PREFERENTIAL SOLVATION OF IONS AND SOLVENT TRANSPORT

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Abstract - In the common binary aqueous mixtures, for example dioxan +
water, an ion induces a non-random equilibrium distribution of solvent
molecules such that close to the ion one solvent component is in excess
of its concentration in the bulk. Thermodynamic, spectroscopic and
transport properties of the solution are influenced by this preferential
solvation. We concentrate here on the transport of one solvent component
with respect to the other in the field of the ion and show how diffusion
and transport measurements can be combined to obtain the transport number
of water, say, with respect to the non-aqueous solvent component, n_w.

It can be shown that $n_w = N \left[\dfrac{(l/q) - 1}{(l/q) + (1/q)} \right]$

where N is the total dynamic solvation number, l is the ratio of water to
non-aqueous component in the transported solvent and q the corresponding
ratio in the bulk.

Values of n_w for alkali-metal and halide ions in solutions of high water
content containing raffinose, dioxan, acetone, methanol, allyl alcohol,
tertiary butanol, dimethysulphoxide and glycine are presented. The n_w
values in the 0.75% (W/W) raffinose + water system probably approach N in
pure water closely; they are $Li^+(16)$ $Na^+(10)$ $K^+(6)$ $Cl^-(4)$ and $H^+(1)$. In
the remaining systems these figures are reduced by competition of the
organic molecule for solvation of the ion; n_w is seen to be influenced by
the ion-molecule (acid-base) interaction, steric and kinetic effects.
Glycine solvates both cations and anions preferentially; DMSO and tertiary
butanol solvate the halide ions preferentially.

Very marked changes in n_w as a function of composition (q) in the DMSO +
water and dioxan + water systems occur for some ions. These can be
explained in terms of changes in N and l/q with the structure of the mixed
solvents.

INTRODUCTION

Let us consider an electrolyte dissolved in a binary mixed solvent. In this lecture we con-
centrate on those binary mixtures that contain water as one component. A typical system
would be sodium chloride - water - dioxan. The non-aqueous "solvent" component need not be
a liquid in its pure state; aqueous solutions of the sugar raffinose and the amino-acid
glycine, for example, are particularly interesting solvent mixtures.

It is of course very appropriate that we should speak of these systems in France when we
think of the important contributions made to this field by French physical chemists.

The equilibrium distribution
Consider a mixed solvent, for example the dioxan - water mixture, containing a certain
definite mol ratio q of water (W) to dioxan (S).

Then $q = \dfrac{\nu_w}{\nu_s} = \dfrac{x_w}{x_s}$ (1)

where the ν are the numbers of mols in a given sample and the x are mol fractions.

When we introduce an ion into the mixed solvent it will normally interact to different extents with the two solvent components; and this will induce a non-random distribution of the solvent molecules with respect to the ion.

At large distances from the ion a volume element will contain the two components in the same ratio, q, as in the bulk mixed solvent; but in shells close to the ion the ratio will change and there will be a higher proportion of one component to the other than in the bulk. We say that the ion is <u>preferentially solvated</u> by that component.

It should be stressed that in many of the common mixed aqueous solvents, like water with alcohols, dioxan and DMSO, the methods available to us suggest that the extent of preferential solvation is usually, though not always, weak, though it can still have very interesting consequences. We shall return to this point, but could briefly consider one example.

Suppose we take a mixed solvent containing one mol of glycine $^+NH_3.CH_2.COO^-$ with 150 mols of water. Our experiments suggest that near to an alkali-metal ion the mol ratio of glycine increases to one in 100 mols of water. This is a weak preferential solvation of glycine, even though the immediate environment of the ions is still markedly aqueous.

Experimental consequences of preferential solvation

The equilibrium distribution will of course determine the <u>thermodynamics of ion solvation</u>. Where the preferential solvation is marked, and in particular in totally non-aqueous mixtures, it has been possible to predict free energies, enthalpies and entropies of transfer from determinations of the stability constants of the ion-solvent complexes [1]. This approach tends not to be so successful in aqueous mixtures; and there is also the problem that thermodynamic quantities for the two ions of a binary electrolyte cannot be separated unambiguously, and this usually makes interpretation difficult, particularly, again, if the preferential solvation is rather weak.

The latter problem can to some extent be overcome in n.m.r. studies [2] where the ionic nucleus is active, for example ^{23}Na or ^{81}Br; and we shall later compare some of our new results with those obtained by n.m.r. techniques.

Solvent transport by ions

We turn now to another type of experiment, and it is this that will occupy the rest of this lecture. When an ion moves under a gradient of electrical potential, as in electrolysis, or of chemical potential, as in diffusion, it will tend to move solvent molecules with it. Those close to it, where the effects of preferential solvation are most marked, are likely to be moved more readily than those further away, so if we can analyse the solvent that has moved with the ion we can infer something about the preferential solvation. We shall see that the measurements have two advantages: they are very sensitive; and they can be made for individual ionic species. On the other hand these are dynamic experiments and we must be careful in relating the results to the equilibrium distribution.

The story begins in the basement of the University library looking up a very famous experiment made by Washburn [3] seventy-five years ago.

Raffinose is a trisaccharide which has a very high specific optical rotation and can therefore be easily analysed. Washburn took aqueous solutions of the alkali-metal chlorides and added a little raffinose to them. He then did an ordinary Hittorf transport number experiment; but, at the end of it, he analysed the electrode compartments for raffinose as well as electrolyte. In this way he found the amount of water transported towards the cathode per Faraday relative to raffinose; it is the net effect of transport in opposite directions by ions of opposite sign. For a uni-univalent electrolyte we write, in modern terminology,

$$w_W = (n_W)_+ \ t_+ - (n_W)_- \ t_- \tag{2}$$

The n_W are the numbers of mols of water transported per mol of ions relative to the second solvent component and the t are the ionic transport numbers. In honour of Washburn we now call w_W the Washburn number of water; we could equally well talk of the Washburn number of raffinose w_S and in fact

$$\frac{w_W}{w_S} = - \frac{x_W}{x_S} \tag{3}$$

Washburn's main aim was to find out something about the hydration of the ions. So he speculated as to whether the raffinose could be regarded as "inert", that is, not moved by the ions at all, in which case the n_w would be true dynamic hydration number for the ions. This is an interesting point to which we shall return.

During the years that followed, Washburn numbers were determined for a number of different aqueous mixtures and it became clear that whether or not an inert reference substance could be found, the Washburn number of a given electrolyte was usually markedly dependent on the nature and concentration of the organic component.

All three of the classical methods for measuring ionic transport can be adapted to the measurement of solvent transport numbers. As well as the Hittorf method, there is a moving boundary method, developed by Longsworth (4); and much of the modern work, including our own, has used the e.m.f. method, which I shall discuss briefly later (5 - 8). Each method has its advantages and disadvantages. The e.m.f. method is precise and applicable to dilute electrolyte solutions, but is not suitable for very low concentrations of organic component, and is limited by the availability of reversible electrodes. The other methods are applicable to almost any electrolyte, but rather high electrolyte concentrations are required in the Hittorf method, and low non-electrolyte concentrations in the moving boundary method.

The Erdey-Grúz experiment
Of course, as Washburn himself noted, without another kind of experiment, or some assumption, we cannot calculate the individual n_w from the Washburn number.

For some years we were all measuring Washburn numbers unaware that the distinguished Hungarian electrochemist Tibor Erdey-Grúz and his co-workers had already solved, or partly solved the problem as early as the 1930's, although there was no publication until 1948 (9).

In electrolysis, cations and anions move in opposite directions. In diffusion, they move in the same direction, so that the relative solvent transport is now the sum of effects for cation and anion. Thus it should be possible to obtain what we call the Erdey-Grúz number

$$\Sigma n_w = (n_w)_+ + (n_w)_- \qquad\qquad (4)$$

from a diffusion measurement; combination of this with the Washburn number will at once yield the individual n_w unambiguously. The procedure is completely analogous to the way in which limiting equivalent conductances are obtained unambiguously. We get two equations because ions transport both mass and charge.

Erdey-Grúz therefore set up a diffusion cell (I)

$$\begin{array}{|c|c|c|} \hline W(1) & W(1) & \\ S(2) & S(2) & \\ MX(3) & & \\ \hline \end{array} \qquad\qquad (I)$$
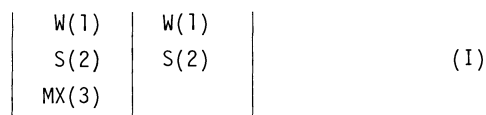
Typically he made up an alcohol + water mixture and separated it from a solution of the salt in a mixture of the same composition on the other side. He reasoned that as the salt diffused it would carry one component with respect to the other. An analysis of the solvent side would reveal how much alcohol, or water, one mol of salt had carried across; this would be the desired number.

Unfortunately, he did not allow for an important effect. The addition of the salt to the mixed solvent changes the chemical potentials of the two components; in most cases that he studied it would raise that of the organic component. This means that a flow of organic component accompanies that of the ions. This effect, or macroscopic coupling (10) is not the one we are interested in, which is rather the microscopic coupling. Usually, the effect of macroscopic coupling is of the same order but greater than that of the microscopic coupling, and Erdey-Grúz concluded that the ions in almost all cases transported the organic solvent in preference to water. Although this can, of course, happen with the right systems, it is not what he expected and it seemed to cause him to abandon these important experiments.

There the matter rested until we read the English edition of his book on Transport Processes, in which these experiments are described rather more clearly than in the 1948 paper, and since 1977 we have been carrying out the Erdey-Grúz experiment in Dublin, but correcting for the macroscopic coupling (11).

Soon after this we met Professor Chemla of Paris and found, in the way that one often does, that he was on the same track (10). It was gratifying to find that he was getting the same sort of answers as we were with a different diffusion technique. In this he examines the flux of electrolyte under a gradient of chemical potential of the organic component, using the capillary method.

Experimental method
Because of changes in its solvation energy the activity of an electrolyte at a given molal concentration will vary with composition of the mixed solvent and we first require inform-ation on activities of the electrolyte in the various mixed solvents relative to a common standard state; usually water is chosen. The extensive work that has been done on free energies of transfer means that this information is often already available. Typically (12) a concentration cell "without transport" is used, for example (II).

$$Ag\text{-}AgCl \mid NaCl(W) \mid Na(Hg) \mid NaCl(W,S) \mid AgCl\text{-}Ag \qquad (II)$$
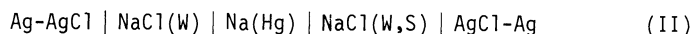
This information is used in two ways. Firstly we find pairs of electrolyte concentrations at which its activities are equal on either side of cell (II) - these would give it a zero e.m.f. - and use them in cell (III) "with transport".

$$Ag\text{-}AgCl \mid NaCl(W) \quad NaCl(W,S) \mid AgCl\text{-}Ag \qquad (III)$$

The e.m.f. of cell (III) is given by

$$E = (2RT/F) \int_{W,S}^{W} t_+ \, d \ln a_+ + (RT/F) \int_{W,S}^{W} w_W \, d \ln a_W \qquad (5)$$

For matched activities ($a_\pm$) the first term of (5) disappears to within experimental error. This leaves the second term which we extrapolate to infinite dilution of the electrolyte; we then obtain the Washburn number using published water activities (a_W). A series of measurements in a given mixed-solvent system leads to Washburn numbers which are average values at the mid-points of small intervals of solvent composition. Another way of getting equal electrolyte activities was suggested by G.N. Lewis (13) and has been used by Schneider (14) and that is to saturate each side of the cell with electrolyte.

The information from cell (II) is also essential to correct for macroscopic coupling in the Erdey-Grúz diffusion cell via the powerful equation (6).

$$\left(\frac{\partial \mu_3}{\partial n_2}\right)_{n_1,n_3,P,T} = \left(\frac{\partial \mu_2}{\partial n_3}\right)_{n_1,n_2,P,T} \qquad (6)$$

We use a diaphragm cell and measure the flux of electrolyte and solvent by conductance and interferometry respectively. Without going into the theoretical details, it is worth mentioning that a complete analysis of the data to obtain all four phenomenological or practical diffusion coefficients, as in the beautiful work of Miller (15) is not necessary in this application, where all we require is a ratio of fluxes.

Meaning of n_W
Combination of the Washburn and Erdey-Grúz numbers gives us n_W for an individual ionic species. What does n_W mean?

Suppose that, on average, an ion carries N molecules of solvent with it, made up of N_S of non-aqueous component and N_W of water. Thus $N = N_S + N_W$. Earlier we defined $q = \nu_W/\nu_S$, that is the mol ratio in the bulk, and we can now define the mol ratio in the transported solvent as $l = N_W/N_S$.

Independently of any molecular model, by considering hypothetical transport experiments, we can show that equation (7) holds:

$$n_W = N\left[\frac{l-q}{l+1}\right] = N\left[\frac{(l/q) - 1}{(l/q) + (1/q)}\right]. \qquad (7)$$

We shall be considering values of q ranging from about 4000 (for 0.75% raffinose solution by weight) to 9 (for 30% dioxan by weight).

The ratio l/q is important.   For strong preferential solvation by water, $l \gg q$, and $n_W = N$;   the relative solvent transport number is then the same as the dynamic solvation number.

For all $l > q$, n_W is positive and preferential solvation is by water.

If $l = q$, $n_W = 0$;   the ion is carrying the solvent components in exactly the proportions present in the bulk mixture.

When preferential solvation is by the non-aqueous component, that is, $l < q$, n_W is negative;   we may prefer then to use the relative solvent transport number of the non-aqueous component, n_S:

$$n_S = -n_W/q$$

Finally, if solvation by the non-aqueous component is very strong, that is if $l \ll q$, we have $n_S = N$.

This treatment of the n is exact, but we see that n is not a very simple quantity conceptually.   Later on we can make a somewhat less exact model that gives figures that are more easily visualised.

Some results
Let us now examine a selection of figures obtained for low concentrations of organic component (Table 1)

TABLE 1. Solvent transport numbers of ions in binary aqueous mixtures

n_W/mol (water) mol (ion)$^{-1}$

(n_S)/mol (organic component) mol (ion)$^{-1}$

	Raffinose	Dioxan	Acetone	TBA	Allyl Alcohol	Methanol	DMSO	Glycine	
%(W/W)	0.75	5	6	5	10	5	5	2.5	
q	3705	93	50	78	29	34	82	163	
Li$^+$	15.5	11.0	–	4.8	3.5	3.3	1.2	-7.3	(0.045)
Na$^+$	9.7	9.2	7.6	4.2	4.1	4.1	4.6	-5.0	(0.031)
K$^+$	5.6	5.7	–	3.0	2.7	2.2	2.4	-3.5	(0.021)
Rb$^+$	–	2.2	–	1.8	–	2.3	3.3	–	–
Cs$^+$	5.0	2.0	–	1.0	–	1.9	2.0	-3.3	(0.020)
H$^+$	1.4	–	–	0.8	–	1.9	2.0	–	–
Cl$^-$	4.2	2.4	1.4	-1.2	-0.7	-0.1	-0.7	-3.6	(0.022)
Br$^-$	–	–	1.1	-2.4	–	-0.3	-3.4	–	–
I$^-$	–	–	–	-3.2	–	-0.7	-5.1	–	–
BPh$_4^-$	–	-100(2)	–	–	–	–	–	–	–
Ref w_W	(4)	(6,20)	(21)	(22)	(20)	(5,6,7)	(8,21)	(20)	
Σn_W	(15)	(17,20)	(17)	(23)	(20)	(17)	(20)	(20)	

Absolute accuracy ±1 except for raffinose ±2.

Relative accuracy among cations or anions in any system much better.

We shall assume that at these concentrations any modification of the water structure by the organic component is negligible; in the course of time we would hope to determine values at infinite dilution of the organic component. We have ranged the systems so that we go from strong preferential solvation by water, in the raffinose system, to preferential solvation by the non-aqueous component, in the glycine system.

Let us first examine the relationship between the equilibrium distribution and the kinetics of flow.

The equilibrium distribution for a given type of ion will be an average over a number of different distributions of varying energies for all the ions of that type. Each different distribution will lead to a different activation energy for flow and the current will be carried preferentially by the ions having the lowest activation energies. This will shift the solvent ratio in the transported solvent from its average values in the near-neighbour shells at equilibrium. It is perhaps helpful, though less exact, to envisage the ion and solvent molecules as forming a range of ion-complexes of different compositions and activation energies for flow.

A good example where a major shift would be expected is the raffinose + water system. Raffinose is large, heavy and strongly bonded to water. Even if a cation made a strong bond to one of its many hydroxyl oxygen atoms, the resulting complex would have a low mobility and would play little part in carrying the current. The relative water transport for this system is, in fact, the largest of any we have studied. The total dynamic solvation numbers N in pure water then are probably close to the values of n_w and pro-

visionally we shall assume that the two are equal, that is, that Washburn was right in treating raffinose as inert. We see that N is the equivalent of 1 - 3 shells of solvent molecules.

The raffinose + water system is a clear-cut limiting case, but in general the interpretation of these figures is complex, and becomes more so at higher non-electrolyte concentrations. Let us try, however to establish a model to explain the main effects.

Years ago, Feakins and Watson examined the free energies of transfer of these ions from water to mixed solvents, and proposed that the dominant interaction in a first shell of orientated solvent is of an "acid-base" type (16). In alcohol + water mixtures, for example, a cation interacts with the oxygen atoms, while anions interact with the hydroxyl hydrogen as in a hydrogen bond. Alcohols are stronger bases and weaker acids than water, and, through co-operative hydrogen bonding, transmit these characteristics to water molecules, so that in the mixtures, all molecules are stronger bases and weaker acids than in pure water.

This "averaging" of "acid-base" properties is important in the present problem for two reasons.

(a) At equilibrium, if both species become of approximately the same basicity, the primary solvation of the smaller cations, for example, may be decided solely on steric grounds and will be by water even though the isolated water molecule is intrinsically the weaker base. This steric effect may be less important for the larger cations.

(b) Kinetically, the concept of averaging of acid-base properties suggests that several quite different distributions around the ions might be close in energy, and this would lead to an average distribution that could change markedly with the perturbations caused by flow or by small changes in solvent composition.

In the present state of knowledge we cannot yet add to this. As with the raffinose system, ion-complexes involving water might carry the current preferentially because of their smaller size. Against this, the incorporation of the non-aqueous component might provide a hydrophobic surface of shear for the ion-complex.

We return now to the figures in Table 1.

Cations
From thermodynamic and gas-phase studies we would expect all the organic species to be stronger bases than water (7,8). Yet in almost all cases the cations transport water in preference to the non-aqueous component for the reasons stated above.

Glycine is a notable exception. The charges are fully developed at both ends of the molecule in the zwitterionic form, making it both a stronger acid and a stronger base than water; it is clear that the strongest interaction in this case will be if the glycine enters the first solvation shell of the ion, whether anion or cation.

The dioxan + water system is more typical. Here the preferential solvation of lithium by water is marked. However, the relative water transport by caesium is much less than in the raffinose system, presumably because the dioxan is now more readily accommodated around the larger ion. We shall see in the case of the anions that "soft-soft" interactions are important and these may also encourage the incorporation of the organic molecule next to the polarisable caesium ion.

It is not possible at this stage to interpret much of the fine structure of Table 1; but if we concentrate on the lithium ion, the trends across the Table are reasonable. The alcohols are more readily accommodated around the ion than dioxan and n_w falls, though less for the bulkier tertiary butanol (TBA) than for allyl alcohol or methanol.

The figures for the caesium ion suggest however, that when steric hindrance is not a problem, TBA is a stronger ligand than the other two alcohols.

Dimethylsulphoxide is a strong ligand in the solvation of lithium, despite an unfacourable stereochemistry. The sterically similar acetone is a weaker ligand, as is demonstrated by the values of n_w for the sodium ion in the two systems.


Anions
We have fewer data for anions (Table 1) but they are very interesting.

On its own is a very exciting result, obtained in Professor Chemla's laboratory, showing very marked preferential solvation of the tetraphenylboride ion by dioxan at very low concentrations of dioxan, easily the strongest such interaction yet demonstrated. This suggests that the practice of using sodium tetraphenylboride as a universal solute is one that should be attended with caution.

The preferential solvation of the chloride ion by glycine in the glycine + water system and by water in both the acetone + water and dioxan + water systems, are the expected results. Less expected is a slight preferential solvation of the halide ions by the alcohols and DMSO; this is most marked with DMSO and the iodide ion; we shall consider this case in detail.

It would be generally accepted (though this does not mean it is true) that a halide ion is in a lower free energy state in pure water than in pure DMSO. Further, at equilibrium, we imagine that iodide can interact with water in a hydrogen-bonding type of interaction like

$$I^- \ \ldots\ldots\ H - O \diagdown_{\displaystyle H}$$
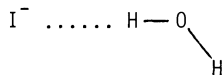
whilst this is not possible with DMSO. Why then is there preferential solvation by DMSO? We must answer this at the usual two levels.

In a DMSO + water mixture the acid strength of the water molecule will be reduced by its interaction with the very basic DMSO, so that water molecule now forms a weaker bond with the ion.

$$I^- \ \ldots\ldots\ H - O \diagdown_{\displaystyle H \cdots O=S-CH_3 / CH_3}$$
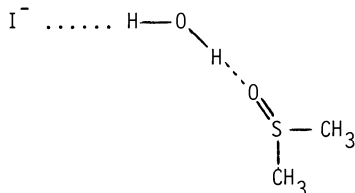
The ion may therefore prefer to bond directly to DMSO <u>via</u> a "soft-soft" interaction - both are highly polarisable species.

The temptation to postulate some actual chemical bonding will for the moment be resisted because, as will be seen, tertiary butanol behaves very similarly.

It is also possible that a complex containing DMSO is kinetically favoured because it provides a shear surface at the methyl groups. We contrast this specific ion-solvent interaction with that of a cation where the DMSO molecule does not have to be adjacent to the ion to exert its basic effect.

Weak preferential solvation of halides by DMSO is consistent with the n.m.r. evidence (18). In methanol + water mixtures, a study of nuclear relaxation times (19) indicates slight preferential solvation of sodium and rubidium ions by water and of chloride and bromide by methanol, as we find here.

In Table 2 the information about these systems is given in a less exact but more revealing way. We identify N, the total dynamic solvation number, with the n_w values in the raffinose + water system and suppose that these values of N will hold for all these highly aqueous systems. We then calculate the ratio l/q; a value greater than unity indicates preferential solvation is by water, and less than unity, by the non-aqueous component. The values deviate little from unity, in other words preferential solvation is weak.

TABLE 2. Values of l/q

	Dioxan	Acetone	TBA	Allyl alcohol	Methanol	DMSO	Glycine
%(W/W)	5	6	5	10	5	5	2.5
Li^+	3.4	-	1.4_5	1.3	1.3	1.1	0.7
Na^+	-	4.6	1.8	1.9	1.7	1.9	0.7
K^+	-	-	2.2	1.6	1.6	1.6	0.6
Cs^+	1.6	-	1.2_5	1.6	1.6	1.6	0.6
H^+	-	-	2.3	-	1.1	0.7	-
Cl^-	2.3	1.5	0.8	0.9	1.0	0.9	0.5
(N=4?) I^-	-	-	0.6	-	0.9	0.4	-

The equation $n_w = N \left[\dfrac{(l/q) - 1}{(l/q) + (1/q)} \right]$ is used

with $N = n_w$ for the raffinose + water system.

We turn finally to the way in which n_w varies with solvent composition.

The detailed information is for the moment limited to two systems, dioxan + water and DMSO + water, and these only at high water content (Figs. 1 and 2). For ease of interpretation we have included figures for only three ions on these graphs.
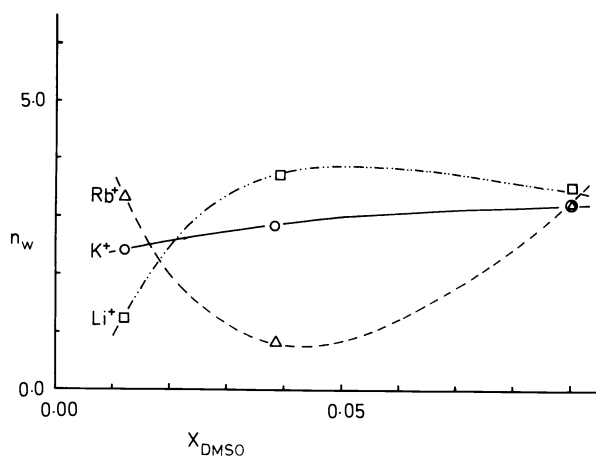

Fig. 1 Dependence of n_w on solvent composition for selected cations; n_w versus mol fraction of DMSO.
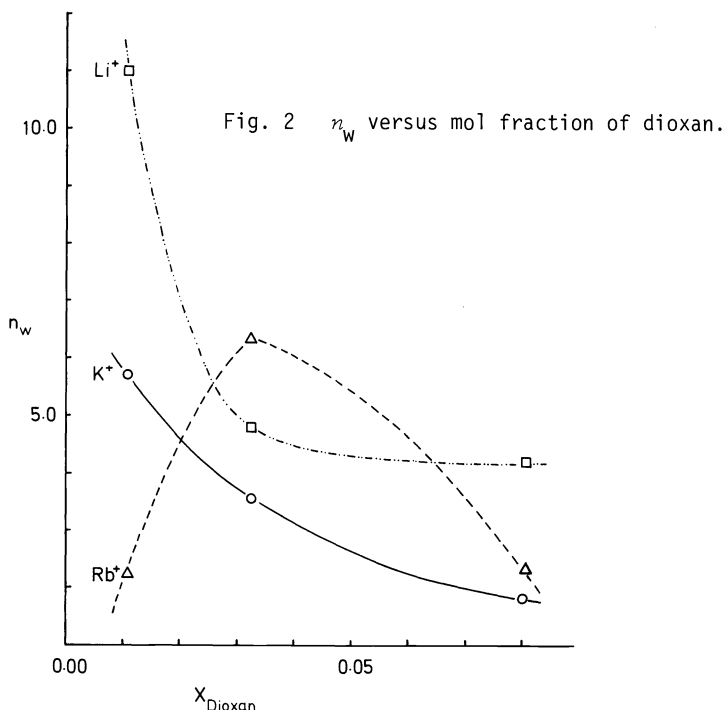
Fig. 2 n_w versus mol fraction of dioxan.

We must be quite frank and say that at this stage we cannot interpret these results with any certainty.

We recall that

$$n_w = N \left[\frac{(l/q) - 1}{(l/q) + (1/q)} \right] \qquad (7)$$

In eqn. (7) the term $(1/q)$ is not important in the present cases.   Thus n_w is a function of the total dynamic solvation number N and of the extent of preferential solvation as measured by l/q.   It is perhaps worth noting that on the simplest kind of Law of Mass Action theory both N and l/q and therefore n_w would be independent of q, the solvent composition.   This is manifestly not the case.

To explain changes as complex as those in Figs. 1 and 2 we shall have to postulate changes in both N and l/q.   Up to now we have dealt with systems so close to pure water that we have been able to assume that N is a constant for a particular ion.

The free energies of transfer of electrolytes in these systems generally vary monotonically with solvent composition (24,25).   Recent work, presented elsewhere at this conference (26) suggests that even the characteristic inflections in the enthalpies of transfer in binary aqueous systems may be explained more simply and uniformly than previously believed.   This disposes us to a largely kinetic explanation of the present phenomena.

We now need to consider the structure of the solvents.   The most striking feature in Figs. 1 and 2 is that the behaviour of the Li^+ and Rb^+ ions is inverted between the two systems. This suggests that there is some fundamental difference between them, and we suggest that it is that dioxan breaks down the structure of water at all concentrations, but that as DMSO is added to water, water structure is at first enhanced and then, at higher concentrations of DMSO, broken down.

When the complex of ion and solvent molecules moves through the solution it encounters a resistance depending on the nature and extent of the solvent structure.   We make only one postulate and that is that ion-complexes will encounter less resistance the smaller their size.   The greater the resistance offered by the solvent, the more will the smaller complexes carry the current;   these will be the ones having the smallest N or highest water content.

Thus the average lithium-solvent complex, already large in pure water, can increase in size as the solvent structure breaks down in the dioxan + water system.   It does this by absorbing more dioxan into the complex, decreasing l/q and hence n_w.   In the DMSO + water

system, the initial rise in n_w is presumably due to the reverse effect, the addition of DMSO at first stiffening water structure and calling for smaller complexes, containing less DMSO, to carry the current.

On the other hand the caesium ion, the extent of whose solvation is limited in water, reacts to the breakdown in solvent structure in the dioxan + water system by first increasing its dynamic solvation number, thus increasing n_w, and then absorbing dioxan into the complex, decreasing n_w again. In the DMSO + water system N will first decrease as solvent structure increases and then increase again with decrease in solvent structure: at higher DMSO concentrations we might predict a maximum in n_w.

Conclusion

It is clear that these suggestions do not explain all the features of Figs. 1 and 2, but at least we are now uncovering previously hidden features of the transport process. The extensions are obvious. For example, the results presented in this talk involve what we believe to be an essentially aqueous regime; there are signs that if the proportion of organic solvent is increased a different pattern of results is obtained (22,23). At the other end we hope soon to be studying very dilute solutions of molecules of biological significance.

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