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Ionic Solute Hydration †

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INTRODUCTION

The last decade has witnessed a rather spectacular revival the field of aqueous electrolyte solutions; new theories and models have been proposed, precise and systematic studies of thermodynamic and transport properties have been accumulating, many spectral techniques, such as IR, RAMAN, NMR, ESR, X-ray and neutron scattering, have been applied successfully to water and aqueous solutions giving a better insight into the molecular nature of solute-solvent interactions.¹⁻⁵ Though this progress has been brought about partly by the improvements in experimental techniques, by the interest generated in related fields, such as analytical chemistry and biochemistry, and by the needs created through problems of pollution and desalination of sea water, it also owes much to the insight and enthusiasm of scientists such as Henry Frank, who this year is celebrating his 70th anniversary.

The properties of ionic aqueous solutions have been studied for well over a century. Most of the non-ideality of these systems was attributed to hydration effects arising from strong charge-dipole interactions,⁶ association and long-range Debye-Hückel type forces. However, with the classical work of Bernal and Fowler,⁷ Eley,⁸ Frank and Evans,⁹ Gurney,¹⁰ Frank and Wen¹¹ and Samoilov,¹² it was realized that the particular nature of the structure of water might also be involved in the solute-solvent and even solute-solute interactions. Despite the strong evidence presented by these authors, the general acceptance of the structural nature of the hydration interactions was slow. This was to a large extent due to the difficulty of distinguishing *coulombic hydration*,¹ arising from strong electrostatic (charge-dipole, charge-quadrupole) interactions, from *structural hydration*, which is related to modifications in the solvent-solvent interactions (hydrogen bond strength and distribution) in the presence of solutes.

† XV^{ème} Conseil International de Chimie Solvay, Brussels, June 1972.

The usual method of studying ion-solvent interactions is to measure systematically one property with different electrolytes and interpret the data in terms of a model. Unfortunately, often conflicting models can explain equally well a particular set of data. Also, it often occurs that the model proposed for the interpretation of one property is in conflict with the interpretation of another, a fact that is usually ignored. To verify completely a model for ion-solvent or ion-ion interactions, it is important to check it against as many physical properties as possible. Here a distinction must be made between bulk and molecular properties. The bulk properties, such as thermodynamic and transport properties, give us no direct information on the molecular nature of solvation, but can discriminate between ion-solvent and ion-ion interactions and lead themselves readily to quantitative calculations. The spectral techniques (IR, NMR, X-ray, etc.), cannot always isolate ion-solvent interactions, but on the other hand can often give specific information on the energetics and dynamics of the molecular interactions in the vicinity of the ions. Ideally, one should therefore test quantitatively a hydration model against most of the bulk properties and qualitatively against the molecular properties.

An examination of all the properties of aqueous electrolyte solutions is well beyond the scope of the present review. The systematized tabulation of properties, such as spectral data, is far from being complete, and there are still many important gaps even with simple systems like alkali halides. However, with most thermodynamic and transport properties, reliable data at 25°C has been accumulating with model electrolyte systems such as alkali halides, tetraalkylammonium halides and *n*-alkylamine hydrobromides. Through a careful examination of these systems, we can in principle determine the influence of the ionic field, size and shape of the ions on hydration. It should then be possible to find the simplest model which is consistent with these properties and which is not in conflict with the findings of the molecular properties.

The theories of ionic solvation will not be reviewed at the present time. A much slower evolution has marked the theories of ion-solvent interactions in comparison with the theories of ion-ion interactions.¹³ This is understandable if we consider that continuous solvent models are applicable to the theories of excess functions but are much less so in the case of hydration effects, which are related to short-range effects; molecular models have therefore more hope of being successful with hydration theories. Also, most of the theoretical calculations have been limited to coulombic hydration. As it will be shown in the present review, structural hydration is far from being negligible, especially with properties such as expansivities, heat capacities and compressibilities, and must be taken into account in any successful theory of hydration. The present state of the solvation theories have been reviewed

in many recent monographs¹⁻⁵ and will not be covered here.

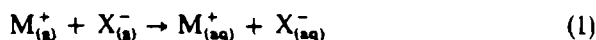
The excess thermodynamic properties will be discussed, but only in relation with ion-solvent interactions. Coulombic hydration will change the effective concentration of the solute, while modification of the structural hydration of ions will cause extra attractive and repulsive forces between ions. While these structural forces can sometimes be small, they can in some cases be predominant and even lead to association.

THERMODYNAMIC AND TRANSPORT DATA

The thermodynamic and transport properties of aqueous electrolyte solutions have been studied for many years. However, much of the earlier data was not accurate enough or too incomplete to distinguish between structural and coulombic hydration. Fortunately, this situation has significantly improved in recent years, and we are now in a position to examine critically the general trends with model electrolyte systems such as alkali halides (MX), tetra-alkylammonium halides (R_4NX) and *n*-alkylamine hydrobromides (RNH_3Br) in H_2O and D_2O at 25°C. The origin and general method of representing the thermodynamic and transport data are summarized below.

a Thermodynamic functions

Partial molal enthalpies and chemical potentials of electrolytes cannot be obtained experimentally. It is possible to measure ΔH for the dissolution process of salts, but this enthalpy is not an additive property of the ions. For this reason, discussion of the influence of ion-solvent interactions on enthalpy usually refers to the hydration functions of gaseous ions



which are both measurable and additive. Similarly, for the same process, it is possible to determine the entropy of hydration: the entropies of ions in the gas phase can be calculated, and the standard partial molal entropies \bar{S}° can be measured with techniques such as electromotive force. From ΔH_h° and ΔS_h° , ΔG_h° is then readily available.

The standard states are often confusing with electrolyte solutions. The standard state for gaseous ions is the hypothetical ideal gas behaviour at 1 atm, and for the dissolved ions it is usually taken as the hypothetical one molal ideal solution. While this latter standard state is identical to the partial molal value at infinite dilution with heats, volumes, compressibilities, expansivities and heat capacities, it does not refer to any well-defined real concentration with free energies and entropies. The problem of the choice of standard states have been well treated in monographs on chemical thermodynamics¹⁴ and in the recent review by Friedman and Krishnan.⁵

Absolute ionic thermodynamic functions of hydration cannot be measured directly and must be obtained indirectly through some non-thermodynamic approximations. Reasonably good values of ionic ΔG_h^0 , ΔH_h^0 and ΔS_h^0 have been tabulated for M^+ and X^{-4} and some R_4N^+ ions.¹⁵

Partial molal volumes are easily derived from density data, and tables of partial molal volumes \bar{V} are available for MX ,¹⁶⁻¹⁸ R_4NX ¹⁹ and RNH_3Br .²⁰ Here again, standard ionic values are available.^{17,18}

Two principal methods have been used to obtain the partial or apparent molal heat capacity (\bar{C}_p or Φ_p) of electrolytes in solution. The direct measurement of the specific heat of the solution is usually limited to fairly high concentrations,²¹ and the extrapolated values to infinite dilution may be largely in error. The indirect method, which is based on the measurement of the standard heats of solutions at different temperatures,²² gives directly \bar{C}_p^0 , the standard partial molal heat capacity. However, with this technique, large differences in temperature are usually required ($\sim 10^\circ C$), and, if the heat capacity is not symmetrical about the mean temperature, significant errors may be introduced. Recently, a differential method has been devised for the measurement of specific heats by flow microcalorimetry,^{23,25} and, with this technique, it has been possible to obtain, in the concentration range 0.01 to 1 molar, the ϕ_c of R_4NBr ,²⁴ of RNH_3Br ³² and of most alkali halides.²⁶

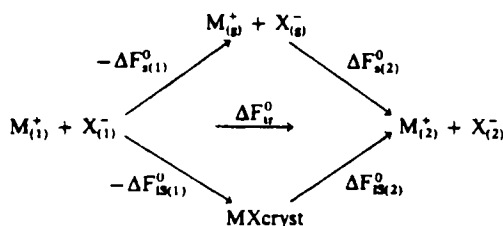
The partial or apparent molal expansivities (\bar{E} or Φ_E) of electrolytes have usually been determined from the variation of \bar{V} or Φ_V with temperature²¹ and consequently suffers from the same drawbacks as the indirect method of measuring \bar{C}_p . The variation of \bar{E} with temperature is usually large and unsymmetrical; the value of $\Delta\bar{V}/\Delta T$ for ΔT of the order of 10 to $20^\circ C$ can therefore be significantly different from the actual \bar{E} at the mean temperature. A more direct measurement with a dilatometer, where a temperature change of only a few degrees would be made, should prove much more satisfactory. However, until such systematic studies are made available, the values of \bar{E} obtained indirectly will have to be used. For this purpose, the data tabulated by Noyes²⁷ on MX and the measurements of Millero and Drost-Hansen²⁸ on R_4NCI will be used. The chlorides may be corrected to the bromides with the data of Dunn.²⁹

Heats of dilution, from which apparent molal relative enthalpies Φ_L can be derived, have been measured by Lindenbaum and Boyd³⁰ and by Wood *et al.*³¹ for R_4NX . Data is also on hand for MX ^{26,32,33} and RNH_3Br .³⁴

b Thermodynamic functions of transfer from H_2O to D_2O

The use of the gas phase as a reference state is often cumbersome; the experimental data is not always accessible with organic ions, and the size of the ions could be different in the gaseous and solution states.³⁵ These difficulties are

avoided if thermodynamic functions of transfer between two solvents are used instead. For example, for the solvents 1 and 2, the standard transfer function ΔF_{tr}^0 is given by the difference in the two standard thermodynamic functions of solvation, $\Delta F_{s(1)}^0$ and $\Delta F_{s(2)}^0$ or by the difference in the two standard integral functions of solution, $\Delta F_{is(1)}^0$ and $\Delta F_{is(2)}^0$



Two approaches have been used in the choice of a reference solvent for transfer functions. An ideal polar solvent with little intermolecular structure, where only coulombic solvation effects should be present, should lend itself more readily to theoretical calculations. Propylene carbonate is often used in this respect.⁵ On the other hand, the effect of coulombic hydration may be eliminated to a large extent if transfer functions from H₂O to D₂O are studied. Both liquids have similar dipole moments and dielectric constants, but D₂O is more structured.³⁶⁻³⁸ A study of this isotope effect will therefore be most sensitive to interactions which depend on the hydrogen bond distribution of the solvent near the ions. Standard enthalpies of transfer ΔH_{tr}^0 are available for most MX,^{39,40} R₄NX³⁹ and RNH₃Br^{41,42} Excess enthalpies of transfer are also available for RNH₃Br.⁴² The ΔV_{tr}^0 and ΔV_{tr}^{EX} of some MX and R₄NBr have been determined by Conway and Laliberté.⁴³ Also ΔC_{ptr}^0 and ΔC_{ptr}^{EX} of R₄NBr and some MX have recently been measured.^{24,44,45}

c Transport properties

The transport properties will yield information on the effect of hydration on the movement of a solute particle. The two properties which have been looked at most systematically are equivalent conductivities and viscosities.

The viscosities are usually discussed in terms of the Jones and Dole equation

$$\eta/\eta_0 = 1 + A_\eta c^{1/2} + B_\eta c \quad (2)$$

or of some extended equations such as

$$\eta/\eta_0 = 1 + A_\eta c^{1/2} + B_\eta c + D_\eta c^2 \quad (3)$$

In both cases, it is the B_η parameter which is related to ion-solvent interactions. The A_η depends on long-range coulombic forces and D_η is an empirical parameter which cannot be interpreted unambiguously.⁴⁶

Kay⁴⁷ has reviewed most of the conductivity and viscosity data available for MX and R_4NX in H_2O and D_2O . To this, we can add the data on RNH_3Br ⁴⁸ and the recent accurate viscosity measurement on MX and R_4NX .⁴⁹

There is no problem in obtaining ionic conductivities since the transport numbers are known. Ionic B_η are somewhat more difficult to estimate, but different methods of separating B_η into its ionic components give approximately the same values.^{10,46} It is therefore probable that the correct ionic B_η are not too different from the suggested ones.

DISCUSSION

Standard thermodynamic functions

The standard thermodynamic functions of hydration at 25°C of M^+ , R_4N^+ and X^- ions are plotted on Figure 1 against the ionic radii. The set of radii suggested by Waddington⁴⁹ were chosen because Masterton *et al.*⁵⁰ have shown that the radii for ions (including R_4N^+) derived from the scaled-particle theory, are consistent with this set. Since the purpose of Figure 1 is only to show the general variation in the thermodynamic functions of hydration with the size of ions, a different scale for ionic radii would not change the qualitative picture, as long as the radii used are self-consistent.

The variation of ΔG_h^0 , ΔS_h^0 and ΔH_h^0 with size on Figure 1 is approximately as expected from a simple electrostatic model. The Born equation predicts that the thermodynamic functions are inversely proportional to the ionic radii, which in general is approximately verified.⁴ Also, if the Born equation is corrected for dielectric saturation in the inner hydration shell, for the difference in size between the gaseous and dissolved state of ions and for the non-electrostatic contribution related to the change in reference state and to interfacial effects, the experimental ΔG_h^0 can be accounted for theoretically.^{4,5} Similarly, molecular models, which take into account charge-dipole and charge-quadrupole type interactions can also explain adequately the experimental ΔH_h^0 .^{4,5,51}

The standard partial molal volumes \bar{V}^0 at 25°C are also plotted on Figure 1 against the ionic radii. \bar{V}^0 varies approximately as the cube of the radius and the deviation from the ideal volume contribution, $4/3\pi r^3 N$, can be accounted for satisfactorily if allowance is made for the free space near the ions, resulting

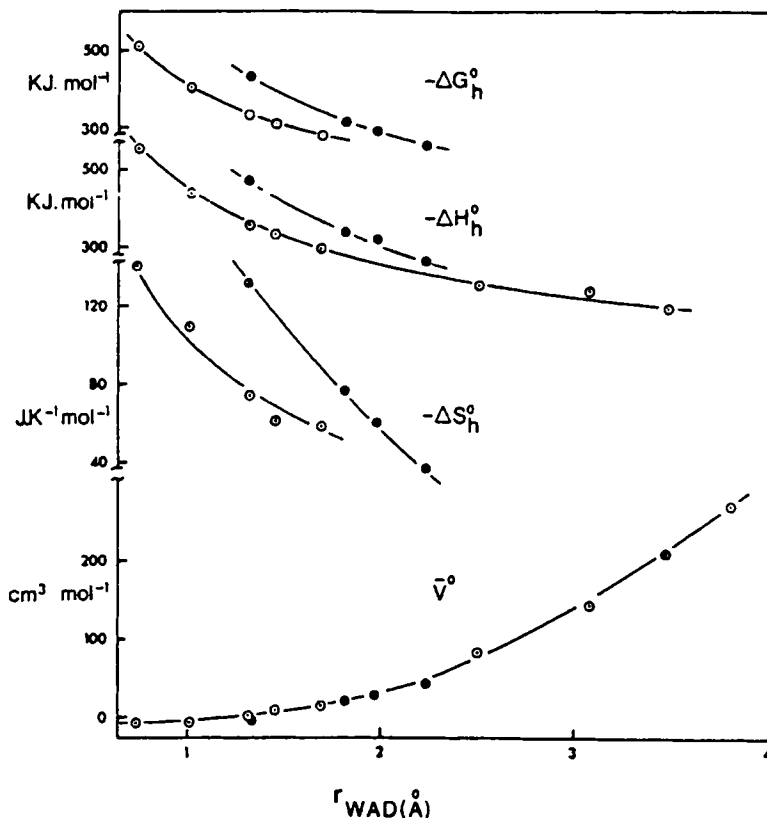


FIGURE 1 Hydration functions of symmetrical monovalent ions in water at 25 C. \circ = cations. \bullet = anions.

from the finite size of the solvent molecules,^{17,18,52} and for electrostriction in the inner hydration shell.^{17,18,53}

The difference in behaviour of cations and anions depends to a large extent on the scale of ionic radii chosen,⁴ and no definite conclusion on the specificity of hydration on the sign of the charge of the ions can be drawn from a plot against ionic radii such as in Figure 1.

It therefore seems that on purely electrostatic grounds it is possible to account, at least semi-quantitatively, for the four thermodynamic hydration functions ΔG_h^0 , ΔH_h^0 , ΔS_h^0 and \bar{V}^0 . For this reason, these functions are often discussed with little, if any, reference to structural hydration effects.⁵⁴ The fair agreement between electrostatic calculations and experimental data does not rule out the existence of structural changes, but it indicates that the structural effects are either absorbed in one of the adjustable parameters (size of the hydration shell for example) or that they are small compared with

the coulombic contribution. Therefore, little information on structural hydration effects can be derived from a study of these functions alone. More sensitive functions will have to be examined. In this respect, functions related to the derivative of \bar{H}^0 , and \bar{V}^0 with respect to temperature or pressure should be more informative.

The standard apparent molal compressibilities ($\phi_K^0 = K^0$), expansivities ($\phi_E^0 = E^0$) and heat capacities ($\phi_C^0 = C_p^0$) of the salts MBr and R_4NBr at 25°C are plotted versus their standard partial molal volume ($\bar{V}_0 = \phi_V^0$) on Figure 2. Ionic values were not used because of the large uncertainty involved in the methods of separating these functions into their ionic components. For example, the ionic ϕ_C^0 of Br^- suggested by Criss and Cobble²² is $-255 \text{ J.K}^{-1} \text{ mol}^{-1}$ while that by Noyes²⁷ is -64 . Partial molal volumes were

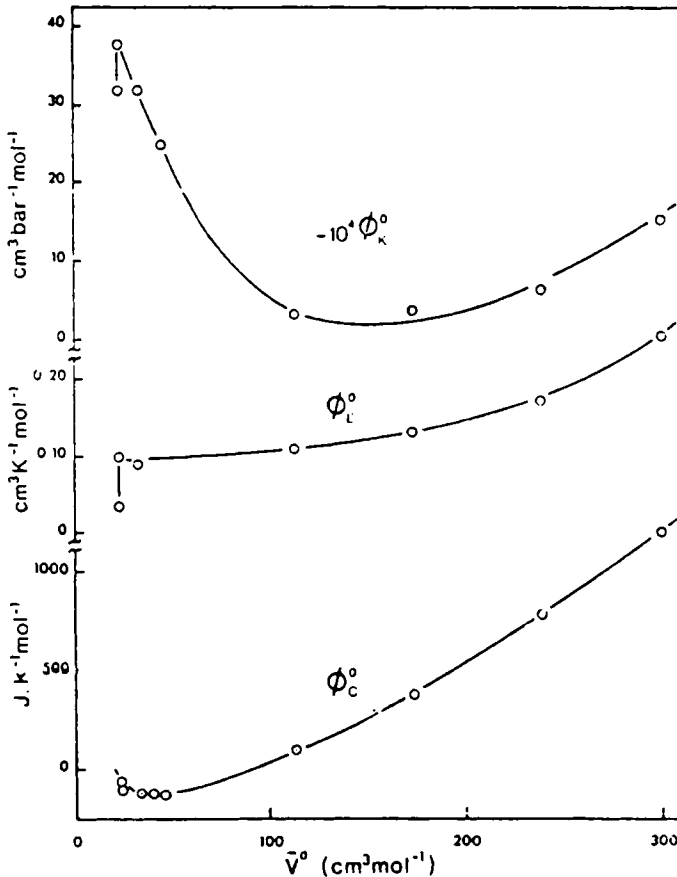


FIGURE 2 Standard apparent molal compressibilities, expansivities and heat capacities of alkali and tetraalkylammonium bromides in water at 25°C.

preferred to molecular weights as a variable proportional to the size of ions, since the density of quaternary ammonium salts is significantly different from that of alkali halides, and hydration effects are function of the dimensions of ions more than of their weight. \bar{V}^0 is proportional to the intrinsic volume and a plot of the above functions against the intrinsic volumes would probably show very similar qualitative trends as in Figure 2.

It is obvious from Figure 2 that no simple electrostatic model will explain satisfactorily the dependence of ϕ_R^0 , ϕ_E^0 and ϕ_C^0 on ionic size.

Any theory based on the ionic field would not predict a minimum in the thermodynamic functions. Still, it would be important to know qualitatively the effect of coulombic hydration on these functions. The Born equation is not a convenient basis for discussion in this respect. A molecular model⁴ is simpler to visualize and can predict at least the sign of the contribution of coulombic hydration on the thermodynamic functions and the influence of the ionic field.

Coulombic hydration

We will assume for the present purpose that an ion placed in the solution will bind firmly h solvent molecules to form a solvated complex, while the rest of the solvent remains unaffected. The number h is therefore the solvation or hydration number. Then, the total volume V of the solution can be written in terms of the molal volume of the hydrated ions V_h and of the molar volume of the pure solvent V_0 ;

$$V = nV_h + (n_0 - nh)V_0 \quad (2)$$

where n and n_0 are respectively the total number of ions and solvent molecules. The total volume can also be related to the apparent molal volume of ions,

$$V = n\phi_v + n_0 V_0, \quad (3)$$

and V_h can be given in terms of the intrinsic volume V_{in} and the volume of the water molecules in the hydration shell V_0^h ,

$$V_h = V_{in} + hV_0^h. \quad (4)$$

Combining Eq. (2) to Eq. (4), the apparent molal volume of an ion at infinite dilution is given by

$$\phi_v^0 = V_{in} + h(V_0^h - V_0) \quad (5)$$

Since the molar volume of a water molecule in the hydration shell is smaller than the molar volume of pure water, ϕ_v^0 is smaller than V_{in} , and this is the well-known electrostriction effect. Also, the diminishing field effect as the size

of the ion increases can be represented as a decreasing value of h . Therefore, the observed general decrease in electrostriction as the size of the ion increases is also accounted for by this simple model.

The contribution of coulombic hydration to ϕ_K^0 and ϕ_E^0 can be deduced from the derivation of Eq. (5) with respect to P and T . If V_{in} , h and V_0^h are assumed to vary to a negligible extent with P and T (the hydrated ion is assumed to be a complex molecule made up of close-packed hard spheres), then

$$\phi_K^0 = - \left(\frac{\partial \phi_V^0}{\partial P} \right)_T = h \left(\frac{\partial V_0}{\partial P} \right)_T = -hV_0\beta_0 \quad (6)$$

and

$$\phi_E^0 = \left(\frac{\partial \phi_V^0}{\partial T} \right)_P = -h \left(\frac{\partial V_0}{\partial T} \right)_P = -hV_0\alpha_0 \quad (7)$$

where β_0 and α_0 are respectively the isothermal compressibility and the expansivity of the pure solvent. Since β_0 and α_0 are positive, this model predicts that coulombic hydration will cause a negative contribution to both ϕ_K^0 and ϕ_E^0 , and that the effect will increase with the ionic field.

The compressibilities of alkali halides (Figure 2) are in qualitative agreement with such a model, and this is why ϕ_K^0 of alkali halides is often interpreted in terms of coulombic hydration.^{4,54,55} However, this hydration model fails to explain the increase in ϕ_K^0 with size in the case of R_4NBr and fails completely to account for the positive values of ϕ_E^0 for both MBr and R_4NBr .

The same model can be used to predict the effect of coulombic hydration on enthalpies and heat capacities. Through a similar derivation, the standard apparent molal enthalpy is given by

$$\phi_H^0 = H_{in} + h(H_0^h - H_0) \quad (8)$$

where the significance of each term can be derived by analogy with the corresponding volume equation (Eq. (5)). Since the passage of a water molecule from the bulk to the hydration shell is exothermic, $H_0^h - H_0$ should be negative and this corresponds to a negative $\phi_H^0 - H_{in}$ or ΔH_0^h , as observed.

The corresponding expression for ϕ_C^0 is obtained by deriving Eq. (8) with respect to T , assuming that h is relatively insensitive to temperature changes:

$$\phi_C^0 = \left(\frac{\partial \phi_H^0}{\partial T} \right)_P = \left(\frac{\partial H_{in}}{\partial T} \right)_P + h \left\{ \left(\frac{\partial H_0^h}{\partial T} \right)_P - \left(\frac{\partial H_0}{\partial T} \right)_P \right\} = C_{pin} + h(C_{p0}^h - C_{p0}) \quad (9)$$

Unlike the intrinsic volume, H_{in} cannot be assumed to be constant, since the internal energy of a molecule is a function of temperature, and this variation is given by the molecular or intrinsic heat capacity C_{pin} . We would expect C_{p0}^h to be larger than C_{p0} , since extra heat would be necessary to raise the

temperature of the water molecules in the hydration complex in order to overcome the binding energy. The term $h(C_{p0}^h - C_{p0})$ of Eq. (9) would therefore be positive and should lead to a positive contribution to $\phi_c^0 - C_{pin}$. Since h is a function of the ionic field, $\phi_c^0 - C_{pin}$ should also decrease with increasing size of ions.

It was assumed that h was relatively insensitive to temperature changes. If this assumption was not made, an extra term, $(H_0^h - H_0)(\partial h/\partial T)_p$ would have to be added to Eq. (9). Since $H_0^h - H_0$ and $(\partial h/\partial T)_p$ are both negative, this term would also lead to a positive contribution to $\phi_c^0 - C_{pin}$.

Examination of ϕ_c^0 in Figure 2 shows that the alkali halides are all negative, contrary to the predictions, although they do tend to decrease with increasing size. Also, the large increase in ϕ_c^0 of tetraalkylammonium bromides (C_{pin} of $n\text{-Bu}_4\text{NBr}$ should be approximately equal to $600 \text{ J.K}^{-1} \text{ mol}^{-1}$) cannot be accounted for at all with the above model. Therefore, coulombic hydration may have some influence on ϕ_c^0 , but it is certainly not the predominant effect.

A comparison of the predictions of this simplified model with the experimental data indicates that it would be dangerous to explain any of the functions ϕ_K^0 , ϕ_E^0 and ϕ_c^0 in terms of coulombic hydration only. The present data indicate that it is necessary to examine other types of interactions such as structural hydration.

Structural hydration

It is generally accepted that solutes can modify the structure of water; the presence of a foreign molecule will increase or decrease the water-water interactions. In the case of the larger alkali and halide ions, the transport properties strongly suggest that there is an increase in fluidity of the solvent near the ions.⁹ More direct evidence for this is supplied by spectroscopic data.⁴ In particular, the recent work of Walrafen⁵⁶ on the Raman spectra of aqueous solutions indicates that the intensity of the bands attributed to unbonded water molecules increases in the presence of structure-breaking ions. This structure-breaking effect can be visualized with the Frank and Wen model.¹¹ In the region where there is a competition between the ionic field orientation and the normal structure of water, the water molecules have more translational and rotational freedom than bulk water. This effect seems to increase with the size of the monatomic ions presumably because there is more space available in the immediate vicinity of the larger ions compared with the smaller ions.

Near hydrophobic solutes there is good evidence that there is a reinforcement of the water-water interactions. While these ideas were suggested by Eley,⁸ Frank and Evans⁹ and Kauzmann⁵⁷ some time ago, it is only in the

last decade that enough reliable experimental data has been gathered to unambiguously fix the importance and nature of hydrophobic hydration. As it will be shown later, most of the thermodynamic and transport properties of RNH_3Br and R_4NX can be interpreted only if it is assumed that there is some kind of increase in the structure of the solvent. The spectroscopic evidence⁴ confirms this. For example Jolicœur *et al.*⁵⁸ have recently shown that the influence of $n\text{-Bu}_4\text{NBr}$ on the structure of water at 25°C is similar to decreasing the temperature of pure water by about 13 degrees. A good indication of the nature of hydrophobic hydration has been given by the work of Wen and Saito,⁵⁹ Glew *et al.*⁶⁰ and Baumgartner and Atkinson.⁶¹ They all showed that the properties of aqueous solutions of hydrophobic solutes as a function of concentration pass through a maximum or minimum at the concentration corresponding to the composition of a time-average clathrate hydrate. Therefore, it seems that, near hydrophobic solutes, the hydrogen-bonded network is strengthened, but the overall average structure may be more that of a clathrate than that of ice I.

While the existence of these structural hydration effects is generally accepted, their importance on the thermodynamics properties is less so. The relative importance of structural and coulombic hydration may vary from one property to another, but both types of interactions must exist in all cases and should have some effect on all properties.

The simplest way of predicting the sign of these structural changes is with a two-state model for liquid water.²⁴ The presence of a solute is assumed to change the distribution of bonded (b) and unbonded (u) water molecules. We will assume that the partial molal thermodynamic function \bar{F} of a water molecule, when it is in the unbonded and bonded state, is given by \bar{F}_{ou} and \bar{F}_{ob} . If the mole fraction of unbonded water molecules in the absence and in the presence of a solute is given respectively by X and X' , then $1 - X$ and $1 - X'$ represents respectively the mole fraction of bonded water molecules in the absence and presence of solute molecules.

The molar thermodynamic function of equilibrium water is obtained from Euler's theorem on homogeneous functions as

$$F_0 = X\bar{F}_{\text{ou}} + (1 - X)\bar{F}_{\text{ob}} = \bar{F}_{\text{ob}} + (\bar{F}_{\text{ou}} - \bar{F}_{\text{ob}})X \quad (10)$$

and

$$F'_0 = X'\bar{F}_{\text{ou}} + (1 - X')\bar{F}_{\text{ob}} = \bar{F}_{\text{ob}} + (\bar{F}_{\text{ou}} - \bar{F}_{\text{ob}})X' \quad (11)$$

Therefore, the effect of the solute on the molar change of the solvent is

$$\Delta F_0 = F'_0 - F_0 = (\bar{F}_{\text{ou}} - \bar{F}_{\text{ob}})(X' - X) \quad (12)$$

In the case of a structure breaker, $X' - X > 0$, and with structure makers, $X' - X < 0$. Therefore, provided $\bar{F}_{\text{ou}} - \bar{F}_{\text{ob}}$ is known, the sign of ΔF_0 can

be predicted. The effect of the structural change on the standard partial molal property of the solute is given by the intrinsic function F_{in} and the overall change in the solvent property;

$$\bar{F}^0 = F_{in} + n\Delta F_0 \quad (13)$$

when n is the total number of moles of solvent.

This model can be applied to enthalpies, entropies and volumes. The sign of $\bar{F}_{ou} - \bar{F}_{ob}$ can be deduced from the sign of the change during the melting of ice, i.e.

$$\begin{aligned} \bar{H}_{ou} - \bar{H}_{ob} &> 0 \\ \bar{S}_{ou} - \bar{S}_{ob} &> 0 \\ \bar{V}_{ou} - \bar{V}_{ob} &< 0 \end{aligned} \quad (14)$$

Therefore, the influence of structural hydration on the thermodynamic functions of ions can be predicted as shown in Figure 3. The heats and entropies of mixing of nonelectrolytes in water confirm the above model. The higher molar entropy of solution of KCl compared with two argon molecules in water⁹ again is consistent with the predictions. The only disagreement is with the volumes of solution of nonelectrolytes in water which are usually negative. Hydrophobic solutes do increase the structure of water ($\Delta V > 0$), but this effect is more than compensated by the loss in free space ($\Delta V < 0$) which results since the solute tends to occupy, at least partially, some of the cavities that are always present in the normal structure of water.^{62,20} Therefore, hydrophobic hydration usually occurs with an economy of space, and this can be represented by an overall negative ΔV_0 with hydrophobic solutes.

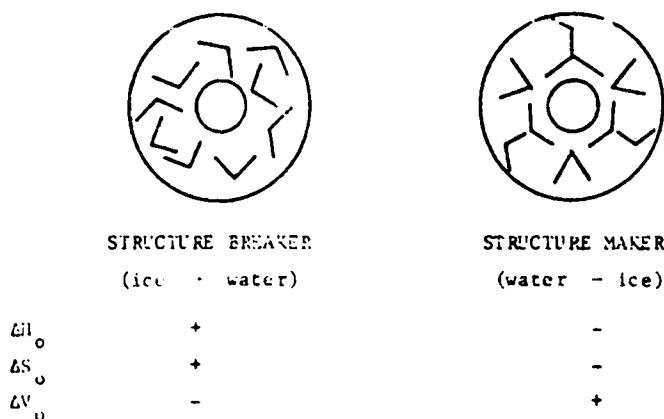


FIGURE 3 Model for the prediction of the sign of the structural hydration effects.

The influence of structural hydration on the functions ϕ_C^0 , ϕ_X^0 and ϕ_E^0 can also be predicted from Eq. (12)†

$$\Delta C_{po} = (\bar{C}_{po} - \bar{C}_{pob})(X' - X) \quad (15)$$

$$\Delta E_0 = (\bar{E}_{ou} - \bar{E}_{ob})(X' - X) \quad (16)$$

$$\Delta K_0 = (\bar{K}_{ou} - \bar{K}_{ob})(X' - X) \quad (17)$$

Contrary to volumes, entropies and heats, the sign of the differences between the partial molal quantities of unbonded and bonded quantities is not obvious for heat capacities, expansivities and compressibilities. However, if these changes are expressed as temperature or pressure derivatives.

$$\begin{aligned} \bar{C}_{po} - \bar{C}_{pob} &= \frac{\partial(\bar{H}_{ou} - H_{ob})}{\partial T} \\ \bar{E}_{ou} - E_{ob} &= \frac{\partial(\bar{V}_{ou} - \bar{V}_{ob})}{\partial T} \\ \bar{K}_{ou} - \bar{K}_{ob} &= \frac{-\partial(\bar{V}_{ou} - \bar{V}_{ob})}{\partial P} \end{aligned} \quad (18)$$

some predictions can be made. The properties of pure water⁶² indicate that the strength of the hydrogen bond most probably weakens as the temperature or pressure increases. It is therefore reasonable to assume that the changes $\bar{H}_{ou} - H_{ob}$ and $\bar{V}_{ou} - \bar{V}_{ob}$ will both decrease in absolute value if the temperature or pressure increases. The sign of the structural contribution to ΔC_{po} , ΔE_0 and ΔK_0 can therefore be deduced. The predicted sign of the structural interactions are summarized in Table I.

With hydrophobic solutes, $\bar{V}_{ou} - \bar{V}_{ob}$ was taken as positive to allow for the fact that hydrophobic hydration usually occurs with an economy of space. In all cases, the contribution of structural hydration to ϕ_C^0 , ϕ_E^0 and ϕ_X^0 will have the same sign as ΔC_{po} , ΔE_0 and ΔK_0 .

The observed (Figure 2) negative ϕ_X^0 , positive ϕ_E^0 and positive ϕ_C^0 of R_4NBr , and the increase in absolute value of ϕ_X^0 , ϕ_E^0 and ϕ_C^0 with the size or hydrophobic character are all consistent with this structural hydration model. In this structural treatment and also in the coulombic hydration model, it was assumed that the ions were incompressible spheres. While this assumption

† Note added in proof It is incorrect to apply eq (12) to ϕ_C^0 , ϕ_X^0 and ϕ_E^0 since this treatment then fails to account for the shift in equilibrium between the water species when the temperature or pressure is changed. The failure of Eq. (12) probably results from the fact that X is related to the equilibrium constant between bonded and unbonded water molecules and is therefore temperature and pressure dependent. It can be shown^{44, 45} that the shift in equilibrium between water species is the main structural contribution to ϕ_C^0 , ϕ_E^0 and ϕ_X^0 , but fortunately the predicted signs of this effect are the same as the ones given here.

TABLE I

Influence of structural hydration interactions on heat capacities, expansivities and compressibilities.

	Structure breaker	Structure maker
$X' - X$	+	-
$\bar{H}_{ou} - \bar{H}_{ob}$	+	+
$\frac{\partial(\bar{H}_{ou} - \bar{H}_{ob})}{\partial T}$	-	-
$\bar{V}_{ou} - \bar{V}_{ob}$	-	+ ^a
$\frac{\partial(\bar{V}_{ou} - \bar{V}_{ob})}{\partial T}$	+	-
$\frac{\partial(\bar{V}_{ou} - \bar{V}_{ob})}{\partial P}$	+	-
$\Delta C_{p,ou}$	-	+
ΔE_0	+	+
ΔK_0	-	-

^a The cavity effect is assumed to be more important than the increase in icelikeness.

is probably good for monatomic ions, it is less so for large organic ions. There is therefore some contribution to ϕ_K^0 and ϕ_E^0 which results from the compressibility and expansivity of the organic molecules themselves.⁵⁵ Both intrinsic compressibilities and expansivities K_{in} and E_{in} should be positive. Therefore, the structural contribution to ϕ_K^0 may be somewhat larger than expected from Figure 2 and ϕ_E^0 somewhat smaller. It is not simple to predict even the order of magnitude of K_{in} and E_{in} since most of the experimental compressibilities and expansivities of pure liquids are due to the increase or decrease of the free space between molecules.

It is easier to estimate the intrinsic contributions to ϕ_C^0 since most of the specific heat of pure liquids is due to the molecules themselves. Since the specific heat of organic liquids are approximately $0.5 \text{ cal. K}^{-1} \text{ g}^{-1}$ or $2 \text{ J K}^{-1} \text{ g}^{-1}$, the intrinsic heat capacity $C_{p,in}$ of R_4NBr should be given approximately by twice the molecular weight: Me_4NBr (300), Et_4NBr (420), $n\text{-Pr}_4NBr$ (530) and $n\text{-Bu}_4NBr$ ($640 \text{ J K}^{-1} \text{ mole}^{-1}$). Comparison of these values with Figure 2 indicates that $\phi_C^0 - C_{p,in}$ is negative for Me_4NBr , approximately nil for Et_4NBr and positive for the two higher homologs. Therefore, the heat capacity data suggests that $n\text{-Pr}_4NBr$ and $n\text{-Bu}_4NBr$ are net structure makers while Me_4NBr is a net structure breaker. Even if the present estimate of $C_{p,in}$ of Et_4NBr is rather crude, it does show that this salt does not have any large net structural influence on the solvent.

Recently, Ben-Naim⁶⁴ has discussed the influence of structural hydration on heat capacities, and he concluded that, with a two-state model for water, it is not possible to predict the sign of the contribution of hydrophobic

hydration. This is actually true only if the assumption that the strength of the hydrogen bond decreases with temperature is not made.

The structural hydration models account qualitatively for the thermodynamic properties of large organic ions. There is no reason to expect that similar interactions should not be important with monatomic ions. To facilitate the discussion, the signs of the coulombic and structural hydration interactions on the thermodynamic properties on ions are summarized in Table II.

The influence of the structure-breaking effects on \bar{H}^0 and \bar{S}^0 is opposite that of the coulombic interactions. Since, experimentally, ΔH_h^0 and ΔS_h^0 of M^+ and X^- are negative, the coulombic contribution must be larger than the structural one with small ions. In the case of \bar{V}^0 , all contributions are negative, and it is not possible from a study of \bar{V}^0 to say which effect predominates. With \bar{C}_p^0 and \bar{E}^0 , a comparison of Table II with Figure 2 indicates that structural interactions are the most important. This is not in contradiction with \bar{H}^0 and \bar{S}^0 , since coulombic interactions are probably much less temperature dependent than structural interactions. The stability of a hydration complex is affected by a temperature or pressure variation but to a much smaller extent than the equilibrium between bonded and unbonded water molecules.

Further examination for the correctness of this interpretation comes from the \bar{C}_p^0 of NaF in water and in a solution of 2 molar KCl.⁶⁵ In the presence of a high concentration of KCl, the aqueous medium has lost much of its structure, and the structural contribution to \bar{C}_p^0 should be less pronounced. This is borne out by the experimental data since \bar{C}_p^0 of NaF, which was

TABLE II

Signs of the coulombic and structural hydration interactions on the thermodynamic properties of ions.

Thermodynamic function	Coulombic hydration	Structure-breaking effect	Structure-making effect
\bar{G}^0	-		
\bar{H}^0	-	+	-
\bar{S}^0	-	+	-
\bar{V}^0	-	-	-
$\bar{C}_p^0 = \left(\frac{\partial \bar{H}^0}{\partial T}\right)_p$	+	-	+
$\bar{E}^0 = \left(\frac{\partial \bar{V}^0}{\partial T}\right)_p$	-	+	+
$\bar{K}^0 = -\left(\frac{\partial \bar{V}^0}{\partial P}\right)_T$	-	-	-
Variation with size	decreases	increases	increases

negative in pure water, becomes positive in the KCl solution, showing the increasing relative importance of the intrinsic heat capacity and possibly coulombic hydration.

All contributions to \bar{K}^0 are negative. It is therefore not possible from an observation of compressibility data to decide on the relative importance of the different contributions. However, by analogy with \bar{C}_p^0 and \bar{E}^0 , we would expect that much of the negative contribution to \bar{K}^0 of alkali halides comes from structural effects and not from coulombic forces as it is usually assumed.

In many of the thermodynamic properties, Li^+ appears to be less hydrated than Na^+ . A suggestion that is often proposed for this apparent anomaly is that, although the field near Li^+ is larger than Na^+ , the coordination number of Li^+ is smaller than that of Na^+ for geometrical reasons, and the overall number of water molecules held by Li^+ is thus smaller.⁴ The present discussion offers an additional possibility. If coulombic hydration decreases while structural hydration increases with the size of the alkali metal ions, a maximum in the property may occur at Na^+ through some compensation of reinforcement effect.

Finally a few words should be said about free energies. Since the change in chemical potential $\mu_{\text{ou}} - \mu_{\text{ob}}$ is zero for any equilibrium situation, Eq. (12) predicts that structural interactions should have no effect on the free energy of hydration of solutes. This is in contradiction with the usual hypothesis that hydrophobic bonding⁵⁷ results from a reduction of the structural contribution to the free energy of hydration of hydrophobic solutes. The origin of this contradiction probably lies in the assumption that was implied in Eq. (10) and Eq. (11) that the introduction of a solute changes the distribution of bonded and unbonded water molecules but has no effect on the partial molal quantities \bar{F}_{ou} and \bar{F}_{ob} . Since we were only interested in the prediction of the sign of the structural interaction, this was an acceptable approximation for most thermochemical properties. This is not so with chemical potentials. Since $\mu_{\text{ou}} = \mu_{\text{ob}}$ by definition

$$\Delta\mu_0 = \mu' - \mu_0 = \mu'_{\text{ou}} - \mu_{\text{ou}} = \mu'_{\text{ob}} - \mu_{\text{ob}} \quad (19)$$

Unfortunately it is not possible from the above two-state model for water to predict the sign of $\Delta\mu_0$. At any rate, we would not expect ΔG_h^0 of alkali halides to be very sensitive to structural hydration effects since it was shown that the leading contribution to ΔH_h^0 and ΔS_h^0 is the coulombic hydration. We would expect that this would be even more so with ΔG_h^0 .

Transfer thermodynamic functions

The thermodynamic functions of transfer from H_2O to D_2O offer another convenient way of emphasizing structural interaction.⁶³ Since the dipole

moments, dielectric constants and variation of the dielectric constants with temperature of both solvents are very similar, it is reasonable to assume that the transfer functions will be rather insensitive to coulombic hydration. On the other hand, since D_2O is more structured than H_2O , D_2O should be more influenced by the presence of a solute. This follows from the second assumption that was made previously in the discussion of structural interactions; a more structured solvent medium is more sensitive to perturbations. We can therefore expect that a study of the transfer function of \bar{H}^0 and \bar{V}^0 will reflect mostly the structural contribution, and, in a way, it should be equivalent to taking the derivative of the functions with respect to temperature or pressure.

In terms of the two-state model, the thermodynamic functions of transfer may be given as

$$\Delta F_{tr}^0 = n\Delta F_{0,tr} \quad (20)$$

where

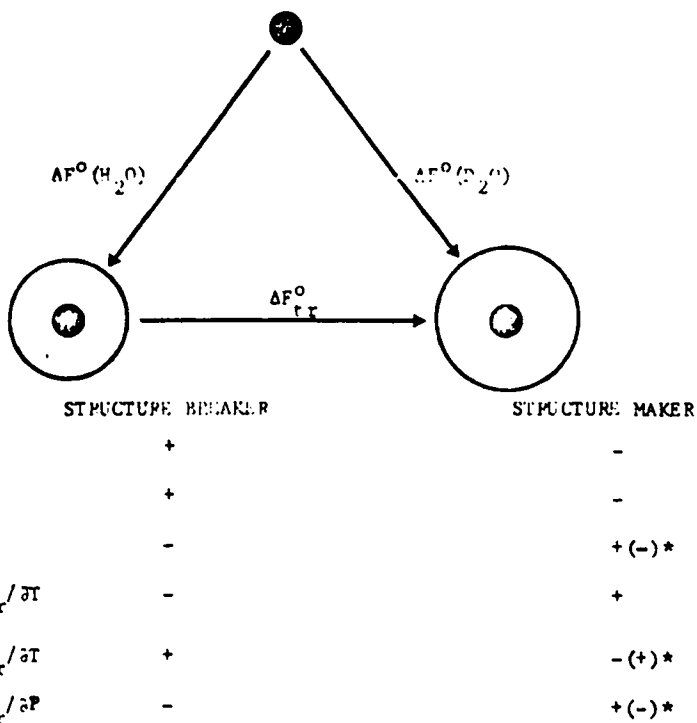
$$\Delta F_{0,tr} = (\bar{F}_{ou} - \bar{F}_b)_{D_2O}(X' - X)_{D_2O} - (\bar{F}_{ou} - \bar{F}_{ob})_{H_2O}(X' - X)_{H_2O} \quad (21)$$

Again, two possible assumptions will lead to the prediction of the sign of $\Delta F_{0,tr}$,

- a) D_2O is more structured than H_2O , which would imply that $(\bar{F}_{ou} - \bar{F}_{ob})_{D_2O} > (\bar{F}_{ou} - \bar{F}_{ob})_{H_2O}$ in absolute value
- or
- b) A more structured medium (D_2O) is more sensitive to any perturbation like the presence of a solute. This second assumption leads to $(X' - X)_{D_2O} > (X' - X)_{H_2O}$ in absolute value.

Either of these closely related assumptions is sufficient to explain the isotope effect on thermodynamic functions. It follows that the transfer function from H_2O to D_2O should always have the same sign as that of the structural hydration in either solvent system. This statement is not limited to ΔH_{tr}^0 but can easily be shown to be applicable to all other thermodynamic functions such as $\Delta C_{p,tr}^0$, ΔE_{tr}^0 and ΔK_{tr}^0 . The isotope effect can easily be visualized with the co-sphere model of Gurney;¹⁰ all structural changes are assumed to occur inside a co-sphere, and the larger effect observed in D_2O can be represented as a larger co-sphere as in Figure 4. The predicted sign of the transfer function is also given for structure breakers and makers in Figure 4.

The standard enthalpies, volumes and heat capacities of transfer from H_2O to D_2O are plotted on Figures 5 for the salts MX and R_4NX against the standard partial molal volumes. While structural effects were not obvious when ΔH_{tr}^0 and \bar{V}^0 were examined (Figure 1), they are definitely in evidence with the transfer functions. The structural contribution to \bar{H}^0 was opposite



Sign predicted if the cavity effect is larger than the increase in ice-likeness

FIGURE 4 Model for the prediction of the sign of the standard thermodynamic functions of transfer from H₂O to D₂O.

that of the coulombic effect (Table II). This is confirmed by ΔH_{tr}^0 which is negative with structure makers and positive with structure breakers. Also the general trend in the dependence of $-\Delta H_{tr}^0$ on the size of ions is very similar to \bar{C}_p^0 , showing the self-consistency of the general structural hydration model.

If $\bar{C}_p^0 - C_{p, in}$ is primarily a measure of the structural effect, then $\Delta C_{p, tr}^0$ should have the same general shape as \bar{C}_p^0 , when plotted against \bar{V}^0 . This is what is observed when Figure 5 is compared with Figure 3. The only surprising part is the large increase in $\Delta C_{p, tr}^0$, as the size of the small cations decreases. The same tendency was observed with ΔH_{tr}^0 . One possible suggestion for this is that coulombic hydration also has some isotope effect which becomes important with small ions like Li⁺, Na⁺ and F⁻ and may neutralize at least partially the structure-breaking effect (ΔH_{tr}^0 or NaF \approx 0).

The volumes of transfer are surprising at first sight. In order to explain \bar{K}^0 and \bar{E}^0 , we had to assume that the main structural contribution to the

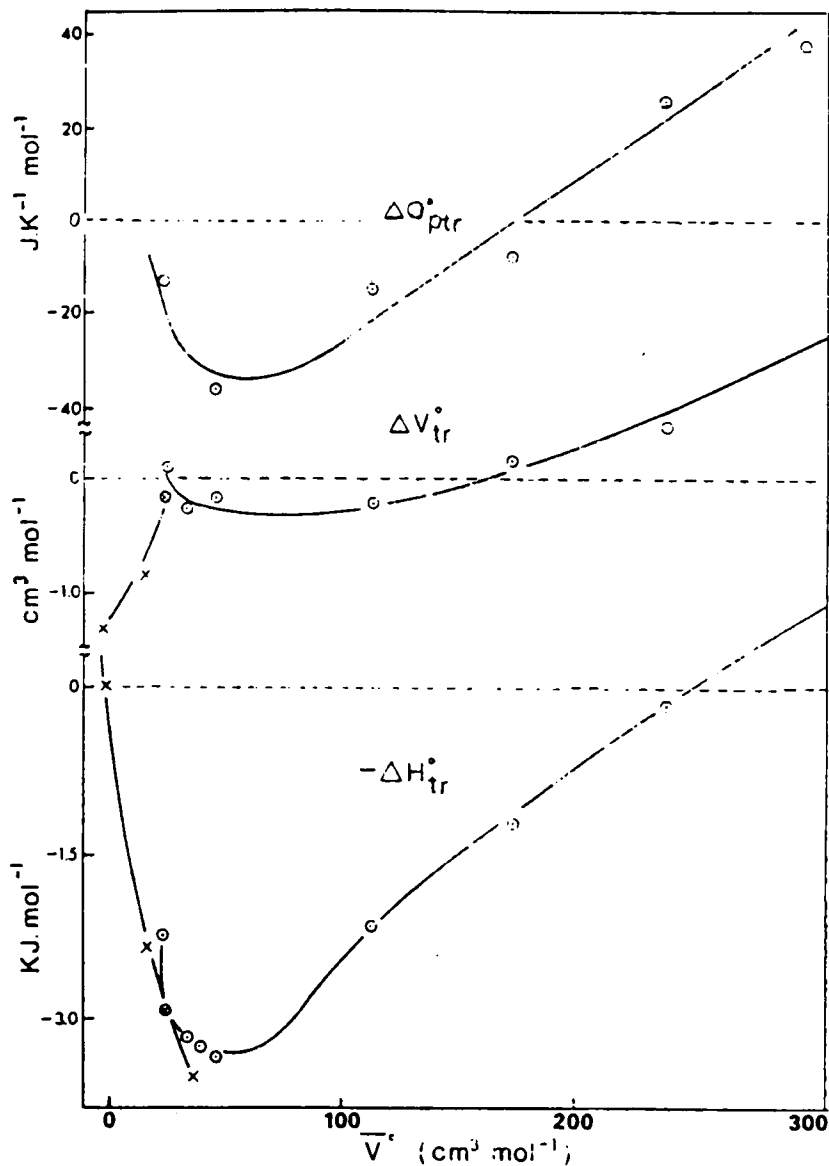


FIGURE 5 Standard thermodynamic functions of transfer from H_2O to D_2O of symmetrical 1:1 electrolytes at 25°C . O = MBr or R_4NBr , X = NaX . Note added in proof. Recently Δ_i° of R_4NBr were repeated²⁴ and were found to be negative as predicted by the structural models.

volume of structure makers was the cavity effect, $\Delta V < 0$. If this is so, ΔV_{tr}^0 of structure breakers and structure makers should both be negative while examination of Figure 3 shows that ΔV_{tr}^0 of *n*-Bu₄NBr is positive, indicating that the increase in icelikeness is the predominant structural effect. The dependence of ΔV_{tr}^0 on size is not opposite that of \bar{K}^0 as we would expect from the analogy between ΔH_{tr}^0 and C_p^0 . On the other hand, the fact that the cavity effect is larger than the increase in icelikeness near hydrophobic solutes does not imply that the cavity effect will necessarily increase in D₂O. The similarity in bond lengths in H₂O and D₂O may very well result in a loss of free space that is approximately the same in both solvents. Therefore, even if the cavity effect is the predominant effect in both solvents, ΔV_{tr}^0 primarily reflects the increase in icelikeness near hydrophobic solutes.

Evidence for this interpretation is furnished by the ΔV_{tr}^0 (H₂O → urea solution). It is usually accepted that structural changes are smaller in an urea-water mixture than in pure water⁶⁶ and that the transfer of an electrolyte from H₂O to an urea solution should be opposite in sign to the transfer from H₂O to D₂O. Also, with hydrophobic solutes, there is no reason to believe that the cavity effect in H₂O and in an urea-water mixture should be the same. Therefore, ΔV_{tr}^0 (H₂O → urea solution) of *n*-Bu₄NBr should have the sign predicted by the cavity effect, and this is what is observed experimentally. ΔV_{tr}^0 (H₂O → 3M urea) of Me₄NBr and *n*-Bu₄NBr are both positive as expected.⁶⁷

In the three transfer functions shown in Figure 5, *n*-Bu₄NBr appears as a net structure maker and Me₄NBr as a net structure breaker, in agreement with $\phi_c^0 - C_{p, in}$. The other two homologous salts sometimes appear as structure makers and sometimes as structure breakers. The net effect of these latter salts seems to depend on the property under investigation. Part of this variation may be due to the relative contribution of the Br⁻, which is not necessarily the same with all properties, and also to the uncertainty in the measurements. Very good experimental techniques are needed to obtain these transfer functions with any precision.

Finally, it should be noted that in all the plots of thermodynamic functions and transfer functions versus \bar{V}^0 of the ion pairs, the cations with a common anion and the anions with a common cation fall on separate lines, indicating that the hydration of small cations and anions is different. This observation is independent of any ionic scale since the properties of ion pairs are used. This therefore supports the general spectroscopic observations⁴ that there is much specificity in the hydration of small cations and anions. With an ion like Li⁺, the interactions is mostly of the charge-dipole type, while with F⁻ there is a possibility of some covalent character. The interaction F⁻—H—O



leads to a delocalisation of charge as in the case of a hydrogen bond and may,

for example, have a much larger isotope effect than the $\text{Li}^+ - \text{O} \begin{array}{l} \text{H} \\ \text{H} \end{array}$ interaction where there is no sharing of electrons.

Transport properties

Not much information can be drawn from a graph of ionic conductivities λ_0 plotted against some function of the size of ions. This is partly due to the non-applicability of the Stokes law⁴⁷ and to the unknown radii of the hydrated ions. Most of these difficulties are eliminated if the temperature dependence or the transfer function of the Walden product are examined instead of λ_0 . The Walden product is very nearly independent of temperature and solvent in non-aqueous systems, but this is not so in water. Kay and Evans^{68,69,47} have defined the function

$$C_{10}^{25} = \frac{(\lambda_0 \eta_0)_{25^\circ\text{C}}}{(\lambda_0 \eta_0)_{10^\circ\text{C}}} \quad (22)$$

which reflects the temperature dependence of the Walden product. Similarly, they³⁸ defined the isotope effect by

$$R = \frac{(\lambda_0 \eta_0)_{\text{D}_2\text{O}}}{(\lambda_0 \eta_0)_{\text{H}_2\text{O}}} \quad (23)$$

A transfer function for the Walden product may also be defined in the usual way by

$$\Delta(\lambda_0 \eta_0)_r = (\lambda_0 \eta_0)_{\text{D}_2\text{O}} - (\lambda_0 \eta_0)_{\text{H}_2\text{O}} \quad (24)$$

The functions C_{10}^{25} and $(\lambda_0 \eta_0)_r$ are both plotted in Figure 6 for M^+ , X^- and R_4N^+ against the Waddington radii.

The B_η viscosity coefficient is also difficult to interpret because of the unknown hydrodynamic volume of the ions.⁴⁶ Here again, the temperature coefficient, $\Delta B_\eta / \Delta T$, may prove more informative.⁴⁷ Also, it was shown⁴⁶ that the difference $B_\eta - 0.0025 \bar{V}^0$ is mostly a measure of the structural ion-solvent interactions. This follows since, for a system which has no net structural influence, \bar{V}^0 should represent the hydrodynamic volume and B_η should obey Einstein's law.

$$B_\eta = 0.0025 \bar{V}^0 \quad (25)$$

A plot of $\Delta B_\eta / \Delta T$ and $B_\eta - 0.0025 \bar{V}^0$ for the ions M^+ , X^- and R_4N^+ show that all four transport functions vary with the size of the ion in a way similar to the thermodynamic functions ϕ_K^0 , ϕ_C^0 , ΔC_{ir}^0 and ΔH_{ir}^0 .

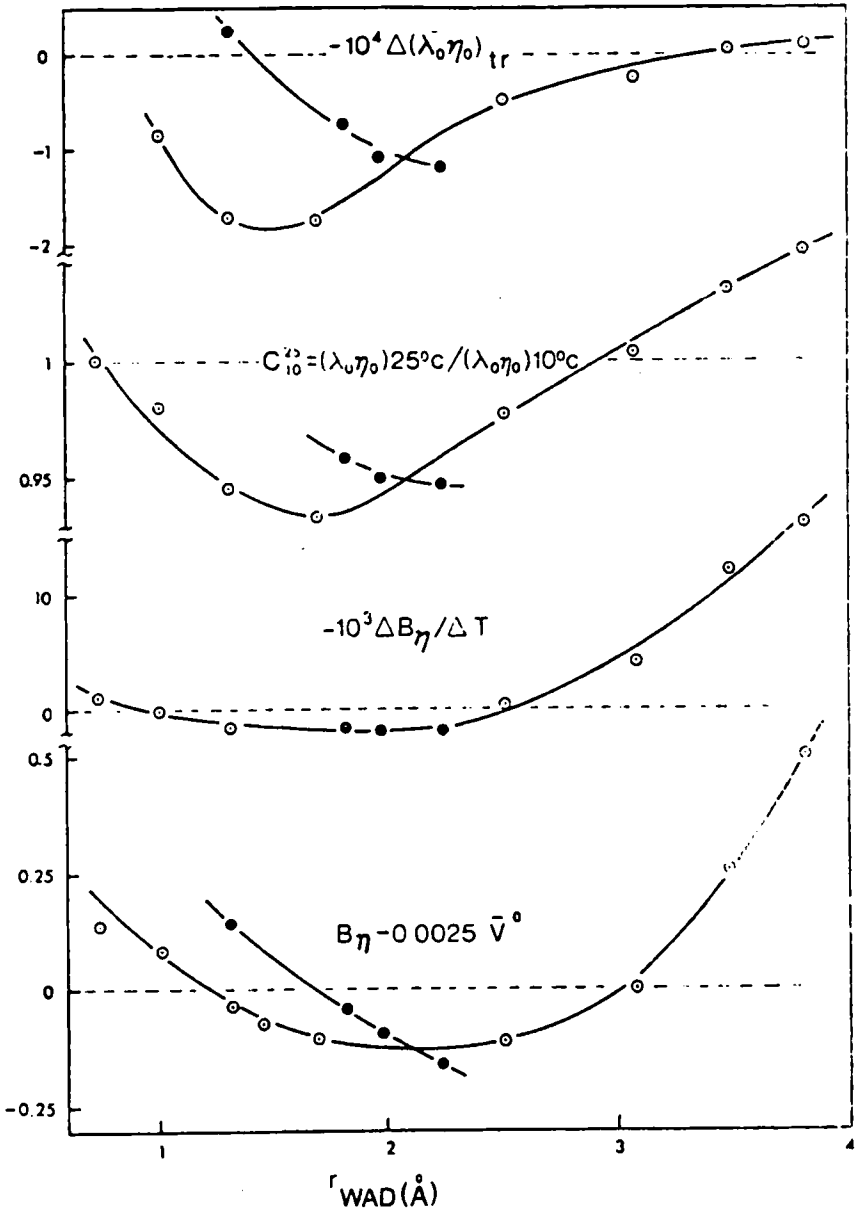


FIGURE 6 Transport properties of symmetrical monovalent ions in water at 25°C. ○ = cations, ● = anions.

The structure-breaking effect will increase the mobility of an ion. By analogy with the discussion on thermodynamic properties, it is reasonable to assume that this extra mobility will be further increased in D_2O and decreased if the temperature is raised. This explains the positive value of $\Delta(\lambda_0\eta_0)_{tr}$ and the negative value of C_{10}^{25} of structure breakers. Again, with structure makers, the opposite effect is expected.

The increase in fluidity near structure-breaking ions causes a negative contribution to B_η (the particle appears smaller); an increase in temperature will decrease this effect. Therefore $\Delta B_\eta/\Delta T$ should be positive with structure breakers, and this is verified experimentally (Figure 6).

Hydrophobic hydration will hinder the movement of the solute particles (positive contribution to B_η) but affect very little the partial molal volume (compensation between the cavity effect and increase in icelikeness). Therefore, as observed, $B_\eta - 0.0025\bar{V}^0$ is positive with hydrophobic structure makers. Similarly, with strong electrostrictive ions, $B_\eta - 0.0025\bar{V}^0$ will also tend to be larger than expected from the Einstein relation; B_η is related to the size of the hydrated ion while, as a result of electrostriction, \bar{V}^0 will be smaller than the intrinsic volume. With structure-breaking ions, there is a negative contribution to both B_η and \bar{V}^0 but B_η is more sensitive to structural changes than \bar{V}^0 since with all structure breakers $B_\eta - 0.0025\bar{V}$ is negative.

As in the case of thermodynamic properties, anions and cations usually fall on two separate lines, and the transition between net structure breakers and net structure makers occurs with an ion which has approximately the size of Et_4N^+ . No conclusion can be drawn about the net hydration effect of strong electrostrictive ions, since it is doubtful if Einstein's law holds with small ions.

n-Alkylamine hydrobromides

The *n*-alkylamine hydrobromides, RHN_3Br , are another set of homologous salts which can be used as model compounds to study the effect of chain length on hydration effects. This series goes from a fairly simple structure breaker, NH_4Br , to a long-chain surfactant, *n*-Oct NH_3Br . The study of these properties at infinite dilution will inform us on the additivity of the methylene group and on the overall structural influence.

The volumes derived from the Stokes radii, \bar{V}^0 , $B_\eta - 0.0025\bar{V}^0$, \bar{C}_p^0 and ΔH_{tr}^0 ($H_2O \rightarrow D_2O$) are all plotted against the number of carbon atoms in the chain on Figure 7. The function $4/3\pi\Sigma r_s^3$, \bar{V}^0 and B_η (not shown)⁴⁸ all vary approximately linearly with chain length, which suggests very strongly that the contribution of the methylene group is additive. On the other hand, such a plot does not give us any information on the overall structural interaction. As in the case of the spherical ions, much more information is obtained

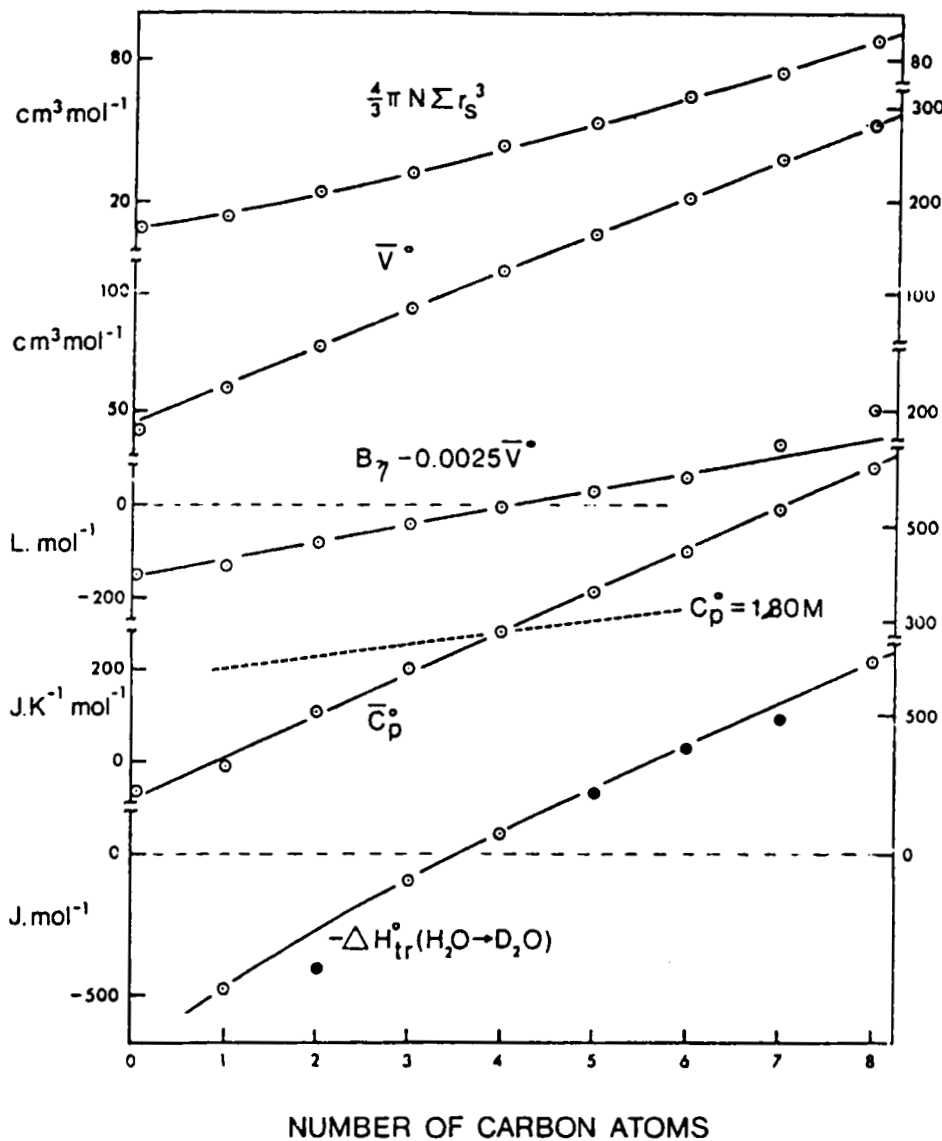


FIGURE 7 Standard thermodynamic and transport properties of RNH_3Br in water at 25 C.

from the other functions plotted on Figure 7; $B_p - 0.0025\bar{V}^0$ changes sign when $R = n$ -Butyl, and the same is approximately true for ΔH_{tr}^0 . The heat capacity is essentially a measure of the intrinsic heat capacity of the unsolvated RNH_3Br and a contribution of the hydration contribution. The specific heat of pure n -Pen NH_3Cl has been measured by Southard *et al.*⁷⁰ and has the value of $1.8066 \text{ J K}^{-1} \text{ g}^{-1}$ at 25°C . As a first approximation, we can therefore assume that $C_{p,n}$ should be given by $1.8 M$ where M is the molecular weight of the salt. This $C_{p,n}$ is also given in Figure 7 and crosses the \bar{C}_p^0 line at approximately n -Bu NH_3Br . This offers extra proof that all salts above n -Bu NH_3Br are overall structure makers while those below are net structure breakers. There is a smooth transition between both types of salts, which implies that the hydration (mostly structure breaking) of the $-NH_3^+$ group and Br^- are, at least as a first approximation, independent of the hydrophobic hydration of the R group. When the chain length reaches n -Butyl, the structure promotion near the R group essentially cancels out the structure-breaking effect near the ionic head and Br

Hydrophilic and Hydrophobic ions

All the thermodynamic and transport properties of spherical ions, M^+ , X^- and R_4N^+ show smooth transitions from Li^+ to n -Bu $_4N^+$ when they are plotted against a suitable function of the ionic size. This implies that there is in fact no sharp distinction between the different types of ions, and, for the stronger structure breaking ions (Cs^+ , I^-), the functions which are considered sensitive to structural hydration are usually found in the minimum or maximum of the curves. These general trends are understandable if we consider the forces that are involved in hydration effects. Near small ions, the ionic field acts on the dipole moment of the solvent molecules; if the interactions are strong enough, they may lead to a partial immobilization of solvent molecules; if they are weaker, they will still interfere with the structure of water and lead to the structure-breaking effect. Therefore, coulombic and structure-breaking hydration have the same origin and are closely related effects.

On the other hand, large organic ions tend to stabilize the hydrogen bond network in the vicinity of the non-polar groups. The origin of this stabilization is partially due to van der Waals forces⁷¹ and to entropy effects; by occupying a cavity in the structure of water, the non-polar group acts as a fifth neighbour to the adjacent water molecules and at the same time hinders the rotation of the water molecules. As it was discussed previously, the time-average structure of the hydrophobic hydration shell may be different from the normal ice-like structure of water, i.e. it probably has a structure resembling more that of a clathrate hydrate than of ice I. If this is true, then the organic ion has to reach

a certain size, or hydrophobic character, before it can overcome the normal structure of water. This would imply that a small extent of structure breaking may also occur from a competition of the clathrate-type orientation by the solute and the normal orientation of water molecules.

It therefore follows that there are probably only two types of ions, which we may call *hydrophilic* and *hydrophobic*. The first is associated with the field effect and the second with the structural stabilization effect. Structure breaking occurs when either of these two orientation forces (but mostly in the case of the field effect) is not strong enough to overcome completely the normal structure of water.

Another problem remains which is related to the coexistence of the coulombic and structure-broken hydration shells. It is usually accepted that divalent ions have a fairly stable hydration inner shell, while they have an outer structure-broken hydration co-sphere as evidenced from the positive $\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$ heats of transfer.⁷² This is in excellent agreement with the Frank and Wen¹¹ model of two regions in the overall hydration co-sphere. The coulombic hydration sphere is relatively unaffected by the isotope effect in comparison with the structure-broken region. In the case of univalent ions, the situation is not as clear. There is little spectroscopic evidence⁴ of the existence of an inner hydration shell, except possibly with the smaller ions Li^+ , Na^+ and F^- . The present comparison of thermodynamic and transport data seems to confirm this. If there were an inner shell of strongly held water molecules, we would not expect such a smooth transition between hydrophilic and hydrophobic ions. While thermodynamic and transport data offer no definite proof of this, they do suggest that the inner hydration shell ceases to exist when the size of the ions reaches approximately that of K^+ or Cl^- .

Hydration numbers

Hydration numbers have for a long time been considered a useful parameter to characterize ion-solvent interactions.^{4,54,73} The hydration number is defined as an effective number of water molecules that have undergone some constant critical change in property related to a suitable definition of hydration.⁴ The justification for the introduction of this parameter is that, if it is determined from one property, it can be used to interpret other properties. Unfortunately, we have shown (see Table II) that different properties measure different extent of coulombic and structure-breaking hydration, and, while in some case both types of hydration oppose each other (λ_o , \bar{S}^0 , \bar{H}^0 , \bar{E}^0 , B_n), with other properties they act in the same direction (\bar{V}^0 , \bar{K}^0). We must therefore conclude that the concept of hydration number is unfortunately of little value, and sometimes even misleading; it can possibly be useful for the

comparison of the hydration of ions when a single property or closely connected properties are considered. In any case, it gives little information about what is really happening near the ion.

Summary of ion-solvent interactions

Interesting conclusions can be drawn from the present analysis of thermodynamic and transport properties of aqueous electrolyte solutions.

1) There are probably only two types of ions, hydrophilic and hydrophobic. Both types can lead to some increase in order of the solvent, when their orienting influence is strong, or to a structure-breaking effect, when the normal structural influence of water is competitive.

2) A stable time-average hydration shell probably exists only with the stronger monovalent hydrophilic ions (Li^+ , Na^+ , F^-); aliphatic ions larger than Et_4N^+ and $n\text{-BuNH}_3^+$ are net hydrophobic structure makers, Et_4N^+ and $n\text{-BuNH}_3^+$ ions have little overall influence on the structure of water and all other intermediate ions are structure breakers.

3) Structural interactions are more sensitive than coulombic hydration to any perturbation (temperature and pressure changes) and to the isotope effect.

4) The hydration of hydrophobic anions is slightly different from that of cations.

THERMODYNAMIC EXCESS PROPERTIES

The coulombic and structural hydration interactions will certainly have some influence on ion-ion interactions. For example, Stokes and Robinson⁷⁴ have shown that the effective removal of water molecules resulting from coulombic hydration causes a positive contribution to the non-ideal free energy or activity coefficient. On the other hand, Frank and Robinson,⁷⁵ Gurney¹⁰ and Frank⁷⁶ have shown that structural interactions may also influence the excess thermodynamic properties. These structural interactions may even be large enough to cause association of two hydrophobic solutes.^{57,63}

Excess thermodynamic properties originate not only from hydration interactions but also from other interactions such as the long-range coulombic forces between ions. With hydrophilic ions, the long-range forces often predominate and may mask hydration effects. Therefore, it would be preferable, in order to isolate hydration effects, to study excess functions relative

to a function which accounts correctly for long-range coulombic forces than to compare them with the equations of an ideal solution (Henry's law).

The best known theory used to account for the long-range forces is that of Debye-Hückel,⁷⁷ which predicts correctly that the logarithm of the activity coefficient should vary with the square-root of concentration or ionic strength I

$$\log f_{\pm} = - \frac{A_f I^{1/2}}{1 + BaI^{1/2}} \quad (26)$$

The parameters A_f and B depend on the temperature and dielectric constant of the solvent and a is the distance of closest approach. The limitations of this theory are now well-known¹³ and can be summarized by a comparison of the Debye-Hückel osmotic coefficient with the MacMillan-Mayer theory solved with the hypernetted chain equation⁷⁸ for NaCl at 25°C (see Figure 8). For the same primitive model, the hypernetted chain and Debye-Hückel equations coincide, but they diverge significantly near 1 molar. Since the experimental data fall in-between the two theories, it is obvious that the use of the Debye-Hückel theory as a reference in the discussion of ion-ion interactions at intermediate concentrations (0.1 to 1 molar) may lead to erroneous interpretation; instead of looking for extra repulsion to explain the experimental data (positive contribution to ϕ) we should be looking for

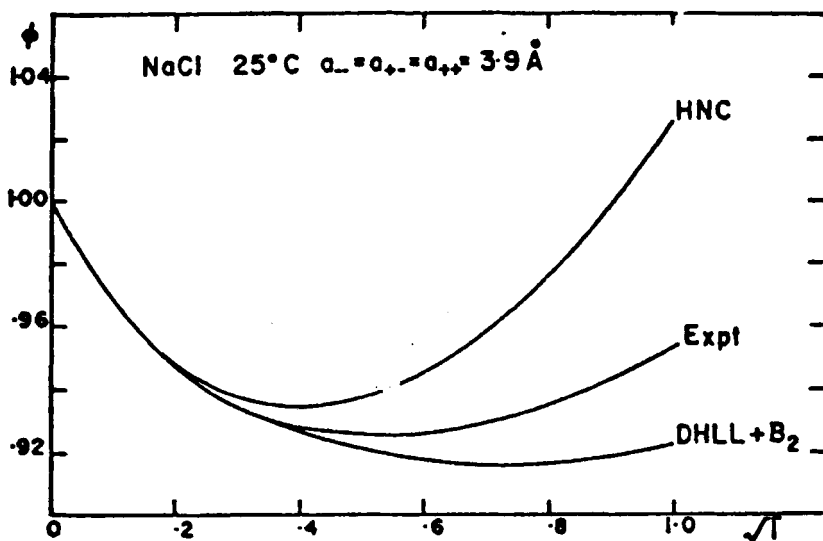


FIGURE 8 Comparison of the Debye-Hückel theory with the hypernetted chain equation for the same primitive model for NaCl in H₂O at 25°C. Rasaiah,⁷⁸ reprinted by permission of the American Institute of Physics.

extra attraction. Therefore, any discussion of the hydration effects on excess thermodynamic properties should really be made with reference to some form of the MacMillan-Mayer theory based on a model which considers repulsive forces when ions are close together, long-range coulombic attractive forces and polarisation or cavity effects.¹³ Unfortunately, such theories are not yet in an analytical form, and the equations have to be solved numerically. Since the purpose of the present review is more to see the general influence of coulombic and structural hydration effects, we will use as a reference the limiting Debye-Hückel theory, which is exact at very low concentrations, and examine the deviations from the limiting slope for families of salts. These deviations will include all interactions not accounted for in the limiting equation (distance of closest approach, cavity and hydration effects) in addition to deviations arising from the poor mathematical treatment. The sign of the deviation, especially when it is small, can often be misleading, but a comparison of the trends with different ion pairs should give some pertinent information on the nature of ion-solvent interactions affecting the excess functions.

The limiting Debye-Hückel slopes and higher terms for activity coefficients,⁷⁴ apparent molal volumes,⁷⁹ apparent molal relative enthalpies²¹ and apparent molal heat capacities²⁴ for volumes in cm³ per mole and energies in Joules per mole are

$$\log \gamma = -0.512m^{1/2} + Bm + Cm^{3/2} - \dots \quad (27)$$

$$\phi_v - \phi_v^0 = 1.867c^{1/2} + B_v c + \dots \quad (28)$$

$$\phi_L = 1975m^{1/2} + B_L m + C_L m^{3/2} + \dots \quad (29)$$

and

$$\phi_c - \phi_c^0 = 28.95m^{1/2} + B_c m + \dots \quad (30)$$

where the B and C parameters account for all the deviations from the limiting Debye-Hückel theory. In the case of ϕ_L and ϕ_c , a term in c or m is usually sufficient to account for the experimental data on MX and R₄NX up to concentrations of approximately 0.5 molar, but with $\log \gamma$ and ϕ_L , higher terms are needed.

Desnoyers *et al.*^{4,16} have compared the activity and excess volume data of all available MX and R₄NX salts (see Figure 9 and Figure 10). Since B_γ cannot be determined unambiguously $\log \gamma - 0.512m^{1/2}$ was taken arbitrarily at $0.2m$. The parameter h in Figure 10 is identical with B_v of Eq. (28).

The trends in excess free energies (Figure 9) and volume data (Figure 10) cannot be accounted for with effects such as coulombic hydration, distance of closest approach or polarisation forces.^{4,16} Most of these interactions would lead to approximately additive deviations from the Debye-Hückel theory and cannot account for the inversions in the order of the fluorides

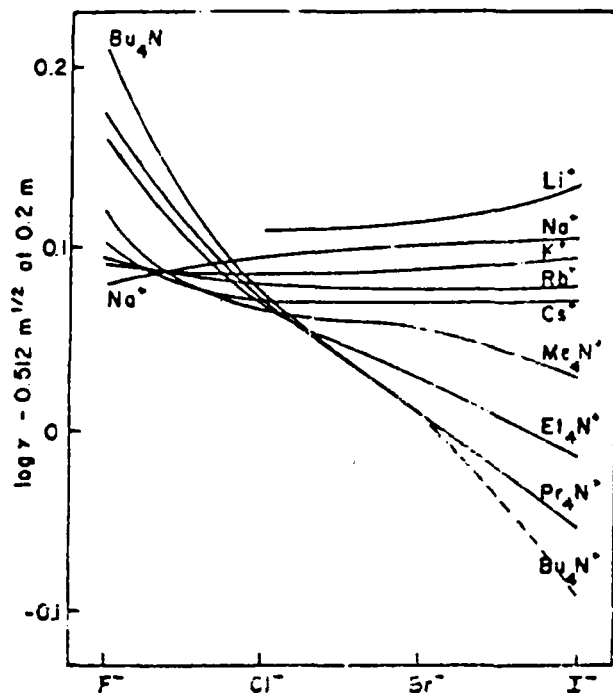


FIGURE 9 Concentration dependence of activity coefficients in H_2O at 25°C . Desnoyers *et al.*¹⁶, reprinted by permission of the American Chemical Society.

when they are compared with the other halides. On the other hand, structural interactions do account for the relative order in Figure 9 and Figure 10. For this purpose, Desnoyers *et al.*¹⁶ have extended the co-sphere model of Gurney,¹⁰ which can be summarized as follows:

1) The influence of an ion on the structure of water can be represented as an imaginary co-sphere (see Figure 3 and Figure 5) and the concentration effect by an overlaps of these co-spheres.

2) Only two type of ions need to be considered: hydrophilic and hydrophobic ions.

3) Two solute will attract each other if their structural influences, or their tendencies to orient water molecules, are compatible with each other: conversely, an incompatibility in these structural influences or tendencies will result in repulsive forces.

4) The sign of the structural contribution to the excess thermodynamic function is obtained by applying the two-state model of water to the overlap region of the co-spheres.

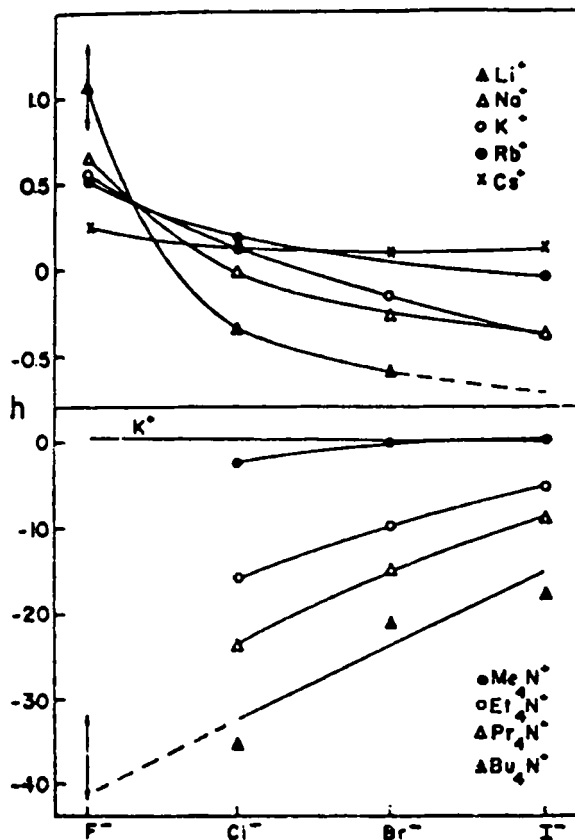


FIGURE 10 Concentration dependence of apparent molal volumes in H₂O at 25°C. Desnoyers *et al.*,¹⁶ reprinted by permission of the American Chemical Society.

Using the same kind of arguments as in the discussion of standard thermodynamic functions, the sign of the structural interactions to excess thermodynamic functions can be predicted and are given in Table III.

A few comments should be made on these predictions. It was shown that the principal structural contribution to \bar{V}^0 of hydrophobic ions was negative due to the cavity effect. However, this cavity effect remains essentially constant as the concentration increases (except when association occurs), and only the increase in ice-likeness is affected giving rise to a negative \bar{V}^{EX} .²⁰ The structural contribution to \bar{H}^{EX} and \bar{S}^{EX} always have the same sign, which is a case of the Barclay-Butler rule.⁸⁰

The strongest hydrophobic-hydrophobic interaction will occur with *n*-Bu₄NI (I-being the weakest hydrophilic ion), the strongest hydrophilic-

TABLE III

Contribution of structural interactions to excess thermodynamic functions.

Interaction	Net effect	\bar{G}^{EX}	\bar{H}^{EX}	\bar{S}^{EX}	\bar{V}^{EX}	\bar{C}_p^{EX}
Hydrophobic-Hydrophobic	attraction	-	+	+	-	-
	less structure promotion					
Hydrophobic-Hydrophilic	repulsion	+	+	+	-	-
	less structure promotion					
Hydrophilic-Hydrophilic (opposite sign)	attraction	-	-	-	+	+
	less structure breaking					
Hydrophilic-Hydrophilic (same sign)	repulsion	+	+	+	-	-
	more structure breaking					

hydrophobic with n -Bu₄NF, the strongest hydrophilic-hydrophilic (opposite sign) with LiF and the strongest hydrophilic-hydrophilic (same sign) with LiI and CsF. The inversion in $\log \gamma - 0.512m^{1/2}$ in Figure 9 when the fluorides are compared with the iodides is consistent with the predictions. Also, the inversion of $h(= B_v)$ of MX and the lack of inversion with R₄NX also confirm the model.

The contribution of structural interaction can also be verified with \bar{H}^{EX} by plotting $\phi_L - 1975m^{1/2}$ at 0.5 molal for different MX and R₄NX on Figure 11. Most of the data on alkali halides comes from the compilation of Parker³² and from some recent measurements in our laboratory.³³ Some of the excess heats in Figure 11 may be in error, but the trends are clear. If structural interactions are the predominant source of non-ideality in excess to the Debye-Hückel theory, then the excess heats on Figure 11 should be the mirror image of the excess volumes (Figure 10), since all the predicted structural interactions of \bar{H}^{EX} are opposite in sign (see Table II). There seems to be an inversion in \bar{H}^{EX} of alkali fluorides when they are compared with the other halides, and \bar{H}^{EX} of Bu₄NF is the most positive of all ion pairs in agreement with the structural hydration interactions. However, the general dependence of \bar{H}^{EX} on the size of the anion seems to be opposite to what we would expect. There seems to be some extra negative deviation from the Debye-Hückel theory which increases with ion size and which is not of structural origin. The distance of closest approach may possibly be responsible for these observed trends.

The difficulty of interpreting unambiguously the excess functions could be resolved if the excess heats of transfer from H₂O to D₂O were available. Since a more structured medium is more sensitive to structural changes, all excess thermodynamic functions will be larger in D₂O than in H₂O (larger co-spheres).

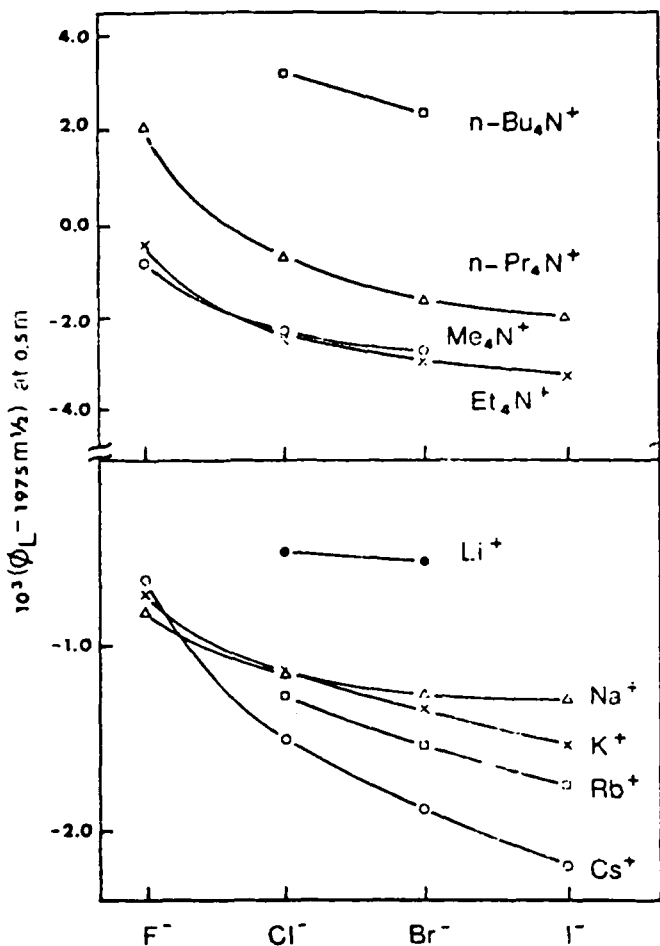
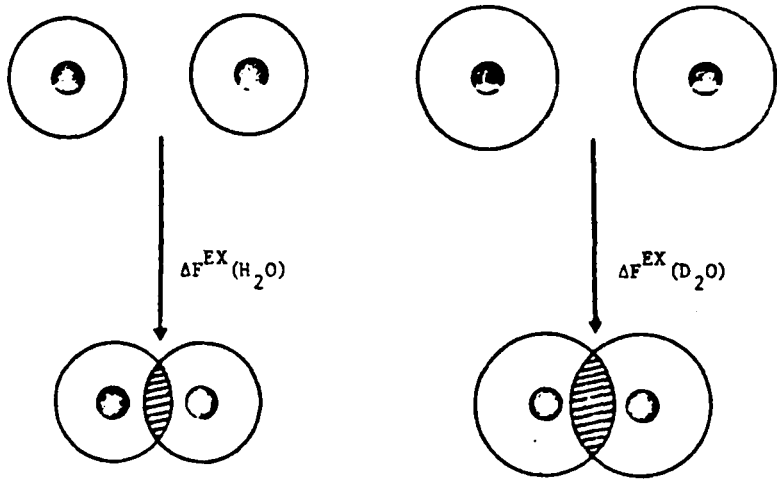


FIGURE 11 Concentration dependence of relative apparent molal enthalpies in H_2O at 25°C .

The isotope effect may therefore be represented by a larger overlap of co-spheres as shown in Figure 12. Provided the transfer is defined from H_2O to D_2O , the sign of the excess transfer function will be the same as the sign of the structural contribution to the excess function in either solvent. The values of \bar{F}_{tr}^{EX} ⁴³ and $\bar{C}_{p,ir}^{EX}$ ²⁴ of R_4NBr are both more negative in D_2O , but the difference does not seem to increase significantly with hydrophobic character. The ΔH_{tr}^{EX} ($\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$) have been measured for the salts RNH_3Br ⁴² and the trends of the transfer function are predicted correctly; they go from a negative value for MeNH_3Br to a positive value for *n*-Oct NH_3Br . The few measurements on excess free energies of transfer of alkali



$$\Delta F_{tr}^{EX} = \Delta F_{tr}^{EX}(D_2O) - \Delta F_{tr}^{EX}(H_2O)$$

	ΔC_{tr}^{EX}	ΔH_{tr}^{EX}	ΔS_{tr}^{EX}	ΔV_{tr}^{EX}	$\Delta C_{p, tr}^{EX}$
Hydrophobic-hydrophobic	-	+	+	-	-
Hydrophobic-hydrophilic	+	+	+	-	-
Hydrophilic-hydrophilic (same sign)	+	+	+	-	-
Hydrophilic-hydrophilic (opposite sign)	-	-	-	+	+

FIGURE 12 Model for the prediction of the sign of the excess thermodynamic functions of transfer from H₂O to D₂O.

halides⁸¹ indicate that $\Delta G_{tr}^{EX}(H_2O \rightarrow D_2O)$ is small and opposite in sign to what is predicted from Figure 12. Unfortunately, this study was limited to a few systems that are rather insensitive to structural interactions. Also, a study of osmotic coefficients of 1:1 electrolytes in *N*-methylacetamide⁸² indicates that the inversions in Figure 9 are not unique to aqueous solutions.

We can therefore conclude that excess thermodynamic functions are influenced by structural hydration interactions. The importance of structural interactions relative to other ion-ion interactions is still somewhat ambiguous especially in the case of \bar{G}^{EX} . Unlike standard thermodynamic functions \bar{F}^0 , there is no additivity of \bar{F}^{EX} , and the values of nearly all MX and R₄NX are needed to observe general trends. Also $\Delta F_{tr}^{EX}(H_2O \rightarrow D_2O)$ are most valuable

to isolate structural effects, but these functions are not easily accessible experimentally.

Once all the trends in \bar{F}^{EX} and ΔF_{tr}^{EX} ($H_2O \rightarrow D_2O$) are known beyond the experimental uncertainty with model electrolytes such as MX and R_4NX for most properties, the role of structural effects on ion-ion interactions will be much clearer and the theoretical treatment of \bar{F}^{EX} , with some modern version of the MacMillan-Mayer theory,^{13,78,83} simplified.

Acknowledgement

I am much indebted to my present and former colleagues, and in particular to C. Jolicoeur, P. Picker, G. Perron, P. R. Philip, P. A. Leduc, J. L. Fortier, M. Arel, R. Francescon, and R. Pagé, whose close collaboration have made this review possible. I am also grateful to the National Research Council of Canada for its financial assistance.

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Discussion of the Report of J. E. Desnoyers

J. E. Mayer I was puzzled by the correction made for what is often called the primitive model, namely for a model of charged sphere inbedded in a dielectric without structure. In your earlier slides you indicated that you subtracted the "limiting law" correction from the activity $A/c^{1/2}$, and the corresponding correction for the other functions. This is, of course, only a small part of the correction at the concentration of 0.2 M or higher, as you mentioned later. However the higher order "Primitive Model" corrections depend on the assumed diameter of the ion, and would be very different for lithium halide and for tetrabutyl ammonium halide. Since your discussion concerns comparison of salts such as these, I have difficulty understanding how the correction is made. Actually you referred to the curve that you showed as the "exact" theory. I wish it were.

J. E. Desnoyers Rasaiah, using the same primitive model as in the extended Debye-Hückel theory, treated it mathematically with the hypernetted chain equation. If we accept that this treatment is more exact, then Figure 8 indicates that we should be looking for extra attraction and not extra repulsion to explain the excess free energies of NaCl in water. Such a comparison does not imply that the primitive model is necessarily a correct representation of electrolyte solutions in moderately concentrated solutions.

J. E. Mayer No! Even with the assumption of the primitive model the calculations are not exact. They are merely the best there is!

J. E. Desnoyers It is obvious that any treatment of excess thermodynamic properties, and especially in the case of free energies and enthalpies, must

include, in addition to the long-range coulombic forces, other effects such as distance of closest approach, mutual salting-out of the ions, dielectric saturation, etc. However, as it was shown previously (see Ref. 4 and 16), even after allowance for these effects, the anomalies noted when the excess thermodynamic properties of the fluorides are compared with those of the bromides and iodides still remain. On the other hand, structural interactions can qualitatively account for these inversions. Also, Friedman (see Ref. 13 and 83) in a more quantitative statistical mechanical treatment considered coulombic forces, repulsion, cavity effects and structural interactions and reached about the same conclusions as we did.

A. R. Ubbelohde Why are experimental studies on electrostatic interactions in aqueous ionic solutions often restricted to uni-univalent ions? Surely the contact repulsion envelopes of ions with higher charges especially of rare earth ions, are quite well established in their crystalline compounds. Studies of their ionic solutions should thus provide much more sensitive tests of various quantitative theories, than with univalent salts since the ions carry a higher charge. Rare earth salts are now quite readily available.

J. E. B. Randles I would like to ask Dr. Desnoyers about the increase of activity coefficient, γ^{\pm} , with concentration shown by many electrolytes and explained by Robinson and Stokes as a "salting out" effect arising from the presence around each ion of a hydration shell which excludes other ions. I believe that he states that the pair-potential treatment of an ionic solution using the primitive model (structureless dielectric medium) can explain this increase of activity coefficient, while the extended Debye-Hückel theory cannot. My question is what physical basis the primitive model can provide for the increase of excess free energy with concentration, unless it is by use of a rather large distance of closest approach.

J. E. Mayer The primitive model is not very realistic, and I have absolutely no doubt that there are effects, and important effects due to the structure of the solvent. Only I do feel that if one seeks an effect due to structure one should correctly subtract the prediction without structure. The general rise of the curve at higher concentrations is predicted in the primitive model. It is due merely to size. One cannot pack hard spheres beyond a certain density. But I am well willing to believe that the experimental behaviour is primarily due to more sophisticated structural effects.

J. E. Desnoyers If ions are truly hydrated (coulombic type), then the Stokes and Robinson's equation can be used to calculate the contribution to activity coefficients of the removal of water molecules from their solvent role.

However, it is incorrect to derive hydration numbers from activity data, with the same equation. For example, if these activity hydration numbers for 1:1 electrolytes in water were compared, they would fall in an order similar to that of the activity data shown in Figure 9, i.e. they would not be additive and would include all the sources of non-ideality not accounted for by the Debye-Hückel theory.

May be we should ask ourselves: is there any evidence that the larger univalent ions have a stable coulombic hydration shell?

R. M. Diamond There are indications of (first-shell) hydration even for some rather large monovalent ions. One may extract tetraalkylammonium salts into a variety of solvents and determine the water coextracted. By using a very large anion such as tetraphenylboride, essentially no water coextracts, showing that the alkylammonium cation carries no water, especially in solvents such as nitrobenzene where the salts are dissociated. Then the water determined with other salts belongs to the anion. Even I^- shows 0.9 moles of water per mole of ions, and, in fact, ClO_4^- gives numbers like 0.2–0.4 in a number of solvents. Smaller ions show larger numbers up to 3.2 for Cl^- . These are not first-shell coordination numbers, but lower limits, the average of a distribution. Fluoride shows values from ≈ 4 at low organic-phase concentrations to ≈ 18 at a few tenths molar concentration, because F^- and H_2O form (hydrogen-bonded) aggregates. Obviously the situation in such an organic phase is different from that in aqueous solution, but these results indicate that monovalent anions larger than F^- can bind water.

D. H. Everett I would first like to comment on the selection of properties which may be most usefully employed as a basis for the development and testing of theoretical models. Second derivative quantities – and in particular the heat capacity – are very sensitive to details of the theoretical model (and unfortunately also to experimental errors!) and perhaps insufficient attention has been paid to them: it turns out that by examining the predictions of theoretical models in relation to heat capacities some important limitations of the range of possible models can be established.

Prof. Desnoyers has said that electrostatic interactions make a negative contribution to the entropy of an ion, but a positive contribution to the heat capacity. This does not seem to me to be correct. The simple Born equation approach – based on a continuous structureless dielectric model – leads to the conclusion that both contributions should be negative. However, the radii which have to be ascribed to the ions to obtain quantitative agreement differ for various properties of the ions, and are often physically unrealistic. However, as far as entropies and heat capacities are concerned, it is predicted that both quantities should in a series of situations vary in parallel –

whereas experimentally it is found that contrary variation is usually observed. This is sufficient to show that no simple continuum theory can be adequate. The next stage is to consider electrostatic calculations based on a simple molecular model. The work of Eley and Evans¹ and of Coulson and Everett² indicates that realistic values for the entropies and heat capacities of ions in water could be based on the simple Bernal and Fowler model.

The numerical values obtained are satisfactory – but it is important to stress that these results depend rather critically on the assumed distribution of electrostatic charge in the water molecule. But once again heat capacity and entropy effects should vary in a roughly parallel fashion. To account for the opposite variation which is observed, some additional effects must be included – these are the so-called “structure effects”. They include the concepts of “hydrophobic bonds,” “structure makers” and “structure breakers” which are still not rigorously defined.

In so far as a separation of the overall phenomenon into additive contributions is possible we have to seek a clearer picture of the origin of these additional effects. One very simple model which may help to understand these factors may be constructed using molecular models of water having tetrahedral bonding joined together with elastic bands to form a three-dimensional network. This enables one to envisage the effect of creating a cavity in the structure: in the model this corresponds to cutting a number of elastic bands and removing one or more water molecules. The structure relaxes with the water molecules neighbouring the cavity moving onwards and increasing the packing density around the cavity. This will contribute to a decrease of entropy. However, the creation of cavities reduces the energy density of the whole assembly so that the structured stability with respect to thermal effects is decreased – this will contribute a positive term to the heat capacity. Perhaps this is the basic origin of the contrary variation of entropy and heat capacity terms.

References

1. D. D. Eley and M. G. Evans, *Trans. of the Faraday Soc.*, **34**, 1093 (1938).
2. C. A. Coulson and D. H. Everett, *Trans. of the Faraday Soc.*, **36**, 633 (1940).

J. E. Desnoyers I unfortunately did not estimate the coulombic contribution to heat capacities from the Born equation. On the other hand, I find it difficult to visualize a solvent molecule partly immobilized in the field of an ion with a lower heat capacity than a bulk solvent molecule, in the case of a structureless solvent. If the coulombic contribution to ϕ_c^0 is negative, it

becomes more difficult to explain the maximum observed at high temperatures when ϕ_c^0 of alkali halides is plotted versus temperature. The usual explanation given is that at low temperatures the increase in ϕ_c^0 is caused by the disappearance of the structure-breaking effect and at high temperatures the decrease of ϕ_c^0 is attributed to the elimination of coulombic hydration.

R. M. Diamond Professor Everett has just mentioned a model which I, too, was going to suggest as a first try. But a comment. We use terms such as "structure-making" or "ice-like" to include two quite different situations. Around a small, highly charged ion, the water molecules are oriented strongly by the ion, leading to a number of effects including a decrease in volume. For somewhat bigger, lower-charged ions, the water near the ion has a relatively equal orientation towards the ion and towards the water structure beyond it, and so is more free rotationally. Such ions are called structure-breakers, as mentioned by Prof. Desnoyers. But for still larger univalent ions, such as the larger tetraalkylammonium cations, the orientation by the water structure is greater than that from the ion itself, and so the water molecules closest to the ion are oriented by the water structure; they are pulled back into that structure away from the ion. These two types of structure-making are quite different and have different effects.

In fact, I wonder if the large ion case cannot be considered as the creation of small surfaces (cavities or bubbles) around each hydrophobic ion, with some of the properties of the water-air interface (taking into account the small radius of curvature, if this is meaningful for such dimensions).

It is known that large hydrophobic ions are pushed out of the bulk water into the surface phase, in contrast to the behaviour of smaller ions. It might be expected that the hydrogen-bonded structure is less complete in the surface, and so the hydrophobic ions are pushed into the surface from the bulk water to minimize the damage to the hydrogen-bonded network.

H. G. Hertz Another simple and qualitative explanation of the hydrophobic hydration may be given as follows: in pure water a given molecule is tetrahedrally surrounded by four other water molecules. Although somewhat distorted, the closest surrounding is fairly symmetric. The electric field will be homogeneous i.e. the field gradient will vanish at the central molecule. Now let us replace one of the four surrounding water molecules by a non polar, inert group, a CH_3 say. The electric field will be that of an electric dipole in the opposite orientation as the original one, located at the methyl group, superposed on the original field. Of course it produces a torque acting on the central molecule.

Now the non-polar group (e.g. CH_3) may be located at the lone-pair site of the central molecule or on the proton site. Due to the electric quadrupole

moment of the water molecule both situations are not equivalent. Thus the average torque does not disappear, the protons of the water molecule point away from the inert surface, this being the configuration of lower potential energy.

J. E. Desnoyers A fair amount of work has been done on the alkaline earth halides in water. Properties such as heats of hydration and partial molal volumes suggest that the divalent ions are strongly hydrated. On the other hand, Greyson (see Ref. 72) has shown that their heats of transfer from H_2O to D_2O are positive as in the case of alkaline earth chlorides. The explanation offered is that, although the divalent cations have a stable hydration shell, the contribution of coulombic hydration to enthalpies is about the same in H_2O and D_2O . The observed transfer functions therefore reflect primarily the structure-breaking effect beyond the hydration shell.

M. Magat We obtained very recently some preliminary results on the Raman spectra of saturated ($\sim 1N$) solutions of thorium nitrate in ordinary water. We choose a tetravalent ion and a concentrated solution in order to have a good chance to obtain intermolecular bands characteristic of the solvation shell. We could not observe the 60 cm^{-1} band because of the Rayleigh wings and are unable to say if it persists or not. The 170 cm^{-1} band is replaced by a band at about $210\text{--}220\text{ cm}^{-1}$. There is no trace of the 500 and 700 cm^{-1} librational bands of water but there appears a rather broad and weak band at about 400 cm^{-1} and broad but more intense band at $\approx 1300\text{ cm}^{-1}$. Of course other experiments (temperature and concentration variation, D_2O , change of anion and etc.) will be necessary before it will be possible to attribute these bands to definite modes.

R. Parsons The strong hydration of multivalent ions can be seen clearly in the case of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ which behaves very much like a molten salt with the ions $\text{Ca}(\text{H}_2\text{O})_3^{2+}$, NO_3^- .

H. G. Hertz We were able to show that ions like CdI_4^{2-} , $\text{Hg}(\text{CN})_4^{2-}$ cause an increase of the fluidity of water, i.e. are structure breakers. Even at sufficiently low temperature $\text{Co}(\text{CN})_6^{3-}$ becomes a structure-breaker.

One sees that for sufficiently small ratio ionic charge/ionic radius and absence of hydrophobic groups, structure breaking effects may be observed.

M. Magat I had recently the privilege of visiting the Bell Telephone Laboratories and to learn there two yet unpublished results that may have a bearing on the present discussion.

1) Dr. Stillinger told me of some preliminary results he has recently obtained in collaboration with his co-workers from Argonne Laboratory concerning solutions of neon in water. They have replaced in the Molecular Dynamic calculations one water molecule by a neon atom. The result is that a kind of cage, like a clathrate cage is built around the neon atom; the life time of this cage, although not yet determined, was definitely significantly larger than the life time of tetrahedral arrangements of water molecules among themselves.

2) Dr. Rentzepis' experimental results concern the rate of solvation of an electrical charge in water. Since this time is of the order of 10^{-12} sec, it is of course impossible to introduce an ion in such a short time and the detection would be difficult. It is however possible to detach an electron from an ion by laser irradiation and to follow the development of the well known and characteristic absorption spectrum of the hydrated electron. This is what Rentzepis did with a picosecond laser disposing of a true resolution of $0.8 \cdot 10^{-12}$ sec. For the first 2 picoseconds no absorption was observed, then appeared an absorption in red, gradually shifting to the green. After $8 \cdot 10^{-12}$ sec Rentzepis observed the classical absorption spectrum with a maximum in the green. In other words $8 \cdot 10^{-12}$ sec. about are necessary for an electron "to dig its own trap" by reorienting the water molecules.†

M. Eigen The time constant you reported is almost identical with the dielectric and ultrasonic relaxation time found in pure water. This would indicate that the rate limiting step of solvation is the same type of structure rearrangement which allows water molecules to librate (cf. dielectric relaxation) or to build up bulky structures (cf. ultrasonic relaxation).

† Hydrogen bonding between neon and water—M. Losonczy, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.*, **59**, 3264 (1973); Relaxation of excess electrons in a polar solvent—P. M. Rentzepis, R. P. Jones, and J. Jortner, *Chem. Phys. Lett.*, **15**, 480 (1972).