys., 1984, 80, 2856. 6. M. J. Blandamer, J. Burgess, H. J. Cowles, I. M. Horn, N. J. Blundell and J. B. F. N. Engberts, J. Chem. Soc., Chem. Comm., 1989, 1233. 7. M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles, J. B. F. N. Engberts, I. M. Horn and P. Warrick Jr., J. Am. Chem. Soc., 1990, in press. 8. D. G. Hall, J. Chem. Soc., Faraday Trans. II, 1972, 68, 25. 9. K. E. Newman, J. Chem. Soc., Faraday Trans. I, 1988, 84, 1387. 10. S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941. 11. J. G. Kirkwood and F. P. Buff, J. Chem. Phys., 1951, 19, 774.

W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C. D. Hubbard and E.-E. A. Abu-Gharib, J. Chem. Soc., Faraday Trans. I, 1986, 82, 1471. 13. J. M. Simonson, D. J. Bradley and R. H. Busey, J. Chem. Therm., 1987, 19, 479. 14. N. C. Patel and S. I. Sandler, J. Chem. Eng. Data, 1985, <u>30</u>, 218. 15. A. J. Easteal and L. A. Woolf, J. Chem. Therm., 1985, 17, 49. 16. E.-E. A. Abu-Gharib, M. J. Blandamer, J. Burgess, N. Gosal, P. Guardado, F. Sanchez and C. D. Hubbard, Trans. Met. Chem., 1984, 9, 306. 17. M. J. Blandamer, J. Burgess, M. Balon, P. Guardado and A. Maestre, Trans. Met. Chem., 1988, 13, 313. 18. J. F. J. Engbersen, Ph.D. Thesis, University of Groningen, 1976. 19. J. Kenttamaa, E. Tommila and M. Marti, Ann. Acad. Sci. Fenn., 1959, AII, 932. 20. M. Sakurai, Bull. Chem. Soc. Japan, 1987, <u>60</u>, 1. 21. T. Moriyoshi, Y. Morishita and H. Inubushi, J. Chem. Therm., 1977, <u>9</u>, 571. 22. H. A. J. Holterman and J. B. F. N. Engberts, J. Am. Chem. Soc., 1982, 104, 6382. 23. H. A. J. Holterman, Ph.D. Thesis, University of Groningen, 1982.

12. M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A.

CHAPTER SIX

A Theoretical Outline of Isochoric Thermodynamic Parameters for Reactions in Aqueous Solutions

6.1 - INTRODUCTION

1935, in a paper concerning In the applications of the transition state theory to kinetics, Evans and Polanyi¹ made the suggestion that kinetic data obtained for reactions carried out at constant volume may readily interpreted than those obtained be more at pressure. They reasoned that at constant constant pressure, the separation between solvent molecules changes when the pressure is changed. Similarly at constant temperature, these distances change when the pressure changes. So, they reasoned that the analysis would be much simpler if the solvent-solvent distance remained constant. This original idea has been taken up by many authors $^{2-8}$ but, despite over 50 years of debate, the precise volume to be held constant remains undefined.

The term "isochoric" has more recently been used to define reaction conditions of constant volume and the associated thermodynamic parameters. The dictionary definition of the term "isochoric" is unhelpful, simply listing isochoric as meaning, "taking place without change in volume; under conditions of constant volume". In much of the early work in this field it was not made totally clear what volume was being held constant^{2,5}, although

many different constant volume thermodynamic parameters were determined. Whalley⁹ acknowledged that there was controversy over what volume should be held constant, stating that "the volume that is kept constant is the volume of an equilibrium mixture of initial and transition states". Williams³, however, claimed that the volume to be held constant was that of the activated complex rather than the volume of the reacting system. More recently, the debate has been rekindled by the suggestion made by Blandamer et al.⁶ that the only meaningful isochoric volume must be the molar volume of the pure solvent. Albuquerque and Reis⁸ counter-claimed this maintaining that a constant concentration of solvent was necessary.

The following work aims to clarify the issue, and show that the isochoric volume must be the molar volume of the pure solvent. In Chapter Seven the theory is applied to experimental data, and activation parameters are calculated describing processes under clearly defined isochoric and isobaric/isothermal conditions¹⁰.

6.2 - CONVENTIONAL ISOBARIC/ISOTHERMAL CONDITIONS

The bulk of thermodynamic parameters reported in the literature involve practical measurements

made under isobaric/isothermal conditions. Before considering isochoric thermodynamic parameters, a few basic equations used for calculating isobaric/isothermal parameters are reported. Throughout this discussion of thermodynamic parameters we are concerned with the behaviour of solute-j in an aqueous solution. The chemical potential of such a solute is given by,

$$\mu_{j}(mix;T;p) = \mu_{j}^{\#}(mix;T;p) + RTln(m_{j}\gamma_{j}/m^{o})$$
 (6.2.1)

where m_j is the molality of solute-j, $m^0 = 1.0 \text{ mol kg}^{-1}$ and $\mu_j^{\#}(\text{mix};T;p)$ is the chemical potential of solute-j for the ideal solution where $m_j = 1.0 \text{ mol kg}^{-1}$ and $\gamma_j = 1.0$ at the same T and p. We can now consider an equation for the chemical equilibrium for a system containing i-solutes,

$$\Delta_{r}G^{\#}(mix;T;p) = -RTlnK^{\#}(mix;T;p)$$

$$= \sum_{j=1}^{i=1} v_{j}\mu_{j}^{\#}(mix;T;p)$$
(6.2.2)

where $\ln K^{\#}(\text{mix};T;p)$ is the equilibrium constant for the reaction, $\Delta_r G^{\#}(\text{mix};T;p)$ is the Gibbs energy of reaction and v_j is the stoichiometric quantity. Similarly, this

leads us to equations for partial molar quantities,

$$\Delta_{r} X^{\infty}(mix;T;p) = \sum_{j=1}^{j=1} v_{j} X_{j}^{\infty}(mix;T;p)$$
 (6.2.3)

where x_j^{∞} is the limiting partial molar quantity where X = H, V, C_p. Similar equations can be obtained where the equilibrium constant K, is replaced by the rate constant k. This leads to the determination of activation quantities. Again, we are concerned with parameters determined "at the same T and p". One final important equation to be mentioned here is the Van't Hoff equation which measures the temperature dependence of equilibrium constants under isobaric conditions,

$$[\partial \ln K^{\#}(\min;T;p) / \partial T]_{p} = [\Delta_{r}H^{\infty}(\min;T;p)] / RT^{2}$$
(6.2.4)

This is an important equation and several $authors^{2,5}$ have considered this equation under isochoric conditions.

6.3 - INTENSIVE AND EXTENSIVE VARIABLES

Thermodynamic parameters such as enthalpy H, and volume V, are defined by a number of different variables including temperature T, and pressure p. The precise definition of these variables is very important, especially when considering the nature of isochoric

reaction conditions. The importance of these variables can be shown by considering the Ideal Gas Equation,

$$pV = nRT$$
 (6.3.1)

This equation describes the relationship between four thermodynamic variables. These variables, or properties, can be either intensive or extensive.

Extensive variables are additive¹¹; the total value for an extensive variable being equal to the sum of all the values of that property within the entire system under consideration, regardless of the way in which it has been subdivided. This means that if the amount of substance within the total system is changed, then the extensive properties of the system will be changed proportionally¹². Examples of extensive variables are mass and volume.

Intensive variables are not additive, meaning that the value of any intensive variable can be measured at any point of a system that has attained equilibrium. Examples of such variables are temperature and pressure.

Returning to the Ideal Gas Equation we can define an equation for the molar volume¹³,

$$V_m^* = V/n = RT/p$$
 (6.3.2)

and we now find that V_m^* is an intensive variable as the ratio between any two extensive variables leads to an intensive variable.

6.4 - SOME APPROACHES TO CONSTANT VOLUME PARAMETERS

6.4.1 - Early Work

The suggestion made by Evans and Polanyi¹ that constant volume parameters were worthy of consideration were not immediately taken up. The first serious work in this area was carried out by Whalley and coworkers^{2,9,14-16}. Whalley² derived a number of equations for reactions involving the formation of a transition state at constant volume rather than at constant pressure.

Transition State Theory¹⁷ yields an equation for the rate constant k, of a one-step chemical

reaction at constant pressure in an ideal solution,

$$k = \kappa (k_{b}T/h) \exp (-\Delta \neq G^{o}/RT)_{p}$$
(6.4.1)

where κ is the transmission coefficient, k_b is Boltzmann's constant, h is Planck's constant and $\Delta^{\neq}G^{\circ}$ is the standard Gibbs energy of activation. For constant volume systems, equation (6.4.1) becomes,

$$k = \kappa (k_b T/h) \exp \left(-\Delta \neq F^{\circ}/RT\right)_{\star}$$
 (6.4.2)

where $\Delta \neq_{F^{\circ}}$ is the standard Helmholtz energy of activation. As the transition state will only be present in very low concentrations, Whalley states that,

$$\Delta^{\neq} G^{\circ} = \Delta^{\neq} F^{\circ} \tag{6.4.3}$$

In other words, the constant pressure and constant volume conditions are essentially the same. Equations (6.4.1) and (6.4.2) can be differentiated with respect to temperature at constant pressure or volume. An equally valid approach would be to differentiate these equations with respect to pressure or volume at constant temperature. Given that

 $(\partial G/\partial p)_{T} = V$ and $(\partial F/\partial p)_{T} = -p$, Whalley finds that,

$$(\partial \ln k / \partial p)_{T} = -\Delta^{\neq} V^{\infty} / RT$$
 (6.4.4)

where $\Delta^{\neq} V^{\infty}$ is the volume of activation. Differentiating with respect to volume gives,

 $(\partial \ln k / \partial V)_{T} = -\Delta^{\neq} p / RT$ (6.4.5)

where $\Delta^{\neq} p$ is the pressure of activation.

Whalley takes equation (6.4.4) as his starting equation as derived by Evans and Polanyi¹ for a one-step chemical reaction showing the effect of pressure on the rate constant k. Similarly for equilibrium constants K,

$$(\partial \ln K / \partial p)_{T} = -\Delta_{r} V^{\infty} / RT$$
 (6.4.6)

where $\Delta_r V^{\infty}$ is the standard volume of reaction. He then uses an operational equation to show relationships between a number of activation parameters at constant pressure or volume,

$$(\partial/\partial T)_{v} = (\partial/\partial T)_{p} + (\alpha/\kappa)(\partial/\partial p)_{T}$$
 (6.4.7)

where α is the isobaric thermal expansivity and κ is the isothermal compressibility. Any property that is pressure and temperature dependent only can be substituted into equation (6.4.7). Whalley substituted $\ln(k/T)$,

$$\left[\frac{\partial \ln (k/T)}{\partial T}\right]_{v} = \left[\frac{\partial \ln (k/T)}{\partial T}\right]_{p} + (\alpha/\kappa) \left[\frac{\partial \ln (k/T)}{\partial p}\right]_{m}$$
(6.4.8)

Equations (6.4.1) and (6.4.2) lead to,

$$[\partial \ln (k/T) / \partial (1/T)]_{p} = -\Delta^{\neq} H^{\infty} / R \qquad (6.4.9)$$

and,

$$[\partial \ln (k/T) / \partial (1/T)]_{v} = -\Delta^{\neq} U_{v} / R \qquad (6.4.10)$$

.

respectively. If these equations combined with equation (6.4.4), are substituted into equation (6.4.8) and the product multiplied by RT^2 , then the result is an equation

which links constant pressure and constant volume conditions,

$$(\Delta^{\neq_{\mathrm{H}^{\infty}}})_{\mathrm{p}} = \Delta^{\neq_{\mathrm{U}_{\mathrm{v}}}} + (\mathrm{T}\alpha\Delta^{\neq_{\mathrm{V}}}/\kappa)$$
 (6.4.11)

a11 of this work Whalley has In maintained 9,18 that the volume held constant is that of an equilibrium mixture of the initial and transition states i.e. an actual reaction volume. However, Whalley 14 did draw attention to a fact which needs to be considered when looking at constant volume parameters where the volume held constant is as described above. This consideration arises for reactions involving dilute solutions with formation of a transition state where a change in volume occurs. If the reaction is carried out under conditions of constant pressure then only the solvent in close vicinity to the transition state will be affected by the change in volume; the bulk of the solvent remaining unperturbed. Where conditions of constant volume of an equilibrium mixture are maintained, the entire solvent will have to undergo change to compensate for the change in volume as the transition state is formed.

At the same time as Whalley was studying constant volume activation parameters for equilibrium mixtures of initial and transition states, Williams³ was

concerned with constant volume parameters where the volume held constant was that of the activated complex. Thus for the generalised reaction,

$$A < --> A^{\neq} --> PRODUCTS$$
 (6.4.12)

the volume which is held constant is V_A^{\neq} . Regarding the equilibrium as an ideal system gives,

$$\Delta H(T;p) = H_A \neq (T;p) - H_A(T;p)$$
 (6.4.13)

and similarly,

$$\Delta V(T;p) = V_{A} \neq (T;p) - V_{A}(T;p)$$
 (6.4.14)

This leads to,

$$(\partial \ln k / \partial p)_{T} = -\Delta V(T;p) / RT$$
 (6.4.15)

and,

$$(\partial \ln k / \partial T)_p = -\Delta H(T;p) / RT^2$$
 (6.4.16)

In equation (6.4.12) it is assumed that the concentration of the activated complex A^{\neq} is very small compared to that of the reactant A. It therefore follows that the volume of the total system V_s , for the equilibrium reaction can be adequately approximated to V_A ,

$$dV_s = dV_A = (\partial V_A / \partial T)_p dT + (\partial V_A / \partial p)_T dP$$
 (6.4.17)

Williams uses these equations to show that the equilibrium can be expressed in terms of the standard states for A and A^{\neq} , and, therefore,

$$Q_{V_s}(T;V_s) = \Delta^{\neq} U^{\circ}(T;V_{A^{\neq}}) + 1/2RT$$
 (6.4.18)

where ${}^Q\!v_s$ is the constant volume activation energy and $\Delta \upsilon$ is the internal energy change. Brummer and Hills's 19 contention that,

$$Q_{V_s} = (\Delta^{\neq} U^{\circ})_{V_s}$$
 (6.4.19)

is, according to Williams, misleading. Williams states that this implies a transformation of A in its standard state to A^{\neq} at constant volume of the system. Williams's own analysis claims to show that $Q_{V_s}(T;V_s)$ in fact measures the formation of A^{\neq} from A where the volume held constant is that of A^{\neq} in its standard state. Hills and coworkers^{4,19,20} also studied constant volume systems and came to the conclusion that an element of caution was necessary when interpreting the results from such calculations.

Lown et al.⁵ measured partial molar volume changes for the ionisation of ethanoic acid and having derived some equations for constant volume thermodynamic parameters, used these results to calculate their isochoric parameters. However, they do not define the volume held constant.

6.4.2 - Comparison Between Constant Pressure and Constant Volume Reaction Conditions

The aim of many authors^{5,14,21} was to compare constant volume parameters with constant pressure parameters in an attempt to discover which set, if either, was the more fundamentally important. Reaction data¹⁴ were recorded and analysed in an attempt to justify the use of constant volume parameters over constant pressure parameters.

For many systems, constant volume parameters are theoretically simpler and more readily interpreted in terms of the reacting system itself and

Evans and Polanyi's¹ interactions within it. This was Adams²² contended for idea. that reactions original carried out under conditions where the volume remains constant, the intermolecular distances between reactants also remains constant as the temperature is changed. This means that the activation energy at constant volume does not contain a term that is dependent on the intermolecular properties of the solvent, but is made up of terms derived from the reaction process itself. However, $Adams^{22}$ went on to say that it was simplistic to say therefore that constant volume parameters were easier to understand than constant pressure ones as this relied on the idea that the solvent had no temperature-sensitive structure. Lown et al.⁵ also pointed out a possible pitfall. For isobaric equilibrium reactions, the Gibbs energy of activation will contain an energy contribution from the thermal expansion of the solution in addition to that due to the effect of temperature on the equilibrium. When the same reaction is studied under isochoric conditions. the system is prevented from expanding by applying pressure. This superficially makes the results easier to interpret, but it must be remembered that whenever the volume change for the reaction is non-zero, the pressure applied to maintain the isochoric state will alter the position of equilibrium.

The differences between isobaric and isochoric parameters revolve around one equation and derivatives thereof; equation (6.4.11). The term which gives rise to the differences between values calculated for isobaric and isochoric conditions is clearly the $T\alpha\Delta V^{\neq}/\kappa$ term. Whilst ΔV^{\neq} is frequently relatively small, the α and κ terms can be very large leading to enormous differences between the parameters for the different reaction conditions. Holterman and $Engberts^{21}$ reiterated the importance of electrostriction in reactions carried out at constant volume. In the case of a reaction with a large, negative ΔV^{\neq} , the electrostriction will also be large. This means that the solvent molecules far from the site of reaction will have to be expanded to compensate for the large electrostriction taking place during activation.

The general conclusion appears to be that neither the constant volume nor the constant pressure parameters can be said to be the more fundamental.

6.4.3 - Constant Solvent Concentration

A recent alternative approach to conditions of constant volume has been made by Albuquerque and Reis⁸. They agree with Blandamer et al.²³ that before studying isochoric reactions it is vital to clearly define what volume is being held constant. Their idea is to consider reactions under conditions of constant solvent concentration, this being isochoric (constant total volume) when suitable standard solutions are used.

The general procedure when studying reactions involving equilibrium formation is to carry the reaction out whilst keeping constant two intensive independent variables. Generally these variables are temperature and pressure. Hence,

$$X_{\rm B}(T;p) = (\partial X / \partial n_{\rm B})_{T,p,n'}$$
 (6.4.20)

where X is an extensive property of the system and n' is the total amount of all reactants excluding component B. Reis²⁴ showed that the condition of constant volume of the reacting system cannot be directly substituted for

pressure in the above equation as such a volume is an extensive variable. Instead, Reis called this a pseudo-partial molar quantity,

$$X_{B}'(T;V_{s}) = (\partial X/\partial n_{B})_{T,Vs,n'}$$
 (6.4.21)

where V_s is the volume of the reacting system. Albuquerque and Reis⁸ attempt to solve this problem by considering an iso-solvent-concentration reaction,

$$X_{B}(T;C_{A}) = (\partial X/\partial n_{B})_{T,C_{A},n'}$$
(6.4.22)

 C_A is the concentration of solvent A and is equal to n_A/V . This principle is applied to systems where solvent A does not take part in the reaction. Under such conditions Albuquerque and Reis claim that as $B \neq A$, the conditions (T;V;n') and $(T;C_A;n')$ become equal. They note however, that for reactions where solvent A is involved, the condition of iso-solvent-concentration will become one of constant-reaction-volume.

6.5 - CONSTANT MOLAR VOLUME OF PURE SOLVENT

Blandamer et $al^{6,23}$ first introduced the idea that the only meaningful isochoric volume could be to hold the molar volume of the pure solvent constant. Two

problems with other volumes which led to this decision were (a) volume is an extensive property whereas the normal reaction variables, temperature and pressure, are intensive; and (b) when equilibrium reactions are considered the system is at a minimum in Gibbs energy (i.e. fixed T and p) and not Helmholtz energy (i.e. fixed T and V). In introducing the idea of constant molar volume of pure solvent as the isochoric condition , Blandamer et al.^{6,23} introduced a new set of isochoric parameters to describe equilibrium and kinetic reactions. The aim of this chapter and the next, is to show that the isochoric volume has to be the molar volume of pure solvent, but to show this without having to use these complex new isochoric parameters.

Throughout these calculations, and in the next chapter where results will be considered, the solvent studied is water. By defining reaction conditions where the volume held constant is the molar volume of pure solvent, extrinsic isochoric parameters are being used, as with Blandamer et al.^{6,23}. An important point when using such a volume is that unlike reaction volumes which are extensive, the molar volume of pure solvent under the defined conditions is intensive. In this analysis these conditions are T = 298.2K and p = 101325 N m⁻².
The method used here is the determination of (T-p) pairs where the molar volume of the solvent is the same. e.g. $(T_1, p_1)^{V*}$, $(T_2, p_2)^{V*}$ This idea is extended in the next chapter to reaction data. Using equilibrium measurements of the dependence of $K^{\#}(aq;T;p)$ on T and p, thermodynamic properties of the system can be calculated for these extrinsic isochoric conditions. e.g. $\Delta_r v^{\infty}[aq;(T_1, p_1)]$, $\Delta_r v^{\infty}[aq;(T_2, p_2)]$

6.5.1 - Liquid Water

For a closed system containing n_1 moles of water, the volume can be given by,

$$V = V(T;p;n)$$
 (6.5.1)

V is extensive here. The molar volume V_1^* is intensive and is given by,

$$V_1^* = V_1^*(T;p)$$
 (6.5.2)

From results reported by Fine and Millero²⁵ the molar volume of water at 298.2K and 101325 N m⁻² can be calculated as $18.0683 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. From the equations reported in (Ref. 25), T-p pairs can be calculated at which V₁^{*} remains constant. These are shown in Figure 6.1.



<u>Figure 6.1</u> - Temperatures and pressures at which the molar volume of water is 18.068 x $10^{-6} \text{ m}^3 \text{ mol}^{-1}$. (N.B. - $p_g = 0 = 101325 \text{ N m}^{-2}$).

Equation (6.5.1) can be rewritten to define the pressure,

$$p = p(V;T;n_1)$$
 (0.3.3)

Consider a solution containing n_1 moles of water and n_j moles of added solute. Equation (6.5.1) becomes,

$$V = V(T;p;n_1;n_j)$$
 (6.5.4)

If the system contained αn_1 moles of water and αn_j moles of added solute-j, then the volume would equal αV . Therefore at fixed T and p,

$$\alpha V(n_1; n_j) = V(\alpha n_1; \alpha n_j)$$
 (6.5.5)

Using Euler's theorem,

$$V = n_1 V_1 + n_j V_j$$
 (6.5.6)

where,

$$V_1 = (\partial V / \partial n_1)_{T,p,nj}$$
 (6.5.7)

and,

$$V_{j} = (\partial V / \partial n_{j})_{T,p,n_{1}}$$
 (6.5.8)

.

 \mathtt{V}_1 and \mathtt{V}_j are partial molar volumes. This means that they are intensive variables and so,

$$V_1(T;p;\alpha n_1;\alpha n_j) = V_1(T;p;n_1;n_j)$$
 (6.5.9)

and similarly for V_j . If we now consider a chemical reaction where substance X is converted to substance P,

$$\Delta_{r} V = V_{p} - V_{x}$$
 (6.5.10)

For an ideal solution equation (6.5.10) becomes,

$$\Delta_{r} V^{\infty} = V_{p}^{\infty} - V_{x}^{\infty}$$
 (6.5.11)

If the reaction mixture contains n moles of X and n moles of P,

$$\Delta V = n \Delta_r V^{\infty}$$
 (6.5.12)

If P is in fact a transition state then,

$$\Delta V = n\Delta^{\neq} V^{\infty} = n [V_{\neq}^{\infty} - V_{x}^{\infty}]$$
 (6.5.13)

Equation (6.5.4) can be rewritten for pressures,

$$p = p(V;T;n_1;n_j)$$
 (6.5.14)

If the system contains αn_1 moles of water and αn_j moles of added solute-j, the pressure will not be αp as pressure is an intensive variable. This means that the above derivations for volumes do not apply for pressures meaning that there cannot be an activation pressure as proposed by Albuquerque and Reis⁸.

6.5.3 - Thermodynamic Functions

Two important thermodynamic equations which show the difference between intensive and extensive variables are,

$$dG = -SdT + Vdp - Ad\xi$$
 (6.5.15)

and,

$$dF = -SdT - pdV - Ad\xi$$
 (6.5.16)

where G is the Gibbs energy, F is the Helmholtz energy and A is the affinity for spontaneous chemical reaction. Consider a closed aqueous system where substance X reacts to form substance Y. When the system is at equilibrium, A = 0, and $d\xi/dt = 0$. At time t = 0, $n_x = n_x^0$ and $n_y = 0$; spontaneous reaction will lead to a decrease in G. The equilibrium condition will be a minimum in G, G^{eq} , with V^{eq} , H^{eq} , n_x^{eq} and n_y^{eq} . By changing T and/or p, the composition of the equilibrium mixture will change.

A similar case can be developed for the Helmholtz energy, equation (6.5.16). However, for this system, V and T are the defined variables and so p changes as the composition changes. When the system reaches a minimum in F, F^{eq} ', there will also be n_x^{eq} ', n_y^{eq} ' and p^{eq} '. Keeping T the same in both of the above examples, then by varying p in the first example and V in the second, it would be extremely unlikely that $n_x^{eq} = n_x^{eq}$ ' and $n_y^{eq} = n_y^{eq}$ '. From this it can be seen that the difference between isobaric (G) and isochoric(F) conditions are far more important than acknowledged by Whallev¹⁸.

Returning to the (T-p) pairs for an aqueous solution containing added solute-j, reference chemical potentials can be defined as $\mu_j^{*}[aq;(T_1,p_1)^{\vee}],$ $\mu_j^{*}[aq;(T_2,p_2)^{\vee}]$ etc

6.6 - DISCUSSION

Evans and Polanyi's¹ suggestion that constant volume parameters may be more readily interpreted than constant pressure parameters is an important one, but before results can be interpreted the correct constant volume must be found. Here, the volume used was the molar volume of the pure solvent. This is extrinsic to the reacting system and, as molar volume is intensive like T and p, it is far more valid than other $proposed^{2,3}$ volumes.

The advantage in studying isochoric systems than rather isobaric ones is that intermolecular separations remain constant. By studying reactions where the molar volume of solvent is kept constant, solventsolvent intermolecular separations will remain constant and so the role of the solvent bathing the solute molecules can be monitored. For example, when studying kinetic reactions, the effect of the solvent structure on the activation process can be studied. By comparing results obtained under isothermal/isobaric conditions with those obtained under isochoric conditions, mechanistic and solvent-related properties can be further probed. This will be developed in the next chapter.

6.7 - REFERENCES

1. M. G. Evans and M. Polanyi, Trans. Faraday Soc., 1935, 31, 875. 2. E. Whalley, Adv. Phys. Org. Chem., 1964, 2, 93. 3. G. Williams, Trans. Faraday Soc., 1964, 60, 1548. 4. G. J. Hills, P. J. Ovenden and D. R. Whitehouse, Disc. Faraday Soc., 1965, 39, 207. 5. D. A. Lown, H. R. Thirsk and Lord Wynne-Jones, Trans. Faraday Soc., 1970, 66, 51. 6. M. J. Blandamer, J. Burgess, B. Clark and J. M. W. Scott, J. Chem. Soc., Faraday Trans. I, 1984, 80, 3359. 7. P. G. Wright, J. Chem. Soc., Faraday Trans. I, 1986, 82, 2557. 8. L. M. P. C. Albuquerque and J. C. R. Reis, J. Chem. Soc., Faraday Trans I, 1989, 85, 207. 9. E. Whalley, Ber. Bung. Phys. Chem., 1966, 70, 958. 10. M. J. Blandamer, J. Burgess, H. J. Cowles, I. M. Horn, J. B. F. N. Engberts, S. A. Galema and C. D. Hubbard, J. Chem. Soc., Faraday Trans. I, 1989,85, 3733. 11. W. J. Moore, "Physical Chemistry", Longman, Great Britain, 1972. 12. S. Glasstone, "Textbook of Physical Chemistry", Mocmillan and Co. Ltd., London, 1956. 13. G. W. Castellan, "Physical Chemistry", 3rd. ed., Addison-Wesley Publishing Co., Reading, Mass., 1983.

14. B. T. Baliga, R. J. Withey, D. Poulton and E. Whalley, Trans. Faraday Soc., 1965, 61, 517. 15. B. T. Baliga and E. Whalley, J. Phys. Chem., 1967, 71, 1166. 16. D. L. Gay and E. Whalley, J. Phys. Chem., 1968, 72, 4145. 17. S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941. 18. E. Whalley, J. Chem. Soc., Faraday Trans. I, 1987, 83, 2901. 19. S. B. Brummer and G. J. Hills, Trans. Faraday Soc., 1961, 57, 1816. 20. G. J. Hills and C. A. Viana, "Hydrogen-Bonded Solvent Systems", ed. A. K. Covington and P. Jones, Taylor and Francis, London, 1968. 21. H. A. J. Holterman and J. B. F. N. Engberts, J. Am. Chem. Soc., 1982, 104, 6382. 22. W. A. Adams, Can. J. Chem., 1968, 46, 1989. 23. M. J. Blandamer, J. Burgess, B. Clark, R. E. Robertson and J. M. W. Scott, J. Chem. Soc., Faraday Trans. I, 1985,**81**, 11. 24. J. C. R. Reis, J. Chem. Soc., Faraday Trans. II, 1982,78, 1595. 25. R. A. Fine and F. J. Millero, J. Chem. Phys., 1973, **59**, 5529.

CHAPTER SEVEN

•

An Isochoric Study of Equilibrium and Kinetic Data

7.1 - INTRODUCTION

In the previous chapter, the possibility was considered of studying reactions under isochoric conditions rather than isobaric/isothermal conditions. This issue has been discussed by many authors¹⁻⁶ following the original suggestion made by Evans and Polanyi⁷. It has now been shown that the volume which must be held constant to satisfy thermodynamic requirements of standard states is the molar volume of the pure solvent^{4,5,8}.

In this chapter some equilibrium and kinetic data for reactions in aqueous solutions are examined with respect to isochoric and isothermal/isobaric conditions^{8,9}. Under isochoric conditions the solvent-solvent intermolecular distance remains constant. This means that the role of the solvent on activation or during the reaction can be discussed and thus le**ad.** to an alternative way of probing reaction mechanisms.

The chemical equilibria considered here are (1) dissociation of ethanoic acid; (2) ionisation of orthophosphoric acid; and (3) self-dissociation of water. The kinetic data describe (a) aquation of [Fe(5-Br-1,10-

phenanthroline)3]²⁺; (b) solvolysis of benzyl chloride; and (c) hydrolysis of two 1-acyl-1,2,4-triazoles. The data describe reactions in aqueous solution.

7.2 - ISOCHORIC STUDY OF EOUILIBRIUM DATA 7.2.1 - Theoretical Outline

As explained in Chapter Six, if the isochoric volume is the molar volume of pure solvent then a series of extrinsic equilibrium constants can be calculated for the isochoric (T-p) pairs, $K^{\#}[aq;(T_1;p_1)^{\vee}]$, $K^{\#}[aq;(T_2;p_2)^{\vee}]$. Related extrinsic isochoric thermodynamic parameters can also be calculated, including $\Delta_r H^{\infty}[aq;(T_1;p_1)^{\vee}]$, and $\Delta_r V^{\infty}[aq;(T_1;p_1)^{\vee}]$.

A Taylor expansion was used 10,11 to express the dependence of equilibrium constants on temperature T, and pressure p. The expansion uses a reference temperature θ , and a reference pressure π ,

$$lnK^{\#}(T;p) = lnK^{\#}(\theta;\pi) + a_{2}[(T-\theta)/\theta] + a_{3}[(p-\pi)/\pi] + a_{4}[(T-\theta)(p-\pi)/\theta\pi] + a_{5}[(T-\theta)^{2}/\theta^{2}]$$
(7.2.1)
+ $a_{6}[(p-\pi)^{2}/\pi^{2}] + a_{7}[(T-\theta)^{2}(p-\pi)/\theta^{2}\pi] + a_{8}[(T-\theta)(p-\pi)^{2}/\theta\pi^{2}]$

To obtain $\Delta_r H^{\infty}(T;p)$, equation (7.2.1) is differentiated with respect to T at fixed p. Similarly, differentiation of equation (7.2.1) with respect to p at fixed T generates $\Delta_r V^{\infty}(T;p)$.

A FORTRAN program was used to analyse the dependence of ln K[#] on temperature and pressure using equation (7.2.1). This led to the determination of lnK[#], $\Delta_r H^{\infty}$ and $\Delta_r V^{\infty}$ under extrinsic isochoric conditions for the three equilibrium mixtures studied. The FORTRAN program included the volumetric parameters calculated from equations reported by Fine and Millero¹² (see Chaper Six).

7.2.2 - Results and Discussion

The first system studied⁸ was the dissociation of ethanoic acid. Lown et al.³ measured the dependence of the acid dissociation constant for ethanoic acid on temperature and pressure. These data were analysed using the FORTRAN program and the results are given in Table 7.1.

Marshall and Frank¹³ and Covington et al.¹⁴ reported data for the water dissociation constant.

The results for the analysis using these data are reported

in Table 7.1.

parameter	HA(aq)	$H_2O(aq)$	H₃PO₄(aq)
<i>θ</i> /K	373.15	323.15	398.15
$\pi/10^5 \text{ N m}^{-2}$	401.01	501.01	1001.01
$a_1 = \ln K^{\bullet}(\theta, \pi)$	-11.1607	-30.2027	- 5.636
	± 0.0055	+0.0083	+0.017
a_2	-2.943	19.401	- 5.129
	± 0.026	± 0.058	+0.074
a ₃	0.2155	0.3420	0.0556
	± 0.0028	± 0.0041	± 0.015
a ₁	0.280	-0.378	0.373
	± 0.015	± 0.038	± 0.105
a ₅	- 5.16	-28.69	-0.735
	± 0.13	± 0.60	± 0.47
$a_{6}/10^{-3}$	-6.72	-12.57	-66.5
	± 0.46	± 0.54	26.9
a ₇	0.204	1.231	
	± 0.036	± 0.147	
$a_8/10^{-2}$	-1.26	2.13	
	± 0.23	± 0.50	
standard error/10-2	1.67	3.90	7.69
$\Delta_{r}H^{-}(\theta,\pi)/kJ \text{ mol}^{-1}$	-9.13	53.12	-16.98
$\Delta_r V^{-1}(\theta,\pi)/\mathrm{cm}^3 \mathrm{mol}^{-1}$	-16.7	-18.34	-18.37

<u>Table 7.1</u> - Calculated thermodynamic parameters for three equilibrium reactions using equation (7.2.1)

The final data used in this analysis to determine extrinsic isochoric parameters were first ionisation constants for the dissociation of orthophosphoric acid. The data used were reported by Read¹⁵. The results are given in **Table 7.1**.

Figure 7.1 shows the isobaric and isochoric equilibrium constants as a function of temperature for the three reactions studied. There are noticeable differences between the dependences for all three reactions, the value of lnK increases under isochoric conditions, this becoming more pronounced as the temperature increases. These plots show the role played by the solvent during the reaction. In these reactions ions are produced. Under isobaric conditions the volume of solvent increases with increase in temperature at fixed pressure. To hold the volume of the solvent constant and hence to conform to the isochoric condition, the pressure must increase. An increase in pressure disrupts water-water interactions. This disruption will favour processes which require strong solute-water interaction. For the reactions considered here this trend favours an increase in equilibrium constant K.

Figure 7.2 gives a comparison between the isobaric and isochoric plots for $\Delta_r H^{\infty}(aq)$ for the self dissociation of water. Here we can see that the two sets of conditions produce very similar trends but with a slightly smaller $\Delta_r H^{\infty}$ as discussed above for the isochoric condition. The differences in equilibrium constants under isobaric and isochoric conditions is, as expected, determined by the entropy terms.



Figure 7.1 - Temperature dependences under isobaric (-----) and isochoric (--) conditions in aqueous solutions for (a) dissociation of ethanoic acid; (b) first dissociation constant for orthophosphoric acid; and (c) self dissociation constant for water.



Figure 7.2 - Dependence of standard enthalpy of dissociation $\Delta_r H^{\infty}$ (aq) for the self dissociation of water on temperature under isobaric (----) and isochoric (---) conditions.

7.3 - ISOCHORIC STUDY OF KINETIC DATA

7.3.1 - Theoretical Outline

The dependence of rate constants on temperature and pressure was expressed using a Taylor expansion with a reference temperature θ , and pressure π ; equation (7.3.1),

$$[\ln k (T;p)/T] = \ln [k (\theta;\pi)/\theta] + a_2 [(T-\theta)/\theta] + a_3 [(p-\pi)/\pi] + a_4 [(T-\theta) (p-\pi)/\theta\pi] + a_5 [(T-\theta)^2/\theta^2] + a_6 [(p-\pi)^2/\pi^2]$$
(7.3.1)
+ $a_7 [(T-\theta)^2 (p-\pi)/\theta^2\pi]$

To take account of Transition State Theory the dependence of $\ln(k/T)$ on temperature and pressure, rather than that of lnk, was fitted to the Taylor expansion¹¹. The derived parameters were used to calculate $\Delta^{\neq}H^{\infty}$ and $\Delta^{\neq}V^{\infty}$ under extrinsic isochoric conditions. The analysis was carried out using a FORTRAN program.

7.3.2 - Results and Discussion (I)

The first kinetic reaction studied was the aquation of $[Fe(5-Br-phen)_3]^{2+}$ (where phen = 1,10-phenanthroline). This complex was prepared by mixing stoichiometric quantities of Iron(II) ammonium sulphate(aq) and 5-bromophenanthroline¹⁶.

This aquation reaction is first-order with the rate-determining step being the loss of the first substituted-phen ligand. 0.01 mol dm⁻³ EDTA was used to scavenge the Fe(II) centre to prevent the reverse reaction. The temperature dependence of the aquation reaction was measured spectrophotometrically at $\lambda_{max} = 512$ nm. The pressure dependence of the aquation reaction was measured as described in (Ref. 17). The results are given in Table 7.2.

T/K	$p/10^{5} \mathrm{N} \mathrm{m}^{-2}$	k/10 ⁻⁴ s ⁻¹
298.15	1.013	2.74
303.15	1.013	6.74
308.15	1.013	13.6
313.15	1.013	31.0
318.15	1.013	64.1
298.15	173.51	2.33
298.15	346.01	1.95
298.15	518.51	1.62
298.15	691.01	1.41
298.15	863.51	1.33
298.15	1036.0	1.10

<u>Table 7.2</u> - Kinetic data for the aquation of $[Fe(5-Br-phen)_3]^{2+}$ cations in aqueous solution.

These data were fitted to equation (7.3.1) and analysed using a FORTRAN program; see Table 7.3.

parameter	Fe ¹¹	$BzCl^a$	
θ/K	298.15	313.15	
$\pi/10^{5}$ N m ⁻²	518.5	501.01	
k/s^{-1}	1.478E-4	9.105E-5	
<i>a</i> ,	-14.452	-15.051	
	± 0.050	± 0.006	
<i>a</i> _a	33.54	33.653	
2	± 1.47	± 0.105	
<i>a</i> ₂	-0.4814	0.1834	
0	± 0.0309	± 0.0040	
<i>a</i> ,	-16.40	0.4136	^a Benzyl chloride.
4	± 0.95	± 0.0568	
<i>a.</i>		-46.308	
5		± 2.295	
$a_c/10^{-3}$		-4.18	
0,		± 0.62	
<i>a</i> _		3.39	
		± 1.45	
standard error/10 ⁻²	17.0	2.51	
$\Delta^{\neq} H^{\infty}(\theta, \pi)/\text{kJ} \text{ mol}^{-1}$	83.14	87.62	
$\Delta^{\neq} V^{\times}(\theta, \pi)/\mathrm{cm}^3 \mathrm{mol}^{-1}$	23.01	-9.5	

Table 7.3 - Calculated thermodynamic parameters for two kinetic

reactions using equation (7.3.1).

The second set of data examined described the solvolysis of benzyl chloride 18-20. These data were used to obtain thermodynamic parameters reported in Table 7.3.

The parameters reported in **Table 7.3** for the two kinetic reactions under consideration were used to yield the temperature dependence of the rate constants; Figure 7.3.

Figure 7.3 shows that for both systems as the temperature increases so the gap between the isobaric and isochoric plots increases. For the Iron(II) reaction, the transition state is more hydrophobic than the initial state as the large, hydrophobic substituted-phen ligands are pushed out into the surrounding medium on activation. At a given temperature the extent of water-water interaction decreases on going from isobaric to isochoric conditions. Therefore this disruption does not favour the expansion of the ligands into the solvent.



Figure 7.3 - Dependence of rate constants on temperature under isobaric (---) and isochoric (---) conditions in aqueous solutions for (a) aquation of $[Fe(5-Br-phen)_3]^{2+}$ cations; and (b) solvolysis of benzyl chloride.

The opposite trend emerges for the solvolysis of benzyl chloride. In this case activation involves a marked increase in solute-solvent interaction in terms of the developing chloride anion. Hence the solute becomes less hydrophobic on activation. At a given temperature, the rate **c**onstant increases on going from isobaric to isochoric conditions.

7.3.3 - Results and Discussion (II)

The second two kinetic reactions studied under extrinsic isochoric conditions were the hydrolysis reactions of two acyl triazoles, 1-acetyl-1,2,4-triazole (SUBSTRATE 1) and 1-benzoyl-3-phenyl-1,2,4-triazole (SUBSTRATE 2)²¹. Figure 7.4 shows the reaction mechanism of this hydrolysis reaction. The reaction involves nucleophilic attack by water at the carbonyl group. Figure 7.4 shows that the reaction is bimolecular with respect to water and trimolecular overall.

The dependences 21,22 of rate constants for acyl triazoles on temperature and pressure were fitted to equation (7.3.1) and the parameters obtained are reported in Table 7.4.



Figure 7.4 - Reaction scheme for the pseudo-first order hydrolysis reaction of substrates (1) and (2).

Parameter	Substrate (1)	Substrate (2)	
θ/Κ	298.15	298.15	
$\pi/10^8$ N m ⁻²	1.0015	1.0015	
	-11.118 ± 0.011	-11.675 ± 0.018	
	15.50 ± 0.60	17.18 ± 0.90	
<i>a</i> ₃	0.6821 ± 0.014	0.689 ± 0.021	
st. error	3.826×10^{-2}	4.96×10^{-2}	
$\Delta^{\ddagger} H^{\infty}(\theta; \pi)/\text{kJ mol}^{-1}$	38.68	42.59	
$\Delta^{\ddagger} V^{\infty}(\theta; \pi) / \mathrm{cm}^{3} \mathrm{mol}^{-1}$	-16.9	-17.06	

Table 7.4 - Calculated thermodynamic parameters for substrates (1) and (2) using equation (7.3.1).

The parameters reported in **Table 7.4** were used to obtain isobaric temperature dependent rate constants and extrinsic isochoric temperature dependent rate constants; **Figure 7.5**.

Figure 7.5 shows that the rate constants increase more rapidly under isochoric conditions as the temperature increases than under isobaric conditions.

Study^{21,23} of the reaction pathway of these acyl triazoles has shown that the transition state is less hydrophobic than the initial state. Hydrophobic solutes enhance water-water interactions. Therefore, the presence of strong water-water interactions will inhibit the hydrolysis reaction of these acyl triazoles, especially as



Figure 7.5 - Dependences of rate constants on temperature for (a) substrate (1); and (b) substrate(2), under isobaric (---) and isochoric (---) conditions.

water is also a reactant. As the temperature increases, the water-water interactions will be disrupted under isobaric and isochoric conditions. However, this disruption will be greater under isochoric conditions as the pressure must also be increased to maintain a constant molar volume. This increase in disruption of the water-water interactions observed for the isochoric case relative to the isobaric case will facilitate the hydrolysis reaction of the acyl triazoles and hence give the increased rate constant under isochoric conditions shown in **Figure 7.5**.

7.4 - DISCUSSION

The results discussed in this chapter show that if the isochoric volume is carefully chosen such that reference state conditions are fulfilled, then the results obtained by use of isochoric conditions can be very helpful in understnding the role played by the solvent in a reaction. The role of the solvent, water in the cases studied here, can be monitored for reactions under isochoric conditions as the solvent-solvent intermolecular distances will remain constant (as envisaged by Evans and Polanyi⁷). Whilst measurements made under isochoric conditions may not necessarily be more fundamental than

those obtained using conventional reaction conditions, the use of isochoric and isobaric reaction conditions together can lead to an insight into the role of the solvent in kinetic and equilibrium reactions.

7.5 - REFERENCES

1. E. Whalley, Adv. Phys. Org. Chem., 1964, 2, 93. 2. G. Williams, Trans Faraday Soc., 1964, <u>60</u>, 1548. 3. D. A. Lown, H. R. Thirsk and Lord Wynne-Jones, Trans. Faraday Soc., 1970, <u>66</u>, 51. 4. M. J. Blandamer, J. Burgess, B. Clark and J. M. W. Scott, J. Chem. Soc., Faraday Trans. I, 1984, 80, 3359. 5. P. G. Wright, J. Chem. Soc., Faraday Trans. I, 1986, 82, 2557. 6. L. M. P. C. Albuquerque and J. C. R. Reis, J. Chem. Soc., Faraday Trans. I, 1989, 85, 207. 7. M. G. Evans and M. Polanyi, Trans. Faraday Soc., 1935, <u>31</u>, 875. 8. M. J. Blandamer, J. Burgess, H. J. Cowles, I. M. Horn, J. B. F. N. Engberts, S. A. Galema and C. D. Hubbard, J. Chem. Soc., Faraday Trans. I, 1989, 85, 3733. 9. J. B. F. N. Engberts, J. Haak, M. J. Blandamer, J. Burgess and H. J. Cowles, J. Chem. Soc., Perkin Trans. II, 1990, 1059. 10. M. J. Blandamer, J. M. W. Scott and R. E. Robertson, J. Chem. Soc., Perkin Trans. II, 1981, 447. 11. M. J. Blandamer, R. E. Robertson, J. M. W. Scott and J. Burgess, Chem. Rev., 1982, <u>82</u>, 259.

12. R. A. Fine and F. J. Millero, J. Chem. Phys., 1973, <u>59</u>, 5529.

13. W. L. Marshall and E. U. Frank, J. Phys. Chem. Ref. Data, 1981, <u>10</u>, 295.

14. A. K. Covington, M. I. A. Ferra and R. A. Robinson, J. Chem. Soc., Faraday Trans. I, 1977, <u>73</u>, 1721.

15. A. J. Read, J. Sol. Chem., 1988, 17, 213.

M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A.
W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez,
C. D. Hubbard and E. -E. A. Abu-Gharib, J. Chem. Soc.,
Faraday Trans. I, 1986, <u>82</u>, 1471.

17. J. Burgess and C. D. Hubbard, J. Am. Chem. Soc., 1984, 106, 1717.

S. J. Dickson and J. B. Hyne, Can. J. Chem., 1971, <u>49</u>,
 2394.

19. R. Lohmuller, D. D. MacDonald, M. MacKinnon and J. B. Hyne, Can. J. Chem. 1978, <u>56</u>, 1739.

20. R. E. Robertson and J. M. W. Scott, J. Chem. Soc., 1961, 1596.

21. J. R. Haak, J. B. F. N. Engberts and M. J. BLandamer, J. Am. Chem. Soc., 1985, <u>107</u>, 6031.

22. J. R. Haak, unpublished results.

23. W. Karzijn and J. B. F. N. Engberts, Tet. Lett., 1978, 1787.

APPENDIX ONE

Experimental Section

Kinetic measurements were carried out using two minicomputer-controlled spectrophotometers. These spectrophotometers measured the change in absorbance at a given wavelength, and then analysed these data to give first order rate constants.

All rate constants discussed in this thesis were determined as first order. Equation (A.1) shows a typical first order reaction,

The integrated rate equation commonly used is ,

$$ln\{[R]_{O}/[R]_{t}\} = kt$$
 (A.2)

where $[R]_t$ is the concentration of reactant-R at time t, $[R]_O$ is the concentration of reactant-R at time t=0 and k is the first order rate constant. This equation can be rewritten as,

$$[R]_{t} = [R]_{0} exp(-kT)$$
 (A.3)

For second order reactions,

$$X + Y ----> P$$
 (A.4)

we have,

$$- d[X]/dt = k[X][Y]$$
 (A.5)

where k is the second order rate constant. If substance-Y is present in far higher concentrations than substance-X then the concentration of Y can be considered constant,

$$k_{ODS} = k[Y]$$
 (A.6)

where k_{ODS} is the observed first order rate constant. This equation becomes,

$$-d[X]/dt = k_{obs}[X]$$
 (A.7)

The reactions are monitored spectrophotometrically by measuring the change in absorbance as the reaction proceeds. Using the Beer-Lambert law,

$$P = \log(I_0/I_t) = \epsilon \lambda I[X]$$
 (A.8)

where P is the absorbance of substance X, I_0 is the intensity of the incident light at the monitored wavelength λ , I_t is the intensity of the transmitted light, ϵ_{λ} is the molar extinction coefficient of X at λ , and l is the path length. For the reaction solution described by equation (A.4), the total absorbance is given by,

$$P = \varepsilon_{X}[X] \mathbf{1} + \varepsilon_{Y}[Y] \mathbf{1}$$
 (A.9)

The reaction will be complete at $t = \infty$, and so equation (A.2) becomes,

$$\ln[(P_{O} - P_{\infty})/(P_{t} - P_{\infty})] = kt$$
 (A.10)

A non-linear least squares method¹ is used to solve equation (A.10).

Rearranging equation (A.10) gives,

$$P_t = (P_O - P_\infty) \exp(-kt) + P_\infty \qquad (A.11)$$

Hence at time t,

$$P_t = P_t[P_0; P_\infty; k]$$
 (A.12)

Differentiation of (A.12) gives,

$$dP = (\partial P_t / \partial P_0)_{P_{\infty}, k} dP_0 + (\partial P_t / \partial P_{\infty})_{P_0, k} dP_{\infty}$$
(A.13)
+ $(\partial P_t / \partial k)_{P_{\infty}, P_0} dk$

The partial differentials from equation (A.13) are,

$$(\partial P_t / \partial P_0)_{p_{\infty}}, k = \exp(-kt) = \alpha_1$$
 (A.14)

,

$$(\partial P_t / \partial P_\infty)_{p_0}, k = 1 - \exp(-kt) = \alpha_2$$
 (A.15)

$$(\partial P_t / \partial k)_{P_{\infty}, P_0} = -t (P_0 - P_{\infty}) exp(-kt) = \alpha_3$$
 (A.16)

Predefined estimates of P_0 , P_∞ and k are entered into the microcomputer prior to starting a kinetic run. At the predefined time interval t, P_t is measured and compared to the previous value of P_t ,

$$dP_t = P_t(obs) - P_t(calc)$$
 (A.17)

At each time-step t, the values $\alpha,\ \alpha_2$ and α_3 are calculated to improve the current fit.

$$Q = \Sigma (dP_t - \alpha_1 dP_0 - \alpha_2 dP_\infty - \alpha_3 dk)^2$$
 (A.18)

The aim is to minimise Q such that dQ/dX = 0,

$$dQ/dP_{0} = \mathbf{2}[\Sigma\alpha_{1}^{2}dP_{0} + \Sigma\alpha_{1}\alpha_{2}dP_{\infty} + \Sigma\alpha_{1}\alpha_{3}dk \qquad (A.19)$$
$$- \Sigma\alpha_{1}dP_{t}] = 0$$

$$dQ/dP_{\infty} = 2[\Sigma\alpha_1\alpha_2dP_0 + \Sigma\alpha_2^2dP_{\infty} + \Sigma\alpha_2\alpha_3dk \qquad (A.20) - \Sigma\alpha_2dP_t)] = 0$$

$$dQ/dk = 2[\Sigma\alpha_1\alpha_3dP_0 + \Sigma\alpha_2\alpha_3dP_\infty + \Sigma\alpha_3^2dk$$

$$- \Sigma\alpha_3dP_t)] = 0$$
(A.21)

This can be written as a matrix,

$$\begin{bmatrix} \Sigma \alpha_1^2 & \Sigma \alpha_1 \alpha_2 & \Sigma \alpha_1 \alpha_3 \\ \Sigma \alpha_1 \alpha_2 & \Sigma \alpha_2^2 & \Sigma \alpha_2 \alpha_3 \\ \Sigma \alpha_1 \alpha_3 & \Sigma \alpha_2 \alpha_3 & \Sigma \alpha_3^2 \end{bmatrix} \bullet \begin{bmatrix} dP_o \\ dP_{\infty} \\ dP_{\infty} \\ dR \end{bmatrix} = \begin{bmatrix} \Sigma \alpha_1 dP_t \\ \Sigma \alpha_2 dP_t \\ \Sigma \alpha_3 dP_t \end{bmatrix}$$
(A.22)

This matrix can be written as,

$$Y = X\beta$$
 (A.23)

Equation (A.23) is solved for β using a linear least squares method². Thus P_o, P_∞ and k are continually improved. This is repeated until Σ [P_t(obs) - P_t(calc)]² is a minimum or is of the same magnitude as the estimated experimental precision.

The first spectrophotometer used was a Pye Unicam SP 1800 UV/VIS spectrophotometer. Figure A.1 shows a block diagram of the spectrophotometer. Readings are taken at predefined t and λ . Reactions in up to three cells can be monitored simultaneously (all at the same λ). The spectrophotometer was connected to a HP 9825A minicomputer via a MIKE interface and a digital voltometer (where MIKE = Microprocessor Instrumentation of Kinetic Experiments). The system was controlled by a Hewlett Packard BASIC program written by Dr. M. J. Blandamer. At the calculated time interval an absorbance reading was made for each cell and at the end of the kinetic run the absorbance data were analysed as outlined above to yield the first order rate constant for each reaction cell. (N. B. - All cells were monitored for at least 2.5 half-lives.).

The cell block required thermostatting to ensure a constant temperature throughout the reaction. The



SP 1800 Spectrophotometer and HP 9825A Apparatus.
cell block was water-cooled using a coiled copper pipe around the outside and **monitor**ed using a platinum resistance thermometer. This was connected to a Wheatstone bridge coiled around an inner copper block.

The second spectrophotometer used was a Hewlett Packard 8451A diode array spectrophotometer. This is shown in Figure A.2. This was a single beam spectrophotometer operated by two microcomputers. The Z80 controlled the internal hardware and carried out the absorbance measurements. The HP85A handled the data. Light was provided by a deuterium lamp and the beam was focussed on the sample cell using an ellipsoidal mirror. The BASIC programs used to control the kinetic runs and analyse the resultant data were written by Dr. M. J. Blanadamer. The data were analysed using the non-linear least squares method¹ outlined above.

198



199

-

REFERENCES

1. P. Moore, J. Chem. Soc., Faraday Trans. I, 1972, <u>68</u>, 1890.

2. D. Z. Arbritton and A. L. Schmeltekoptf, "Modern Spectroscopy, Modern Research II", ed. K. N. Rao, Academic Press, New York, 1976.

APPENDIX TWO

-

Flow Diagrams

FLOW DIAGRAM OF KIRKWOOD-BUFF PROGRAMS



FLOW DIAGRAM OF ISOCHORIC PROGRAM

