Experimental Studies on the Structure of Aqueous Solutions of Hydrophobic Solutes

By T. S. Sarma and J. C. Ahluwalia
DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY,
KANPUR-16, INDIA

1 Introduction

The study of the structure of water and of aqueous solutions is important from both theoretical and practical points of view. It has been recognized that the structure of water plays an important role in deciding the conformations of proteins and other biopolymers in their aqueous solutions. In addition, the recent interesting observations that mixed binary aqueous solvent systems behave in a peculiar fashion compared with the mixed non-aqueous systems have given a new impetus to a detailed study of the structure of water and of aqueous solutions. In the recent literature there are many review articles and books which deal extensively and critically with the subject of the structure of liquid water.[1-10]

Theoretical models proposed to depict the bulk structure of water can be broadly classified into (i) continuum models[11,12] and (ii) mixture models.[13-21]

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[2] (*a*) H. S. Frank, *Science*, 1970, 169, 635; H. S. Frank, *Fed. Proc. Fedn. Amer. Chem. Soc.*, 1971, **6**, 217; (*b*) H. S. Frank, *Fed. Proc. Fedn. Amer. Soc. exp. Biol.*, 1965, **24** (Part III), S-1.

[3] R. A. Horne, 'Marine Chemistry', Wiley Interscience, New York, 1969.

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[19] C. M. Davis and T. A. Litovitz, *J. Chem. Phys.*, 1965, **42**, 2563.

[20] H. S. Frank and A. S. Quist, *J. Chem. Phys.*, 1961, **34**, 604.

[21] V. Vand and W. A. Senior, *J. Chem. Phys.*, 1965, **43**, 1869, 1873, 1878.

Continuum models treat liquid water as a uniform dielectric medium, and when averaged over a large number of molecules the environment about a particular molecule is considered to be the same as about any other molecule, so that the behaviour of all molecules is equivalent. According to mixture models liquid water contains two or more distinguishable species.

Even among the supporters of the mixture approach towards defining the intermolecular structure of water there are differences of opinion about the particular form of the species. As a result many models have been proposed which can be categorized under the mixture concept. The complexity in the properties of water and its atypical nature precludes a simple model for representation of its structure. However, the presence of a bulky four-co-ordinated species has been universally agreed upon. Whether the particular form of this species is ice-like or similar to any other form of cage or crystalline structure is still an open question. It is also not yet established whether the denser monomeric water molecules (the second species proposed in the various mixture models of liquid water, the existence of which is still not accepted by the proponents of the continuum models) exist in the interstitial sites provided by hydrogen-bonded lattice or are dispersed among the clusters of the bulky hydrogen-bonded water molecules.

The different models proposed, although able to account for a number of distinctive features of liquid water, are contradictory in many respects.[4] As a result, in spite of the exhaustive amount of work done on the properties of water,[1,22–25] the understanding of the structure of water is far from complete. Nevertheless, it may be hoped that the changes in the structure of water brought about by solutes may help towards better understanding of the structure of water, as any acceptable model should be able not only to account for the various properties of water but must also stand the rigorous test of interpreting the behaviour of aqueous solutions.

Excellent reviews have appeared in recent years which discuss the effects of various kinds of solutes on the structure of water.[3,4,7,8,26–32] However, a broad survey of all the important properties of aqueous solutions of hydrophobic solutes (solutes containing non-polar groups) is not available. The purpose of

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this review is to provide such a comprehensive summary of the investigations done on the properties of aqueous solutions of hydrophobic solutes.

The model that is most commonly adopted, especially in the field of solution chemistry, is the 'flickering cluster' model of Frank and Wen[18], developed by Namethy and Scheraga.[5] Even though this model is not entirely adequate,[7] it has still been able to account for the properties of aqueous solutions more satisfactorily than any other model.[33] Accordingly, emphasis is given to this model in the discussions presented here. In the picture given by this model (Figure 1), there are short-lived liquid clusters of varying extent consisting of highly hydrogen-bonded molecules which are mixed with, and which alternate roles with, non-bonded monomers. The half-life of the clusters is assumed to be about 10^{-11} s, which is short enough to produce a single relaxation time observed for water,[34] but sufficiently long to ascribe a meaningful existence to the clusters, as the half life is 10^2—10^3 times the molecular vibration time.

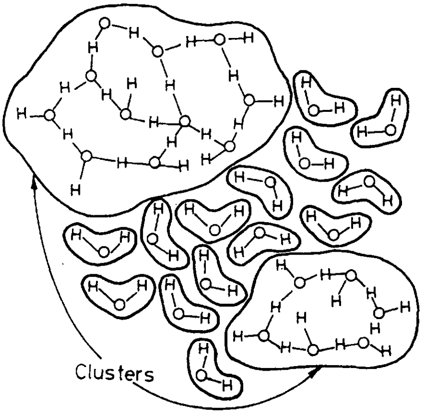

Figure 1 *Frank–Wen flickering cluster model of liquid water*
(Reproduced by permission from *J. Chem. Phys.*, 1962, **36,** 3382)

2 The Concept of Structure-making and Structure-breaking Effect of Solutes

According to the hypothesis given above, the water molecules can be considered to be in dynamic equilibrium between the bulky tetrahedrally hydrogen-bonded clusters and the denser monomer molecules, as represented by $(H_2O)_b \rightleftharpoons (H_2O)_d$ and the statistical degree of ice-likeness (or whatever its structure in water is) is considered to be proportional to the half-life of the clusters, which is of the order of 10^{-11} s in pure water.[18] When a solute is put into water, it is assumed that the former may shift the equilibrium in either direction. A solute which causes a

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[34] C. H. Collie, J. B. Hasted, and D. M. Ritson, *Proc. Phys. Soc.*, 1948, **60,** 145.

shift so as to increase the number and the average half-life of the clusters is termed a structure-maker, and a solute which has an effect in the opposite direction is called a structure-breaker.[18] Although the concept of structure-making and -breaking effects of solutes is not entirely satisfactory, it has proved useful in discussing the effects of solutes on water structure. These effects can be detected experimentally by observing the changes brought about by the solutes in the properties of water, such as fluidity (reorientation time, viscosity, conductance *etc.*) and heat capacity. For instance, structure-makers are shown to decrease the fluidity of water (by causing an increase in reorientation time and increase in viscosity) and result in positive excess partial molal heat capacities in water. The reverse is true for structure-breakers. It has been shown by these methods that ions of simple electrolytes such as LiF and $MgCl_2$, having high charge-density, act as net structure-makers and ions with low charge-density, such as of CsI and KBr, behave as net structure-breakers. Frank and Wen, in order to explain these phenomena, visualized[18] a picture (see Figure 2) in which an ion is surrounded by concentric regions of water molecules. The innermost region A consists of water molecules polarized, immobilized, and electrostricted by the ion. The water molecules in the region C have the normal liquid structure which is polarized in the usual way by the ionic field which at this range will be relatively weak. The intermediate region B is the region in which water is less ice-like, *i.e.* more randomly ordered than the normal water. The decreased structure in this region is presumably due to the approximate balance of two competing forces, namely, the normal structure-orienting influence of the neigh-

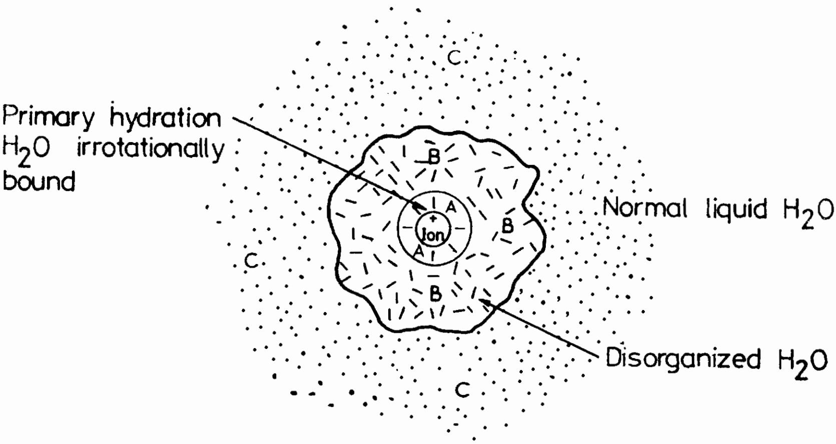

Figure 2 *Frank–Wen zone model of water in the neighbourhood of a simple ion* (Reproduced by permission from 'Membranes and Ion Transport', Wiley-Interscience, London, 1970, Vol. 1)

bouring water molecules, and the radially orienting influence of the electric field of the ion, which act simultaneously on any water molecule in this region. The latter ionic influence predominates in the region A, and the former in region C, and between A and C there should be a region of finite width in which more orientational disorder should exist than in either A or C. Now, it was assumed in the flickering cluster model[18] of water that the lifetime of a cluster is essentially dependent on the fluctuations of energy produced in the liquid water. An ion with its first layer of water molecules will be a disturbing centre which would both interfere with the initiation of clusters and hasten their disruption. Ions with low charge-density have relatively weak electrostatic fields, which makes the region A very small thereby causing net decrease in structure. In the case of structure-making ions of high charge-density, the region A of immobilization exceeds region B, which results in a net structural increase around these ions.

3 Hydrophobic Hydration

An entirely different kind of behaviour is shown by non-polar solutes[35] such as hydrocarbons and solutes or ions having non-polar groups such as substituted hydrocarbons and alkylammonium salts.[34] The relatively low solubility of hydrocarbons and noble-gas molecules is considered to be linked with the large decrease in entropy which makes the free energy of their solution positive in spite of their endothermic dissolution in water. In fact the entropy of transfer of noble gases from an organic solvent to aqueous solution is found to have a large negative value which decreases as the temperature is increased, so that $\bar{C}_{p2}^{\circ}\left(= T\dfrac{\mathrm{d}S_2^{\circ}}{\mathrm{d}T}\right)$ has large positive values.[5,18,36] The large entropy decrease resulting from addition of non-polar groups to water indicates a small number of configurational states for a given energy, which means that the packing of water molecules around dissolved groups is somewhat tighter than in pure water. This situation is called a structure increase.[37] However, one must realize that the abnormally low partial molal entropies of solution of non-polar solutes need not originate exclusively from a decrease in the number of configurations available to solvent molecules. Most probably a contribution towards $-\bar{S}_2$ also arises from the changes in the occupancies of the hydrogen-bonded vibrational and librational energy levels.[38]

The water-structure stabilization by solutes having large non-polar groups is in contradiction to the earlier formulation that solutes having low charge-density are structure-breakers. This has been explained by Frank and Wen[18] as being due to the relative incapability of such solutes in producing or transmitting the cluster disruptive influences, on account of the relative feebleness of their polarizability and of the electrostatic influences into which they can enter. An 'ice-like patch', therefore, should be able to form more readily in a volume element bound

[35] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1495, **13**, 507.
[36] D. M. Himmelblau, *J. Phys. Chem.*, 1962, **63**, 1803.
[37] H. G. Hertz, ref. 30, pp. 226.
[38] F. Franks, ref. 30, p. 224.

by the non-polar solute particle, and once formed should have a longer half-life by virtue of having a part of its boundary protected from the high-energy attack which tries to dissolve it. This would, on average, produce extra structure in the solution. According to Frank and Evans,[35] structure that is formed around the non-polar solutes may or may not be similar to the structure existing in pure water at low temperatures. Increase in structure by non-polar solutes only means that the number of hydrogen bonds is greater than in pure water, and this has been termed as 'ice-berg' formation[35] or 'hydration of second kind' (to differentiate from the hydration of the first kind occurring around the polar ions of normal electrolytes) or 'the hydrophobic hydration'.

Nemethy and Scheraga have extended[33] their statistical thermodynamic treatment[5] of the cluster model to aqueous solutions of non-polar solutes. Owing to relatively weak interaction between the non-polar groups and water molecules compared with that between water molecules themselves, the energy levels of molecules having four hydrogen bonds are lowered and those of other species with 0, 1, 2, and 3 hydrogen bonds are increased; as a result there is a net shift of the first-layer water molecules from the higher levels into the lower levels in accordance with Boltzmann distribution law with a corresponding increase in their ice-likeness. In other words the net number of water molecules in the clusters near the surface of non-polar solute molecule is increased.

Wicke[7] finds the above two-state cluster model to be inadequate and has given a slightly different explanation for the effect of solutes on the structure of water on the basis of his proposed concept of non-tetrahedral hydrogen bonds in liquid water, though the essential picture of hydration remains the same. Around solute molecules containing non-polar species the water molecules tend to bind more between themselves in order to protect the charge going into the non-polar region of the solute molecules, because otherwise an appreciable ionic field will be passing in a region of low dielectric constant. Wicke[7] argues that particularly effective shielding can be obtained by formation of non-tetrahedral hydrogen bonds between the water molecules.

There is no direct evidence for the formation of 'ice-bergs' or cages around solutes containing non-polar groups. However, the most impressive evidence for the formation of some kind of definite structure in aqueous solution is probably the existence of solid gas hydrates[39,40] and clathrates.[41] A number of hydrates of the noble-gas atoms, hydrocarbons, halogens, and of many other simple molecules are known to exist.[39–43] Several amines,[44] ethers,[45,46] and salts[47] of tetra-

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[39] M. V. Stackelberg and H. R. Muller, *Z. Electrochem.*, 1954, **58**, 25.

[40] G. G. Malenkov, *J. Struct. Chem.*, 1962, **3**, 206.

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[42] W. F. Claussen, *J. Chem. Phys.*, 1951, **19**, 259, 662, 1425.

[43] L. Pauling and R. E. Marsh, *Proc. Nat. Acad. Sci., U.S.A.*, 1952, **38**, 112.

[44] D. Panke, *J. Chem. Phys.*, 1968, **48**, 2990.

[45] D. W. Davidson, M. M. Davies, and K. Williams, *J. Chem. Phys.*, 1964, **40**, 3449.

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[47] (*a*) R. K. McMullan and G. A. Jeffry, *J. Chem. Phys.*, 1959, **31**, 1231; 1963, **39**, 3295; (*b*) M. Banamico, G. A. Jeffrey, and R. K. McMullan, *ibid.*, 1962, **37**, 2219; (*c*) D. Feil and G. A. Jeffrey, *ibid.*, 1961, **35**, 1863; (*d*) P. T. Beurskens and G. A. Jeffrey, *ibid.*, 1964, **40**, 2800.

alkylammonium and trialkylsulphonium ions form clathrate compounds. In some of these hydrates, such as the one formed by Et_2NH and Me_3N, the guest molecule is hydrogen-bonded to the framework lattice.[44] In the case of R_4N^+ salts, size and spacial orientation of the guest molecules seem to be rather specific because only tetrabutylammonium and tetraisoamylammonium salts form clathrates. Hydrate formation of hydrocarbon gases has been proposed as a basis for the development of commercial desalination of sea water.[7]

Since the elucidation of the structure of gas hydrates,[42,43] many investigators[48,49] have taken the view that in aqueous solutions of non-polar substances the increase in structure may be preformation of solid hydrated structure. Thermodynamic calculations show that free energy, enthalpy, and entropy of transfer of ice to empty hydrate structure[50,51] have small values which indicate the possibility of the existence of such structures in aqueous solution. It is not known, however, to what extent structures that are stable in the solid state are retained in the liquid state.[27] Frank has pointed out that the induced ice-likeness cannot consist of clathrate formation in the liquid phase, although ice-like structures could be transitory fragments of clathrate-like aggregates.[52] The view that the hydrophobic hydration consists of fluctuating cage structures also seems to receive some support from the recent ultrasonic absorption studies on aqueous solutions of some organic solutes.[53]

4 Experimental Observations

There are many physicochemical methods which can give an insight into the structure of aqueous solutions with the help of which one can verify the formulations made above. In the following sections some representative studies on the properties of aqueous solutions are discussed with greater emphasis on the solution behaviour of non-electrolytes and amphiphilic electrolytes (electrolytes with large non-polar groups as molecular segments), with brief reference to the properties of normal electrolytes in water, for the sake of comparison. Many of the typical phenomena of hydrophobic hydration are retained in the aqueous solutions of the solutes of the former type, with the added advantage of greater solubility which makes them susceptible to study of the solution properties with greater ease and accuracy than for pure hydrocarbons or noble gases.

A. Thermodynamic Properties.—Thermodynamics of the aqueous solutions of R_4N^+ salts is one of the most widely studied aspects of the field of structure of aqueous solutions. The results of heats of dilution,[54,55] heats of transfer from

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[48] W. F. Claussen and M. F. Polglase, *J. Amer. Chem. Soc.*, 1952, **74**, 4817.

[49] D. N. Glew, H. D. Mak, and N. S. Rath, in 'Hydrogen-Bonded Solvent Systems', ed. A. K. Covington and P. Jones, Taylor-Francis, 1968, p. 195.

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[54] S. Lindenbaum, *J. Phys. Chem.*, 1966, **70**, 814; 1970, **74**, 3027.

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water to non-aqueous solvents,[56] and heats of mixing[57] have been interpreted in terms of enhancement of water structure, except in the case of Me_4N^+ salts which are termed as structure breakers.[55] The order of structure-breaking action of the halide ions for the same cation is $I^- > Br^- > Cl^- > F^-$, F^- acting as a structure-maker. The structure enhancement by R_4N^+ ion increases with increase in the size of the ion. However, the results derived from the studies on apparent molal entropies[58,59] calculated from the activity coefficients are indicative of increasing structure-making order for larger cations, when the anion is either chloride or fluoride, and of reverse order with bromide or iodide as anion. These results are explained[58] by the concept of 'water structure enforced ion-pairing by large cations and anions'[60] for dilute solutions and by a micelle formation concept for concentrated solutions. Recently the temperature dependence of apparent molal entropies has been calculated by Lindenbaum *et al.*[61] from the change in activity coefficients of some R_4N^+ salts in the range 25—65 °C. It has been found that the structure-making tendency decreases from 25 to 65 °C for the salts studied except from Bu_4NF and Bu_4NI. It has been observed that it may be possible to interpret the previous results for the apparent molal entropies of R_4N^+ salts without invoking special concepts.

The thermodynamic properties of aqueous solutions of organic compounds,[30,62] such as alcohols, cyclic ethers and amines at infinite dilution, has been represented by Barclay–Butler[63] plots of $\Delta\bar{H}_2{}^\circ$ *vs.* $\Delta\bar{S}_2{}^\circ$ (Figure 3) and the results have been interpreted in terms of immobilization of water molecules in the vicinity of solute molecule.[29,30,35] From the results of excess thermodynamic functions ΔG^E, $T\Delta S^E$, and ΔH^E, two types of systems exhibiting different behaviour have been distinguished: 'typically aqueous' and 'typically non-aqueous' systems[64] (Figure 4). In 'typically non-aqueous' systems (*e.g.* aqueous solutions of amides and nitriles) the deviations from Raoult's law are determined by the sign of ΔH^E whose magnitude is always greater than $T\Delta S^E$. On the other hand, for 'typically aqueous' mixtures (*e.g.* mixtures of water with amines, ethers, and alcohols) the deviations from Raoult's law are controlled by ΔS^E and are positive in spite of large negative heats of mixing. Thus in solutions of these compounds the predominating factor appears to be non-polar-group–water interactions. The results based on lower critical solution temperature measurements and on thermodynamic transfer functions[62] also indicate that their thermodynamics are governed by entropy factors.

Heat capacity measurements extrapolated to infinite dilution have been recognized as a very potent method of detecting structural changes in water in

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[56] Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, 1966, **70**, 2020.
[57] R. H. Wood and H. L. Anderson, *J. Phys. Chem.*, 1967, **71**, 1871.
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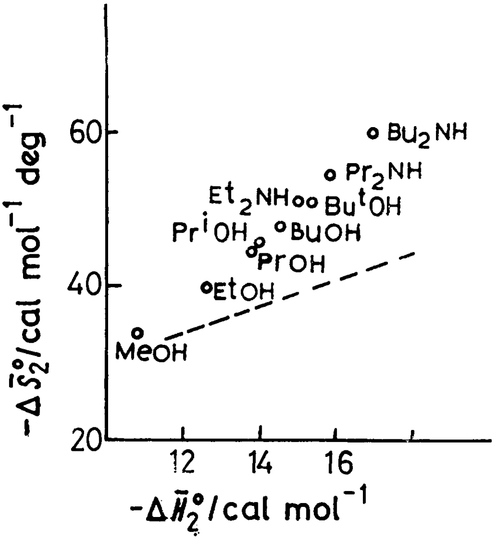

Figure 3 *Barclay–Butler plot for alcohols and amines in aqueous solutions. The dotted line represents the data for simple gases*
(Reproduced by permission from 'Hydrogen-Bonded Solvent Systems', Taylor-Francis, London, 1968)

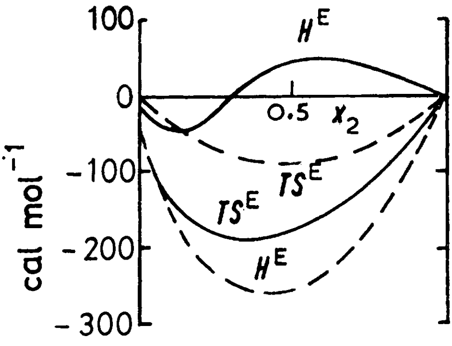

Figure 4 *Excess enthalpies and entropies of 'typically non-aqueous' and 'typically aqueous' mixtures at 75 °C. Broken line refers to* H_2O–H_2O_2 *and full line to* H_2O-EtOH *system*
(Reproduced by permission from 'Hydrogen-Bonded Solvent Systems', Taylor-Francis, London, 1968)

the presence of solutes.[65,66] Partial molal heat capacity ($\bar{C}_{p_2}{}^\circ$) values of all the normal 1:1 electrolytes except those having small ions are negative.[67–69] This means that the heat capacity of water in these electrolyte solutions is much lower than in pure water. Since the abnormally high heat capacity of water is due to the thermal decay of hydrogen bonds, the above shows that fewer bonds are present in solutions of electrolytes than in pure water, *i.e.* a large number of hydrogen bonds have been broken by the ions of electrolytes. Similarly the structure increase in solutions of non-polar solutes has been derived from their high partial molal heat capacities (which give rise to positive partial molal excess heat capacity) as shown by measurements on aqueous solutions of amines,[30] alcohols,[70] cyclic ethers,[71] and sodium salts of fatty acids and alkylammonium chlorides,[72] hydrocarbons and substituted hydrocarbons.[73] The values of the excess partial molal heat capacity, $\Delta C_p{}^\circ$, for some tetra-alkylammonium salts[66] and tetra-aryl-phosphonium and -arsonium salts[74] in water derived from the 'integral heat method'[65] are positive (except for tetramethylammonium salts) and increase with the size of the alkyl group, showing that the structure promotion is greater for solutes having larger alkyl groups. An increment in $\Delta C_p{}^\circ$ by 15—20 cal deg^{-1} mol^{-1} is observed with the addition of one CH_2 group in the side chain of alkylammonium and fatty acid salts. However, when the alkyl group R is larger than C_4H_9 in R_4N^+ salts the increment is much larger (*ca.* 30 cal deg^{-1} mol^{-1} of CH_2 group).[74]

The temperature dependence of $\Delta C_p{}^\circ$ is quite different for different types of solutes. None of the models advanced to explain the properties of aqueous solutions of non-polar solutes seems adequate to account quantitatively for the experimental values. The interstitial model of Eley[75] predicts a negative temperature coefficient of $\Delta C_p{}^\circ$ whereas, according to the flickering cluster model of Nemethy and Scheraga,[33] $\Delta C_p{}^\circ$ should increase with temperature. However, the experimental results show that in the case of normal 1:1 electrolytes,[67–69] sodium salts of fatty acids, and alkylammonium salts,[73] $\bar{C}_{p_2}{}^\circ$ or $\Delta C_p{}^\circ$ increases up to about 50 °C and decreases after about 80 °C, reaching maximum between 50 and 80 °C. This type of behaviour has been explained by Wicke[7] in terms of the breakdown of clusters at moderate temperatures, which is replaced by the break-

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[66] T. S. Sarma, R. K. Mohanty, and J. C. Ahluwalia, *Trans. Faraday Soc.*, 1969, **65**, 2333.
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[72] Th. Ackermann and F. Schreiner, *Z. Elektrochem.*, 1958, **62**, 1143.
[73] L. A. D'Orazio and R. H. Wood, *J. Phys. Chem.*, 1963, **67**, 1435.
[74] R. K. Mohanty and J. C. Ahluwalia, *J. Chem. Thermodynamics*, 1972, **4**, 53.
[75] D. D. Eley, *Trans. Faraday Soc.*, 1939, **35**, 1281, 1421.

down of the non-tetrahedral aggregates at higher temperatures. The experiments carried out on aqueous solutions of alcohols and amines extend only to temperatures slightly above room temperature and they show a decrease in $\Delta C_p{}^\circ$ at higher temperatures, giving support to Eley's model.[30,70]

The temperature dependence of heat capacity of the salts Me_4NBr,[76] $Bu^n{}_4NBr$,[77,78] $Am^n{}_4NBr$,[79] Bu_4PBr,[80] Ph_4PBr,[80] Ph_4AsCl,[80] and $NaBPh_4$[65] has been reported on a larger scale of temperature. In the plots of ΔC_p *vs.* temperature (Figure 5) large variations are observed, supporting none of the above predictions. Only the behaviour of Me_4NBr is simple in that it can be attributed to that of a normal electrolyte. On the other hand, although the salts $Bu^n{}_4NBr$, $Am^n{}_4NBr$, Bu_4PBr, Ph_4PBr, Ph_4AsCl, and $NaBPh_4$ have large positive $\Delta C_p{}^\circ$ values throughout the temperature range studied, ΔC_p–T curves for salts containing aryl non-polar groups and $Am^n{}_4NBr$ show a complex behaviour depicting maxima and minima, in contrast to those for $Bu^n{}_4NBr$ and Bu_4PBr. It is interesting to note that although $Bu^n{}_4NBr$ and $Am^n{}_4NBr$ belong to the same class of solutes, the temperature-dependence characteristics of their heat capacities are quite different. The above studies indicate that although these amphiphilic electrolytes containing alkyl and aryl non-polar groups have strong structure-making propensities, they seem to enforce water structure in different ways. The simple flickering cluster model seems to be inadequate to explain these results. An analysis of the low-temperature properties of R_4N^+ salts suggests[77] the necessity of a 'three-state' model such as the one proposed by Wicke,[7] in order to define the intermolecular structure of water.

B. Transport Properties.—The molecular movements of water molecules in aqueous solutions are reflected in transport properties such as relaxation of the dielectric polarization and of spin through the lattice, conductance, viscosity, and self diffusion. In general the rate of movement of water molecules decreases if there is a structural increase due to increased rigidity and increases in a molecular environment of less structure.

Although the static dielectric constant measurements are of little use in distinguishing the effects of different solutes on the structure of water,[7] the dielectric relaxation times which are closely related to the average reorientation time of H_2O molecules are very useful, because in this case the effect of solutes is more specific than are the effects on the static dielectric constant.[81] Aqueous solutions give dispersion curves which can be regarded, as in the case of pure water, as a uniform relaxation process with a single relaxation time. Alcohols, amines, diethyl ketone and dioxan,[81] heterocyclic compounds[82] and R_4N^+

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[76] M. J. Mastroianni and C. M. Criss, *J. Chem. Thermodynamics*, 1972, **4**, 321.
[77] T. S. Sarma and J. C. Ahluwalia, *J. Phys. Chem.*, 1970, **74**, 3547.
[78] (*a*) T. S. Sarma and J. C. Ahluwalia, *Trans. Faraday Soc.*, 1971, **67**, 2528; (*b*) T. S. Sarma, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India, 1971.
[79] R. K. Mohanty, S. Sunder, and J. C. Ahluwalia, *J. Phys. Chem.*, 1972, **76**, 2577.
[80] S. Sunder, B. Chawla, and J. C. Ahluwalia, to be published.
[81] G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, 1952, **20**, 1452.

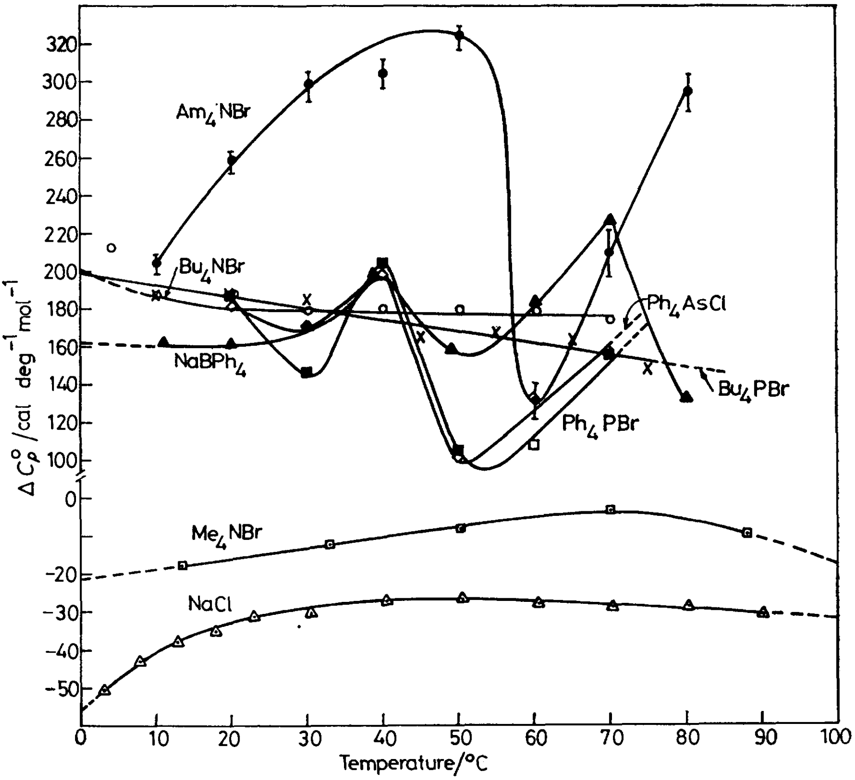

Figure 5 *Temperature dependence of excess partial molal heat capacity* $\Delta C_p{}^\circ$, *of* NaCl (*ref. 69*), Me_4NBr (*ref. 76*), $Bu^n{}_4NBr$ (*ref. 77*), Bu_4PBr, Ph_4PBr, Ph_4AsCl (*ref. 80*), $NaBPh_4$ (*ref. 65*) *and* $Am^n{}_4NBr$ (*ref. 79*)

salts,[81,83] increase the relaxation time of water, the effect being a function of non-polar groups in the solute molecule, which has been interpreted as due to increased rigidity towards the re-orientation of H_2O molecules in solution of these solutes. Alkali-metal halides,[81] on the other hand, reduce the average relaxation time, showing a decrease in structure, in the same order as depicted by other methods, although the origin of structure-forming–structure-breaking scale is displaced towards the side of structure-breaking compared with the other methods probably because of the difference in the method of averaging in the relaxation measurement.[7] Some of the recent measurements on dioxan–water

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[82] R. Pottel and U. Kaatze, *Ber. Bunsengesellschaft phys. Chem.*, 1969, **73**, 437.
[83] R. Pottel and O. Lossen, *Ber. Bunsengesellschaft phys. Chem.*, 1967, **71**, 133.

mixtures by Smyth *et al.*[84] as a function of concentration and temperature have indicated the presence of two relaxation processes. This has been attributed as due to the change in the environments of some of the water molecules by dioxan, which thereby introduces a second relaxation time in the mixture.

Spin–lattice relaxation rates for the proton nuclear spins of H_2O molecules were shown to provide, like the dielectric relaxation rate, information about the average time required for the H_2O molecules to execute one hindered rotation.[85,86] R_4N^+ salts in D_2O solutions and other deuteriated organic molecules in H_2O solution increase the relaxation times of D_2O and H_2O molecules respectively.[85–87] In the presence of R_4N^+ ions (Figure 6) the reorientation of D_2O molecules becomes increasingly rigid on passing from methyl to propyl groups. With salts of butyl groups, however, the effect decreases, perhaps because of coiling or micelle formation.[85,86] Furthermore, on the basis of the increased activation energy calculated from the temperature dependence (40—80 °C) of the relaxation rates in D_2O solutions of $Bu^n{}_4NBr$ compared with the value of the activation energy in pure D_2O, it was inferred that these solutions contain D_2O molecules whose reorientation is more strongly restricted than in pure water. Qualitatively similar results were arrived at from the studies of the relaxation rates of the ^{17}O nucleus[88] in aqueous solution of electrolytes and non-electrolytes, and of the relaxation rates of the proton of the water molecule and the solute molecule in aqueous solution of sodium alkyl sulphates.[89] From ^{79}Br nuclear relaxation measurements[90] in aqueous solutions of R_4NBr salts it was shown that the binding properties for the bromide ions in the presence of R_4N^+ ions are very different from those in the presence of ions of ordinary electrolytes. This was attributed to the increased anion–water interaction in the vicinity of R_4N^+ ions.

Self-diffusion coefficients D^* of water molecules in aqueous solutions of electrolytes obtained either from the tracer method or from the n.m.r. spin-echo method are less than in pure water[91–93] and decrease further with increase in concentration, indicating an increase in the fluidity of water. Aqueous solutions of alcohols[94] and dioxan[95] exhibit minima in the D^* (x_2) isotherm, which was interpreted as being due to increase in water structure in dilute solutions, which collapses after the minimum point. Solutions of R_4NCl salts show a

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[84] (*a*) C. J. Clemett, E. Forest, and C. P. Smyth, *J. Chem. Phys.*, 1964, **40**, 2123; (*b*) S. K. Garg and C. P. Smyth, *ibid.*, 1965, **43**, 2959; (*c*) J. Crossley and C. P. Smyth, *ibid.*, 1969, **50**, 2259.

[85] (*a*) H. G. Hertz and M. D. Zeidler, *Ber. Bunsengesellschaft phys. Chem.*, 1963, **67**, 774; 1964, **68**, 821; (*b*) H. G. Hertz, *ibid.*, 1964, **68**, 907.

[86] H. G. Hertz, *Ber. Bunsengesellschaft phys. Chem.*, 1963, **67**, 311.

[87] C. J. Clemett, *J. Chem. Soc.* (*A*), 1969, 761.

[88] F. Fister and H. G. Hertz, *Ber. Bunsengesellschaft phys. Chem.*, 1967, **71**, 1032.

[89] (*a*) J. Clifford, *Trans. Faraday Soc.*, 1965, **61**, 1276; (*b*) J. Clifford and B. A. Pethica, *ibid.*, 1965, **61**, 182.

[90] B. Lindman, S. Forsen, and E. Forslind, *J. Phys. Chem.*, 1968, **72**, 2805.

[91] D. W. McCall and D. C. Douglas, *J. Phys. Chem.*, 1965, 69, 2001.

[92] J. H. Wang, *J. Phys. Chem.*, 1954, **58**, 686.

[93] L. Devell, *Acta Chem. Scand.*, 1962, **16**, 2177.

[94] K. A. Valiev and M. I. Emelyanov, *Zhur. strukt. Khim.*, 1964, **5**, 7.

[95] C. J. Clemett, *J. Chem. Soc.* (*A*), 1969, 458.

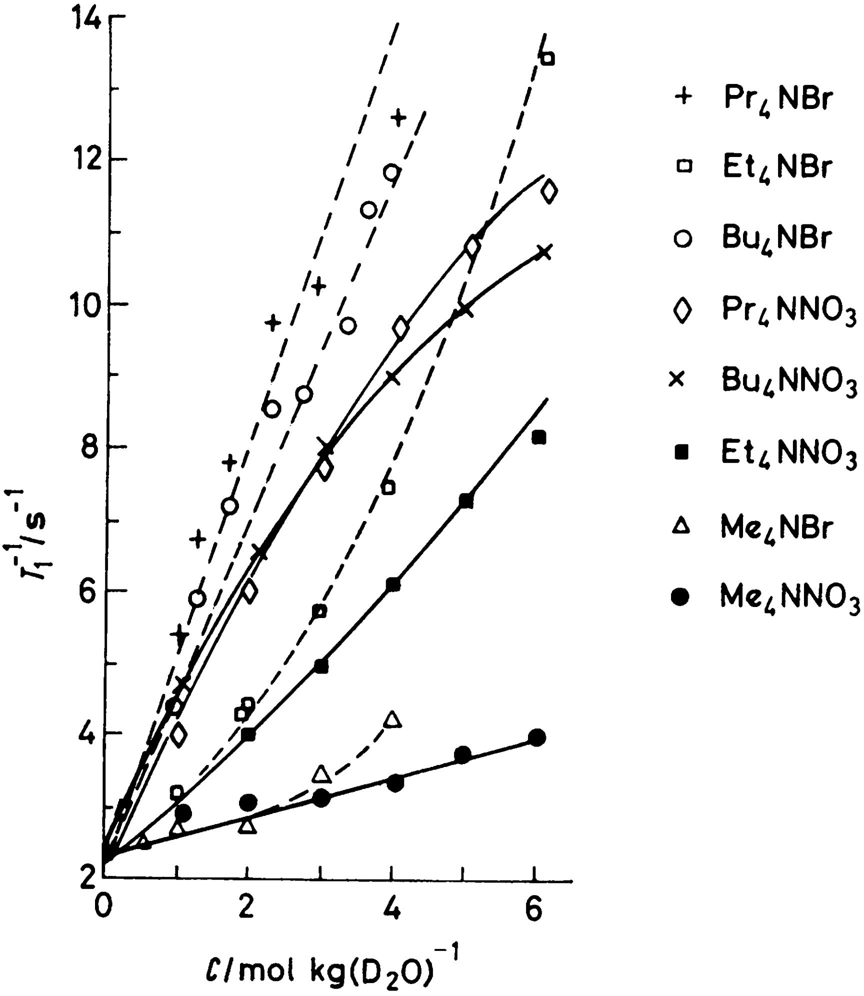

Figure 6 *Relaxation rate* $1/T_1$ *of the nuclear quadrupole resonance of the* D_2O *deuterons in solutions of tetra-alkylammonium salts in* D_2O *at* 25 °C
(Reproduced by permission from *Angew Chem. Internat. Edn.*, 1966, **5**, 106)

rapid decrease in D^* with increasing concentration.[96] A comparison of D^* values of water and of solutes in these solutions gave no evidence for the existence of a rigid long-lived hydration sphere around the cation.

Viscosities of dilute salt solutions relative to pure water can be expressed as a

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[96] H. G. Hertz, B. Lindman, and V. Siepe, *Ber. Bunsengesellschaft phys. Chem.*, 1969, **73**, 542.

function of the concentration of solute in the form of the Jones–Dole equation:[97]

$$\frac{\eta}{\eta_0} = 1 + A\,C^{1/2} + B\,C$$

where η and η_0 are the viscosities of the solution and the solvent respectively, C is the concentration and A and B are constants. The B coefficient is known to be sensitive both in magnitude and sign[97] to the effect of solutes on the structure of water, and for electrolytes can be divided into B ionic coefficients on the basis of some simple assumptions.[98] A negative B coefficient implies a decrease in viscosity in the presence of the solute and hence an increase in fluidity, which is the result of net decrease in the structure of water. Conversely, an increase in structure increases the rigidity and hence the viscosity of water, resulting in a positive B coefficient. Similarly, structure-makers will have negative values of $\mathrm{d}B/\mathrm{d}T$ and structure-breakers positive values. Thus for aqueous solutions of electrolytes the B ionic coefficients of small alkali and halide ions are positive and decrease with increase in size to reach negative values. Similarly, $\mathrm{d}B/\mathrm{d}T$ is negative for small ions, positive for larger ones, and almost equal to zero for ions of medium radii.[97] For large amphiphilic electrolytes[99] and amino-acids[100] it has been emphasized that $\mathrm{d}B/\mathrm{d}T$ is a more important criterion for determining the solute–solvent interactions, as the positive B coefficients obtained for aqueous solutions of these salts can be interpreted as being merely due to their large size. Kay *et al.*[99] have deduced, on the basis of viscosity B coefficients measurements of R_4NBr salts in water as a function of temperature and by comparison with the B values in methanol solutions, that Bu_4NBr and Pr_4NBr are strong structure promoters, whereas Me_4NBr is a structure-breaker and Et_4NBr has almost no effect on the structure of water. Tsangaris and Martin[100] have classified twelve dipolar amino-acids into structure-makers and -breakers on the basis of signs of $\mathrm{d}B/\mathrm{d}T$ in aqueous solutions. In the studies on viscosities of non-electrolytes the usual trend is to plot the absolute viscosity or log (viscosity) as a function of mole fraction of the non-electrolyte. Such plots for the systems water–ethanol, water–dioxan,[101] water–diethylamine, a series of amide–water systems,[102] and the DMSO–water system[103] have shown maxima in the vicinity of integer mole ratios which are taken to be the compositions of the organic molecule–water complexes. However, several experimental results[104,105] for the DMSO–water system seem to be in conflict with such an explanation.[103]

Structural effects on the conductance of ions in aqueous solutions are derived by a comparison of their Walden products (conductance–viscosity products) in

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[97] R. H. Stokes and R. Mills, 'Viscosities of Electrolytes and Related Properties', Pergamon Press, New York, 1965.

[98] M. Kaminsky, *Discuss. Faraday Soc.*, 1957, No. 24, 171.

[99] R. L. Kay, T. Vituccio, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, 1966, **70**, 2336.

[100] J. M. Tsangaris and R. B. Martin, *Arch. Biochem. Biophys.*, 1965, **112**, 267.

[101] J. A. Geddes, *J. Amer. Chem. Soc.*, 1933, **55**, 4832.

[102] P. Assarsson and F. R. Eirich, *J. Phys. Chem.*, 1968, **72**, 2710.

[103] S. A. Schichman and R. L. Amey, *J. Phys. Chem.*, 1971, **75**, 98.

[104] R. K. Wolford, *J. Phys. Chem.*, 1964, **68**, 3392.

[105] J. J. Lindberg and C. Majani, *Acta Chem. Scand.*, 1963, **17** (5), 1477.

aqueous and non-aqueous solutions and at different temperatures and pressures.[97,106] Thus, the large Walden products, their large negative temperature coefficients, and small positive pressure coefficients of aqueous solutions of larger alkali and halide ions in comparison with similar values in methanol solutions have been attributed to decrease in the structure of water in the presence of these ions. On the other hand, structure-making ions like Li^+, F^-, and even Na^+ have low Walden products which are practically independent of temperature and decrease slightly with pressure. The larger R_4N^+ ions and Ph_4B^- ion in aqueous solutions have very low Walden products which increase with temperature. As a result, these ions are classified as structure-makers. The Walden products and their temperature dependence observed for the aqueous solutions of Me_4N^+ and Et_4N^+ ions show that the Me_4N^+ ion acts as a structure-breaker and that the Et_4N^+ ion has very little effect on the structure of water.[106] Similarly, the lower homologues of dipolar amino-acids show a structure-breaking tendency that decreases as the separation of charge increases in the higher homologues which behave as strong structure-makers.[107]

An analysis of the Walden products of electrolytes in aqueous solutions in the light of the Zwanzig theory for ionic mobilities, which is based on the continuum model, shows that the theory fails to explain the experimental results. For the alkali-metal and halide ions experiment shows (Figure 7) an increasing temperature coefficient of the Walden product with increase in the ion size, whereas theory predicts a reverse order. Furthermore, no adjustment of the parameters in the derived equations will explain the positive temperature coefficients of the larger R_4N^+ ions and the Ph_4B^- ion.[106]

C. Volumetric Properties.—Studies on the volumetric properties of aqueous solutions can provide information about solute–water interactions and include studies on partial molal volumes, their pressure dependence (compressibility and thermal expansibility), and on temperature of maximum density.

The excess partial molal volume $\overline{V}_2{}^{\circ E}$ of electrolytes and non-electrolytes in aqueous solutions is generally negative, reflecting the open structure of water which allows the solute molecules to occupy some of its void volumes.[29,30,108] Even solutes of non-polar character show this behaviour, which has been attributed to the fact that the net volume decrease due to occupation of voids by these solutes offsets the volume increase caused by the increase in the structure.[33] Its magnitude appears to depend not so much on the molar volume of the solute as on the ratio of polar and non-polar groups within the molecule. The importance of this ratio is also reflected in the concentration dependence of $\overline{V}_2{}^{\circ}$. Since $\partial\overline{V}_2/\partial x_2$ at low concentration reflects mainly solute–solute interactions, a negative limiting slope in the $\overline{V}_2$ *vs.* x_2 plot (Figure 8) is identified[30] with a long-

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[106] (*a*) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 1966, **70**, 366, 2325; (*b*) R. L. Kay, G. P. Cunningham, and D. F. Evans, ref. 30, p. 249.

[107] L. G. Longworth, *J. Phys. Chem.*, 1963, **67**, 689.

[108] F. Franks and M. J. Quickenden, *Chem. Comm.*, 1968, 388.

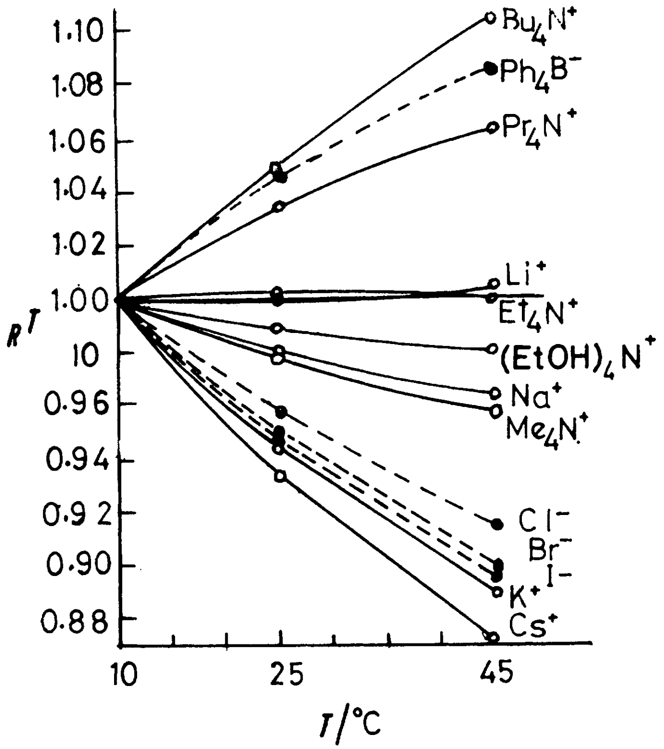

Figure 7 *The temperature dependence of the ionic Walden products for aqueous solutions.* $R^T{}_{10}$ *represents the ratio of Walden products at* T °C *and* 10 °C (Reproduced by permission from 'Hydrogen-Bonded Solvent Systems', Taylor-Francis, London, 1968)

range co-operative structure promotion and has been observed for aqueous solutions of alcohols,[29] R_4N^+ salts,[109,110] and cyclic ethers.[111] A zero limiting slope in conjunction with a negative $\bar{V}_2{}^{0E}$ indicates that although the solute interacts with water, no co-operative effect can be present, at least in dilute solutions. This type of behaviour is exhibited by H_2O_2 and DMSO. Positive slopes are interpreted as indicating structure-breaking effects and this is observed in aqueous solutions of normal electrolytes and in all aqueous solutions at high concentrations. The minimum point thus produced in $\bar{V}_2$ *vs.* x_2 plots is attributed to the upper limit to the region where structural stabilization takes place.[30]

Millero has published recently an excellent review[112] on the partial molal

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[109] W. Y. Wen and S. Saito, *J. Phys. Chem.*, 1964, **68**, 2639.
[110] F. Franks and H. T. Smith, *Trans. Faraday Soc.*, 1967, **63**, 2586.
[111] K. Nakanishi, N. Kato, and N. Maruyama, *J. Phys. Chem.*, 1967, **71**, 814.
[112] F. J. Millero, *Chem. Rev.*, 1971, **47**, 147.

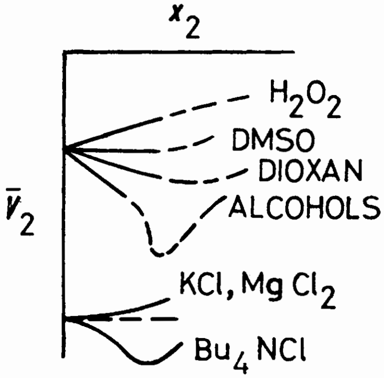

Figure 8 *Variation of* $\bar{V}_2$ *with concentration for aqueous solutions of electrolytes and non-electrolytes*
(Reproduced by permission from 'Hydrogen-Bonded Solvent Systems', Taylor-Francis, London, 1968)

volumes of electrolytes in aqueous solutions. In the plots of apparent molal volume *vs.* $C^{1/2}$ the limiting law behaviour is followed by many normal electrolytes in dilute solutions[113] and by alkali halide solutions up to high concentrations[110] at room temperature. Negative deviations are shown by $NaBPh_4$,[114] Ph_4AsCl,[114] and R_4N^+ salts[110,115] (except Me_4N^+ salts) and these are greater for salts having larger cations, though the limiting law behaviour is approached in very dilute solutions. Such behaviour is attributed[110] to the presence of hydrophobic bonding induced by co-operative ion–water interactions.

The plot of $\bar{E}_2°$, the partial molar expansibility ($\partial\bar{V}_2°/\partial T$), of R_4N^+ salts was found to be a non-linear function of the molecular weight of the cation, although such a plot of $\bar{V}_2°$ was observed to be linear.[116] $\bar{E}_2°$ values of $Pr^n{}_4NCl$ and Bu^nNCl appeared to be too high compared with Me_4NCl and Et_4NCl and this effect decreased at high temperatures. This was explained by assuming that the $\bar{E}°$ value of any salt can be divided into intrinsic, electrical, and structural contributions[116] (similar to the division of $\bar{V}°$) and the last was quite large for large cations. With increase in temperature, owing to the decrease in the structure-making capacity of the salt the contribution from the structural effects was reduced.[116]

Hepler[117] has developed a method of examining the sign of $(\partial^2\bar{V}_2°/\partial T^2)_p$ for various solutes in terms of long-range structure-making and -breaking of solutes in aqueous solutions using the general thermodynamic equation

[113] F. Vaslow, *J. Phys. Chem.*, 1969, **73**, 3745.
[114] F. J. Millero, *J. Chem. and Eng. Data*, 1970, **15**, 562; 1971, **16**, 229.
[115] (*a*) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, **62**, 2738; (*b*) R. E. Verrall and B. E. Conway, *J. Phys. Chem.*, 1966, **70**, 3961.
[116] F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, 1968, **72**, 1758.
[117] L. G. Hepler, *Canad. J. Chem.*, 1969, **47**, 4613.

$$(\partial \bar{C}_p{}^\circ/\partial P)_T = -(\partial^2 \bar{V}_2{}^\circ/\partial T^2)_p$$

On the basis of this equation it has been deduced that structure-making solutes should have positive $(\partial^2 \bar{V}_2{}^\circ/\partial T^2)_p$ values and structure-breaking solutes should have negative values. Hepler[117] has discussed in detail how this criterion can be applied to the aqueous solutions of different solutes. For example, the data presented by a number of workers[118–120] have revealed that all alcohols have positive values over a large range of temperature. The values of $(\partial^2 \bar{V}_2{}^\circ/\partial T^2)_p$ for R_4NI salts as reported by Gopal and Siddiqui[121] are also positive in the temperature range of 25—80 °C, the magnitude increasing as the size of the R group increases from methyl to butyl. However, the conclusions drawn by these authors, which indicate Me_4N^+ ion also to be structure-making, have been subjected to some criticism.[117]

Another volumetric property which is useful in elucidating the structural effects of solutes on water is the effect of pressure on the molal volumes of the solutes in aqueous solutions, *i.e.* the effects of the solute on the compressibility of water.[122] Addition of alcohols to water leads to a decrease in the compressibility, which passes through a minimum at the same alcohol concentration at which the minimum in $\bar{V}_2$ is observed,[29] and the explanation offered is the same as for the changes in the partial molal volume. R_4N^+ salt solutions have high values of apparent molal compressibility at infinite dilution $[\phi^\circ_{K(s)}]$ compared with the aqueous solutions of common electrolytes and those for R_4N^+ salts with a common anion decrease, though in a non-linear fashion, as the number of carbon atoms of the molecules increases.[115] Conway *et al.*[115] have concluded from their results that the electrostrictive effect of the anion decreases with decrease in anion size, and the effect that increases with the size of cation is due to hydrophobic hydration.

The change in the temperature of maximum density of water has been considered as a good criterion for determining the structural changes in liquid water[30] brought about by solutes. Since the temperature of maximum density (TMD) of water is described as the temperature at which the rate of volume decrease due to structural collapse balances the normal thermal expansion, if a solute influences the structure in water it should produce a change in the value of TMD. Structure-making solutes should elevate the TMD and the structure-breaking solutes should depress the TMD of water. However, in practice all solutes except monohydric alcohols[123] in dilute solutions are known to produce a depression in TMD and this has been successfully explained by Franks and Watson's equation.[124] Even R_4N^+ salts decrease the TMD and the depression is

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[118] F. Franks and H. T. Smith, *Trans. Faraday Soc.*, 1968, **64**, 2962.
[119] M. E. Friedman and H. A. Scheraga, *J. Phys. Chem.*, 1965, 69, 3795.
[120] D. M. Alexander, *J. Chem. and Eng. Data*, 1959, **4**, 252.
[121] Ram Gopal and M. A. Siddiqi, *J. Phys. Chem.*, 1968, **72**, 1814.
[122] B. E. Conway and R. E. Verrall, *J. Phys. Chem.*, 1966, **70**, 3952.
[123] G. Wada and S. Umeda, *Bull. Chem. Soc. Japan*, 1962, **35**, 646.
[124] F. Franks and B. Watson, *Trans. Faraday Soc.*, 1967, **63**, 329.

greater for salts containing larger R_4N^+ ions.[125,126] This led Darnell and Greyson[126] to conclude that R_4N^+ salts which are strong structure-makers at room temperature behave as structure-breakers at temperatures near TMD. However, this conclusion does not seem to be justified because these authors have not taken into account the effects of ideal mixing and structural contributions on the lowering of TMD of water by the dissolved solutes.[77]

D. ***X*-Ray Diffraction Studies.**—Probably the most direct method for determining the presence or lack of structure is by the use of *X*-ray diffraction techniques. However, there have not been many such investigations of aqueous solutions. Among electrolytes, solutes whose aqueous solutions have been studied in detail by this method are the halides of ammonia,[127,128] and Bu^n_4NF in concentrated solutions.[129] The observed intensity distributions for these aqueous solutions are almost similar to that for pure water with small but significant differences in the position of the peaks. From these shifts in the peak position it has been concluded that the number of hydrogen bonds in pure water is relatively unaffected by NH_4^+ and F^- ions. The average strength and the average number of hydrogen bonds per water molecule are less in the chloride, bromide, and iodide solutions of the NH_4^+ ion than in pure water whereas Bu^n_4NF solutions contain stronger hydrogen bonds, which is in line with the views of Frank and Evans.[35] A comparison of experimental results with the calculated intensity distribution functions on the basis of the ice-I model of Samoilov[6] modified by Danford and Levy,[14] and of the gas hydrate model of Pauling,[16] shows that the experimental results agree fairly well with the former and deviate considerably from the latter, especially at high concentrations. Other models of water structure were reported to be either incompatible with observed *X*-ray scattering data or insufficiently defined for adequate testing.[127–129]

The *X*-ray diffraction studies of water–ethanol and water–dioxan systems indicate structure promotion of water by ethanol and structure disruption by dioxan.[30]

E. Spectroscopy.—(i) *N.m.r. Chemical Shift.*—Important advances in the problem of the structure of water and aqueous solutions have been achieved with the aid of nuclear magnetic resonance spectroscopy.[7] The chemical shift of the water proton is a measure of the extent to which the proton is shielded by the surrounding electrons. As the hydrogen bonding changes this electron density, the chemical shift of the water proton should be direct evidence of the extent of the structure in the liquid. Thus it has been deduced that in aqueous solutions the structure-making solutes should shift the water proton signal downfield and

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[125] (*a*) G. Wada and S. Umeda, *Bull. Chem. Soc. Japan*, 1962, **35**, 1797; (*b*) G. Wada and M. Miura, *ibid.*, 1969, **42**, 2498.

[126] A. J. Darnell and J. Greyson, *J. Phys. Chem.*, 1968, **72**, 3021.

[127] A. H. Narten, *J. Phys. Chem.*, 1970, **74**, 765.

[128] M. D. Danford, 'Diffraction Pattern and Structure of Aqueous NH_4F Solutions', Oak Ridge National Laboratory, Report 4244, 1968.

[129] A. H. Narten and S. Lindenbaum, *J. Chem. Phys.*, 1969, **51**, 1108.

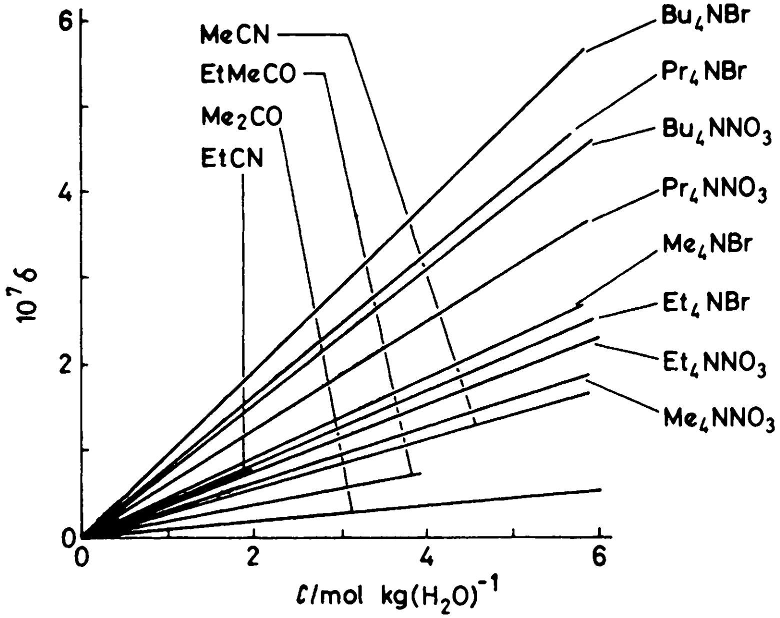

Figure 9 *The chemical shift of* H_2O *protons in aqueous solutions of substances containing hydrocarbon groups at* 25 °. $\delta = (H_c - H_0)/H_0$ [H_c = *resonance field of* H_2O *protons in a solution of concentration* c, H_0 = *resonance field in pure water*]

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structure-breaking solutes upfield. But experimental results show that although the chemical shifts of the water proton in aqueous solutions of normal electrolytes, which are structure-breakers, are upfield compared with the pure water proton signal[86] as expected, the *only* solutions which are found to send the proton resonance line downfield are those of NaF, KF, $MgCl_2$,[86,130] Ph_4AsCl, Ph_4PCl,[131] R_4NF,[132] and those of monohydric alcohols,[133,134] acetone, and some ethers,[134] at 0 °C and low concentrations. Almost all other solutes including those having multivalent ions (such as Sr^{2+}, Ba^{2+}, Ca^{2+}), R_4N^+ ions,[130] Ph_4B^- ion,[131] and alkyl sulphate ions[133] give rise to upfield shifts, instead of downfield. Furthermore, for R_4N^+ ions and other substances containing hydrocarbon groups (which exhibit an upfield shift) the upfield chemical shift is greater for solutes containing

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[130] H. G. Hertz and W. Spalthoff, *Z. Elektrochem.*, 1959, **63**, 1096.

[131] J. F. Coetzee and W. R. Sharpe, *J. Phys. Chem.*, 1971, **75**, 3141.

[132] M. M. Marciacq-Rousselot, A. de Trobriand, and M. Lucas, *J. Phys. Chem.*, 1972, **76**, 1455.

[133] J. Clifford and B. A. Pethica, *Trans. Faraday Soc.*, 1964, **60**, 1483.

[134] D. N. Glew, H. D. Mak, and N. S. Rath, *Chem. Comm.*, 1968, 264.

a greater number of carbon atoms and at higher concentrations (Figure 9). The recent n.m.r. results[132] for R_4N^+ salts at 2, 25, and 43 °C show the same trend for bromide and chloride salts but for fluoride salts a downfield shift increasing with increasing concentrations is observed at all temperatures. However, the overall downfield proton chemical shift order $Me_4NF > Pr_4NF > Bu_4NF$ at 25 and 43 °C is reversed at 2 °C. Thus these results contradict the conclusions drawn from the thermodynamic and relaxation studies. Wicke[7] has attempted to explain this controversy by assuming that the intensified structure in the neighbourhood of non-polar groups does not involve ice-like structures. Instead, the adjacent H_2O molecules are joined by linkages with stronger electrostatic screening of protons. This type of linkage, according to Wicke,[7] can be achieved by the presence of non-tetrahedral hydrogen-bonded molecular aggregates (which was proposed as a 'third state' in water) around the non-polar molecules. These molecular aggregates will give positive chemical shifts and at the same time give rise to a higher heat capacity and shorter relaxation time. Hertz,[27] on the other hand, has pointed out that one may be able to give a better explanation if different contributions from polar and non-polar groups can be separated.

Recently, attempts have been made to separate the ionic contributions of amphiphilic electrolytes.[131,135] In the case of R_4N^+ salts, it has been found that cationic shifts at low temperature are downfield and increase with the size of the cation.[135] With increase in temperature these cation shifts move upfield. Coetzee and Sharpe,[131] on the basis of their results from n.m.r. and i.r. spectra, have concluded that water as well as other solvents discriminate among the solutes Ph_4As^+ (or Ph_4P^+), benzene, and Ph_4B^- in their specific interaction with these solutes. This means that the interaction of hydrophobic solutes with water may differ from one hydrophobic solute to another even though these solutes may broadly be classified as structure-makers, a conclusion in line with the heat capacity measurements.[78]

(ii) *Infrared and Raman Spectra.* Investigations on the vibration picture of electrolyte solutions have led to certain conclusions regarding the water structure problem but the information obtained is very limited.[27] In the uncoupled Raman and i.r. spectra of aqueous solutions of electrolytes, only small shifts in the symmetrical stretching frequency have been observed.[136] Regarding the nature of the influence of alkyl groups on the vibration spectra of water there is conflicting evidence in the literature. The frequency of the O–H stretching vibration in the i.r. spectrum has been found to increase with the length of alkyl chain for R_4N^+ salts in D_2O, indicating breakage of hydrogen bonds,[137] whereas the frequency of the vibration in the Raman spectra of alkyl sulphates in H_2O is reported to decrease as the number of carbon atoms increases, indicating formation of new hydrogen bonds.[138] However, on the basis of the changes in ratio of absorbance

[135] J. Davies, S. Ormondroyd, and M. C. R. Symons, *Chem. Comm.*, 1971, 1204.

[136] T. T. Wall and D. F. Hornig, *J. Chem. Phys.*, 1967, **47**, 784.

[137] K. A. Hartman, jun., *J. Phys. Chem.*, 1966, **70**, 270.

[138] J. Clifford, B. A. Pethica, and W. A. Senior, *Ann. New York Acad. Sci.*, 1965, **125**, 458.

at 1.416 and 1.55 μm bands in the uncoupled i.r. spectra of aqueous solutions, Worley[139] has classified R_4N^+ salts and sodium salts of carboxylic acids as structure-makers (the structure-making capacity increasing with the increase in size of the salt) and many other inorganic ions as structure-breakers. Bunzl[140] has recorded shifts in the combination band of water at 0.97 μm towards low frequency for the solutions of R_4NBr salts, and the results have been attributed to structural increase in these solutions. The existing experimental data on the far-i.r. and Raman spectra of aqueous solutions are not extensive. However, results for the alkali halide solutions show the expected behaviour with regard to structure formation and structure-breaking.[141,142] Recently, Walrafen[143] has made an intensive study of the effects of solutes and pressure on the Raman spectra of the fundamental O–H/O–D vibration. It has been concluded that the ions of inorganic metal salts tend to break water structure (except the F^- ion) and that the $Bu^n{}_4N^+$ ion exerts a structuring effect. Specific ion–water interactions are also observed. The results are reported to support a mixture model.

(iii) *Electron Paramagnetic Spectra.* Changes occurring in the e.p.r. spectral lines of hydrophobic radicals when transferred from an organic solvent to water have been used to elucidate some information about the interaction of the hydrophobic groups with water.[144,145] However, the experimental data in this direction are too limited to arrive at any definite conclusions.

(iv) *Ultrasonic Studies.* Velocity of sound and absorption of sound in aqueous solutions has proved to be relatively important in the studies of structural aspects of liquids, since the compressibility is intimately concerned with this. In the studies on the absorption of ultrasound[146,147,52] and hypersound[148] in mixtures of water with several alcohols, the curves in the plot of a/f^2 *vs.* x_2 (where a is the amplitude absorption coefficient, f the frequency) have shown marked and sudden maxima in the highly aqueous portion of the plot, the composition of which corresponds to the point where maxima in compressibilities were found. Similar maxima were also obtained in the plots of velocity of ultrasound against the mole fraction of the cosolvent in dilute aqueous solutes of propene oxide, tetrahydrofuran, and t-butyl alcohol.[53] The occurrence of these maxima is explained[53,148] in terms of a model in which solute molecules are absorbed initially in the clathrate-like cavities of water, thus enhancing the structure present in water and after the maximum is crossed, and then these solute molecules dissolve

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[139] J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, 1966, **45**, 2868.
[140] K. W. Bunzl, *J. Phys. Chem.*, 1967, **71**, 1358.
[141] D. A. Draegert and D. Williams, *J. Chem. Phys.*, 1968, **48**, 401.
[142] G. E. Walrafen, *J. Chem. Phys.*, 1964, **40**, 3249; 1966, **44**, 1546.
[143] G. E. Walrafen, *J. Chem. Phys.*, 1971, **55**, 768.
[144] P. Jolicoeur and H. L. Friedman, *J. Phys. Chem.*, 1971, **75**, 165.
[145] T. J. Stone, T. Buckman, P. L. Nordio, and H. M. McConnell, *Proc. Nat. Acad. Sci. U.S.A.*, 1965, 1010.
[146] C. J. Burton, *J. Acoust. Soc. Amer.*, 1948, **20**, 186.
[147] (*a*) M. J. Blandamer, N. J. Hidden, M. C. R. Symons, and N. Treloar, *Trans. Faraday Soc.*, 1968, **64**, 3242; (*b*) M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symons, *Chem. Comm.*, 1966, 62.
[148] J. Stone and R. E. Pontinen, *J. Chem. Phys.*, 1967, **47**, 2407.

by substitution, resulting in collapse of the co-operative structure of water. Calculated concentration dependence of the adiabatic compressibility at 25 °C for the tetrahydrofuran–water system on the basis of the assumption of stabilization of clathrate-like water structure by the non-polar solute is in fair agreement with that derived from the experimental values of the velocity of sound at low concentrations.[53] Similar maxima in excess sound absorption obtained in dioxan–water is attributed to the formation of dihydrate of dioxan.[149] The ultrasonic absorption properties of aqueous solutions of R_4N^+ salts were studied by Blandamer *et al.*[150] and the results obtained for the aqueous solutions of tetrabutylammonium chloride and bromide salts indicate changes in the sound absorption properties at concentrations around 8M, which corresponds to the composition of clathrates of these salts. The results were attributed to the changes in water structure at this concentration, which may modify the rotational processes in aqueous solutions.

F. Ternary Systems.—In recent years, studies on ternary systems of aqueous solutions are gaining popularity because it is sometimes difficult to arrive at any definite conclusion from studies on the binary systems alone. The ternary system should act as a better example than the binary system for the interesting studies on the reaction mechanisms and rates of solvolysis of certain organic compounds in mixed aqueous solvents and on the denaturation of proteins by certain reagents, since both these studies are carried out as ternary systems. In a ternary system the properties of a model compound are studied in an aqueous binary solvent system, in order to determine the response of the modified water structure caused by the cosolvent to the presence of the model compound.

Results based on the studies of ternary systems[151] have in some instances supported and in others contradicted the conclusions arrived at from the properties of binary systems, some of which will be enumerated here very briefly. Arnett *et al.*[152] have made detailed thermodynamic studies on a series of normal and amphiphilic electrolytes. Endothermic maxima for enthalpies of solution have been observed for all solutes regardless of their size, charge, or substituent groups, and the position of the maxima is dependent only on the cosolvent, being nearly independent of the solute. However, recent studies[79,153] on the transfer of $Bu^n{}_4NBr$ and $Am^n{}_4NBr$ from water to aqueous solvent mixtures indicate that the solute also plays an important role in determining the trend of enthalpies (Figure 10) and heat capacities (Figure 11) of the solute as a function of the cosolvent composition. The enthalpy and heat capacity maxima obtained

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[149] K. Arakawa and N. Takenaka, *Bull. Chem. Soc. Japan*, 1969, **42**, 5.

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

[151] For a detailed discussion on ternary systems, see references 79, 152 and 153 and the references cited therein.

[152] E. M. Arnett, in 'Physico-Chemical Processes in Mixed Aqueous Solvents', ed. F. Franks, Heinemann, London, 1967, p. 105.

[153] R. K. Mohanty, T. S. Sarma, S. Subramanian, and J. C. Ahluwalia, *Trans. Faraday Soc.*, 1971, **67**, 305.

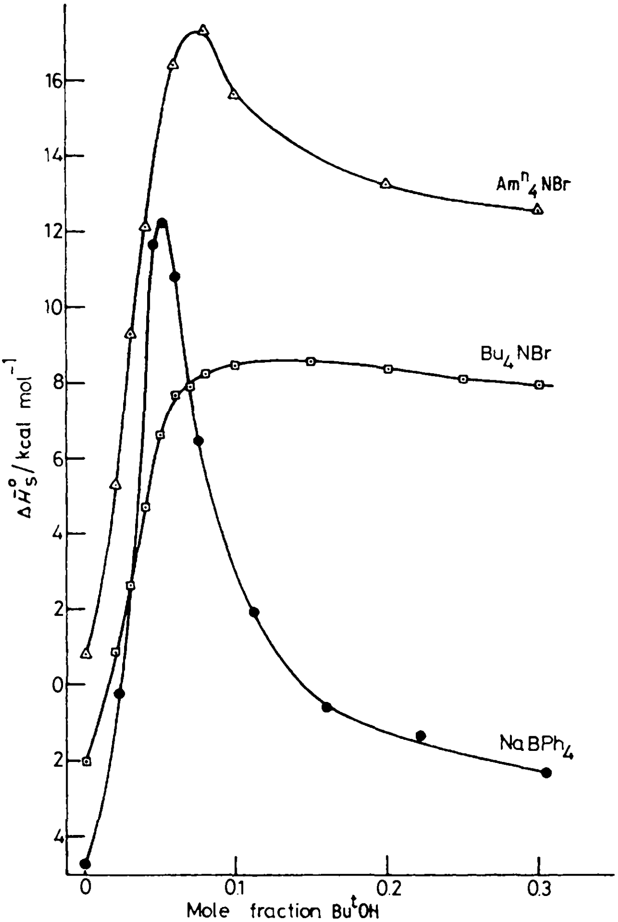

Figure 10 *Partial molal enthalpy of* Am$^n_4$NBr (*ref. 79*), NaBPh$_4$ (*ref. 152*) *and* Bu$^n_4$NBr (*ref. 153*) *in t-butyl alcohol–water mixtures*

in these studies are explained in terms of a model adopted for interpreting the similar extrema obtained in properties such as partial molal volume and sound absorption of the aqueous solutions of the cosolvent in binary systems.[29,30] The effects of non-electrolytes on water structure by the conductance method have been studied by considering the changes in ionic mobilities produced by the addition of the non-electrolyte in question to the aqueous solutions of electrolytes.[106,154] By studying the solubility of argon in aqueous solutions of a series

[154] F. Accascina, R. De Lisi, and M. G. Offredi, *Electrochem. Acta*, 1970, **15**, 1209.

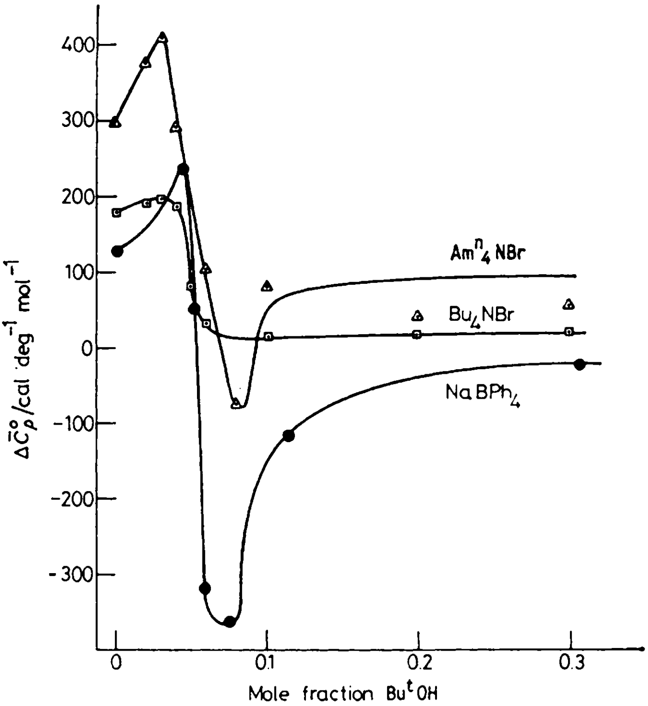

Figure 11 *Partial molal heat capacity of* Am^n_4NBr (*ref.* 79), $NaBPh_4$ (*ref. 152*), *and* Am^n_4NBr (*ref. 153*) *in t-butylalcohol–water mixtures*

of alcohols, dioxan, glucose, and sucrose, Ben-Naim[155] has concluded that the cosolvents containing inert groups stabilize water structure whereas others have an opposite effect. The results[156] on diffusion properties of iodine in ethyl alcohol–water and t-butyl alcohol–water have been interpreted in terms of the structural anomaly of alcohol–water solution. From a comparison of the ionization constants of acetic acid[157] and trihydroxyacetic acid[158] in water and aqueous methanol–water mixtures, the latter acid is shown to break water structure.[158] Based on the heat capacities of nitromethane[159] and solubilities of argon[160] in pure water and aqueous solutions of normal electrolytes, it has been concluded that these structure-making solutes make less structure in electrolyte solutions than in pure water. The increase in solubility of hydrocarbons caused by R_4N^+ salts in water has been attributed to the salting-in effect of R_4N^+ salts in aqueous

[155] A. Ben-Naim, *J. Phys. Chem.*, 1965, **69**, 3245.
[156] K. Nakanishi and T. Ozasa, *J. Phys. Chem.*, 1970, **74**, 2956.
[157] T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, 1956, **60**, 151.
[158] S. Goldman, P. Sagner, and R. G. Bates, *J. Phys. Chem.*, 1971, **75**, 826.
[159] J. H. Stern and J. T. Swearingen, *J. Phys. Chem.*, 1970, **74**, 167.
[160] H. L. Clever and C. J. Holland, *J. Chem. Eng. and Data*, 1968, **13**, 411.

solution. Similar hydrocarbon solubility studies at high concentrations of R_4N^+ salts have indicated micelle formation.[161–165]

One of the most useful applications of the study of ternary systems is in structural studies of aqueous urea solutions. There has been no general agreement about the nature of interaction of urea with water. The views of biochemists[166] tend towards water structure-breaking whereas dielectric constant studies[167] have been interpreted in terms of structure promotion by urea; heat capacity experiments[168] and ultrasonic absorption measurements[169,170] indicate a small decrease in the structure of water in the presence of urea at low temperature. Results based on the properties of ternary systems, such as the effect of urea on the solubilities of hydrocarbons[171] and R_4N^+ salts[172] in water, and on critical micelle concentration of certain surfactants,[173] support the view that urea breaks water structure and that this tendency increases with increase in concentration of urea. The results of Wetlaufer *et al.*[171] on the solubility of hydrocarbons in aqueous urea have been interpreted by Frank and Franks[174] by proposing a model in which urea is termed as a 'statistical structure breaker' and the structure-breaking action of urea, which is unlike that of normal electrolytes, is due to the dissolution of urea in the dense monomer species of water, causing a shift of some water clusters into non-bonded molecules. This view, that urea acts as good structure-breaker in large concentrations and that this structure-breaking action is in accord with the Frank and Franks model,[174] is supported by the recent studies on the heat capacities of transfer, $\Delta C_{p_{tr}}$, of $Bu^n{}_4NBr$ and $Am^n{}_4NBr$ from water to aqueous solutions of urea and sodium chloride.[175–177] As shown in Figure 12, $\Delta C_{p_{tr}}$ for $Bu^n{}_4NBr$[175] and $Am^n{}_4NBr$[177] from water to aqueous urea is always negative and continuously increases in the negative direction with increasing concentration of urea, classifying urea as a structure-breaker at all concentrations. On the other hand, these $\Delta C_{p_{tr}}$ values from water to aqueous sodium chloride are significantly positive and reach a maximum value around 2M-NaCl.[176] The conclusions

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[161] W. Y. Wen and J. H. Hung, *J. Phys. Chem.*, 1970, **74**, 170.

[162] N. C. Deno and C. H. Spink, *J. Phys. Chem.*, 1963, **67**, 1347.

[163] S. Saito, M. Lee, and W. Y. Wen, *J. Amer. Chem. Soc.*, 1966, **88**, 5107.

[164] J. E. Gordon and R. L. Thorne, *J. Phys. Chem.*, 1967, **71**, 4390.

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

[166] J. F. Brandt, *J. Amer. Chem. Soc.*, 1964, **86**, 4302.

[167] M. Abu-Hamdiyyah, *J. Phys. Chem.*, 1965, **69**, 2720.

[168] (*a*) S. Subramanian, D. Balasubramanian, and J. C. Ahluwalia, *J. Phys. Chem.*, 1969, **73**, 266; (*b*) S. Subramanian, T. S. Sarma, D. Balasubramanian, and J. C. Ahluwalia, *ibid.*, 1971, **75**, 815.

[169] K. Arakawa and N. Takenaka, *Bull. Chem. Soc. Japan*, 1967, **40**, 2739.

[170] G. G. Hammes and P. R. Schimmel, *J. Amer. Chem. Soc.*, 1967, **89**, 442.

[171] D. B. Wetlaufer, S. K. Malik, L. Stoller, and R. L. Coffin, *J. Amer. Chem. Soc.*, 1964, **86**, 508.

[172] F. Franks and D. L. Clarke, *J. Phys. Chem.*, 1967, **71**, 1155.

[173] M. J. Schick, *J. Phys. Chem.*, 1964, **68**, 3585.

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

[175] T. S. Sarma and J. C. Ahluwalia, *J. Phys. Chem.*, 1972, **76**, 1366.

[176] B. Chawla and J. C. Ahluwalia, *J. Phys. Chem.*, 1972, **76**, 2582.

[177] B. Chawla and J. C. Ahluwalia, *J. C. S. Faraday I*, 1973, **69**, 434.

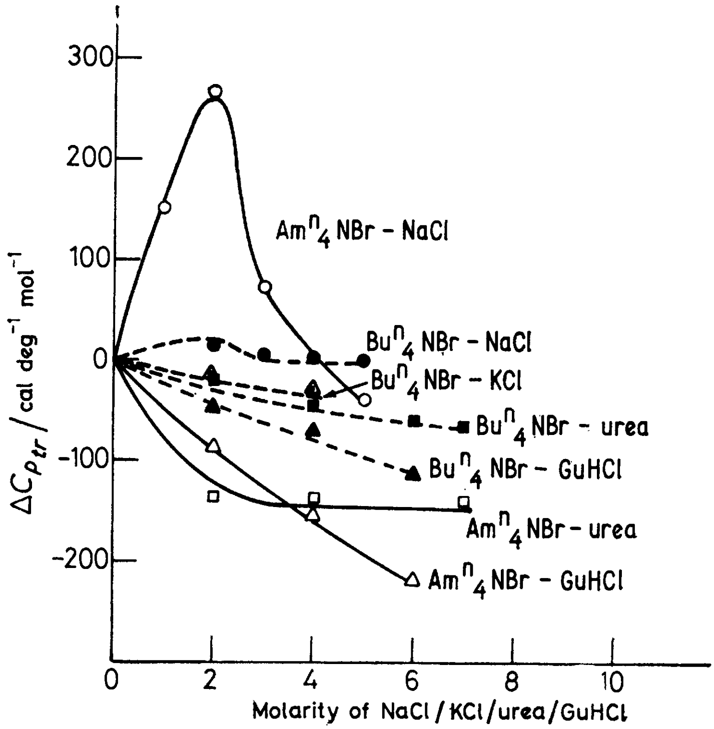

Figure 12 *Partial molal heat capacity of transfer of* Bu^n_4NBr *and* Am^n_4NBr *from water to solutions of aqueous urea (refs. 175, 177), sodium chloride (ref. 176), potassium chloride, and guanidine hydrochloride (ref. 179)*

drawn from a recent detailed n.m.r. study[178] of aqueous urea solutions also support the above view on urea–water interactions.

Recently some attempts[179,180] have also been made to look into the possibility of a correlation existing between the effectiveness of solutes in reducing hydrophobic hydration and their effectiveness in protein denaturation. The results on the heat capacities of transfer of Bu^n_4NBr and Am^n_4NBr from water to aqueous solutions of NaCl, KCl, urea, and guanidine hydrochloride (GuHCl) (see Figure 12) indicate that the increasing order of NaCl < KCl < urea < GuHCl in effectiveness of reducing hydrophobic hydration (as indicated by the negative $\Delta C_{p_{tr}}$ value) or structure-promoting ability of Bu^n_4NBr and Am^n_4NBr correlates well with the increasing effectiveness of these solutes in protein denaturation.[179] These results support the conclusion, drawn from the studies[180]

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[178] E. G. Finer, F. Franks, and M. J. Tait, *J. Amer. Chem. Soc.*, 1972, 94, 4424.

[179] B. Chawla, S. Sunder, and J. C. Ahluwalia, *J. Phys. Chem.*, to be published.

[180] M. J. Mastroianni, M. J. Pikal, and S. Lindenbaum, *J. Phys. Chem.*, 1972, **76**, 3050.

on the heats of dilution of solution of $Bu^n{}_4NBr$ in NaCl, DMSO, and urea, that the order NaCl < DMSO < urea < GuHCl is both the order of increasing effectiveness as a protein denaturant and the order of increasing effectiveness in destroying the structure-making ability of Bu_4NBr.

5 Theoretical Studies on the Structure of Hydrophobic Hydration

Since the classic paper by Nemethy and Scheraga[33] there have been several attempts to explain on a theoretical basis the increase in the structure of water in the presence of non-polar solutes[181–185] and of alcohols.[185] The results obtained from the calculations on thermodynamic properties are in good agreement with the experimental studies. In a one-dimensional model presented for aqueous solutions of noble gases, it is shown that cluster formation is promoted by a noble gas only if the molecules can occupy the interstitial sites in the clusters of water.[183] However, it is not certain to what extent the assumed models correspond to real systems.[27]

6 Conclusions

Since the concept of ice-berg formation was proposed, the structure of hydrophobic hydration has been speculative. With regard to the structural changes in water caused by non-polar solutes, the studies on the water proton chemical shifts, partial molal expansibilities, and static dielectric constants of aqueous solutions of such solutes lead to views that are in contradiction with the thermodynamic and relaxation studies. These contradictions can be rationalized if it is assumed that the structure of hydrophobic hydration is different from that of ice-I. It is possible that the hydration sheath around a non-polar solute molecule resembles Pauling-type clathrates, or some other polymorphic modification of ice, or perhaps contains some kind of non-tetrahedrally hydrogen-bonded water species. The inference that can be drawn from the various studies reported in the literature is that the structural elements around a particular class of solute may be different from those around another type of solute. In addition, there seem to be major differences in the mechanism of dissolution of different types of solutes in water. Non-electrolytes such as alcohols and amines are thought to dissolve first interstitially and then by substitution; hydrocarbons, on the other hand, are thought to dissolve in both clusters and monomer species, and urea only in the denser species of water.

The properties of aqueous solutions seem to be understandable only in terms of some kind of a mixture model for liquid water. However, the exact nature and number of constituent species in liquid water are not clearly established. For example, some of the experimental data on the thermodynamic, volumetric, and magnetic properties of aqueous solutions cannot be explained on the simple

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[181] A. Ben-Naim, *J. Phys. Chem.*, 1965, **69**, 1922.
[182] A. Ben-Naim, *Trans. Faraday Soc.*, 1970, **66**, 2749.
[183] R. A. Lovett and A. Ben-Naim, *J. Chem. Phys.*, 1969, **51**, 3108.
[184] R. B. Herman, *J. Phys. Chem.*, 1971, **75**, 363.
[185] N. Laiken and G. Nemethy, *J. Phys. Chem.*, 1970, **74**, 3501.

two-state mixture model but force us to turn towards a 'three-state model'. Also, none of the mixture models proposed so far seem to be defined sufficiently to account for the recent studies on the temperature dependence of excess partial molal heat capacities of hydrophobic solutes in water. Thus the understanding of the structure of hydrophobic hydration and water appears to be in its preliminary state and further studies are needed to arrive at any definite conclusions.