The Thermodynamics of solutions

David Feakins, Fiona M. Canning, James J. Mullally and W. Earle Waghorne

Department of Chemistry, University College Dublin, Belfield, Dublin 4,
Republic of Ireland.

Abstract - This paper explores the relationship between thermodynamics and two
other types of investigation. Structure determinations by neutron diffraction
and computer simulation give a clear picture of first-shell solvation for a number
of cations in water. Replacement of a water molecule in the complex $M(H_2O)_n^+$ by
an organic ligand S in a mixed aqueous solvent $S-H_2O$ may result in distortion
which raises the free energy of transfer $(\Delta_t G^{\ominus})$ of the cation M^+ from water above
that expected from an unhindered base-line. The sequence of these deviations is
that predictable from the known geometries, i.e. $Li^+ > Na^+ > Cs^+ > Ag^+$, H^+. The
relative viscosities of solutions are examined by Transition-State Theory.
Electrolytes like CsCl lower the free energy, and markedly, the enthalpy and
entropy of activation for viscous flow of water, but do not necessarily break down
solvent structure as in the classical view. Enchanced co-ordination of solvent
to the ions could occur in a transition-state solvent more weakly structured and
bonded than the ground-state solvent. Enthalpies of transfer of the "hydrophobic"
solute tert-butanol in methanol-water mixtures suggest that TBA makes strong
solute-solvent bonds, but breaks solvent-solvent bonds. The large positive
activation parameters for viscous flow in highly aqueous mixtures suggest that
water encages this type of solute in the ground state, thereby enhancing the
solute-solvent interaction.

INTRODUCTION

Our basic thermodynamic process is the transfer of a solute between standard states in two
different solvents; it will be accompanied by changes in the free energy, $\Delta_t G^{\ominus}$, enthalpy,
$\Delta_t H^{\ominus}$, and entropy, $\Delta_t S^{\ominus}$, of the system, which reflect differences in the solvation of the
solute in the two solvents (ref. 1). Most of our solutes will be electrolytes. Most of
the transfers will involve binary aqueous mixtures. We shall first show how recent
structural studies (refs. 2 & 3) help us to understand steric influences on the free
energies of transfer, $\Delta_t G^{\ominus}$, of some simple electrolytes from water to mixed aqueous solvents.
We shall then discuss briefly a simple theoretical model (ref. 4) for the enthalpy of
transfer, $\Delta_t H^{\ominus}$, in binary solvent systems. Finally, we shall consider viscous flow (ref. 5).
This process played a crucial part in the development of the established models (refs. 6 &
7) for ions in solution. It can be treated quasi-thermodynamically, by Transition-State
theory (ref. 8). Our transfer quantities now involve something we call the transition-
state solvent. This access to an unusual type of solvent helps us to a clearer under-
standing of the solvation process.

STRUCTURES AND MODELS FOR IONS IN SOLUTION

A very significant recent development has been the use of neutron diffraction with isotopic
substitution by Enderby and others (ref. 9) to determine the geometries of ion-solvent
complexes in aqueous solution unambiguously. They can tackle many common ions, like Li^+
and Ca^{2+}, in this way. Sometimes, as with Na^+ and F^-, the method cannot be used because
suitable isotopes do not exist. Whilst a laboratory-based X-ray method linked to the
neutron technique is being developed for such cases (ref. 10) we can turn meanwhile to
computer simulation of the solution (ref. 3). Using comparatively simple intermolecular
potentials, Molecular Dynamics, for example, reproduces geometries known experimentally
and so gives reliable answers if none are experimentally available.

Some of this information is in Table 1; it relates to the lowest salt concentration for
which data are available. Co-ordination numbers (n) are taken to the nearest integer.

There is a very clear picture for Li^+ (ref. 12) which is co-ordinated by the oxygen atoms
of six water molecules. We also focus on Ca^{2+} (ref. 13) for which $n=10$. In both cases,
the distances between adjacent oxygen atoms in the complexes are about twice the

TABLE 1.   Structural data for ion-water complexes in aqueous solution

Ion	Pauling radius/Å	$\underline{n}$	M-O/Å	(O-O/Å)[a]	(O-M-O)[a]	Method
Li^+	0.60	6	1.95	2.76	$90°$	D
Ca^{2+}	0.99	10	2.46	2.80	$69.5°$ (mean)	D
Na^+	0.95	6	2.3_5	3.3	$90°$	$C^{[b]}$
K^+	1.33	6–8				D
		7				C
Cs^+	1.69	8	3.2	3.9	$74.5°$	C
Ag^+	1.26	4	2.41	3.94	$109.5°$	D
H_3O^+				~ 4.5	~$109.5°$	
Sr^{2+}	1.13	$\geqslant 10$	2.6	$\leqslant 2.9$	$\leqslant 69.5°$	A
Ba^{2+}	1.35	$\geqslant 10$	2.8	$\leqslant 3.2$	$\leqslant 69.5°$	A

[a] Based on standard geometries for circumscribing polyhedra, see ref. 11.
D – neutron diffraction, references in text;   C – computer experiments;
[b] calculated $\underline{n}$-values are means of figures given for Monte Carlo and
Molecular Dynamics methods in ref. 3.   A – figures for Sr^{2+} and Ba^{2+} are
by analogy to Ca^{2+}.

van der Waals radius of oxygen, i.e. 1.4Å, so that both ions are close-packed by the water
ligands. Na^+ has about the same ionic radius as Ca^{2+}, and so has space for about ten
water molecules too.   Yet, according to Molecular Dynamics (ref. 3) $\underline{n}$ is only 6.   Why is
this?   As well as the short-range forces between the ligands which determine their van
der Waals radii, there are longer-range electrostatic repulsions.   If we reduce the
charge on the central ion, the total attractive ion-molecule interaction energy is also
reduced.   The co-ordination number must then fall to reduce the ligand-ligand repulsion
energy, and the complex re-equilibrates at a lower value of $\underline{n}$.   There is a second factor,
particularly in a structured solvent like water: the ability of the ion, also charge-
related, to pull solvent molecules away from their attraction to other solvent molecules
in the bulk solvent.   Among common solvents, water, with its special three-dimensional
structure, is generally thought to be particularly able to resist the centrosymmetric
demands of the ion, and so limit $\underline{n}$.

Frank (ref. 7) however, went beyond the idea of a mere limitation of the centrosymmetric
region, proposing that outside it there is a "region B" in which the water structure is
actually broken down by the incompatible structural demands of the ion and the bulk water.
Region B, present for all, but particularly important for large, weakly polarising ions
like Cs^+, could explain a key fact of classical electrochemistry, namely that certain
electrolytes reduce the viscosity of liquid water.   Whether or not there is a region of
structural breakdown, and people are looking for it (refs. 2 & 14) we shall later show
that its existence is not in fact necessary to explain the viscosity phenomena.

With K^+ there is rapid exchange of solvent molecules between the ion complex and the bulk,
and the original paper (ref. 15) on the neutron diffraction experiments does not contain a
value of $\underline{n}$; the results are not inconsistent with an $\underline{n}$ value of 6–8 (ref. 16).   The value
of 8 for Cs^+ is from Molecular Dynamics.   Heinzinger (ref. 3) notes that the first
hydration shell is "less pronounced" than for the smaller alkali-metal ions; the nearest
neighbour oxygen atoms are distributed over a wider range of distances both radially and
over the ionic surface; the range of orientations of the ligands has also increased.

Ag^+ has a co-ordination number of 4, giving a very open structure around the ion (ref. 7).
The Ag-O distance corresponds to an ionic radius of about 1.0Å compared with the Pauling
value of 1.26Å.

Some thermodynamic consequences of structure.   We now examine some values of the free
energy of transfer, $\Delta_t G^{\ominus}$, of chlorides of univalent cations from water to methanol-water
mixtures (Table 2).   The cations are the alkali-metals, Ag^+ and H^+.   The values for
AgCl are important in what follows; they were obtained by e.m.f. measurements (ref. 21)
of the thermodynamic solubility products.

$\Delta_t G^{\ominus}$ in the alkali-metal series invariably increases from Li^+ to Na^+ and falls again from
Rb^+ to Cs^+.   The values for Ag^+ are just above those for Li^+; those for H^+ always lie
lowest.   Variations in these patterns with methanol content are small, as they are also

TABLE 2.   Free energies of transfer, $\Delta_t G^{\ominus}$/cal, molar scale, from water to methanol-water mixtures with radial parameters ρ_i/Å. (1cal = 4.184J)

% Methanol W/W	$\Delta_t G^{\ominus}$/cal							ρ_i/Å		
	HCl	LiCl	NaCl	KCl	RbCl	CsCl	AgCl	ρ_H	ρ_{Ag}	ρ_{Cs}
10	182	313	437	428	428	395	354	0.97	1.30	1.41
20	351	623	883	876	861	803	710	0.97	1.30	1.42
30	507	(940)	1328	–	–	–	1058	0.96	1.29	–
40	666	1268	1785	1804	1753	1651	1432	0.95	1.29	1.44
50	837	(1618)	2291	–	2279	2136	1885	0.95	1.32	1.45
60	1065	1992	2790	2866	2809	2683	2320	0.95	1.32	1.49
80	1883	2845	3968	4174	4167	4033	3480	1.01	1.38	–
							Means	0.97	1.31	1.44
								±0.02	±0.03	±0.03

Sources: HCl, see ref. 18;   alkali-metal chlorides, ref. 19;   AgCl, ref. 20.

for other basic co-solvents, for example dioxan and acetone (Table 3).

A simple acid-base theory (ref. 1) proposed that the organic molecule is a stronger Lewis base than water; by co-operative hydrogen-bonding it can to some extent transmit its basicity to the water molecules in the mixture so that all the molecules in the mixture are on average stronger bases than the water molecules in pure water.   The dominant cation-ligand interaction is electrostatic and lowers the free energy of the cation in the mixed solvent relative to its energy in water.   (The overall values of $\Delta_t G^{\ominus}$ for the chlorides are positive mainly because of the influence of the chloride ion (ref. 1)).

In a series of ions of closely related electronic structure, an electrostatic interaction of this type should be stronger the smaller the ion; this explains the relative values for Li^+ and Na^+.   The deviations of the larger ions from this pattern could be at least partly due to van der Waals interactions increasing in importance with the size of the ion.   In 1972 (ref. 19) we had a limited success in modelling these interactions.   Once again solubility data were valuable; we used the solubilities of the noble gases in methanol-water mixtures (ref. 26) to estimate the appropriate contributions to $\Delta_t G^{\ominus}$.   The upward drift of n from Li^+ to Cs^+, detected in the MD calculations for aqueous solutions, is also due to the increasing importance of these van der Waals interactions.   Interestingly enough, this will also tend to lower $\Delta_t G^{\ominus}$ for the larger ions by increasing the number of attractive electrostatic interactions.

TABLE 3.   Free energies of transfer, $\Delta_t G^{\ominus}$/cal, molar scale, from water to 20% (W/W) organic solvent-water mixtures. (1 cal= 4.4184 J)

20% (W/W) aqueous	HCl	LiCl	NaCl	KCl	RbCl	CsCl	AgCl
Methanol	351	623	883	876	861	803	710
Dioxan	427	631	755	778	778	734	639
Acetone	371	710	820	825	825	741	696
tert-Butanol (TBA)	433	910	1089	1065	1022	945	764
Dimethyl sulphoxide (DMSO)	25	282	509	523	514	501	82

Sources: refs. 22, 23, 24, 25.

Ag^+ (Table 3) appears to interact with the solvent ligands in two distinct ways.   The $\Delta_t G^{\ominus}$ of AgCl lie exceptionally low in DMSO- water, no doubt due to d_π-p_π interactions between Ag^+ and DMSO (ref. 25).   In the remaining systems, no multiple-bonding between ion and ligand is possible, but even here the interaction is stronger than with an alkali-metal ion of a similar size.   Twenty years ago, we attributed this (ref. 26) following Nyholm

(ref 27) to the relatively poor screening of the silver nucleus by the d-electrons.   Thus the strong silver-oxygen interaction, first detected thermodynamically, is now confirmed in the short Ag-O distance which has been found for the aqueous complex.

Steric hindrance.   A powerful connection between structure and thermodynamics is seen in the effects of steric hindrance on solvation (ref. 28).   Consider a cation in an alcohol-water mixture.   Molecular models show that even for the smallest ion, Li^+, there is no steric problem about replacing one or more of the water molecules in the aqueous complex by methanol molecules.   However, replacement of water in the lithium complex by tert-butanol (TBA) is impossible without severe steric strain.   Any method of relieving that strain will raise the free energy of the ion relative to a hypothetically unhindered state. For example, the ion could adopt predominantly aqueous complexes.   However even if there is some averaging of basicities over the components of the mixtures, the stronger ion-molecule interaction is likely to be with the alcohol;   in addition, even if preferential solvation is neutral enthalpically, it is disfavoured entropically.

To investigate this quantitatively we begin with the strongly interacting ions Li^+, Na^+, Ag^+ and H^+.   The van der Waals interactions (ref. 19) are small for Li^+ and Na^+ so that their interactions are mainly electrostatic and can be treated by the simple "acid-base" theory (ref. 1).   This gives the leading term in the free energy of transfer (ref. 28) as $-N_A \Delta q \underline{n} (z e) R^{-1}$.   The charge on the ion is $z e$:   we take $z = 1$ for Li^+ and Na^+ and $z > 1$ for a poorly shielded univalent ion.   The ionic charge is separated by a distance R from the effective charge $\underline{q}$ in the ligand lone-pair orbital, which changes by Δq when the ion is transferred. $R = \underline{r}_i + \delta$, where $\underline{r}_i$ is the Pauling radius and $\delta = 0.6\text{Å}$; δ here is based on the ST2 model of water used in the MD calculations;   its exact value is not critical.   Thus we can write equation (1).

$$\Delta_t G^{\ominus}(MCl) = -\underline{N_A} \Delta \underline{q} \, \underline{n} \, (\underline{z} \, e) \underline{R}^{-1} + \underline{b} \tag{1}$$

where $\underline{b}$ includes any terms in $\Delta G^0(M^+)$ that are independent, or nearly independent of $\underline{R}$, as well as $\Delta_t G^{\ominus}(Cl^-)$. Li^+ and Na^+ have the same $\underline{n}$ and $\underline{z}$ so we can put

$$\Delta_t G^{\ominus}(MCl) = -\underline{a} \, \underline{R}^{-1} + \underline{b} \tag{2}$$

and so determine $\underline{a}$ and $\underline{b}$.   Now $\underline{z}$ would be uncertain for Ag^+, and $\underline{n}$ and $\underline{R}$ for H^+, so we bring these ions into correspondence with Li^+ and Na^+ by assigning radial parameters ρ determined from $\underline{a}$, $\underline{b}$ and $\Delta G^{\ominus}_t(MCl)$ using equation (3)

$$\Delta_t G^{\ominus}(MCl) = -\underline{a}\rho^{-1} + \underline{b}. \tag{3}$$

We find that essentially the same radial parameter for H^+ fits the data for HCl over the range 0-80% methanol;   the same is true for Ag^+;   we show these parameters in Table 2. Though not as reproducible as that of the smaller ions, the behaviour of the larger alkali-metal ions in this respect is also more consistent than we would have expected. This is particularly so for Cs^+, so we include radial parameters for it in Table 2.

Steric crowding when ions are transferred to mixed solvents with bulky organic ligands is more likely the shorter the distance, O-O, between, and the smaller the angle subtended at the ionic nucleus, O-M-O, by the oxygen atoms of adjacent ligands.   Thus among monovalent ions the close-packed Li^+ will be especially vulnerable, but Ag^+ and H^+ (as H_3O^+ or SH^+) with low $\underline{n}$ and high O-O and O-M-O, particularly invulnerable to such crowding.   We note especially that, though Cs^+ is larger than Ag^+, its high $\underline{n}$ gives it about the same O-O and a lower O-M-O, making it the more vulnerable to crowding (Table 1).

Figure 1 shows plots of $\Delta_t G^{\ominus}$ against ρ^{-1} for 20% (W/W) aqueous mixtures of three organic components;   these are representative of many data for other solvent compositions.   In the methanol-water system all points are collinear by definition.   When the organic ligand is the bulkier acetone, the points for H^+, Ag^+, Na^+ and Cs^+ chlorides are collinear, with that for LiCl strongly displaced in a positive direction, indicating some steric hindrance to solvation of Li^+ by acetone.   If in the TBA-water system we take the line joining the points for AgCl and HCl as defining an unhindered baseline, then the points for NaCl and CsCl also lie above it, the displacements indicating steric hindrance in the expected order $Li^+ > Na^+ > Cs^+$.

Rather more detailed examination (ref. 28) is required if the effects are relatively small, as in the dioxan-water system;   however, reference to Table 2 shows that $\Delta_t G^{\ominus}(LiCl)$ shifts to a higher value relative to $\Delta_t G^{\ominus}(AgCl)$ as methanol is replaced by dioxan, thus showing some steric hindrance to solvation of Li^+ by dioxan;   the trend continues in the order methanol < dioxan < acetone < TBA.

The simple theory outlined above would predict that $\frac{1}{2}\Delta_t G^{\ominus}(MCl_2) < \Delta_t G^{\ominus}(MCl)$ for chlorides of alkaline-earth and alkali-metal ions of the same radius, since the alkaline-earth ions have
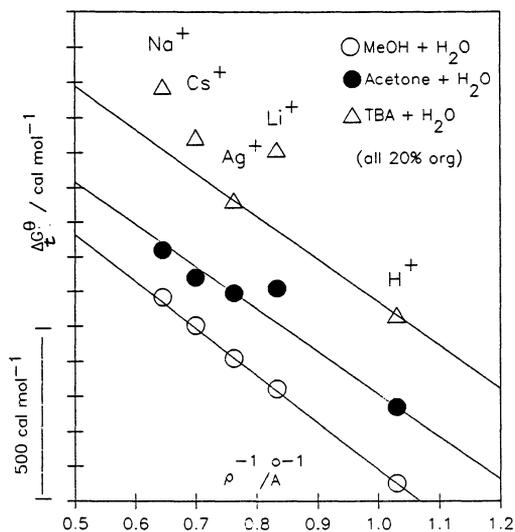
Fig.1. Free energy of transfer, $\Delta_t G^\ominus$, of chlorides vs ρ^{-1}
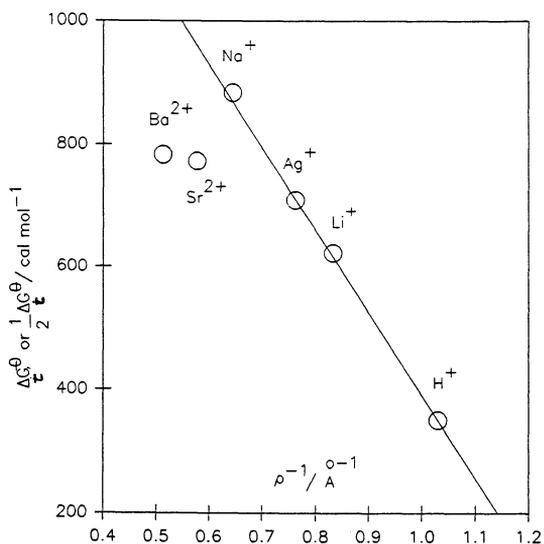
Fig.2. $\Delta_t G^\ominus$ (MCl) or $\frac{1}{2} \Delta_t G^\ominus$ (MCl$_2$) vs ρ^{-1} for 20% methanol + water
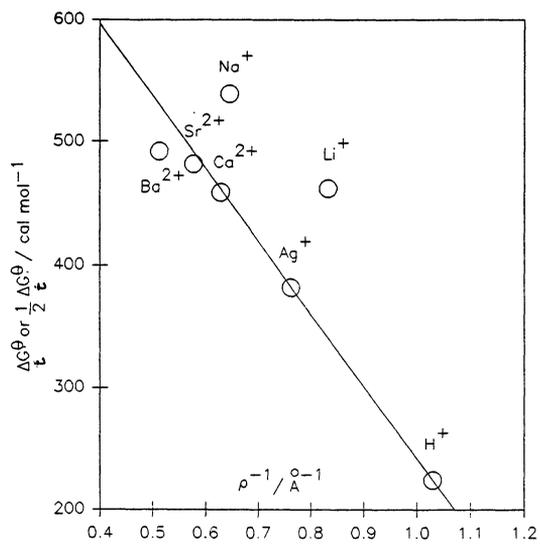

Fig.3. $\Delta_t G^\ominus$ or $\frac{1}{2} \Delta_t G^\ominus$ (MCl$_2$) vs ρ^{-1} for 10% TBA + water
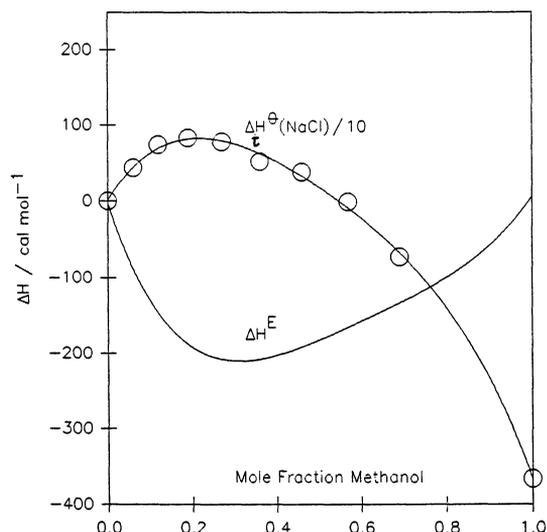
Fig.4. Enthalpy of transfer, $\Delta_t H^\ominus$ and of mixing, ΔH^E for methanol + water

the larger $\underline{n}$ (Table 1). In the unhindered situation in 20% methanol-water, the points for the alkaline-earth ions do, in fact, lie well below those for the monovalent ions (Fig. 2). If Li$^+$ and Na$^+$ are both hindered, then Ca^{2+}, Sr^{2+} and Ba^{2+} which all have O-O distances less than those in Na$^+$, and small O-M̂-O (Table 1) must also be. In the corresponding plot for TBA-water (Fig. 3) the points for the alkaline-earth chlorides now lie on, or only slightly below, the Ag$^+$-H$^+$ line.

THE ENTHALPY OF TRANSFER. A MODEL FOR $\Delta H^\ominus$ (ref. 4)

When a solute (3) enters a solvent (1) it changes the solvent-solvent interactions if only because it breaks solvent-solvent bonds to make a cavity for itself. The resulting enthalpy change we call $\Delta \underline{H}_{11}^\ominus$. The solute then interacts with each solvent molecule in its new position, giving the enthalpy change $\Delta \underline{H}_{13}^\ominus$. The enthalpy of solvation is the sum of these two contributions

$$H^\ominus = \Delta \underline{H}_{11}^\ominus + \Delta \underline{H}_{13}^\ominus. \tag{4}$$

We interpose here the Compensation Principle (ref. 29) which often enables us to simplify our discussions. When we treat free energy functions, it states that the solvent-solvent contribution to the enthalpy change is approximately compensated by the corresponding contribution to the entropy change, equation (5)

$$\Delta \underline{G}^{\ominus}_{11} = \Delta \underline{H}^{\ominus}_{11} - T\Delta \underline{S}^{\ominus}_{11} \approx 0. \tag{5}$$

The free energy change is thus dominated by the solute-solvent or (1,3) interactions.

Let us return to the term $\Delta \underline{H}^{\ominus}_{11}$. To make a cavity for the solute we must break solvent-solvent bonds. If $\Delta \underline{H}^{\ominus *}_{11}$ is the molar enthalpy of intermolecular bonding then the increase in enthalpy on cavity formation is $-\alpha \underline{n} \Delta \underline{H}^{\ominus *}_{1}$. $\Delta \underline{H}^{\ominus *}_{1}$ is negative and is the molar enthalpy of vaporisation of the liquid to zero pressure with the sign reversed. The number of nearest neighbours of the solute is $\underline{n}$ and α is the fraction of bonds broken by each solvent molecule. A similar term $\beta \underline{N}$ takes care of any further making or breaking of bonds in all shells affected by the ion, thus

$$\Delta \underline{H}^{\ominus}_{11} = -(\alpha \underline{n} + \beta \underline{N})\Delta \underline{H}^{\ominus *}_{1}. \tag{6}$$

Suppose now we consider the transfer of a solute from water (1) to mixtures of methanol (2) with water. The average strength of the intermolecular bonds in the mixture will clearly be related to the strengths of those in pure liquids, $\Delta \underline{H}^{\ominus *}_{1}$ and $\Delta \underline{H}^{\ominus *}_{2}$, through the enthalpy of mixing ΔH^{E}. If we assume that (i) $(\alpha \underline{n} + \beta \underline{N})$ is independent of solvent composition (ii) there is no preferential solvation and (iii) the "ion-solvent" interactions are linear in $\underline{x}_2$, the mole fraction of the alcohol, we derive equation (7) for the enthalpy of transfer

$$\Delta_t H^{O} = \underline{x}_2 (\Delta \underline{H}^{\ominus}_{23} - \Delta \underline{H}^{\ominus}_{13}) - (\alpha \underline{n} + \beta \underline{N})\Delta \underline{H}^{E} + \underline{x}_2 (\alpha \underline{n} + \beta \underline{N})(\Delta \underline{H}^{\ominus *}_{1} - \Delta \underline{H}^{\ominus *}_{2}). \tag{7}$$

In this equation there are two unknowns, which can be obtained by curve-fitting; these are $(\Delta \underline{H}^{\ominus}_{23} - \Delta \underline{H}^{\ominus}_{13})$ and $(\alpha \underline{n} + \beta \underline{N})$.

Equation (7) explains very well the main features of the enthalpies of transfer of the alkali-metal halides in the methanol-water system (ref. 4), which is one for which the assumptions made are likely to be reasonable approximations. First $(\alpha \underline{n} + \beta \underline{N})$ ranges from about 6 for chlorides to 10 for iodides; these positive values indicate that a net breaking of solvent-solvent bonds is required if a cavity for the solute is to be formed. Second, $H^{\ominus}$ for NaCl as a function of $\underline{x}_2$ has a maximum (Fig. 4) which is often discussed from a structural standpoint. However, casting equation (7) in the form

$$\Delta_t H^{\ominus} = \underline{a}\underline{x}_2 - \underline{b}\Delta \underline{H}^{E}$$

shows that the maximum in $H^{\ominus}$ merely reflects the minimum in $\Delta \underline{H}^{E}$, also sketched in Fig. 4, and may have no other significance.

The analysis is not always as simple as this. We have analysed a number of systems using an extended equation which allows for preferential solvation; and it would appear, for example, that the n-propanol-water system must be divided into two ranges, "aqueous" and "non-aqueous", having different properties and fitting parameters (ref. 30).

We can use the simpler methanol-water system to see what our measurements, first calorimetric and later viscometric, tell us about another classical problem of solution chemistry, namely the so-called hydrophobic effect. Just as Frank (ref. 7) thought that caesium ions "melted" water, he also suggested that water structure was enhanced or "frozen" around alkyl groups. As solute we used a non-electrolyte, tert-butyl alcohol (TBA) and found that a value of $(\alpha \underline{n} + \beta \underline{N})$ of around 16 will fit the enthalpy of transfer over the whole range of solvent composition (ref. 31). Yet this value poses a problem.

First, there is a net breaking, not making, of solvent-solvent bonds as the solute enters the liquid. Quantitatively, the enthalpy required to make a suitable cavity in water as solvent is given by $-(\alpha \underline{n} + \beta \underline{N})\Delta \underline{H}^{\ominus *}_{1}$ and is about 170 kcal per mole if $(\alpha \underline{n} + \beta \underline{N})$ is 16. Yet the enthalpy of solvation is only -15 kcal. This means that we must find an attractive interaction equivalent to about 185 kcal to offset this value of $\Delta \underline{H}^{o}_{11}$. According to equation (4) this can only come from a (1,3) interaction between the solute and the solvent molecules. Presumably this is of the van der Waals type. An approximate cancellation of the solute-solvent $(\Delta \underline{H}^{o}_{13})$ and solvent-solvent $(\Delta \underline{H}^{o}_{11})$ terms in equation (4) in not unreasonable since the solvent-solvent interactions between $\underline{n}$ pairs of solvent molecules that disappear in making the cavity will be replaced by an equal number of interactions between the solute and the $\underline{n}$ nearest neighbour solvent molecules. There is in these results then no evidence for "freezing" of the solvent around the alkyl groups, or indeed for any particular structural role for the solvent; however, we may discover the latter when we examine the viscosity results.

VISCOSITY

Classically the tendency for large singly charged ions to decrease the viscosity of water seemed to require, as we have already indicated, the notion that they break down solvent structure. It is timely to ask whether this is the only explanation or whether indeed it is a reasonable explanation at all.

Precise measurements of the relative viscosities η_r of solutions yield the Jones-Dole $\underline{B}$-coefficient from equation (8)

$$\eta_r = 1 + \underline{A}\,\underline{c}^{\frac{1}{2}} + \underline{B}\,\underline{c}. \tag{8}$$

The $\underline{B}$-coefficient is difficult to use in precise argument. It is, however, easily related to the quasi-thermodynamic treatment of Eyring (ref. 8). In Eyring's simple model the molecules move one-by-one from their equilibrium positions through their transition states, in which intermolecular bonds are stretched, to other equilibrium positions. For a pure liquid he found the equation

$$\eta_1 = (h\,\underline{N}_A/\bar{\underline{V}}_1)\,\exp\,(\Delta\underline{G}_{-1}^{\ddagger}/\underline{R}\,\underline{T}) \tag{9}$$

In equation (9), $\bar{V}_1$ is the molar volume of the liquid and $\Delta\underline{G}_1^{\ddagger}$ the free energy of activation.

When a solution flows, both the solute (3) and the solvent (1) molecules move under the shearing force. At high dilution of the solute, we can write eqn (10) for the activation energy per mole of solution,

$$\Delta\underline{G}_{13}^{\ddagger} = \underline{x}_1\Delta\mu_1^{o\ddagger} + \underline{x}_3\Delta\mu_3^{\ominus\ddagger} \tag{10}$$

We identify $\Delta\mu_1^{o\ddagger}$ with $\Delta\underline{G}_1^{\ddagger}$, the free energy of activation of the _pure_ solvent, so that $\Delta\mu_3^{\ominus\ddagger}$ as _defined_ by equation (10) includes any change in the free energy of activation of the solvent molecules caused by the presence of the solute, as well as a contribution from the movement of the solute itself.

The $\underline{B}$-coefficient is related to $\Delta\mu_3^{\ominus\ddagger}$ by equation (11)

$$\underline{B} = \frac{\nu\bar{\underline{V}}_1^{o} - \bar{\underline{V}}_3^{o}}{1000} + \frac{\bar{\underline{V}}_1^{o}}{1000\,\underline{R}\,\underline{T}}\left[\Delta\mu_3^{\ominus\ddagger} - \nu\Delta\mu_1^{o\ddagger}\right] \tag{11}$$

The $\bar{V}$ are partial molar volumes; $\nu = 1$ for a non-electrolyte, 2 for a (1,1) electrolyte and so on; it was incorrectly omitted from the original formulation (ref. 34).

Table 4 gives values of $\Delta\mu_3^{\ominus\ddagger}$ for alkali-metal chlorides in water and dimethylsulphoxide (DMSO) as a typical non-aqueous solvent. The criterion for a positive B-coefficient is $\Delta\mu_3^{\ominus\ddagger} > 2\Delta\mu_1^{o\ddagger}$ and conversely for a negative B-coefficient. In aqueous solution $\Delta\mu_3^{\ominus\ddagger} < 2\Delta\mu_1^{o\ddagger}$ for the chlorides of K$^+$, Rb$^+$ and Cs$^+$, but in DMSO all the electrolytes have positive $\underline{B}$-coefficients and $\Delta\mu_3^{\ominus\ddagger} > 2\Delta\mu_1^{o}$. In water the enthalpic and entropic contribution to the corresponding parameters for the solution are almost uniformly negative; in DMSO they are all positive.

The transition-state solvent (ref. 5). Every solvent molecule in one mole of solution interacts more or less strongly with the solute. Each solvent molecule must pass through the transition state, in which it must also interact with the solute. A contribution to the activation energy therefore arises from the interaction of the solute with every solvent molecule in its transition state; this is equivalent to the interaction of the solute with a transition-state solvent whose thermodynamic and structural properties differ from those of the ground state solvent. For example, the enthalpy of activation for viscous flow of water is 3.86 kcal mol^{-1} compared with an enthalpy of vaporisation of 10.52 kcal mol^{-1}, so that on average 37% of the intermolecular bonds present in the ground state have been broken down in the transition state. Thus, $\Delta\mu_3^{\ominus\ddagger}$ contains the free energy of transfer of the solute from the ground- to the transition-state solvent. It will also contain another term. When the ion itself moves through the transition state the probability that any of the solvent molecules will be independently in its transition-state is small, so the ion moves effectively in a solvent unperturbed by external fields, as in conductivity or self-diffusion. The parallel with these processes would place the contribution to $\Delta\mu_3^{\ominus\ddagger}$ in a very narrow range, around 3-4 kcal mol^{-1} for most singly charged ions and small non-electrolytes in water. The specificity in the behaviour of the alkali-metal chlorides in water must therefore arise from the transfer of the electrolyte from the ground- to the transition-state solvent. Since the diffusive-type of contribution to $\Delta\mu_3^{\ominus\ddagger}$, say about 6 kcal mol^{-1} for a binary electrolyte, is greater than $\Delta\mu_3^{\ominus\ddagger}$ for KCl, RbCl and CsCl the transfer term is actually negative for these electrolytes.

If the Compensation Principle is correct, trends in $\Delta\mu_3^{\ominus\ddagger}$ cannot be explained in terms of changes in solvent-solvent interactions as in the Frank and Wen model. This suggests the following mechanism for ions like caesium. The structural resistance to the co-ordination

TABLE 4.   B-coefficients and solute contributions to the activation parameters for viscous flow for alkali-metal chlorides at 25°C.

	Solvent: Water			
	B/dm^3mol^{-1}	$\Delta\mu_3^{\ominus\ddagger}$/kcal	$\Delta\bar{H}_3^{\ominus\ddagger}$/kcal	$T\Delta\bar{S}_3^{\ominus\ddagger}$/kcal
LiCl	0.143	8.45	$8._1$	$-0._4$
NaCl	0.079	6.31	$-3._2$	$-9._5$
KCl	-0.014	3.62	-16	-20
RbCl	-0.037	3.0_4	-18	-21
CsCl	-0.049	2.9_2	-18	-21
	$2\Delta\mu_1^{\ominus\ddagger}$/kcal	$2\Delta\bar{\underline{H}}_1^{\ominus\ddagger}$/kcal	$2T\Delta\underline{S}_1^{\ominus\ddagger}$/kcal	
$2H_2O$	4.38	7.7_2	3.3_4	

	Solvent: DMSO			
	B/dm^3mol^{-1}	$\Delta\mu_3^{\ominus\ddagger}$/kcal	$\Delta\bar{\underline{H}}_3^{\ominus\ddagger}$/kcal	$T\Delta\underline{\bar{S}}_3^{\ominus\ddagger}$/kcal
LiCl	0.866	13.04	$24._3$	$11._4$
NaCl	0.792	12.52	$25._3$	$12._8$
KCl	0.802	12.64	$23._9$	$11._3$
RbCl	0.781	12.52	$22._0$	$9._5$
CsCl	0.750	12.31	$21._8$	$9._5$
	$2\Delta\mu_1^{\ominus\ddagger}$/kcal	$2\Delta\bar{\underline{H}}_1^{\ominus\ddagger}$/kcal	$2T\Delta\underline{\bar{S}}_1^{\ominus\ddagger}$/kcal	
2DMSO	7.96	6.2	-0.6	

Sources: see ref. 33.   Figures for the activation parameters will differ from earlier tabulations because of different bases of calculation (see text).

of ions in the ground-state of water is decreased in the more weakly bonded transition-state solvent.   This leads to an increase in the co-ordination of the ion, whether by an actual increase in its co-ordination number, or by a reduction of the rotational freedom of the co-ordinated molecules.   This strengthens the ion-solvent interaction and lowers the free energy, enthalpy and entropy in the transition state, as observed.

In this bond-making mechanism, the ion is seen as bridging the motion of a solvent molecule from one equilibrium site to another.   It is likely, though, that even in the field of the Cs^+ ion, some solvent molecules break ion-solvent bonds when they move.   Such an ion-solvent bond-breaking mechanism will be dominant for a strongly polarising ion like Li^+ which has less scope for increasing its co-ordination in the transition state.

The remarkable uniformity of the activation parameters for all the electrolytes in DMSO is consistent with the idea that such a solvent offers little structural resistance to ground-state co-ordination of the ions.   There is therefore little further scope for bond-making in the transition-state, which is reached by bond-breaking in all cases.

Mixed solvents.   Here we shall concentrate on some of the simpler and more striking aspects.   We have seen (Fig. 4) that the enthalpy of mixing, ΔH^E, is a minimum at a mole fraction of alcohol x_2 about 0.3.   This, and other evidence suggested to Ives (ref. 33) that the alcohol enhances the structure of water up to this composition, after which there is a breakdown to a structure of lower order.   For the present purpose we can make a simpler structural assumption, that when methanol is added to water, a three-dimensional water-like structure is at least maintained over the early part of the range of solvent composition.

The viscosity behaviour of CsCl in this system (Fig. 5) is consistent with this postulate (ref. 34).   Up to about x_2 = 0.16, $\Delta\mu_3^{\ominus\ddagger}$ remains at or below the value in pure water; this indicates that the mixed solvents can still resist the formation of centrosymmetric structure in the ground-state solvent, and can lower $\Delta\mu_3^{\ominus\ddagger}$ by ion-solvent bond-making in the transition state.   At higher methanol concentrations the value of $\Delta\mu_3^{\ominus\ddagger}$ rises steadily towards the sort of values characteristic of non-aqueous solvents.
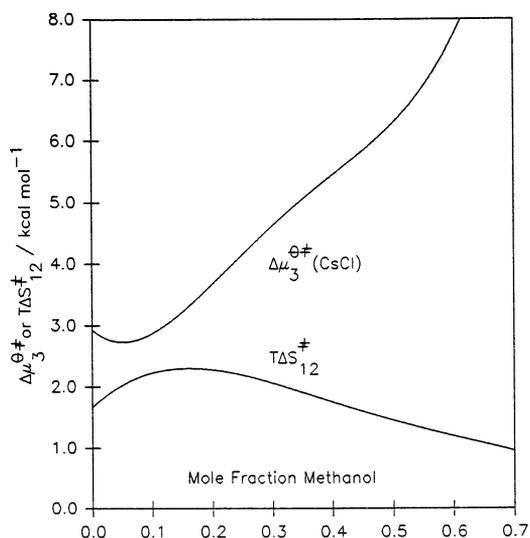
Fig.5. $\Delta\mu_3^{\theta\ddagger}$(CsCl) and $T\Delta S_{12}^{\ddagger}$ for viscous flow in methanol + water
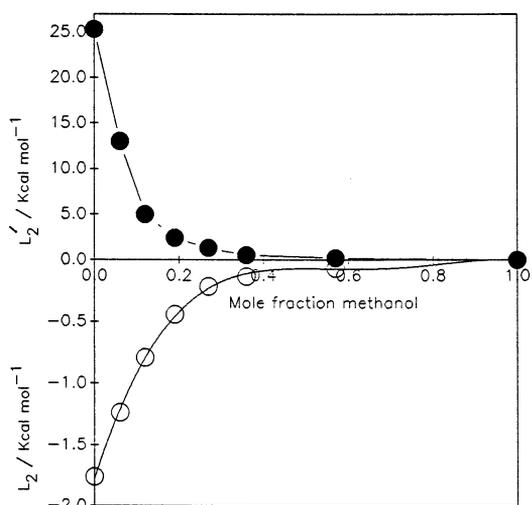
Fig.6. L_2 & L_2' for methanol + water
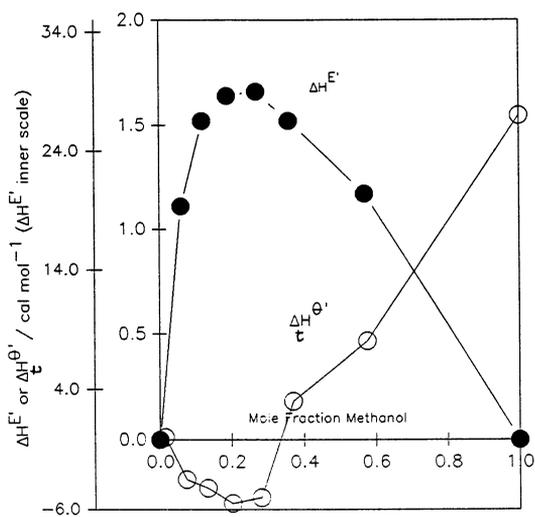
Fig.7. $\Delta H^{E'}$ and $\Delta_t H^{\theta'}$ (CsCl) for methanol + water
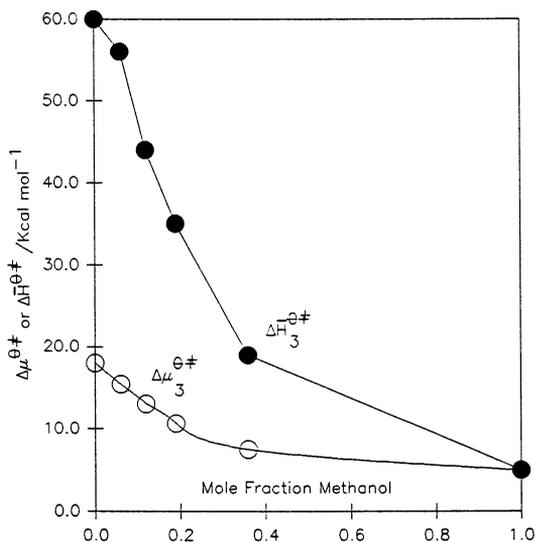
Fig.8. $\Delta\mu_3^{\theta\ddagger}$ and $\Delta\bar{H}_3^{\theta\ddagger}$ for TBA in methanol + water

The slight minimum in $\Delta\mu_3^{\theta\ddagger}$ at a mole fraction of around 0.06 could be a displaced reflection of a property of the binary mixtures that occurs at a slightly higher mole fraction ($x_2 = 0.1$) namely a maximum in the mean entropy of activation for viscous flow, $\Delta S_{12}^{\ddagger}$. At this composition the break-up of the transition-state solvent with respect to the ground-state solvent is a maximum so that here or near here the relative stabilisation of the electrolyte in the transition state should be a maximum, too.

The mixed solvent transition-states can be constructed in principle from the transition-states of the pure alcohol and pure water, a process which can be described by the familiar thermodynamic mixing functions. Fig. 6 shows, as an example, the behaviour of the relative partial molar enthalpy of the alcohol in the transition state solvent, L_2'. L_2' is a magnified mirror image of L_2, the corresponding ground-state function. Again the excess enthalpy in the transition state, $\Delta H^{E'}$, has a pronounced maximum as a function of x_2, and not like ΔH^E in the ground state, a minimum. The enthalpy of transfer of an electrolyte, $\Delta_t H^{\theta'}$, in the transition state should now show a minimum as a function of mole fraction if its dependence on $\Delta H^{E'}$ is similar to that of ΔH_t^{θ} on ΔH^E, namely

$$\Delta_t H^{\theta'} = a' x_2 - b' \Delta H^{E'} \tag{12}$$

Figure 7 shows exactly this dependence for CsCl.

Finally, we look at TBA as solute. $\Delta\mu_3^{\ominus\ddagger}$ and $\Delta\overline{H}_3^{\ominus\ddagger}$ are plotted as functions of solvent composition in Fig. 8.   All the values are positive, very large in water and much smaller in pure methanol.   Let us concentrate on $\Delta\mu_3^{\ominus\ddagger}$.   Classically the large value found in water would have been explained by postulating the "freezing" of the solvent around the solute. But, firstly, we could find no evidence from the enthalpy of transfer for any such freezing: rather, any stabilisation of the solute arose from direct (1,3) ion-solvent interactions. Secondly, $\Delta\mu_3^{\ominus\ddagger}$ is a free energy function and is not, according to the Compensation Principle, influenced by changes in solvent-solvent interactions.   Thus we see the $\Delta\mu_3^{\ominus\ddagger}$ (and $\Delta\overline{H}_3^{\ominus\ddagger}$) arising essentially from the breaking of solute-solvent bonds in the transition-state.   The values are large because the original solute-solvent interaction in the ground state is large.   Yet the strong solvent specificity of the activation parameters, large in water but falling rapidly as methanol is added, does suggest a structural role for the solvent, and in particular for water.   We tentatively suggest that with this type of solvent very little rearrangement of the solvent occurs, but the solvent structure simply closes on the solute like an elasticated net, trapping the solvent and bringing the solvent molecules close to it, enhancing their mutual van der Waals interactions.   This effect is likely to be most marked for water.   It is lost in the transition-state solvent and contributes to high values of the activation parameters.

Acknowledgements   We thank Professor J.E. Enderby and Dr. G.W. Neilson for valuable information on the neutron diffraction experiments.

REFERENCES

1.   D. Feakins and P. Watson, <u>J. Chem. Soc.</u>, 4734 (1963).
2.   J.E. Enderby, <u>Ann. Rev. Phys. Chem.</u>, <u>34</u>, 155 (1983).
3.   K. Heinzinger, <u>Pure and Applied Chem.</u>, <u>57</u>, 1031 (1985).
4.   E. de Valera, D. Feakins and W.E. Waghorne, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>79</u>, 1061 (1983).
5.   D. Feakins, W.E. Waghorne and K.G. Lawrence, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>82</u>, 563 (1986).
6.   J.D. Bernal and R.H. Fowler, <u>J. Chem. Phys.</u>, <u>1</u>, 515 (1933).
7.   H.S. Frank and Wen-Yang Wen, <u>Discuss. Faraday Soc.</u>, <u>24</u>, 133 (1957).
8.   S. Glasstone, K.J. Laidler and H. Eyring, <u>The Theory of Rate Processes</u> (McGraw Hill, New York, 1941), p. 477.
9.   A.K. Soper, G.W. Neilson, J.E. Enderby and R.A. Howe, <u>J. Phys. C.</u>, <u>10</u>, 1793 (1977).
10.   N.T. Skipper, S. Cummings, G.W. Neilson and J.E. Enderby, <u>Nature</u>, <u>321</u>, 52 (1986).
11.   M.G.B. Drew, <u>Co-ordination Chemistry Reviews</u>, <u>24</u>, 179 (1977).
12.   J.R. Newsome, G.W. Neilson and J.E. Enderby, <u>J. Phys. C.</u>, <u>13</u>, L293 (1980).
13.   N.A. Hewish, G.W. Neilson and J.E. Enderby, <u>Nature</u>, <u>297</u>, 138 (1982).
14.   H.G. Hertz, <u>Pure and Applied Chem.</u>, <u>54</u>, 2297 (1982).
15.   G.W. Neilson and N. Skipper, <u>Chem. Phys. Letters</u>, <u>114</u>, 35 (1985).
16.   G.W. Neilson, private communication.
17.   M. Sandstrom, G.W. Neilson, G. Johansson and T. Yamaguchi, <u>J. Phys. C.</u>, <u>18</u>, L1115-L1121, (1985).
18.   D. Feakins and P.J. Voice, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>69</u>, 1711 (1973).
19.   D. Feakins and P.J. Voice, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>68</u>, 1390 (1972).
20.   (a) D. Feakins, K.G. Lawrence, P.J. Voice and A.R. Willmott, <u>J. Chem. Soc. A</u>, 837 (1970);   (b) H.N. Parton and D.D. Perrin, <u>Trans. Faraday Soc.</u>, <u>41</u>, 579 (1945); (c) J-P. Morel, Thesis, University of Clermont-Ferrand, 1969, 99.
21.   B.B. Owen, <u>J. Amer. Chem. Soc.</u>, <u>60</u>, 2229 (1938).
22.   D. Feakins, B.E. Hickey, J.P. Lorimer and P.J. Voice, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>71</u>, 780 (1975);   H.S. Harned, <u>J. Amer. Chem. Soc.</u>, <u>60</u>, 336 (1938);   ref. 20(a).
23.   D. Feakins, B.E. Hickey and P.J. Voice, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>75</u>, 907 (1979).
24.   K.P. Anderson, E.A. Butler and E.M. Woolley, <u>J. Phys. Chem.</u>, <u>75</u>, 93 (1971); D. Feakins, P.J. McCarthy and T.A. Clune, <u>J. Electroanalytical Chem.</u>, <u>84</u>, 199 (1977) and unpublished data.
25.   D. Feakins, M. Knox and B.E. Hickey, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>80</u>, 961 (1984).
26.   J.T. Law, Ph.D. Thesis and A.J. Beckwith, M.Sc. Thesis (University of New Zealand, 1949).
26.   D. Feakins, K.G. Lawrence and R.P.T. Tomkins, <u>J. Chem. Soc. A</u>, 753 (1967).
27.   R.S. Nyholm, <u>Proc. Chem. Soc.</u>, 273 (1961).
28.   D. Feakins, B.E. Hickey, M. Knox, P.J. McCarthy and W.E. Waghorne, <u>J. Chem. Soc. Chem. Comm.</u>, 611 (1987).
29.   See, <u>e.g.</u> D.J.G. Ives and P.D. Marsden, <u>J. Chem. Soc.</u>, 649 (1965).
30.   G. Carthy, D. Feakins and W.E. Waghorne, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>83</u>, 2585 (1987).
31.   J. Mullally, Thesis, National University of Ireland, 1987.
32.   D. Feakins, D.J. Freemantle and K.G. Lawrence, <u>J. Chem. Soc. Faraday Trans. 1</u>, <u>70</u>, 795 (1974).
33.   A.C. Brown and D.J.G. Ives, <u>J. Chem. Soc.</u>, 1608 (1962).
34.   F.M. Canning, Ph.D. Thesis, National University of Ireland, 1987.