Structure and Properties of Aqueous Salt Solutions

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Many properties of aqueous salt solutions can be qualitatively linked with molecular models for these solutions. This review examines some properties of salt solutions with reference to the properties and possible structures of the solvent, water.[1,2] Initially the properties of salts in standard states in solution and methods for evaluating single ion properties are considered. Modification of these properties by ion–ion interactions in real solutions are then examined. This review will only examine aqueous solutions of closed shell ions, *e.g.* alkali metal, halide, and alkylammonium ions. This greatly simplifies the task of interpretation since in the first limit, these ions can be characterised by their size, shape, and charge. Once the properties of these ions in water are understood, then the properties of other ions, *e.g.* those formed by transition metals, can be examined, although here quantum mechanical forces assume a greater importance.

1 Interionic Distances

A simple model for a salt solution[3a] assumes that the ions of a 1 : 1 electrolyte are randomly distributed at the centres of cubes, volume d^3. If the concentration (mol m^{-3}) of salt is c, the average distance between ion centres equals $9{\cdot}399(c)^{-1/3}$ nm. This distance, d, can be compared with ionic radii, r_i, estimated from molecular models [3b] and crystallographic data,[4] *e.g.* $r[(C_4H_9)_4N^+] + r(Br^-) = 0{\cdot}689$ nm. Although radii of ions in solution are not precisely known,[5] this simple calculation shows that where $c > 10^3$, $d < 0{\cdot}94$ nm, there can be few water molecules (approx. diam. 0·28 nm) between the ions. There is indeed a close link between the properties of these systems[6] and corresponding solid salts. However, in very dilute solutions, *e.g.* $c = 10^{-6}$, $d \approx 10^3$ nm, the ions are separated by many water molecules. Thus the properties of these solutions will probably be extensively influenced by the structure of water, and the structure of water by the ions.

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[1] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

[2] For recent reviews of models for liquid water see for example, (*a*) H. J. C. Berendsen, 'Theoretical and Experimental Biophysics', Arnold, London, vol. 1, 1967; (*b*) D. J. G. Ives and T. H. Lemon, *Roy. Inst. Chem. Rev.*, 1968, **1**, 62; (*c*) D. Eisenberg and W. Kauzmann, 'The Structure and Properties of Water', Oxford University Press, Oxford, 1969.

[3] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions', Butterworth's Sci. Publ., London, 2nd edn. (revised), 1965, (*a*) p. 15, (*b*) p. 125, (*c*) p. 73, (*d*) p. 133, (*e*) p. 245.

[4] L. Pauling, 'The Nature of the Chemical Bond', Oxford Press, 1960, 3rd edn., (*a*) p. 514, (*b*) p. 469.

[5] K. H. Stern and E. S. Amis, *Chem. Rev.*, 1959, **59**, 1.

[6] (*a*) C. Deverell and R. E. Richards, *Mol. Phys.*, 1966, **10**, 551; (*b*) F. Fister and H. G. Hertz, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 1032.

2 Analysis of Experimental Results

A valid approximation for very dilute solutions (*e.g.* $c < 1$ for 1 : 1 electrolytes in water at 298 K, where $d > 9{\cdot}4$ nm)[7,8] is to assume that ion–ion interactions occur through long-range electrostatic forces. The effects of these interactions on thermodynamic properties of salt solutions can be examined using the Debye–Huckel theory.[3c] Properties of a salt in its standard state in solution, *i.e.* in the absence of ion–ion interactions, can then be calculated from the properties of real salt solutions. Thus the Debye–Huckel theory can predict the slope of a plot of apparent molar volume, ϕ_V (determined from the densities of a series of salt solutions of differing concentrations) *vs.* $(c)^{1/2}$, which can then be extrapolated[9] to give the standard partial molar volume, $V_2^{\ominus}$, *e.g.* $V_2^{\ominus}(\mathrm{KCl}) = 26{\cdot}90 \times 10^{-6}$ m^3 mol^{-1}, at 298·15 K.[10]

Unfortunately in some cases there is no simple theoretical model on which to base an analysis of the results. The simplest procedure is to plot the variation of an observed quantity against salt concentration. In favourable instances, the plot is a straight line and the slope is measured. If the plot is a smooth curve, the limiting slope as $c \rightarrow 0$ is measured. These slopes depend on and, for given set of observations, characterise each salt. This procedure has been used to analyse dielectric data[11] and n.m.r. spectra.[6b,12,13]

3 The Solvent—Water

The term 'hydration' can apply either to the interaction between an ion and the nearest neighbour water molecules, the primary hydration shell, or to the interaction between an ion and the solvent (solution) over the range $0 < r < \infty$. Indeed the arrangement of water molecules, 'the structure of water', is affected at some distance from an ion, *i.e.* beyond the nearest neighbour water molecules.[14-16] The failure of the simple Born equation for Gibbs functions for ionic hydration[17] and of Walden's rule for ionic mobilities[8,18] shows that the solvent in aqueous solutions cannot be treated as a bulk continuum.

Water is not a typical liquid.[2] For example the molar volume of liquid water is smaller than the solid, ice-Ih (common ice), at 273·15 K and 101 325 N m^{-2}.

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[7] H. S. Frank and P. T. Thompson, 'The Structure of Electrolyte Solutions', ed. W. J. Hamer, Wiley, New York, 1959, p. 113.

[8] H. S. Frank, 'Chemical Physics of Ionic Solutions', ed. B. E. Conway and R. G. Barradas, Wiley, New York, 1966, p. 60.

[9] O. Redlich and D. M. Meyer, *Chem. Rev.*, 1964, **64**, 221.

[10] F. Franks and H. T. Smith, *Trans. Faraday Soc.*, 1967, **63**, 2586.

[11] (*a*) R. Pottel, ref. 8, p. 584; (*b*) G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, 1952, **20**, 1454; (*c*) J. B. Hasted, D. M. Ritson, and C. H. Collie, *ibid.*, 1948, **16**, 1.

[12] (*a*) J. Burgess and M. C. R. Symons, *Quart. Rev.*, 1968, **22**, 276; (*b*) J. F. Hinton and E. S. Amis, *Chem. Rev.*, 1967, **67**, 357.

[13] G. Engel and H. G. Hertz, *Ber Bunsengesellschaft phys. Chem.*, 1968, **72**, 808.

[14] H. S. Frank, *Z. phys. Chem.* (*Leipzig*), 1965, **228**, 364.

[15] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507.

[16] H. S. Frank and W-Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

[17] D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

[18] (*a*) R. L. Kay, 'Trace Inorganics in Water', (Advances in Chemistry, no. 73) American Chemical Society, 1968, p. 1; (*b*) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 1966, **70**, 2325.

Further the liquid contracts on warming until $T = 277{\cdot}13$ K (the temperature of maximum density) and then expands. The molar heat capacity C_p is significantly larger for the liquid than for the solid and has a minimum near 310 K. At 298 K, the viscosity decreases as the pressure is increased and only increases, the normal behaviour, when the temperature exceeds 300 K. The larger relative permittivity and high melting and boiling points of water have long been taken as evidence for the importance of intermolecular hydrogen bonding. From this basic premise, many detailed molecular theories have been evolved. Nevertheless most theories fall into one of two general classes,[2] mixture[1] and uniform[16] models. Uniform models propose that each water molecule has the same molecular environment as every other water molecule in the liquid. For example, Pople's model (see reference 2*c*), a classic of this type, requires that every water molecule is hydrogen bonded to four other water molecules and that each hydrogen bond can independently bend without breaking. However, by far the greater number of models are mixture models and these have been extensively used in rationalizing the properties of water and, more importantly in the present context, of aqueous solutions. It is envisaged that no (or little) hydrogen bond bending can occur and that there are many broken hydrogen bonds in liquid water. Consequently water molecules exist in different molecular environments in water. For example there may be water molecules involved in 4, 3, 2, 1, or 0 hydrogen bonds.[19a] An important proposal[16] is that hydrogen bonding between water molecules is a co-operative process. Association of two water molecules by hydrogen bonding stimulates association of these molecules with other water molecules, the lifetime of a cluster of water molecules being *ca.* 10^{-11}s. In water at low temperatures there are low-density (large molar volume) networks of hydrogen-bonded water molecules. Consequently, at a particular temperature and pressure, liquid water has some degree of structure. With increase in temperature, the extent of intermolecular hydrogen bonding decreases, *i.e.* the intensity of water–water interactions decreases, and the structure breaks down. Conversely with decrease in temperature the structure increases. These changes in temperature result in 'structure breaking' and 'structure making' respectively. The structure of water can also be affected by adding a solute, and one aim in this field is to bring together the effects of added polar and non-polar solutes in a series of related general models for these solutions.

The low solubility of non-polar solutes in water is linked with a large entropy decrease which accompanies dissolution.[15,16,19b,20] This makes ΔG (and $\Delta G^{\ominus}$) positive. A characteristic of some aqueous systems is the importance of entropy changes. A major part of the entropy decrease is attributed to enhancement of water–water interactions around solute particles. This enhancement, sometimes called hydrophobic hydration, means that these solutes are 'structure formers'. The structure of this water does not necessarily resemble the structure of ice-Ih

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[19] G. Nèmethy and H. A. Scheraga, (*a*) *J. Chem. Phys.*, 1962, **36,** 3382; (*b*) *ibid.*, 1962, **36,** 3401; (*c*) *ibid.*, 1964, **41,** 680; (*d*) *J. Phys. Chem.*, 1968, **66,** 1773.

[20] H. S. Frank and F. Franks, *J. Chem. Phys.*, 1968, **48,** 4746.

or the many other ice polymorphs.[21] Other possible structures include those based on pentagonal dodecahedra of water molecules, *cf.* the structure of clathrate hydrates containing non-polar guests.[4b,22] In real solutions, regions of enhanced water structure interact and can, through co-operative interactions, mutually enhance the water structure.[10]

4 Ionic Properties

An important problem in this subject is the derivation of standard partial molar quantities for ions from the corresponding quantities for salts, *e.g.* $V^{\ominus}(K^+)$ and $V^{\ominus}(Cl^-)$ from $V^{\ominus}(KCl)$. The determination is not straightforward and several techniques have been applied.[23]

A. Relative Quantities.—The most direct approach assumes that the value for one ion, usually the hydrogen ion, is zero, *e.g.* $V^{\ominus}(H^+) = 0$, and the standard partial molar entropy, $S^{\ominus}(H^+) = 0$. Similarly, in the interpretation of the ionic molal shifts,[8] *cf.* ^{17}O n.m.r. shifts of salts in $H_2{}^{17}O$, $\delta(NH_4{}^+)$ has been equated to zero[24] in a number of investigations.

B. Theoretical Analysis.—Experimental data can be fitted to equations derived from theoretical models for ion–water interactions. In most cases the ionic radius is a variable parameter. Gibbs functions for ionic solvation can be derived assuming that the Born equation[25] is valid. The ionic parameters are obtained by subdividing the values for the salts into the corresponding ionic solvation parameters such that when plotted against the reciprocal of 'corrected' radii, the points fall on the predicted straight line.[26,27] Clearly the validity of derived ionic values depends on the validity of the model adopted at the outset.

C. Intuitively Derived Quantities.—An important example of this approach concerns analysis of *B*-viscosity coefficients.

Viscosities of dilute salt solutions, η, relative to that of pure water, can be fitted to an equation of the form:[28]

$$\eta/\eta_o = 1 + A(c)^{1/2} + Bc \tag{1}$$

B-Viscosity coefficients are characteristic of each salt and each *B*-coefficient can be divided, in principle, into individual *B*-ionic coefficients. These ionic coefficients reflect the effect of each ion on solvent structure. Since K^+ and Cl^- are approximately the same size (and isoelectronic), it was suggested that in water at 298 K[29] and over the range 288—318 K,[30] $B(K^+) = B(Cl^-)$.

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[21] B. Kamb, 'Structural Chemistry and Molecular Biology', ed. A. Rich and N. Davidson, Freeman, San Francisco, 1968.

[22] G. A. Jeffrey and R. K. McMullan, *Progr. Inorg. Chem.*, 1967, **8**, 43.

[23] B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Z. phys. Chem. (Leipzig)*, 1965, **230**, 157.

[24] Z. Luz and G. Yagil, *J. Phys. Chem.*, 1966, **70**, 554.

[25] M. Born, *Z. Physik*, 1920, **1**, 45.

[26] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, 1939, **7**, 108.

[27] For other comments see K. J. Laidler and C. Pegis, *Proc. Roy. Soc.*, 1957, *A*, **241**, 81.

[28] R. H. Stokes and R. Mills, 'Viscosities of Electrolytes and Related Properties', Pergamon Press, London, 1965.

[29] R. W. Gurney, 'Ionic Processes in Solution', McGraw-Hill, New York, 1953.

[30] M. Kaminsky, *Discuss. Faraday Soc.*, 1957, **24**, 171.

Such ionic coefficients can be used to calculate other ionic quantities. If the standard partial ionic entropies, $S_i^\ominus$ and B-viscosity coefficients are both indicative of the effects of an ion on water structure, then $S_i^\ominus$ and B_i should be linked. If $S^\ominus(\mathrm{H})$ equals $-23{\cdot}03$ J mol^{-1} K^{-1}, rather than zero, then in a plot of $S_i^\ominus$ *vs.* B_i, data points for both cations and anions fall on one line.[29] These new ionic entropies depend on the initial assumption that $B(\mathrm{K}^+) = B(\mathrm{Cl}^-)$.

An extension of this approach involves examining a series of related salts, *e.g.* with common anion, and developing a graphical analysis such that the required ionic property is obtained as an intercept.[31,32] For example,[31b] the standard partial molar volumes for tetra-alkylammonium iodides, $V^\ominus(\mathrm{R_4N^+I^-})$, in water (and water–ethanol mixtures[32]) fall on a straight line when plotted against the molecular mass of the cation, M_+. The intercept at $M_+ = 0$ gives the standard partial molar volume of iodide, $V^\ominus(\mathrm{I}^-) = 42{\cdot}3 \pm 0{\cdot}2 \times 10^{-6}$ m^3 mol^{-1}.[32a]

D. Absolute Ionic Quantities.—Some ionic quantities can be unambiguously obtained. The molar conductance of a salt, Λ, together with the transport number of one ion, t_i in a solution gives the ionic conductance, $\lambda_i = t_i\Lambda$ and $\lambda_i^\ominus = t_i^\ominus\Lambda^\ominus$.[3,33a,33b] Absolute ionic partial molar volumes can be obtained by measuring ultrasonic vibration potentials,[33c] *e.g.* $V^\ominus(\mathrm{H}^+)$ at 298·15 K $= -5{\cdot}5 \pm 0{\cdot}5 \times 10^{-6}$ m^3 mol^{-1}.

Some experimental techniques measure the properties of single ions in extremely dilute solution where there is little evidence of changes due to ion–ion interactions. The charge-transfer-to-solvent (c.t.t.s.) spectra of iodide ions in water are extremely intense and the frequency of absorption maximum for the low-energy absorption band[34] is very sensitive to temperature, solvent, and pressure. An additional advantage is that the solvent plays an important part in defining the energy of the excited state and c.t.t.s. spectra can, therefore, be used to probe the arrangement of solvent molecules around an ion.

5 Ion–Solvent Interactions

The interaction between an ion and water is extremely intense.[35] The enthalpy

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[31] (*a*) H. P. Bennetto and D. Feakins, 'Hydrogen Bonded Solvent Systems', ed. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 235; (*b*) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, **62**, 2738.

[32] I. Lee and J. B. Hyne, *Canad. J. Chem.*, 1968, **46**, 2333.

[32a] See also estimation of absolute enthalpies of hydration, H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, **59**, 1126.

[33] (*a*) H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolyte Solutions', 3rd edn., Reinhold, New York, 1958; (*b*) J. Barthel, *Angew. Chem. Internat. Edn.*, 1968, **7**, 260; (*c*) R. Zana and E. Yeager, *J. Phys. Chem.*, 1966, **70**, 954 (see also P. Mukerjee, *J. Phys. Chem.*, 1966, **70**, 2708).

[34] M. J. Blandamer and M. F. Fox, *Chem. Rev.*, in press.

[35] (*a*) B. E. Conway and J. O'M. Bockris, 'Modern Aspects of Electrochemistry', vol. I, Butterworths, London, 1954, p. 47; (*b*) W. M. Latimer, *Chem. Rev.*, 1936, **18**, 349; (*c*) B. E. Conway, *Ann. Rev. Phys. Chem.*, 1966, **17**, 481; (*d*) B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Proc. Roy. Soc.*, 1964, *A*, **256**, 389.

changes, $\Delta H^{\ominus}$, for the process salt + water → solution, are small and sometimes negative,[35a] owing to the similarity between the interaction energies for an ion with a solvent and a salt lattice. Many treatments of ion–water interactions accept that the intense electric field, *ca.* 10^8 V m^{-1} at a distance of 0·6 nm from the centre of an ion, aligns nearest neighbour solvent molecules such that the dipolar axis passes close to or through the ion centre. These solvent molecules are called electrostricted water molecules.

Arising from the charge on an ion, the enthalpies of evaporation for ions (solution → water + ion in gas phase) are very different from those for non-polar solutes having similar size.[15] However, the corresponding entropies, $\Delta S_V^{\ominus}$ (at 298·15 K and 101·325 N m^{-2}) for both classes of solutes are very similar. Thus for potassium chloride, $\Delta S_V^{\ominus}$ is 217 J mol^{-1} K^{-1} while for two moles of argon, the corresponding entropy change is 253 J mol^{-1} K^{-1}. Release of electrostricted water molecules from ions should, on evaporation, contribute a significant increase in entropy. Nevertheless, the entropy change for the salt is less than that for the argon atoms. Therefore, in a solution of potassium chloride there is too much entropy, and this excess is traced to some degree of disorder in the arrangement of water molecules beyond the layer of electrostricted water molecules.

These observations are generalised for all simple ions in aqueous solutions by use of a model which identifies three zones of water structure around each ion.[16] Two concentric spheres are drawn around the centre of an ion. The zone between the surface of the ion and the first sphere, zone A, contains all those water molecules for which ion–water interactions dominate, *i.e.* the electrostricted water molecules. Zone C extends from the outer sphere to infinity and includes those water molecules which have essentially the same arrangement as in pure water. These water molecules experience a weak electrostatic field from the ion and the associated entropy contribution to $\Delta S_V^{\ominus}$ can be calculated by treating this liquid as a bulk continuum.

The water between the two concentric spheres, zone B, is subjected to the competing demands of water structures associated with zone C, bulk water, and with zone A, the hydration shell. Generally, these two influences will differ and the water structure in this fault zone[36] is broken down. This structure-broken layer is the source of the excess entropy in the example discussed above, potassium chloride in water.

This rather formal structural model represents essentially an instantaneous picture of the arrangements of water molecules around an ion in the same way that mixture models tackle the structure of liquid water. Zone B increases with increase in ion size and consequently the extent of water structure breaking increases. Conversely with decrease in ion size, zone B contracts until for small ions, *e.g.* lithium and fluoride, zone B disappears. In these systems the hydrated ions are accommodated within the structure of water. Such ions are (electrostrictive) structure formers.

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[36] E. Wicke, *Angew. Chem. Internat. Edn.*, 1966, **5**, 106.

The above model rationalises in a straightforward way possible competing influences of ion–water and water–water interactions. The importance of this balance is apparent, for example, in the relative enthalpies of solution for salts in water–alcohol mixtures, *i.e.* essentially $\Delta H^\ominus$ (salt + solvent → solution) − $\Delta H^\ominus$ (salt + water → aqueous solution). Addition of small amounts of an alcohol to water, particularly t-butyl alcohol and to a lesser extent ethanol, enhances water–water interactions.[37,38] When small amounts of ethanol are added to water the relative enthalpies of solution for potassium chloride, potassium bromide, and potassium iodide become increasingly endothermic.[39] Here ion–water interactions become weaker as the water–water interactions become more intense.

6 Application of Structural Models

These qualitative models have been extensively used in the interpretation of experimental data and have also been fruitfully extended to include the properties of solutes which are biochemically important.[40] A few examples are given to show how the model is used.

The standard partial molar heat capacities of non-polar solutes are positive and increase with increase in size of the solute molecule.[19b] In contrast these heat capacities for alkali-metal halides in water at 298·15 K are negative and become increasingly negative with increase in ion size. This is associated with structure breaking in zone B. (Above 310 K heat capacities show a reverse trend with increase in ion size.[36])

Tracer amounts of $H_2{}^{18}O$ diffuse more rapidly through aqueous solutions of potassium iodide than of potassium chloride:[41] this is expected if iodide breaks the structure more effectively than chloride. Furthermore, added potassium iodide increases the diffusion coefficient more markedly the lower the temperature, showing that at the lower temperature the ions have more structure to break. Interpretation of translational properties of ions in water is, however, not straightforward. There is, for example, evidence that alkali-metal cations and halide ions diffuse by different mechanisms.[8,42]

An example of a clear link between thermodynamic data and structural models is found in the transfer functions, $\Delta G^\ominus$, $\Delta H^\ominus$, and $T\Delta S^\ominus$, for salts between deuterium oxide and water.[43] The properties of these two solvents are very

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[37] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[38] M. C. R. Symons and M. J. Blandamer, ref. 31*a*, p. 211.

[39] (*a*) E. M. Arnett and D. R. McKelvey, *Rec. Chem. Progr.*, 1965, **26**, 185; (*b*) E. M. Arnett, 'Physico-Chemical Processes in Mixed Aqueous Solvents', ed. F. Franks, Heinemann, London, 1967, p. 105.

[40] See for example (*a*) M. Kennerley, H. J. V. Tyrell, and M. Zaman, *J. Chem. Soc.*, 1966, 1041; (*b*) M. Kennerley and H. J. V. Tyrell, *ibid.*, 1968, 607.

[41] (*a*) J. H. Wang, *J. Phys. Chem.*, 1954, **58**, 686; (*b*) J. Tamás and K. Újszászy, *Acta Chim. Acad. Sci. Hung.*, 1966, **49**, 377.

[42] J. N. Agar and J. C. R. Turner, *Proc. Roy. Soc.*, 1960, **255**, *A*, 307.

[43] J. Greyson, *Desalination*, 1967, **3**, 60; *J. Phys. Chem.*, 1962, **66**, 2218; 1967, **71**, 259.

similar except that at a given temperature and pressure, more structural order exists in deuterium oxide than in water.[19d] For transfer of salts from standard states in deuterium oxide to standard states in water, $\Delta G_2^\ominus$ is negative, *i.e.* the transfer is thermodynamically favourable. In water, water–water interactions are less intense than in deuterium oxide and so, as expected, ion–water interactions are relatively more intense. Nevertheless, $\Delta G_2^\ominus$ is relatively insensitive to the salt whereas more marked differences occur in $\Delta H^\ominus$ and $T\Delta S^\ominus$ quantities. The trends agree with the model discussed above in that the structure breaking sequences are $K^+ > Na^+ > Li^+$ and $I^- > Br^- > Cl^- > F^-$. A structure breaking salt is more effective in deuterium oxide where there is more structure to break.

The relative insensitivity of the Gibbs function in the above example, coupled with a greater sensitivity in the associated entropy and enthalpy quantities, is not uncommon and these phenomena are more widely known as compensation effects.[44] In fact the effects of structural changes in water on ionic properties are generally not readily apparent in Gibbs functions and associated parameters such as equilibrium and rate constants. They are much more noticeable in associated ΔH, $T\Delta S$[45] and, quite markedly, in C_p-quantities.[44]

Although the properties of solutions containing alkali-metal cations and halide ions have been used in the above examples, the properties of other ions have been discussed in a similar fashion. For example, NO_3^- and ClO_4^- are water structure breakers. The planar structure of NO_3^- cannot be easily accommodated into the water structure. The concept of a structure-breaking ion has also been related to the idea of 'negative hydration'.[46] This approach to ionic solvation considers the motion of solvent molecules in the neighbourhood of an ion. If, in comparison to those in pure water, the motion is more rapid, the ion is negatively hydrated whereas if less rapid, the ion is positively hydrated. This model is particularly useful in the interpretation of proton T_1 relaxation times in aqueous solution.[13]

7 Arrangement of Water Molecules in Zone A

The assumption that every simple ion in water is surrounded by a layer of electrostricted water molecules is widely but not universally held.[6b,14,29,46,47] Some authors suggest that for iodide in water, zone A is absent so that zone B extends from the surface of the ion and the water adjacent to the ion is more fluid than in pure water.[48] The existence of an electrostricted layer of water molecules is supported, however, by other observations. For example, the decrease in relative permittivity of water when salts are added is attributed to the restriction of dipolar reorientation for a number of water molecules by electro-

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[44] D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.

[45] S. Lindenbaum, *J. Phys. Chem.*, 1966, **70**, 814.

[46] O. Ya. Samoilov, (*a*) *Discuss. Faraday Soc.*, 1957, 24, 141; (*b*) 'Structure of Aqueous Electrolyte Solutions and the Hydration of Ions', Consultants Bureau, New York, 1965.

[47] D. Rosseinsky, *Chem. Rev.*, 1965, **45**, 467.

[48] H. G. Hertz and M. D. Zeidler, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 774.

strictive forces.[10,11,49] Similarly, the effect of added salts on the Raman spectra has been linked to the electrostriction of water, particularly by anions.[50] These electrostricted water molecules form a potential energy well which provides a well-defined energy level for the excited state of c.t.t.s. absorption spectra of anions.[34] The n.m.r. spectra of ions in some non-aqueous solvents have detected solvent molecules attached to cations, and it has been possible to determine the number of attached solvent molecules and their rate of exchange with the bulk solvent.[12,51]

The arrangement of water molecules in zone A is, however, still unknown.[47] In some models, the dipolar axis of each solvent molecule passes through the ion centre, *e.g.* $\ominus\ +\!\!\!\rightarrow$ and $\oplus\ \leftarrow\!\!\!+$, where $+\!\!\!\rightarrow$ represents the molecular dipole moment of one of the nearest neighbour water molecules. This structure is generally used in the context of cation hydration. However, some treatments use a model where the interaction for anions occurs through one hydrogen of water, $\ominus \cdots \mathrm{H{-}O(H)}$, such that one hydrogen can still hydrogen bond with other water molecules outside the primary hydration layer.[52,53] Interaction between a cation and a nearest neighbour water molecule might also involve a non-bonding doubly filled orbital on oxygen.

Some insight into the arrangement of water molecules around an ion is given by the structures of various hydrates. In tetrabutylammonium fluoride clathrate hydrate, $\mathrm{Bu^n{}_4N^+F^-,32{\cdot}8H_2O}$, each fluoride ion replaces a water molecule in the host lattice and has tetrahedral co-ordination.[54] The structure of the monoclinic hydrate, $\mathrm{KF,4H_2O}$, contains $\mathrm{K^+(H_2O)_6}$ and $\mathrm{F^-(H_2O)_6}$ octahedra; each water molecule has a tetrahedral co-ordination of either two fluoride ions, one potassium ion, and one water molecule or two potassium ions, one fluoride ion, and one water molecule.[55]

A related problem to that concerning arrangement of water molecules in the electrostricted layer concerns possible differences in the hydration energies of a cation and an anion having the same size. Most authors accept that the difference is quite large.[47] However, if the hydration energies are compared with ionic radii derived from electron density measurements on crystals, the differences between these hydration energies are small.[56] This conclusion seems to be supported by analysis of the mass spectra of hydrated ions, a novel but important way of studying ion–water interactions.[57]

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[49] F. E. Harris and C. T. O'Konskii, *J. Phys. Chem.*, 1957, **61**, 310.

[50] (*a*) G. E. Walrafen, *J. Chem. Phys.*, 1962, **36**, 1035; 1966, **44**, 1546; (*b*) R. E. Weston, *Spectrochim. Acta*, 1962, **18**, 1257.

[51] J. H. Swinehart and H. Taube, *J. Chem. Phys.*, 1962, **37**, 1579.

[52] E. J. W. Verwey, *Rec. Trav. chim.*, 1942, **61**, 127.

[53] F. Vaslow, *J. Phys. Chem.*, 1963, **67**, 2773.

[54] R. K. McMullan, M. Bonamico, and G. A. Jeffrey, *J. Chem. Phys.*, 1963, **39**, 3295.

[55] G. Beurskens and G. A. Jeffrey, *J. Chem. Phys.*, 1964, **41**, 917.

[56] M. J. Blandamer and M. C. R. Symons, *J. Phys. Chem.*, 1963, **67**, 1304.

[57] (*a*) P. Kebarle, *Adv. Chem. Ser.*, 1968, **72**, 26; (*b*) P. Kebarle, M. Arshadi, and J. Scarborough, *J. Chem. Phys.*, 1968, **49**, 817.

8 Alkylammonium Ions

A great deal of interest has been aroused by the often strange properties of alkylammonium salts in aqueous solutions.[14,35c,58] For example, the apparent partial molar heat capacity of tetra-n-butylammonium bromide in water at 293·15 K is large and positive, being more characteristic of non-polar solutes in water than ionic solutes.[16] By comparison with ion size and heat capacities of alkali-metal halides, a large negative value would be expected. This break in a pattern of behaviour is found in other properties. The *B*-viscosity coefficients increase and the electrical mobilities decrease with increase of size of the cation.[18] In addition, the Walden products, $\lambda^{\ominus}\eta$, for alkylammonium ions are markedly dependent on temperature.

There is a close link between the properties of alkylammonium ions and those of non-polar solutes. For example, the partial molar volumes $V^{\ominus}(R_4N^+Br^-)$ increase through the series (R =) methyl < ethyl < n-propyl < n-butyl < n-amyl.[59] The increase in volume per CH_2 group is similar to the increase observed for the partial molar volumes of n-alkanes in water.[59]

These observations are explained by a structural model in which the alkyl groups enhance water–water interactions, the extent of this enhancement increasing with increase in size of the alkyl group. (This model is widely but not universally accepted.[60]) These alkylammonium ions are therefore structure formers.

These ions enhance water structure for probably very similar reasons to non-polar solutes. The lack of a readily available site on a large alkylammonium ion for specific ion–water interactions means that the interactions between the water lattice and ion are weak van der Waals forces. These forces stabilise those water molecules involved in a hydrogen bonded lattice type structure, such water structures being able to form sufficiently large cavities to accommodate the alkyl chains. This structure forming is consequently quite different from the electrostrictive structure forming of lithium and fluoride ions. The extent of structure making for alkylammonium ions according to the above model follows the order, $Me_4N^+ < Et_4N^+ < Pr^n{}_4N^+ < Bu^n{}_4N^+$, and this order agrees with most experimental observations. Actually, tetramethylammonium is thought to be an electrostrictive structure breaker[10,18] (*cf.* action of Cs^+ [61]), whereas in the tetraethylammonium ion the structure enhancement by the ethyl groups and the electrostrictive structure breaking effects cancel.

When a site for specific ion–solvent interactions is introduced into the alkyl group, these special properties of alkylammonium ions are lost.[59] The hydroxy-groups in tetra-(2-hydroxyethyl) ammonium (*cf.* tetrapropylammonium – an ion of similar size) destroys the hydrophobic character of the alkyl chains. The *B*-viscosity coefficient is now relatively insensitive to temperature and there is

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[58] F. Franks, ref. 31*a*, p. 31.

[59] W-Y. Wen and S. Saito, *J. Phys. Chem.*, 1964, **68**, 2639; 1965, **69**, 3569.

[60] H. E. Wirth, *J. Phys. Chem.*, 1967, **71**, 2922.

[61] Y-C. Wu and H. L. Friedman, *J. Phys. Chem.*, 1966, **70**, 2020.

some evidence that the tetraethanolammonium ion should be considered a structure breaker.[18]

The above model, derived for alkylammonium ions, has been successfully extended to account for properties of aqueous solutions of trialkylsulphonium ions[62] (*e.g.* $Pr^n_3S^+$ is a structure former whereas Me_3S^+ is a structure breaker) and of sodium tetraphenylboron, $Na^+B^-Ph_4$.[63]

9 Very Dilute Aqueous Salt Solutions ($0 < c < 0{\cdot}1$)

So far we have considered ion–water interactions where the ions are effectively separated by an infinite amount of solvent. When the properties of real solutions are considered, the effects of ion–ion interactions on the properties of each ion must be included in a discussion of structural models for real solutions. The derivation of ionic properties can also involve new problems. As noted above, single ionic conductances can be calculated from a knowledge of molar conductance and a transport number of one ion in the solution. The spectrum of an ion in solution also provides information about ionic properties. However, the case for evaluating single-ion activity coefficients[64] remains seriously in doubt.[65]

The Debye–Huckel treatment of ion–ion interactions is satisfactory for these dilute solutions and equations for the activity coefficient of the salt, and osmotic coefficients of the solvent in a solution can be conveniently calculated. In general, the limiting law is used and the predictions are compared with the properties of real solutions.

The limiting law is quite successful in accounting for the variation in properties of solutes in real solutions at low concentrations, Even, for example, the apparent molar volume of alkylammonium salts in water at very low concentrations[10] follows closely the trend predicted. However, the experimental points rapidly deviate from the predicted dependence as the concentration of salt is increased. The deviations for other salt solutions are not so large but are well outside experimental error.

The limiting law can also be used to predict the dependence of thermodynamic excess functions on composition.[66] These excess functions, *e.g.* G^{ex}, H^{ex}, and TS^{ex}, refer to the difference between the property of the real solution and the corresponding ideal solution. If the properties of the real solution follow the limiting law, values of G^{ex}, H^{ex}, and TS^{ex} can be calculated. These are compared in the Table for an aqueous solution and a salt solution in a hypothetical solvent for which the temperature and pressure coefficients of the relative permittivity[67] are zero.

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[62] (*a*) D. F. Evans and T. L. Broadwater, *J. Phys. Chem.*, 1968, **72**, 1037; (*b*) S. Lindenbaum, *J. Phys. Chem.*, 1968, **72**, 212.

[63] S. Subramanian and J. C. Ahluwalia, *J. Phys. Chem.*, 1968, **72**, 2525.

[64] M. Alfenaar and C. L. DeLigny, *Rec. Trav. chim.*, 1967, **86**, 829.

[65] E. A. Guggenheim, *J. Phys. Chem.*, 1929, **33**, 842.

[66] R. H. Fowler and E. A. Guggenheim, 'Statistical Thermodynamics', Cambridge University Press, 1949, Chap. 9.

[67] H. L. Friedman, *J. Chem. Phys.*, 1960, **32**, 1351.

Table *Thermodynamic excess functions*[a] *for salt solutions at* 298·15 K *according to the Debye–Huckel limiting law* (*ref.* 67).

	Water	Hypothetical Solvent
G^{ex}	$-3874I^{3/2}$ J	$-3874I^{3/2}$ J
H^{ex}	$+1975I^{3/2}$ J	$-5812I^{3/2}$ J
S^{ex}	$+19{\cdot}71I^{3/2}$ J K^{-1}	$-6{\cdot}489I^{3/2}$ J K^{-1}

[a] Excess functions derived with respect to a kilogram of solvent.

The total Gibbs function decreases with increase in ionic strength, I, and this decrease in water is a result of an increase in enthalpy and an increase in entropy. This indicates again the importance of entropy changes in aqueous solutions. The increase in entropy, predicted by the limiting law, can be linked with the release of solvent molecules from the electrostatic fields, since the fields from anions and cations will partially cancel[67] as the concentration increases.

10 Higher Concentrations

Agreement between theory and experiment can be extended to higher salt concentrations if the full Debye–Huckel equations are used and also by including additional terms in the expressions relating log $\gamma_\pm$ and salt concentration. Another approach[7,8,68] treats the solution as an expanded salt lattice. The predicted linear interdependence of log $\gamma_\pm$ and $(c)^{1/3}$ is shown by potassium chloride in water at 298·15 K where $1 < c < 100$. Another method[3e] is to add to the Debye–Huckel equation for log $\gamma_\pm$ another term which measures the number of moles of water, h, bound to the two ions. Unfortunately the dependence of h on salt is not easily accounted for (see also ref. 35*c*).

Compensation effects between enthalpy and entropy quantities also occur in real solutions such that the corresponding Gibbs function is relatively insensitive to the salt. This is shown by the excess functions (per mole of salt) for salts in water and deuterium oxide (Figure 1).[69,70] The differences between G^{ex} for a given salt in the two solvents are much smaller than in the associated H^{ex} and TS^{ex} quantities.

Despite these compensation effects, the patterns shown in plots of log $\gamma_\pm$ *vs.* $(m_2)^{1/2}$, where m_2 is the molality, show several interesting trends. For example, when $m = 2{\cdot}25$, the order of log $\gamma_\pm$ for chlorides is Li > Na > K > Rb > Ca, *i.e.* increasing with decreasing size of the cation. However, the order for lithium salts is I > Br > Cl, *i.e.* increasing with increase in anion size, but for caesium salts, Cl > Br > I.[71]

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[68] (*a*) J. C. Ghosh, *J. Chem. Soc.*, 1918, **113**, 449, 707; (*b*) E. Gluekauf, ref. 7, p. 97; (*c*) M. H. Lietzke, R. W. Stoughton, and R. M. Fuoss, *Proc. Nat. Acad. Sci.*, 1968, **59**, 39.

[69] Y-C. Wu and H. L. Friedman, *J. Phys. Chem.*, 1966, **70**, 166.

[70] See also trends in enthalpies of dilution: (*a*) 'The Structure of Electrolyte Solutions', ed. W. Hamer, Wiley, New York, 1959, p. 135; (*b*) E. Lange and A. L. Robinson, *Chem. Rev.*, 1931, **9**, 89.

[71] R. M. Diamond, *J. Amer. Chem. Soc.*, 1958, **80**, 4808.

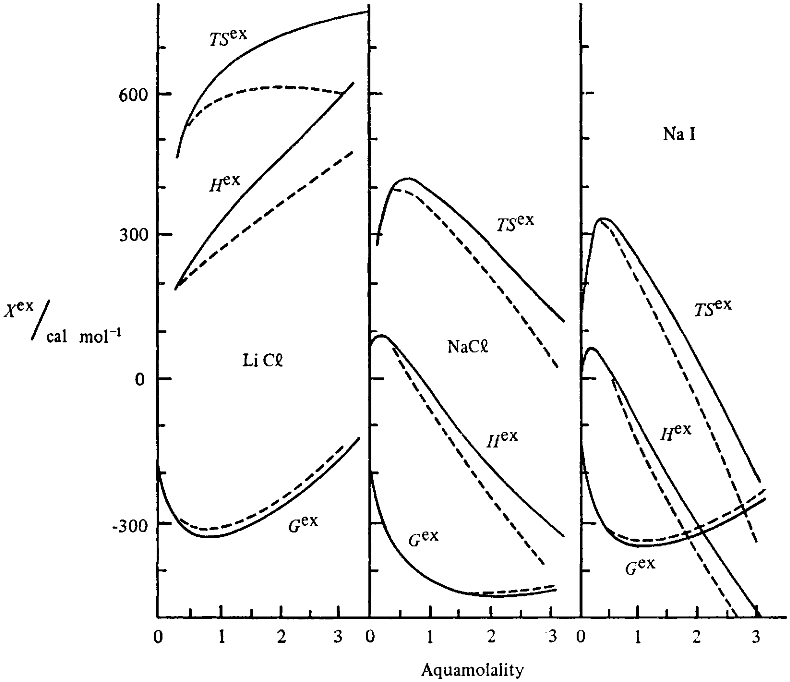

Figure 1 *Total excess thermodynamic functions X^{ex} per mole of solute for three salts in water* (—), *and deuterium oxide* (- - -), *at* 298·15 K; *aqua molality is the number of moles of salt in* 55·51 *moles of solvent* (*taken from ref.* 69). (Reproduced by permission from *J. Phys. Chem.*, 1966, **70**, 166.)

One structural model[14,29] which aims to rationalise these trends examines the response of water structure when ions approach each other, *i.e.* as the concentration increases. Each ion is placed at the centre of a co-sphere of water molecules; the sphere encompasses all those water molecules whose arrangement differs from that of bulk water. With increase in salt concentration, these co-spheres start to overlap. The problem is to decide how the various structural influences associated with each ion react in the region of overlap.[8] The experimental data are fairly consistent with the following generalisations. Anions and cations having similar structural influences (*e.g.* both electrostrictive structure makers or both electrostrictive structure breakers) salt each other in, *i.e.* decrease the activity coefficient. For example, log γ (CsCl) < log γ (LiCl). Two ions having different structural influences, salt each other out, *i.e.* increase the activity coefficient. For example, log γ (LiI) > log γ (CsI). In the above context an electrostrictive structure former, *e.g.* fluoride, and a hydrophobic structure former, *e.g.* $Bu^n_4N^+$ have different structural influences and salt each other out.[72]

Changes in (co-operative) water–water interactions coupled with ion–water interactions are particularly important in the properties of alkylammonium salt solutions. Following an increase in the relative apparent molar volume, $\phi_2 - V^\ominus_2$, for $Bu^n_4N^+Br^-$ with increase in salt concentration as required by the limiting law, the volume decreases and $\phi_2 - V^\ominus_2$ has a minimum close to $m = 1{\cdot}0$ corresponding to a stoicheiometry $Bu^n_4N^+Br^-,(60 \pm 10)H_2O$. This decrease reflects a mutual stabilisation of water structure around the alkyl groups as the alkylammonium ions come together.[10] The structures of the salt solutions, particularly at low temperatures, probably resemble those of the corresponding alkylammonium clathrate hydrates,[22] *e.g.* $Bu^n_4N^+Br^-,34H_2O$. In these crystals the alkyl groups are held in cages formed by hydrogen bonded water molecules. When the temperature is increased, the minimum in $\phi_2 - V^\ominus_2$ becomes less well defined due to the competing thermal breakdown of water structure.[72] When more salt is added, there is insufficient water to form these structures. New properties are now observed. The solubility of benzene in these solutions[73] and the ultrasonic absorption of these solutions[74] increase rapidly as more salt is added.[75]

11 Mixed Salt Solutions

The foregoing models have also been used in discussions of the properties of mixed salt solutions, particularly solutions of two salts having one common ion.

The trends in heats of mixing of two solutions containing alkali-metal halides lead to a set of generalisations.[76] Mixing of two solutions containing either electrostrictive structure makers or electrostrictive structure breakers is endothermic (assuming Na^+ is a structure maker), whereas a structure breaker and a structure maker give exothermic mixing. However, if one solution contains a large alkylammonium ion, *e.g.* tetra-n-propylammonium, the effect of this ion dominates and the mixing is exothermic. The importance of these ammonium ions on thermodynamic properties is confirmed in an analysis of volumes of mixing[77] involving alkylammonium and potassium bromide solutions. When

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[72] For further discussions on effect of alkylammonium salts on water solutions see (*a*) H. G. Hertz and M. D. Zeidler, *Ber. Bunsengesellschaft Phys. Chem.*, 1964, **68,** 821; (*b*) F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, 1968, **72,** 1758; (*c*) R. Gopaland and M. A. Siddiqi, *J. Phys. Chem.*, 1968, **72,** 1814; (*d*) W-Y. Wen, S. Saito, and C. Lee, *J. Phys. Chem.*, 1966, **70,** 1244; (*e*) B. E. Conway and R. E. Verrall, *J. Phys. Chem.*, 1966, **70,** 1473; (*f*) R. M. Diamond, *J. Phys. Chem.*, 1963, **67,** 2513; (*g*) S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, 1964, **68,** 911; (*h*) K. W. Bunzl, *J. Phys. Chem.*, 1967, **71,** 1358; (*i*) J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, 1966, **45,** 2868; (*j*) G. E. Boyd, A. Schwarz, and S. Lindenbaum, *J. Phys. Chem.*, 1966, **70,** 821; 1967, **71,** 573.

[73] H. E. Wirth and A. LoSurdo, *J. Phys. Chem.*, 1968, **72,** 751.

[74] M. J. Blandamer, M. J. Foster, N. J. Hidden, and M. C. R. Symons, *Trans. Faraday Soc.*, 1968, **64,** 3247.

[75] For other evidence of structural effects in real solutions, see F. Vaslow, *J. Phys. Chem.*, 1966, **70,** 2286; 1967, **71,** 4585.

[76] R. H. Wood and H. L. Anderson, *J. Phys. Chem.*, 1966, **70,** 992, 1877; 1967, **71,** 1869, 1871.

[77] W-Y. Wen and K. Nara, *J. Phys. Chem.*, (*a*) 1967, **71,** 3907; (and for solutions in D_2O) (*b*) 1968, **72,** 1137; (*c*) W-Y. Wen, K. Nara, and R. H. Wood, *J. Phys. Chem.*, 1968, **72,** 3048.

these two solutions are mixed in different proportions but at constant ionic strength, there is an overall increase in volume (Figure 2). The volume increase is a maximum when the component salts have equal concentrations. Here the

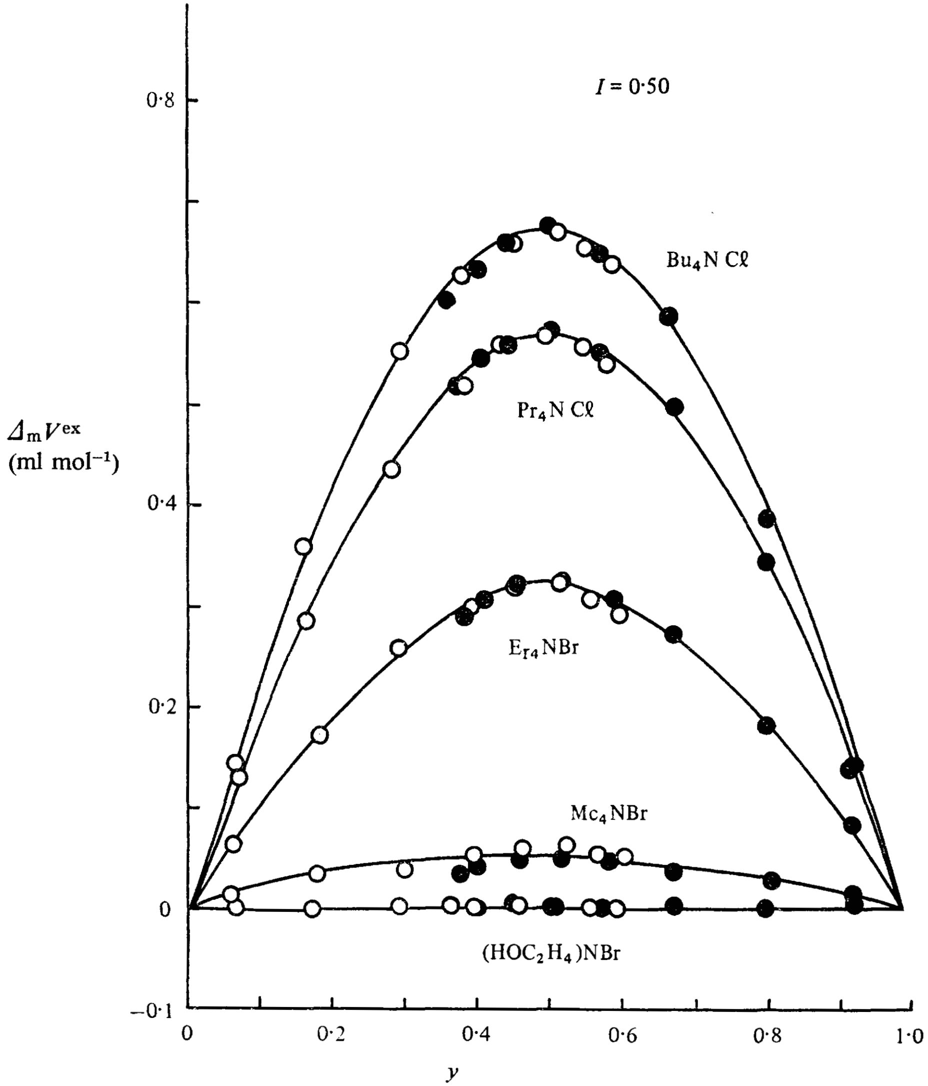

Figure 2 *Excess volumes of mixing for quaternary ammonium salt solutions and potassium bromide solutions at* 298·15 K *and a total ionic strength* 0·5; *y is fraction of ionic strength, I, due to the salt* $R_4N^+Br^-$ *in the mixed salt solution* (*taken from ref.* 77*a*). $\Delta_m V^{ex}(y,I) = V^{ex}(y,I) - (1-y)V^{ex}(0,I) - yV^{ex}(1,I)$ *where* $V^{ex}(y,I)$ *is the excess volume whose composition is specified by y and I* (Reproduced by permission from *J. Phys. Chem.*, 1967, **71**, 3907.).

structure-breaking potassium bromide does maximum damage to water structure enhanced by the alkylammonium ions. The importance of these structural influences, as opposed to ion size effects, is confirmed by the essentially zero excess volumes of mixing for $(HOC_2H_4)_4N^+$ and potassium salt solutions (Figure 2).

In surveying a large subject within the limits of the space allowed, I have had, unfortunately, to omit many important contributions by workers in this field.

I thank colleagues in this Department and Dr. F. Franks for their valuable comments.