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APPROACHES TO THE PROBLEMS OF SOLVATION IN PURE SOLVENTS AND PREFERENTIAL SOLVATION IN MIXED SOLVENTS

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Abstract - Of paramount importance to the understanding of the behaviour of solutes in solvent media is the problem of solute-solvent interaction (solvation), or, in solvent mixtures, of solvent-sorting in the solvation sphere of the solute (preferential solvation). Different techniques and theoretical approaches have been developed but the relation of these to classical thermodynamics has rarely been critically discussed. Theories of solute-solvent interaction can be broadly divided into continuum models and models which acknowledge the molecular nature of the solvent. In the latter, the arrangement of the solvent is often treated in terms of discrete structure only in the solvation sphere, or, more generally, through distribution functions which can be obtained in principle from X-ray and neutron scattering experiments. Unfortunately theoretical approaches based on the nature and extent of intermolecular forces have not yet reached the state of development, in spite of the power of modern high speed computers, that they can be of real use in interpreting the properties of systems of experimental and technological importance. By highlighting the interrelations between the different approaches, the possible origin of some recently reported discrepancies in the interpretation of systems studied by two or more experimental methods may become apparent.

INTRODUCTION

The interaction of ions with solvent molecules is clearly of absolute fundamental importance in almost every field of pure and applied solution chemistry. Some examples are given in Fig. 1. Reference should be made to the symposium monograph edited by Furter (1) and to

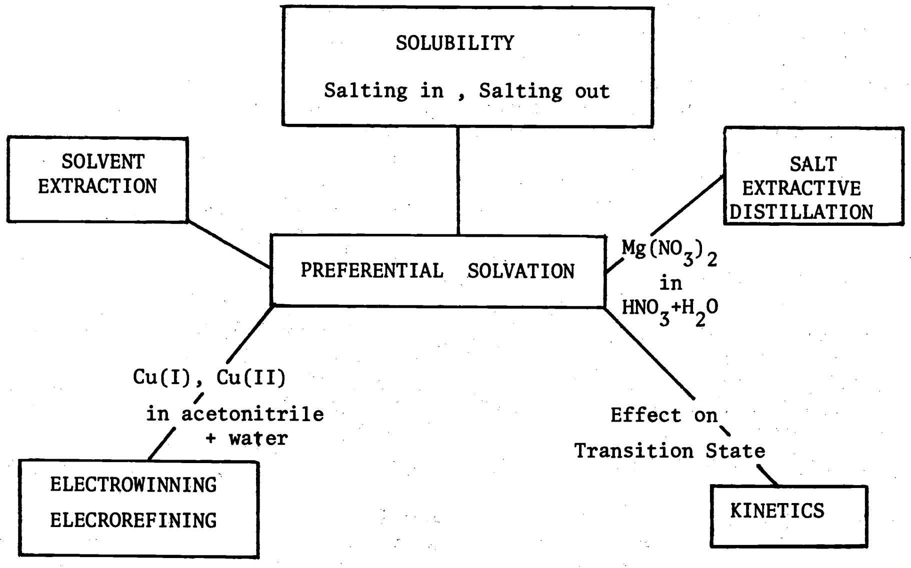

Fig.1 Importance of preferential solvation.

Parker's review (2) for details of these and other applications.

One of the earlest attempts to understand the changes in thermodynamic properties of electrolytes with change in solvent is due to Born (3) in 1920, who equated the solute chemical potential with the work done in charging a conducting sphere, of radius equal to that of the ion, in a dielectric continuum. This work has been subjected to much evolution (4) since then, particularly the idea of adjusting the ionic crystal radius to take into account the effect of completely immobilised, and hence dielectrically saturated, solvent close to the ion, but the short-comings in the theory become very apparent when: (a) the temperature dependence of the charging process is considered and related to the enthalpies of solvation, and (b) mixed solvents rather than pure solvents are considered.

In 1927, Debye (5) introduced, within the general dielectric continuum approach, the idea that in a mixed solvent, the component with the higher relative permittivity (dielectric constant) will be found preferentially close to the ion. The thermodynamic basis of this is that the lowering of the free energy, due to the more favourable charging process with a higher dielectric constant component, is balanced by an unfavourable raising of the free energy due to 'demixing' the solvent. Such ideas have been explored more recently by Koenig (6), Frank (7) and Padova (8,9), and the charging of a sphere in a mixed dielectric continuum at constant solvent chemical potential where solvent sorting is included has been discussed by Covington, Hall and Newman (10).

A basic limitation of such dielectric continuum or BBB models, as Frank (7) has called them, is that they neglect the molecular nature of solvation. That is, although the electrostatic interaction is long range, the most important contributions are those due to solvent molecules close to the ion. In this region, short range 'chemical' forces operate and the concept of a macroscopic dielectric constant loses its validity.

'Chemical' models have long been used to interpret solution thermodynamic properties since Arrhenius' classic interpretation of the conductance of weak acids. Similar association models have been frequently used in treating ion-association and very non-ideal non-electrolyte solutions in terms of dimer, trimer etc. formation. Stokes and Robinson (11) and later Glueckauf (12) have used a solvation model to interpret the activity coefficient behaviour of aqueous electrolytes, particularly of the 2:1 charge type, where the upturn in activity coefficient with increase in concentration is otherwise hard to interpret.

The applicability of a chemical model as opposed to a more rigourous statistical mechanical approach will be mentioned later. An attempt to unify these two approaches through a Mayer activity expansion has been discussed by Wood, Lilley and Thompson (13). The basis of chemical models is that the non-ideality results from clustering of the various components and the formation of such clusters can be formulated in chemical equilibria terms. The clusters can be regarded as behaving ideally in a thermodynamic sense and thus the conventional thermodynamic parameters can be related to the various equilibria between clusters. Stokes and Robinson (11) initially used a constant solvation number approach for concentration up to 2 mol kg^{-1} but the solvation numbers obtained were often non-integral and sometimes very small, and thus intuitively unsatisfactory. This approach has since been extended to very concentrated solutions where the solvation number must be less since there are insufficient solvent molecules to solvate the ions as fully as in dilute solutions. A difficulty is the problem of ion-ion interactions at moderate concentrations, which is ignored in the Stokes and Robinson approach, and this limits its validity. Essentially, both ion-ion and ion-solvent interactions lead to linear dependence of the logarithm of the activity coefficient on concentration and are difficult to separate.

In 1960, Grunwald and co-workers (14) published as an appendix to a paper on the effect of salts on the vapour pressures of dioxan + water mixtures, an analysis of the effect of solvent-sorting on the solute chemical potentials. This paper proved to be the keystone to further work (15) on the thermodynamics of electrolytes in mixed solvents, and in this review attempts will be made to explore the relationship between this work and subsequent developments.

Around the same time, but totally independently, spectroscopic measurements, notably by ultra violet (16) and n.m.r. techniques (17-19), began to yield qualitative evidence of preferential solvation. As theoretical and experimental advances have been made, it has become possible to estimate the composition of the ionic solvation shell in mixed solvents and to relate this to thermodynamic parameters (16). Of particular importance is the fact that by spectroscopic methods it is possible to obtain information about the solvation of single ions, something which is impossible by thermodynamics alone. In Fig. 2 some of the experimental and theoretical approaches to solvation have been summarised, and this figure will form the basis of further discussion later in this review.

EVIDENCE FOR THE FORMATION OF SOLVATES AND THE STRUCTURE OF THE SOLVATION SHELL

N.m.r. techniques have provided a very powerful tool for studying solvation phenomena. It had long been thought that the strong electrostatic field in the vicinity of ions immobilised the solvent molecules but the radiotracer work of Taube (20) showed that solvent exchange was in fact very fast with water. This was confirmed by proton m.r. measurements. However, with certain ions on lowering the temperature, the exchange is sufficiently slowed that separate proton signals from bound water to, for example, Al^{3+} and bulk water can be

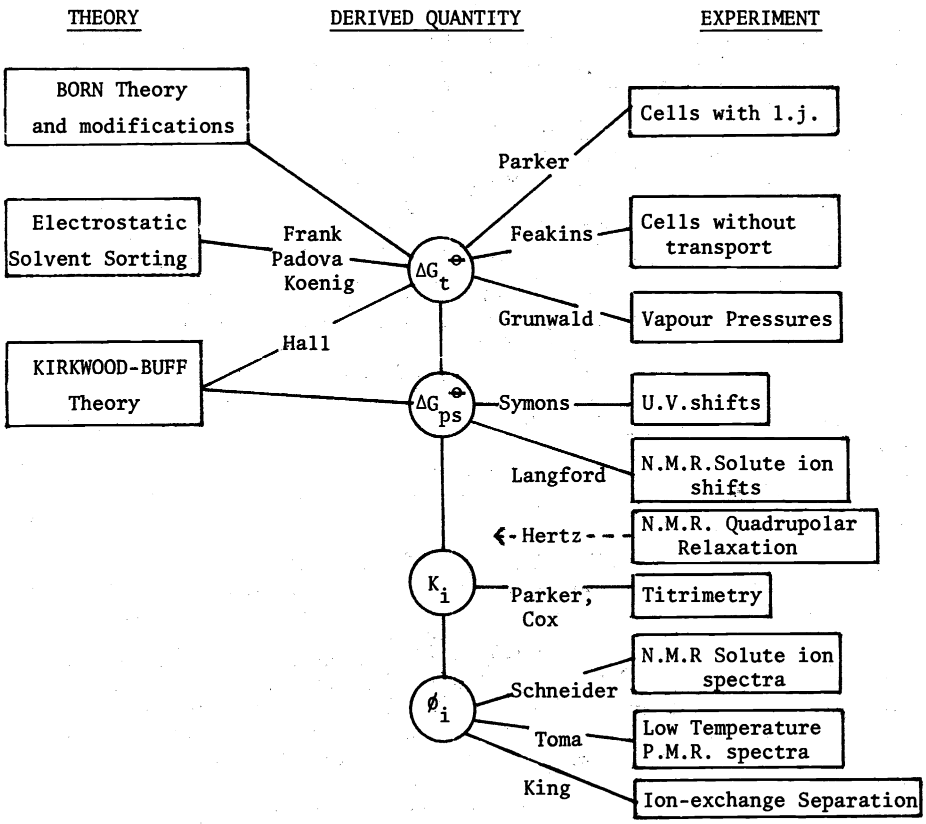

Fig.2. Theoretical and experimental approaches to preferential solvation and derived quantities.

distinguished (21). In mixed solvents, it may be possible to see both bound and bulk signals from both solvents (22). Since the area under each proton resonance is proportional to the proton concentration of each species , it is possible to derive solvation numbers for both components from such spectra. This can also be done with ^{13}C n.m.r. (23). A third n.m.r. technique uses not solvent spectra but solute ion-spectra, and can be illustrated by the work of Schneider (24) on ^{27}Al spectra of aluminium perchlorate in dimethylformamide (DMF) + dimethylsulphoxide (DMSO) mixtures, which also show separate peaks of bound and bulk solvent. Further, the existence of separate solvates and even isomeric solvates may be distinguished (25). This can also be done for p.m.r. spectra by lowering the temperature even further (26) and is illustrated in Fig. 3 for the system magnesium perchlorate in methanol + water mixtures at 230 K.

No amount of cooling produces separate solvate signals for the alkali metal ions or the halide ions in solution in water or in non-aqueous solvents because the solvent exchange on these ions is too fast. Nevertheless it is reasonable to suppose that solvate species have a real existence in such solutions and this is the basis for the thermodynamic analysis outlined in the next section. Another important technique that should be mentioned at this stage is the ion-exchange separation and identification of solvates that can be achieved if the solvent exchange is very slow. This technique has been developed and discussed by King (28).

It has usually been assumed, but only recently has it been confirmed by ab initio quantum mechanical calculations (29), that the orientation of a water molecule in the hydration sphere is in accordance with its dipole charge, that is with the oxygen inwards for cations and hydrogen inwards (one or both) for anions. With water as with other hydrogen bonding molecules there is then the possibility of interactions with a second or third layer of solvent molecules around the ion. Such interactions are impossible with dipolar aprotic solvent molecules as pointed out by Parker (2). The solvation shell structure is therefore very different in these two cases. Problems obviously arise when solvent mixtures protic + dipolar aprotic are considered, for not only may the solvation number change with the composition of the mixed solvent but also probably the volume of the solvation shell.

Although the concept of primary and secondary solvation shells was introduced (30) to explain the different values of solvation numbers obtained by the application of different techniques having different spheres of influence is probably still valid, the idea of the separate existence of discrete primary and secondary solvation shells has been somewhat overemphasized and is a weakness in some of the theoretical treatments developed. There is good evidence

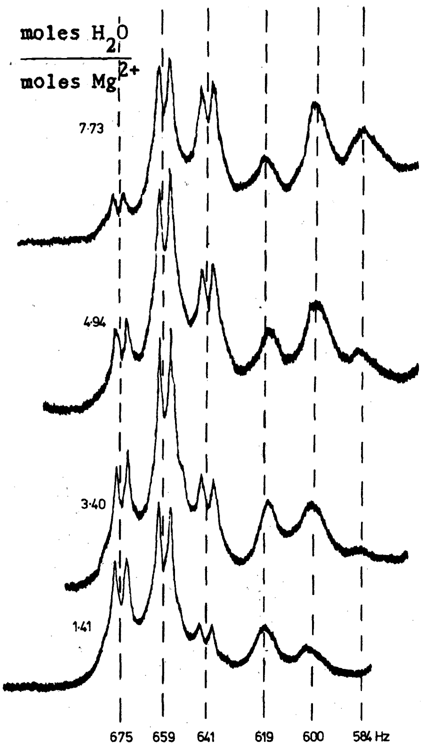

Fig. 3 P.m.r. spectra for magnesium perchlorate in methanol + water at 230 K.

that n.m.r. shifts are influenced essentially by near neighbour interactions and hence provide evidence about primary solvation. This does not mean that secondary effects will be entirely absent. A good illustration of this comes from Schneider's work mentioned above (24), where the addition of a supposedly inert solvent, nitromethane, to DMF + DMSO changed the distribution of Al^{3+} solvates dramatically.

THERMODYNAMICS OF PREFERENTIAL SOLVATION

The basis of the thermodynamic treatment of preferential solvation is that the free energy of the solution is independent of the way the composition (species distribution) is formulated. Following, the treatment of Grunwald, Baughman and Kohnstam [GBK] (14), Covington, Newman and coworkers (31-3) in a series of papers have provided a detailed elaboration, which has been reviewed by these workers (15) and by Schneider (34).
The starting point of the thermodynamic treatment is the fact that the free energy of a solution is independent of whether the ionic solute is considered solvated or not. Consider a solution containing w° moles of solvent W, p° moles of cosolvent P and a moles of solute X. The Gibbs free energy of the system is then

$$G = a\mu_X + w^\circ\mu_W + p^\circ\mu_P \tag{1}$$

If, however, the solute X is considered as solvated, and the general formula of the solvated species is XW_jP_i existing as a fraction ϕ_{ij} , then the average solvation numbers for W and P are defined as

$$h_W = \sum_i^{n_P} \sum_j^{n_W} j\phi_{ij} \tag{2}$$

$$h_P = \sum_i^{n_P} \sum_j^{n_W} i\phi_{ij} \tag{3}$$

$$\text{and} \quad \sum_i \sum_j \phi_{ij} = 1 \tag{4}$$

where n_W, n_P are the solvation numbers of W and P.
In terms of the solvated species, the Gibbs free energy of the solution is (c.f. GBK equation (49))

$$G = a\sum_i \sum_j \phi_{ij}\mu_{ij} + p\mu_P + w\mu_W \tag{5}$$

where $$w = w^\circ - a\sum_i \sum_j j\phi_{ij} \tag{6}$$

and $$p = p^\circ - a\sum_i \sum_j i\phi_{ij} \tag{7}$$

Equating equations (1) and (5) gives (c.f. GBK equation (53))

$$\mu_X = \sum_i \sum_j \phi_{ij}\mu^{\ominus}_{ij} + RT\sum_i \sum_j \phi_{ij}\ln \phi_{ij} - \sum_i \sum_j j\phi_{ij}\mu_W - \sum_i \sum_j i\phi_{ij}\mu_P \tag{8}$$

putting $$\mu_{ij} = \mu^{\ominus}_{ij} + RT \ln \phi_{ij} \tag{9}$$

In equations (2) - (9), i and j can both take the value of zero corresponding to the unsolvated ion. However, the concept of an ion with no solvent round it in a solution is hard to rationalise; indeed in terms of a radial distribution function it has no meaning.
To obtain from (8) an equation for the chemical potential of X in the standard state, $\mu^{\ominus}_X$, we note the definition for a mol fraction standard state

$$\mu^{\ominus}_X = \lim_{a\to 0} (\mu_X - RT \ln x_X) \tag{10}$$

or $$\mu^{\ominus}_X = \lim_{a\to 0} (\mu_X - RT \ln c_X) \tag{11}$$

for a molarity standard state, giving for either choice of standard state

$$\mu^{\ominus}_X = \sum_i \sum_j \phi^\circ_{ij}\mu^{\ominus}_{ij} + RT\sum_i \sum_j \phi^\circ_{ij}\ln \phi^\circ_{ij} - \sum_i \sum_j j\phi^\circ_{ij}\mu_W - \sum_i \sum_j i\phi^\circ_{ij}\mu_P \tag{12}$$

where ϕ°_{ij} refers to the solvated species fraction for vanishingly small solute concentration. The difference in the two standard states lies in the different significance of the $\mu^{\ominus}_{ij}$ term. Equation (12) is too general to be useful and it is usual to make the assumption that only molecules in the first solvation shell are considered in the solvation process and all solvent beyond can be treated by continuum models. Further, if the total number of molecules in the solvation shell is assumed constant (n) and the same for both pure solvents, the generalised solvated species can be written as $XW_{n-i}P_i$, then equation (12) simplifies to

$$\mu^{\ominus}_X = \sum_i \phi^\circ_i\mu^{\ominus}_i + RT\sum_i \phi^\circ_i \ln \phi^\circ_i - \sum_i (n-i)\phi^\circ_i\mu_W - \sum_i i\phi^\circ_i\mu_P \tag{13}$$

where $\sum_i \phi^\circ_i = 1$, for both choices of standard state. Note that unsolvated species are now precluded.
It is usual to measure transfer free energies from a chosen solvent such as W, defined as

$$\Delta G^{\ominus}_{t(X)} = \mu^{\ominus}_X - \mu^{\ominus}_{X(W)} \tag{14}$$

thus $$\Delta G^{\ominus}_{t(X)} = \sum \phi^\circ_i\mu^{\ominus}_i - \mu^{\ominus}_{X(W)} + RT\sum \phi^\circ_i \ln \phi^\circ_i - \sum (n-i)\phi^\circ_i\mu_W - \sum i\phi^\circ_i\mu_P \tag{15}$$

To proceed further (31) it is necessary to make the assumption of the division of $\mu^{\ominus}_X$ into long and short range ('chemical') terms

$$\mu_i^{\ominus} = \mu_i^{\ominus\,\mathrm{int}} + \mu_i^{\ominus\,\mathrm{elec}} + \mu_i^{\ominus\,\mathrm{chem}}$$

where $\mu_i^{\ominus\,\mathrm{int}}$ is an intrinsic contribution from the bare ion which disappears on taking a difference as in equation (14). Thus equation (15) can be rearranged to

$$\Delta G^{\ominus}_{t(X)} = \sum \phi^{\circ}_i\mu_i^{\ominus\,\mathrm{elec}} - \mu_{0(W)}^{\ominus\,\mathrm{elec}} + \sum \phi^{\circ}_i[\mu_i^{\ominus\,\mathrm{chem}} - \mu_{0(W)}^{\ominus\,\mathrm{chem}} - i\mu_P^{\ominus} + i\mu_W^{\ominus}] - \sum i\phi^{\circ}_i RT\ \ln x_P$$
$$+ \sum i\phi^{\circ}_i RT\ \ln x_W - nRT\ \ln x_W + \sum \phi^{\circ}_i RT\ \ln \phi^{\circ}_i \qquad (17)$$

by making the substitutions assuming ideal solvent solution behaviour

$$\mu_W = \mu^{\circ}_W + RT\ \ln x_W \qquad (18)$$

$$\mu_P = \mu^{\circ}_P + RT\ \ln x_P \qquad (19)$$

and noting $\sum \phi^{\circ}_i = 1$.
The transfer free energy $\Delta G^{\ominus}_{t(X)}$ refers to the removal of X from solvent W with the breaking of all interactions and transfer to new solvent P with the formation of new ion-solvent interactions. A related process would be changing the solvation shell of n molecules of W around X step by step until it contains n molecules of P. The general step in such a process can be written

$$XW_{n+1-i}P_{i-1} + P \overset{K_i}{\rightleftharpoons} XW_{n-i}P_i + W \qquad (20)$$

with stepwise or consecutive constant K_i (shown for n = 4 in Fig. 6a) or

$$XW_n + iP \overset{\beta_i}{\rightleftharpoons} XW_{n-i}P_i + iW \qquad (21)$$

with overall or gross constant $\beta_i = \pi K_i = \phi^{\circ}_i x_W^i / \phi^{\circ}_0 x_P^i$

It may be noted that the term in [ ] in equation (17) is thus $-RT\ \ln \beta_i$, so

$$\Delta G^{\ominus}_{t(X)} = \sum \phi^{\circ}_i\mu_i^{\ominus\,\mathrm{elec}} - \mu_{0(W)}^{\ominus\,\mathrm{elec}} - RT\ \ln[\beta_i x_P^i / \phi^{\circ}_i x_W^i] - nRT\ \ln x_W$$
$$= \sum \phi^{\circ}_i\mu_i^{\ominus\,\mathrm{elec}} - \mu_{0(W)}^{\ominus\,\mathrm{elec}} + RT\ \ln \phi^{\circ}_0 - nRT\ \ln x_W \qquad (22)$$

From equation (20), the fraction of W solvated species,

$$\phi^{\circ}_0 = \frac{m_0}{\sum m_i} = \frac{m_0}{m_0 + m_0K_1Y + m_0K_2Y\ldots\ldots} = \frac{1}{1 + \sum\limits_n Y^i \Pi\ K_i} = \frac{1}{1 + \sum Y^i \beta_i} \qquad (23)$$

where $Y = x_P/x_W$,

so $$\Delta G^{\ominus}_{t(X)} = \sum \phi^{\circ}_i\mu_i^{\ominus\,\mathrm{elec}} - \mu_{0(W)}^{\ominus\,\mathrm{elec}} - RT\ \ln[1 + \sum \beta_i Y^i] - nRT\ \ln x_W \qquad (24)$$

This is related to the equation derived by Cox, Parker and Waghorne (35) which contained only the third and fourth terms on the right hand side. These workers, in their coordination model of ionic solvation (35), also applied a chemical model based on successive equilibria starting from an equation for μ_X in terms of the concentration of unsolvated metal ion. They also chose to use volume fractions instead of mol fractions for the solvent components. Their derivation, which is not without its ambiguities, was intended to apply to reaction in an inert solvent, and hence effectively to an isodielectric medium and the first two terms of equation (24) would be negligible. It has been tested in this form (36). It may be noted that K_i and β_i in equations (20) and (21) are dimensionless and hence independent of the chosen concentration scale. However, the transfer free energy does depend on the concentration scale (standard state conditions) adopted, and the difference must lie in the electrostatic contribution.

Equation (22), which suggests that for isodielectric mixtures the transfer free energy is a function only of the fraction of W solvated species, the mol fraction (or activity) of W and the solvation number n, is a particularly simple and interesting one. One may recall the Feakins and French plot (37) of $\Delta G^{\ominus}_{t(X)}$ against water activity from which values of n were estimated. Comparison suggests that this is valid for solutions where the fully water solvated species is dominant ($\phi^{\circ}_{0} \simeq$ constant). Kondo and Tokura (38) have also used a chemical model of successive equilibria. Their final equation differs from (17) and we have so far not succeeded in relating the two treatments.

Making the assumption that values of K_i for equation (20) are statistically related, that is

$$K_i = K^{1/n}(n + 1 - i)/i \qquad (25)$$

where $K = \Pi K_i$ relates to the process

$$XW_n + nP \longrightarrow XP_n + nW \qquad (26)$$

and is in turn related to the free energy of preferential solvation (31) by

$$\Delta G^{\ominus}_{ps} = -nRT \ln K^{1/n} = -RT \ln K \qquad (27)$$

gives from equation (24)

$$\Delta G^{\ominus}_{t(X)} = \sum \phi^{\circ}_i \mu_i^{\ominus\,elec} - \mu^{\ominus\,elec}_{0(W)} - nRT \ln (1 + K^{1/n}Y) - nRT \ln x_W \qquad (28)$$

since in the denominator of equation (23)

$$1 + \sum Y^i \Pi K_i = (1 + K^{1/n}Y)^n \qquad (29)$$

If, as shown in the next section, the solute ion chemical shift δ in a solution of mol fraction x_P and its value δ_P at $x_P = 1$ are related to K through the equation

$$K^{1/n}Y = \frac{\delta/\delta_P}{(1 - \delta/\delta_P)} \qquad (30)$$

then equation (28) becomes

$$\Delta G^{\ominus}_{t(X)} = \sum \phi^{\circ}_i \mu_i^{\ominus\,elec} - \mu^{\ominus\,elec}_{0(W)} - nRT \ln \frac{1}{1 - \delta/\delta_P} - nRT \ln x_W \qquad (31)$$

which is equation (28) of reference (31) and (67) of reference (15). Also from equation (30) and (27)

$$\Delta G^{\ominus}_{ps} = -nRT \ln[\delta/(\delta_P - \delta)][(1 - x_P)/x_P] \qquad (32)$$

Covington and co-workers (31) made the assumption of statistical distribution of solvate species at an earlier stage than introduced here. The present derivation is simpler, less restrictive than equation (28), illustrates the relation of the Cox, Parker and Waghorne (35) equation (24) to the overall thermodynamic treatment of solvation (15), and highlights the significant and simple equation (22).

RELATION TO EXPERIMENT

The n.m.r. chemical shift is a measure of the change in magnetic field at the resonating nucleus. For ionic solutes the effects of solvent on solute nuclei chemical shift are unlikely to extend beyond the first solvation shell. The observed shift is a weighted average of the intrinsic shifts (δ_i) arising from all possible arrangements around the ion if the exchange rate is fast. Hence, the observed shift

$$\delta = \sum_{i=1}^{n} \phi_i \delta_i \qquad (33)$$

It is now necessary to assume that the contribution to each δ_i from each P and W solvent molecule is additive (31), namely

$$\delta_i = i\delta_P/n \tag{34}$$

where δ_P is the shift for $x_P = 1$.
Combining equations (33) and (34) gives

$$\frac{\delta}{\delta_P} = \sum_1^n i\phi_i/n \tag{35}$$

A similar relation is assumed for u.v. frequency shifts, which is less soundly based theoretically, and usually applied as wavelength shifts (15). It is easy to show, assuming either Gaussian or Lorentzian line shapes that u.v. shifts are only additive if there is no change in band width with solvation change (39).
The general expression for ϕ_i° is (31)

$$\phi_i^\circ = m_i/\sum_0^n m_i \qquad \text{for } 0 < i < n \quad (\text{i.e. excepting } \phi_0^\circ)$$

$$= Y^i\Pi K_i/(1 + \sum Y^i\Pi K_i) \tag{36}$$

which, substituted in equation (35) assuming statistical distribution of solvate species (equation (25)), gives

$$\frac{\delta}{\delta_P} = \frac{K^{1/n}Y}{1 + K^{1/n}Y} \tag{37}$$

and this rearranges to give the previously quoted form (equation (30)). Mathematically this is a rectangular hyperbola and is reducible to a straight line plot by the reciprocal form

$$\frac{1}{\delta} = \frac{1}{\delta_P}\left(1 + \frac{1}{K^{1/n}Y}\right) \tag{38}$$

A plot of $1/\delta$ against $1/Y$ serves for the evaluation of K (and hence of $\Delta G^\ominus_{ps}$) as shown earlier (40) and this has been referred to as a Covington plot (41). There are, however, close parallels with the treatment of weak molecular interactions by Benesi-Hildebrand (42) and Scatchard plots (43). A recent application to solvation is described by Nagy and coworkers (44). There are also similarities with binding-site studies, and kinetics, of enzymes and Lineweaver-Burk plots (45). In Fig. 4, a Scatchard plot (43) of the transformation of equation (38) into

$$\frac{\delta}{Y} = \delta K^{1/n} - \delta_P K^{1/n} \tag{39}$$

is shown for the data of Covington et al. (40) on ^{19}F shifts in $H_2O_2 + H_2O$ giving $K^{1/n} = 2.41 \pm 0.02$, $\delta_P = 25.46 \pm 0.14$ compared with 2.38 ± 0.02 and 25.86 respectively from a graphical plot of equation (38). The Scatchard plot is preferred for statistical reasons (46). For alkali metal, fluoride (47) and chloride (48) ions in $H_2O_2 + H_2O$, an isodielectric mixture, good agreement was found between values of $\Delta G^\ominus_{ps}$ (equation (32)) and values of $\Delta G^\ominus_{t(X+Y)}$ determined from measurements with ion-selective electrodes, assuming $n = 4$.
For methanol + water, $\Delta G^\ominus_{ps}/n$ was obtained from n.m.r. shift measurements as shown earlier (31), but attempts to relate this to $\Delta G^\ominus_{t(X+Y)}$ from e.m.f. measurements by calculating the electrostatic contribution by Born theory, were less successful (31) in that the curvature with mol fraction was in the opposite sense to that observed from cell measurements, even though the value for the transfer between the two pure solvents agreed for reasonable choice of n for the ions.
The first application of n.m.r. shifts to the study of preferential solvation was by Frankel, Stengle and Langford (17). The concept of equi- or iso-solvation point has been widely used. This is defined as the mol fraction (x_i) where $\delta = \delta_P/2$. Inserting this in equation (37) gives

$$K^{1/n} = \frac{1}{x_i} - 1 \tag{40}$$

As indicated on Fig. 2, other routes to the related parameters $\Delta G^\ominus_{ps}$, K_i and ϕ_i are low temperature p.m.r., solute-ion spectra where solvates are resolvable, ion-exchange separation when exchange is very slow, and titrimetric studies similar to those developed in complex-ion chemistry. These have been discussed elsewhere (15, 35, 36).

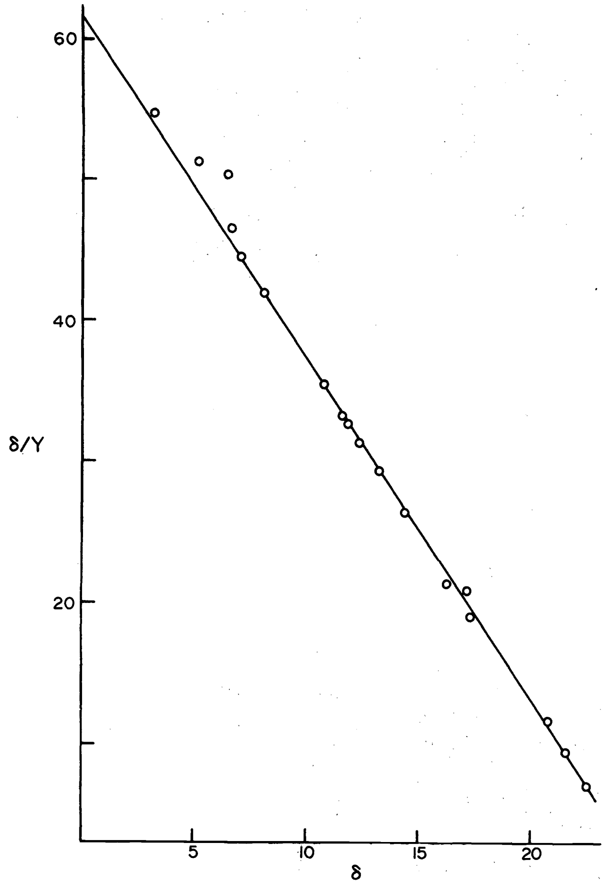

Fig. 4. Scatchard plot of equation (39) for data from Ref. 40 on ^{19}F shifts for NaF in H_2O_2 + H_2O.

CRITICISMS OF THE PRESENT APPROACH

There are several assumptions made in the treatment outlined above which require further discussion:-

1) Separation of long range (electrostatic) and short-range effects.

Although essentially an artificial separation on a molecular level, this is a common assumption in electrolyte theory and one which is best discussed from the point of view of radial distribution functions and Kirkwood-Buff theory (49, 50-2). Its validity is hard to assess but it may be more reasonable for solvation by dipolar aprotic solvents than it is for hydrogen bonding solvents where there is interaction between the primary solvation shell and the rest of the solvent.

2) Mol fractions or activities of the solvent components.

In the derivation given here, for simplicity, ideal behaviour of the solvent mixture was assumed (equations (18) and (19)) but it is a simple matter to replace mol fractions by activities. This point has been extensively discussed elsewhere (15) and it was pointed out that to use measured activities led to over compensation. Langford (53) has criticised the use of mol fractions as in serious error and considers that the least likely of several alternative approximations is that the non-ideality of the components of the solvation shell and bulk solvent is the same. Whilst this is correct, nevertheless some cancellation of effects does occur. He considers that the transfer of water between solvation sphere and bulk solvent depends primarily on the bulk solvent behaviour. If this were so, then preferential solvation curves for all ions in a given solvent mixture would reflect the shape of the partial vapour pressure curves of the mixed solvent, which is untrue.

3) Choice of standard state and the solvation shell.

In previous work, which started with H_2O_2 + H_2O mixtures (40), the aquamolality (a 'corrected' mol fraction scale) was chosen. From a statistical mechanical view point, the number density is the more fundamental quantity. A treatment described elsewhere (52) utilising Kirkwood-Buff theory yields essentially the same equations for the transfer free energy as obtained from the thermodynamic treatment based on mol fractions. The conventional Born equation can also be shown to be valid for the molar standard state, but in applying this it is necessary to assume that the radii of all solvated species are the same.

Molecular model considerations suggest (26) that the volume change of the solvation shell is quite large (an order of magnitude) for the system water + acetone. Orientational effects may also be important and solvate isomers have been observed (25, 54). An interesting effect was observed (55) for the system sodium tetraphenylborate in nitromethane (NM) + hexamethylphosphotriamide (HMPT) as shown in Fig. 5 where ^{23}Na spectra are illustrated. The signal disappears for small additions of HMPT to NM and vice versa. This effect is attributed to quadrupolar relaxation arising from the nuclear quadrupole moment of ^{23}Na nucleus in an asymmetric solvating field. For reasons that are not understood, Greenberg and Popov (56) were able to measure shifts in this system. It is possible that the presence of a little water speeds up the exchange.

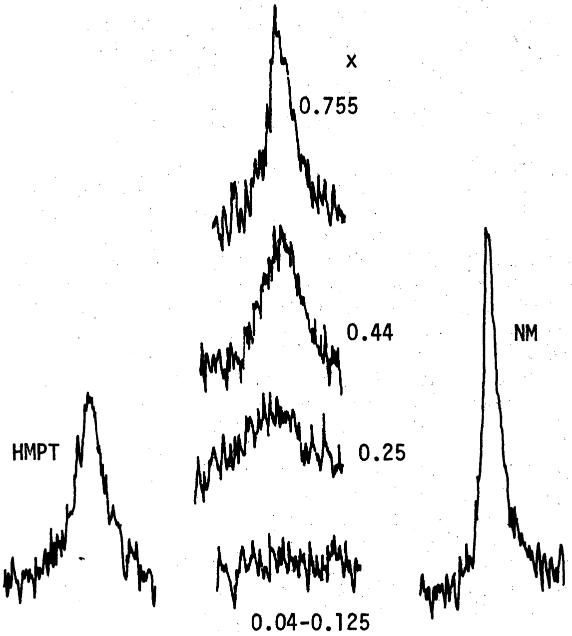

Fig. 5 ^{23}Na spectra from 0.18 mol kg^{-1} solution of sodium tetraphenylborate in NM+HMPT (x = mol fraction of HMPT)

4) Change in solvation number.

As discussed earlier, the treatment involving a varying solvation number with solvent composition is too general to be tractable. The assumption of constant solvation number may be expected not to fit data for some systems. Covington and coworkers (32) explored the simple case of halving or doubling of solvation number, which is equivalent to monodentate versus bidentate solvating-liquid equilibria. This approach has been followed up by Detellier and Laszlo (57, 58), who have studied ^{23}Na chemical shifts in various oxygenated solvents with results shown in Table 1 interpreted on the basis of Fig. 6 b and c for successive solvate formation. Confirmation of the correctness of the interpretation of the intermediate solvate species (AB) was obtained from line-width studies. For fast exchange, the observed viscosity-corrected line width is a weighted average

$$\nu = x_A\nu_A + x_{AB}\nu_{AB} + x_B\nu_B \tag{41}$$

The mol fraction of AB was obtained from the known mol fractions x_A, x_B and the equilibrium constants K_1, K_2 determined from the shift studies. Therefore a plot of $\nu - x_A\nu_A - x_B\nu_B$ against x_{AB} should be linear. This was fulfilled for diglyme + tetrahydrofurfuryl alcohol and triglyme + tetrahydrofurfuryl alcohol mixtures but not for some other solvent mixtures. Laszlo and coworkers (58) have extended their studies to a tridentate solvent ligand (diethylene triamine) with a monodenatate (tetrahydrofuran), again demonstrating the existence of a single mixed solvate.

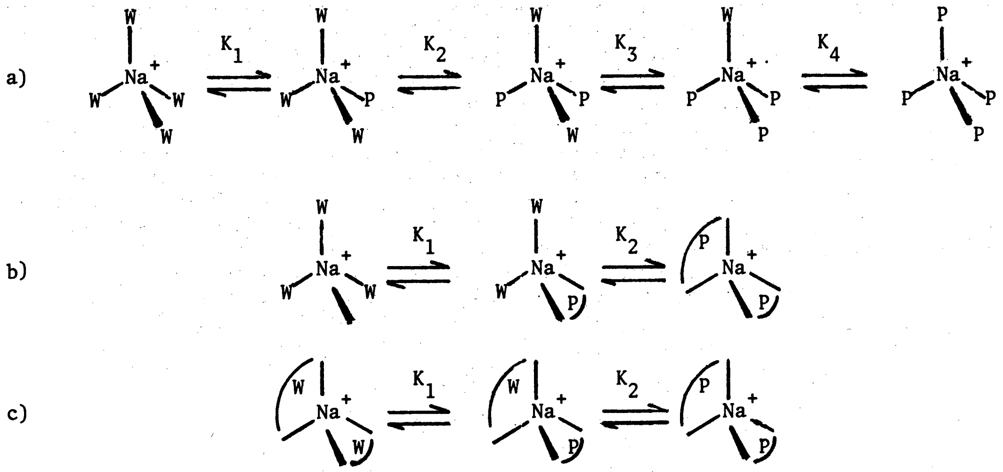

Fig. 6 Models for the solvation of Na^+ with n=4. a) Monodentate-monodentate b) monodentate-bidentate c) bidentate-bidentate.

5) Intrinsic shifts of solvates proportional to cosolvent content (equation (34)).
Some evidence for the validity of this assumption comes from work on alkali metal halide crystals as discussed by Van Geet (59). Other evidence comes from measured shifts of solvates which can be prepared in the solid form. Fig. 7a show the shifts obtained for Al^{3+} solvates of certain organic phosphorus-compound-water solvates by Delpuech and coworkers (60) are linear in the number of water molecules contained. Similar evidence for the additivity of u.v. intrinsic shifts comes from the ion-exchange studies of King (61) where determined molar absorbances (extinction coefficients) at two wavelengths for Cr^{3+}-DMSO-H_2O solvates are linear in the number of water molecules per solvate (Fig. 7b). It should be noted that $K^{1/n} = 5$ for this system and not as stated with caption to Fig. 21 of reference (15). This value lies in the range 3.5 - 5.9 given by King (26) for his discrimination factor.

TABLE 1. Equilibrium constants from ^{23}Na shift measurements (57)

Monodentate-bidentate (Fig 6b)		
	K_1/mol l^{-1}	K_2/mol l^{-1}
THF + THFu	710	20
THF + THPu	600	21
THF + EG	580	115
Bidentate-bidentate (Fig 6c)		
	K_1	K_2
Monoglyme + THFu	18	2
Diglyme + THFu	2.7	0.7
Triglyme + THFu	1.2	0.3

Key: THF = tetrahydrofuran, THFu = tetrahydrofurfuryl alcohol,
THPu = 2-methanoltetrahydropyran.

FURTHER DEVELOPMENTS

a) Thallium ion solvation.
Considerable interest from several groups (62-65) has been shown in the solvation of Tl^+ in a variety of solvents. Unusually, this ion can be studied by several spectroscopic methods

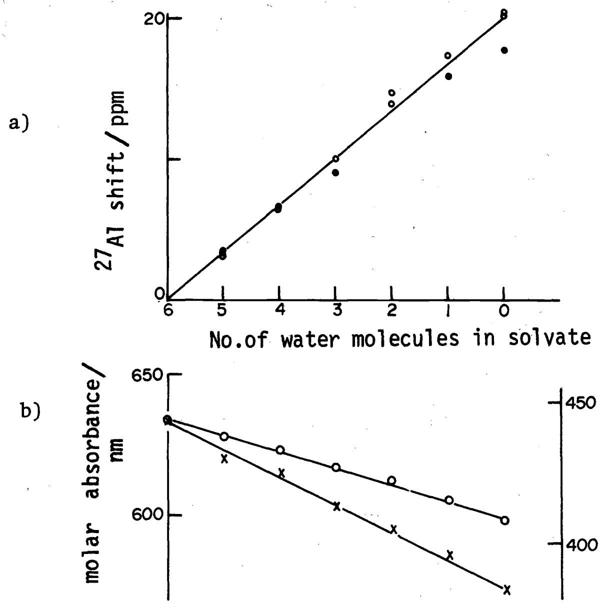

Fig. 7 a) ^{27}Al shifts for Al^{3+} solvates of water and certain organophosphorus compounds (60)
b) Molar absorbances for Cr^{3+} solvates containing water and DMSO (61)

viz. ^{205}Tl n.m.r., u.v. shifts and fluorescence shifts. In view of previous problems in attempting to understand methanol + water solvent (31) this solvent mixture was chosen for a study of Tl^+ solvation by all three aforementioned techniques, and by measurement of transfer free energies of thallous fluoride with cation responsive glass and LaF_3 fluoride ion-selective electrodes (65). ^{205}Tl n.m.r. shifts indicated preferential hydration of Tl^+. At higher concentrations of TlF than 0.02 aquamolal, the shift goes through a maximum at about x_p = 0.8 due to ion-pair formation (Fig. 8) and the same effect was noted in the electrochemical measurements (Fig. 9). For the successive equilibria treatment to be applied, the n.m.r. shifts used must be extrapolated to zero solute ion concentration, for even at low concentrations the interpretation can be obscurred by specific ion-ion interaction and ion-pair formation . That identical shifts are obtained with different co-anions is an inadequate safeguard. Dechter and Zink (63) observed shift maxima in systems involving HMPT or water but most of their work was done at 0.2 mol l^{-1} Tl salt. In methanol + water, their results (63), in spite of these being at fairly high concentration, and those mentioned above (65) support the preferential hydration of Tl^+ (Fig. 8). The value for $\Delta G^{\ominus}_{ps}/n$ for Tl^+ is compared with others for the methanol + water system in Table 2. Both u.v. shifts

TABLE 2. N.m.r. solvation parameters for ions in methanol + water

Ion	$\Delta G^{\ominus}_{ps}/n$ kJ mol^{-1}
Na^+	1.28 ± 0.05
Rb^+	0.89 ± 0.05
Cs^+	0.66 ± 0.06
Tl^+	1.2 ± 0.3
F^-	0.13 ± 0.05
Cl^-	0.96 ± 0.06

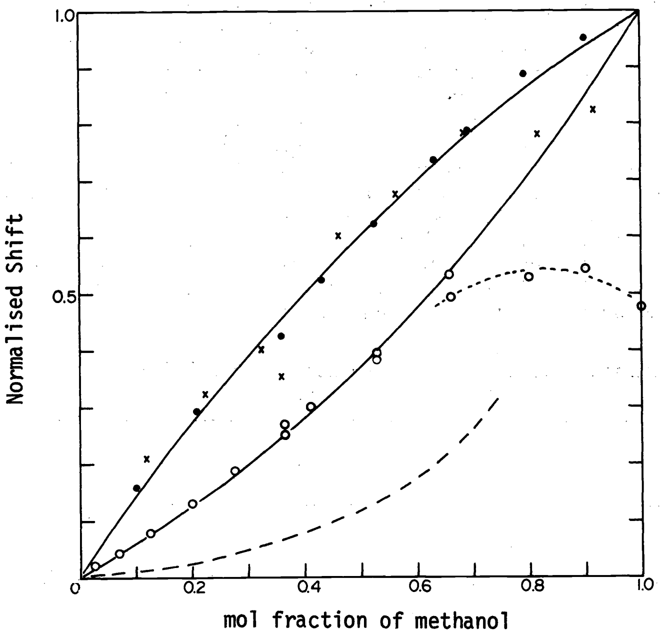

Fig. 8. Normalised shifts for thallous fluoride in water + methanol mixtures (65).
x fluorescence shifts ; ● ultra-violet shifts ; O n.m.r. shifts
--------- effect of ion-pair formation on n.m.r. shifts
— — — — — n.m.r.shifts for thallous acetate at 0.2 mol l^{-1} (63).

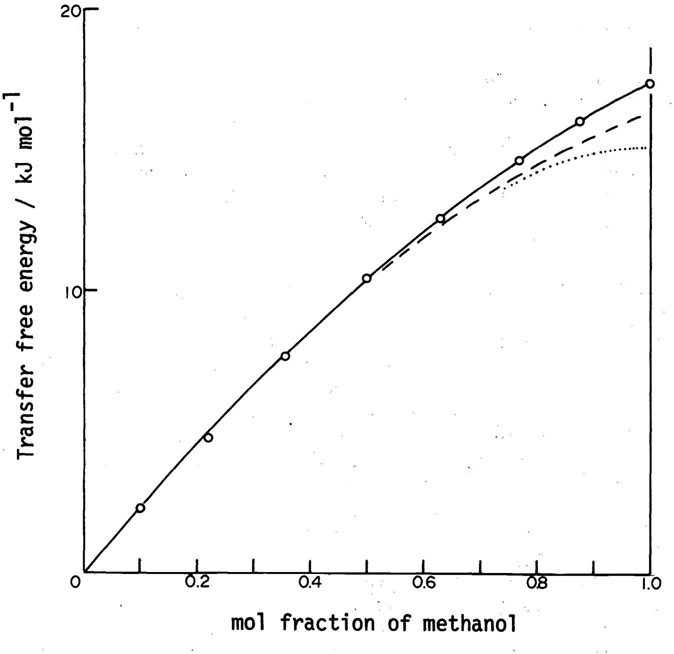

Fig. 9. Transfer free energy of thallous fluoride from water to water+ methanol mixtures determined from e.m.f. measurements (65).
——— 10^{-3} aquamolal ; — — — — 3×10^{-3} aquamolal ;
.... 10^{-2} aquamolal .

(219 nm in water) and fluorescent shift measurements (368 nm) have the opposite curvature to the n.m.r. shifts suggesting preference for methanol in the solvation sphere of Tl^+ ($K^{1/n} = 1.9 \pm 0.2$). The n.m.r. based conclusion is preferred for reasons given elsewhere (65). Using the same analysis as previously described (31) for NaCl and CsCl in methanol + water, namely application of the Born equation, n = 6 and noting that F^- is not preferentially solvated in this solvent mixture, reasonable agreement is obtained between the determined and calculated transfer free energies between pure solvents but again the wrong curvature is obtained as with NaCl, CsCl (Fig. 10). As further evidence of the problems of failing to obtain n.m.r. shifts at sufficiently low concentrations, the constants log $K^{1/n}$ determined for a variety of binary solvent combinations involving pyridine or dimethylformamide (DMF) by Dechter and Zink (63) are not additive as required (Table 3). Some of the results of Briggs and Hinton (64) in solvent mixtures involving DMSO, water, pyridine and certain amide solvents show unsymmetrical shift behaviour which cannot be fitted by the simple model and a treatment of Covington and Thain (33) would need to be applied. An exception is formamide + DMF, which shows no preferential solvation for Tl^+.

TABLE 3. Experimental values of relative solvating ability for Tl^+ (Dechter and Zink (63))

Solvent	Log $K_{DMF}^{1/n}$	Log $K_{Py}^{1/n}$	Difference
Pyrrolidine	1.127	0.898	0.229
HMPT	0.987	0.334	0.653
DMSO	0.560	0.279	0.281
Pyridine (Py)	0.161	0	0.161
DMF	0	-0.114	0.114
Tributylphosphate	-0.431	-0.108	-0.323
THF	-0.686	-0.458	-0.228
Acetone	-0.967	-0.717	-0.250

b) Nuclear magnetic relaxation rate measurements.

N.m.r. relaxation measurements can provide information about preferential solvation. Holz, Weingartner and Hertz (66) have obtained from line width measurements relaxation rates ($1/T_1$) of ^{35}Cl, ^{21}Br, ^{127}I, ^{23}Na and ^{87}Rb in methanol + water mixtures over the complete mol fraction range and extrapolated them to zero salt concentration to remove ion-ion interaction effects. Making some assumptions from the theory of Hertz (67), it was shown that the relaxation rate in the mixed solvent is given by

$$(1/T_1)_{mix} = (1/T_1)^\circ_W\ (1 - h/n)\ \tau_W/\tau^\circ_W + (1/T_1)^\circ_P\ (h/n)\ \tau_P/\tau^\circ_P \qquad (42)$$

where ° refers to pure P or W, τ is the rotational correlation time of solvate molecules, h is the solvation number of P in solvent mixture of mol fraction x_P, and n the constant total solvation number. Setting $\tau_W = \tau_P \simeq \tau$ (the last is measurable from ^2H relaxation times in $CH_3OD + D_2O$) and calculating τ°_W, τ°_P from other measurements, then $(1/T_1)_{mix}$, $(1/T_1)^\circ_W$, $(1/T_1)^\circ_P$ are measured and extrapolated to m = 0. Thus for non-preferential solvation, the solvation shell has the same composition as the bulk solvent, and

$$(1/T_1)_{mix}\ 1/\tau = (1/T_1)^\circ_W\ x_W/\tau^\circ_W + (1/T_1)_P\ x_P/\tau^\circ_P \qquad (43)$$

Equation (43) is used as the theoretical form against which to compare the experimentally obtained curves. For Na^+, the isosolvation point was 0.87 indicating preferential hydration. For Rb^+ no conclusion could be reached but for the Br^- and Cl^-, the isosolvation points were both at 0.30 indicating preferential solvation by methanol in strong contrast to the finding from solute ion n.m.r. shifts discussed earlier. It was concluded that I^- was non-preferentially solvated. A second paper (68) gave details of a study of ^{23}Na and ^{81}Br relaxation rates in amide solvents. It was concluded that Na^+ is non-preferentially solvated in H_2O-formamide and H_2O-NMF, although in the latter mixture there may possibly be slight preferential hydration. For Br^-, deviations from the theoretical form (equation (43)) were attributed to hydrophobic hydration effects in the water-rich mixtures since the measured relaxation rates exceed the value expected if the component with the larger field

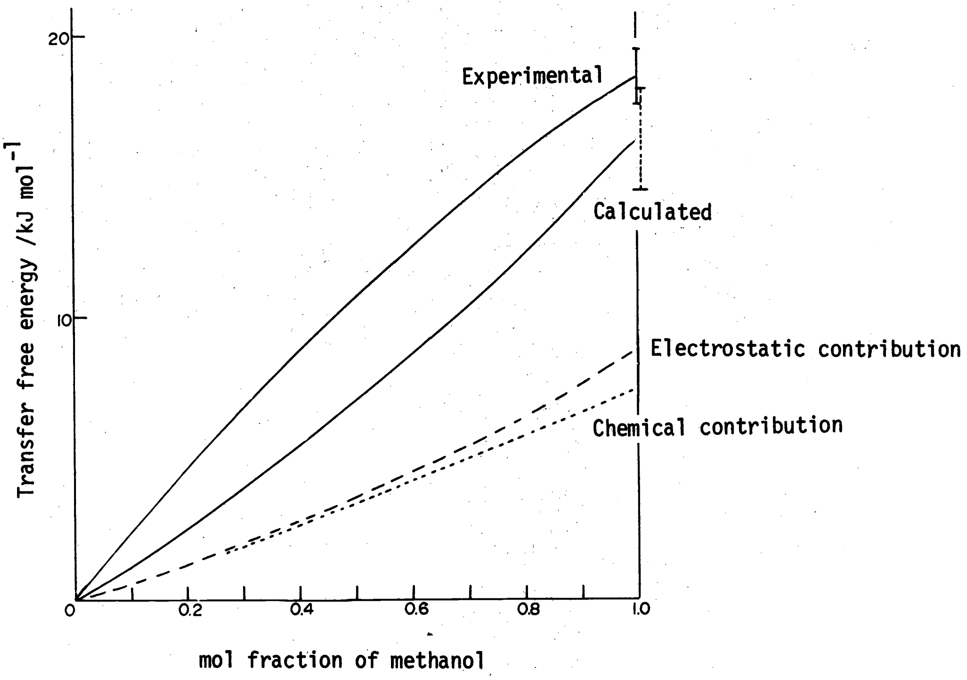

Fig. 10 Comparison of calculated free energy of transfer for thallous fluoride from water to methanol + water mixtures with experimental values obtained using ion-selective electrodes (65).

gradient were completely solvating the anion over the whole range of composition. In two more recent papers (69, 70), Hertz and coworkers have attempted to obtain further information about preferential solvation in methanol + water mixtures by proton relaxation methods. It was concluded that there was evidence for the preferential hydration of K^+ and Rb^+.

c) Isotope effects.

The substitution of D_2O for H_2O should have a large effect on $(1/T_1)$ for a preferentially hydrated ion. Holz (71) has shown that in a mixed solvent the ratio $R(x_P)$ of relaxation rates, in solvent mixtures with a given composition, containing H_2O or D_2O at constant salt concentration, which gives information about the ratio of reorientation times of D_2O and H_2O molecules in the solvation shell of an ion, is given by

$$R(x_P) = \frac{(1/T_1)^{D\ mix}}{(1/T_1)^{H\ mix}} = \frac{(1 - h/n)\tau_W^{D\ mix} + M(h/n)\tau_P^{D\ mix}}{(1 - h/n)\tau_W^{H\ mix} + M(h/n)\tau_P^{H\ mix}} \qquad (44)$$

where h is the solvation number of P in the mixture of mol fraction x_P, M is the ratio of the square of the relative electric moments to relative approach distances of ion and dipole = 0.87. Holz then assumes

i) $\tau_W^{D\ mix}/\tau_W^{H\ mix} = (1/T_1)^D/(1/T_1)^H = R(x_P{=}0)$

That is the reorientation time at the ion of H_2O is reduced relative to that of D_2O molecules by the same factor as in pure water.

ii) $\tau_P^{D\ mix} = \tau_P^{H\ mix}$

That is that the water isotope effect does not influence the molecular orientation of component P. Finally

$\tau_P^{D\ mix}/\tau_W^{H\ mix} = 1.65$

is obtained from ^{17}O line width measurements. Substituting gives

$$R(x) = \frac{(1 - h/n)\, R(x_p = 0)/1.65 + 0.87(h/n)}{(1 - h/n)/1.65 + 0.87(h/n)} \qquad (45)$$

from which h/n can be obtained.

It was concluded that in methanol + water mixtures in the water-rich region that Na^+ was preferentially hydrated but for Br^- there was weak preferential solvation by methanol with an isosolvation point of 0.7 in good agreement with the value derived by the previously discussed method. Fig. 11 summarises the available results on solvation in methanol + water and highlights the very considerable discrepancies between the conclusions from chemical shift and relaxation rate measurements. This points to problems arising from the validity of the theories and the assumptions made before applying them. Holz (71) also reports that Rb^+ is preferentially hydrated in F + H_2O whilst Br^- is non-preferentially solvated, and Na^+ is solvated by DMSO in DMSO + H_2O.

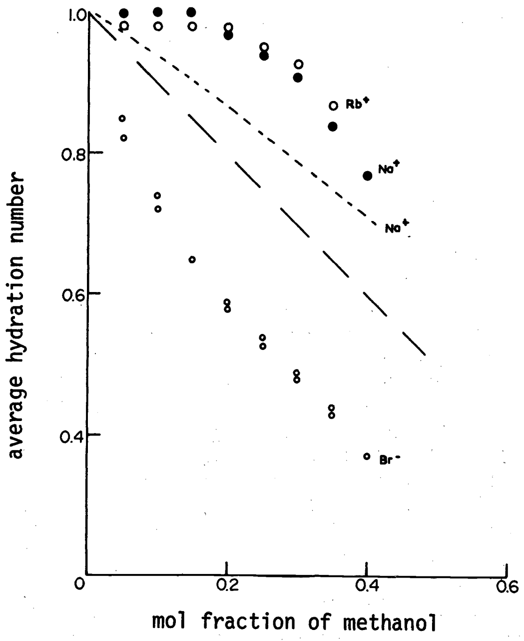

Fig. 11. Plot of the average hydration number (n - h)/n for sodium, rubidium and bromide ions in water + methanol mixtures as determined by Holz (71) compared with that obtained from chemical shift studies (31) shown by --------- . The hatched line _ _ _ indicates non-preferential solvation.

Lindman and coworkers (41) have suggested the water isotope effect on solute-ion chemical shifts should be a direct measure of ion-water contact and thus provide information on preferential solvation. They studied ^{133}Cs shifts in DMF-H_2O and DMF-D_2O mixtures. Maxima in the shift curves with DMF mol fraction caused them to cast doubt on the validity of the intrinsic shift assumption. However, it must be realised that the observed shifts in this system are very small (∿1 - 2 ppm) compared with solvent shifts usually observed for caesium (∿100 ppm), and in this case are indicative of secondary effects. From a plot of equation (38) for the difference in shifts for the two iostopic systems which was linear they concluded that $K^{1/n} = 1.6$ for the preferential solvation of Cs^+ by DMF.

CONCLUSIONS

Considerable progress has been made in understanding the phenomenon of preferential solvation during the 1970's. Whilst there are some aspects which require further attention and discrepancies exist for some systems, the correlation of approaches by various techniques establishing them in a thermodynamic or statistical mechanical framework has led to important unification of approach instead of isolated and fragmentary studies. It is to be hoped that other methods which in principle can yield information about preferential solvation, namely limiting conductance in mixed solvents (72) and Washburn numbers (73) can be refined and applied to the study of systems about which information is available from spectroscopic techniques. Methanol + water is probably the most difficult type of system to understand because of hydrogen bonding - second shell interactions which vary with bulk composition. Isodielectric systems may afford a simplification but one which may be misleading if the components differ in polarity.

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