Effect of Ions on the Structure of Water: Structure Making and Breaking

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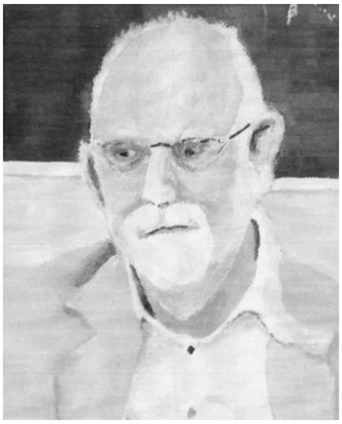
1. Introduction

Water is a ubiquitous liquid substance in our world and has by all accounts striking properties that set it aside from other liquids. A monumental collective set of volumes, edited by Franks[1] some 30 odd years ago, was devoted to water and solutions in it. There exists consensus among researchers that water is a highly structured liquid due to an extensive network of hydrogen bonds. Still, agreement does not exist on how the structure is to be defined and on how the extent of hydrogen bonding is to be measured or computed.

A rise in the temperature of a liquid causes its expansion and a decrease of its density, whereas rising pressures above ambient cause an increase in the density. The structure of water, however defined, is known to depend on the temperature and the external pressure. When either the temperature of water (above 4 °C) or the pressure on it is increased, the water structure is diminished according to whatever measure of this structure is considered. But, again, no quantitative description of the structural effects caused by increasing temperatures or pressures is generally accepted.

Electrolytes dissolved in water dissociate into ions that are hydrated. The large electric field around the (smaller) ions causes the dipolar water molecules to rearrange themselves in the hydration shell(s) around the ions with structures differing from that in bulk water. The electrostrictive effect of the ionic field, meaning the pressure exerted by it, causes the water in the hydration shell(s) to have a larger mean density than neat water. This is a clear effect of the ions on the structure of water. However, when the water structural effects of the ions are discussed, effects beyond their hydration shells are generally meant. The appellations “structure making” and “structure breaking”, ascribed to



Yizhak Marcus was born in Germany but received all his education in Jerusalem, where he obtained his Ph.D. from the Hebrew University in 1956. He was a researcher at the Soreq Nuclear Research Institute, dealing mainly with actinide chemistry, ion exchange, and solvent extraction. From there he was called in 1965 and appointed Professor of Inorganic and Analytical Chemistry at the Hebrew University. There he taught and did research till his retirement in 1999, but he continues with research as Professor Emeritus. His main interest is solution chemistry: aqueous, nonaqueous, and mixed solvents, and solutions of electrolytes and nonelectrolytes. He has published in this and neighboring fields 6 books and over 280 papers in refereed journals. Over the last four years, he has taken up painting, and the photo is a recent selfportrait.

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Gurney,[2] have been applied to various ions. These notions (not necessarily so named) have already been mentioned in previous studies of the effects of ions on the structure of water, such as those of Kujumzelis,[3] Stewart,[4] Frank et al.,[5,6] and Corey.[7] The more or less equivalent terms "kosmotrope" and "chaotrope" for the structure makers and breakers have more recently been introduced in biophysical contexts by Collins and Washbough,[8] but the nuances in their respective use are not dwelt on here.

Since the publication of Gurney's book,[2] the concepts of "structure making" and "structure breaking" by ions as their effects on the water structure have been generally accepted and applied to the explanation of a variety of phenomena exhibited by electrolyte solutions. In recent years, however, these notions have been challenged, among others by Lyubartsev et al.[9] and Bakker et al.,[10,11] but mainly concerning rather concentrated solutions. Their validity for dilute solutions was reaffirmed by other authors, among them Schwenk et al.[12] and Mancinelli et al.[13]

A further question in this connection is the relation of the empirical Hofmeister series[14,15] to the water-structure-affecting properties of ions. This series relates to the minimal concentrations of various salts required to precipitate a given protein from aqueous solution at typically molar concentrations (1 M $\equiv$ 1mol dm^{-3}). The effects mediated by the solvent, water, are approximately additive over all the dissolved ionic species and are dominated by the properties of the anions. The effect appears to be minimal for NaCl, even at high concentrations.[15]

The question over what distances in the aqueous solutions do the ions exert any influence over the structure of the water has not been settled so far either. First hydration shells exist around most ions, even large univalent ones, and well defined second hydration shells are common around more highly charged ions. But the characteristics of these hydration shells in terms of the ion$-$O$_W$ (water oxygen atom) and ion$-$H$_W$ (water hydrogen atom) as well as O$_W-$O$_W$, O$_W-$H$_W$, and H$_W-$H$_W$ intermolecular distances and the orientations of the water molecules with respect to the ion and to each other in these shells have only been determined quite recently in a satisfactory manner by diffraction measurements and computer simulations.[16] Whether and how much influence an ion has beyond the hydration shell(s) is still an open question.

In order to assess the relevance of the structure of the hydration shells of ions to the question of the effects of the ions on the structure of water, it is necessary to consider the spatial constraints present in aqueous electrolyte solutions. The average distance apart, d/nm, of the centers of the ions in a c M solution of a symmetrical electrolyte is

$$d/\mathrm{nm} = [10^{-3}\ (\mathrm{m}^3/\mathrm{dm}^{-3}) \times 10^{27}\ (\mathrm{nm}^3/\mathrm{m}^3)]/ [2c\ (\mathrm{mol\ dm}^{-3})\ N_\mathrm{A}\ (\mathrm{mol}^{-1})]^{1/3} = 0.94[c/\mathrm{mol\ dm}^{-3}]^{-1/3} \quad (1)$$

where N_A is Avogadro's constant. The dependence of d on log c for univalent ions is shown in Figure 1. In a 1 M solution, $d = 0.94$ nm, permitting a water molecule (diameter $d_W = 0.276$ nm) to be located between the hydration shells of hydrated cations and anions. In a 2 M solution, the mean distance between the ion centers is $d = 0.75$ nm only, the hydration shells of even small ions become contiguous (the radii of hydrated Na$^+$ and Cl$^-$ are $d_{\text{ion-W}} + r_W \approx 0.240 + 0.138 = 0.378$ and $0.320 + 0.138 = 0.458$ nm, respectively[17]), and there is no space for "free" water molecules between them.

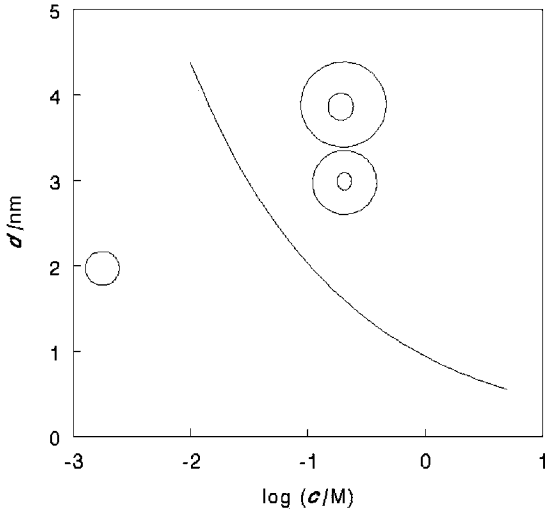

Figure 1. Average distance apart, d, of two ions of a symmetrical electrolyte as a function of its concentration, c. On the left-hand side of the curve is a representation of a water molecule, and on the right-hand side are shown fully hydrated Na$^+$ and Cl$^-$ ions in contact.

In this review, relevant information published to the end of 2007 is considered, and emphasis is placed on the effects of ions on the structure of water in dilute homogeneous solutions at ambient conditions: 25 °C ($T = 298.15$ K) and $P° = 0.1$ MPa.

2. Water as a Structured Liquid

Although it is generally accepted that water is a highly structured liquid, there is little agreement on how to express the structure quantitatively and how to measure it experimentally. The experimental methods commonly employed to ascertain the molecular structure of liquids, namely X-ray and neutron diffraction, yield the structure factors and indirectly (after Fourier transformation) the total pair correlation function $g(r) = f(r/\sigma)$, where r is the linear distance from the center of a given particle and σ is the diameter of the particle. Application of these methods results in the structure of liquid water resembling that of liquid argon, a nonstructured liquid by all accounts, as demonstrated by Marcus.[18] There is, thus, more in the notion of the structure of water than what is measurable by $g(r)$, which is dominated by the strong repulsion of molecules that are too closely packed together. Partial pair correlation functions, such as all three $g(\mathrm{O_W-O_W}, r)$, $g(\mathrm{O_W-H_W}, r)$, and $g(\mathrm{H_W-H_W}, r)$ provide more information on the molecular structure of water, as discussed below.[16]

The notion of "structuredness" that was introduced by Marcus[19] relates to more subtle interactions characterizing bulk properties of a liquid, and these were described in terms of the "stiffness", "openness", and "order" of a liquid in general by Bennetto and Caldin,[20] and in the case of water also in terms of the "extent of the hydrogen bonding" suggested by Ben-Naim.[21]

"Stiffness" of a liquid is measured by the work that must be expended to create a cavity in the liquid (to accommodate a solute particle or one of the liquid itself condensing into it from the vapor). It can be expressed in terms of the difference between the cohesive energy density (the square of the Hildebrand solubility parameter) δ_H^2 and the internal pressure P_i according to Marcus:[22]

$$\delta_H{}^2 - P_i = [\Delta_{vap}H - RT]/V - [T\alpha_P/\kappa_T - p] \qquad (2)$$

In this expression, the thermodynamic quantities characterizing the liquid are its molar enthalpy of vaporization $\Delta_{vap}H$, its molar volume V, its isobaric expansibility α_P, its isothermal compressibility κ_T, and its vapor pressure p, all at the temperature of interest T. In this respect, water is very "stiff" with $\delta_H{}^2 - P_i = 2129$ MPa at 25 °C, much beyond other liquids.

The "openness" of a liquid is related to its free volume, the difference between its bulk molar volume and the intrinsic molar volume. The van der Waals molar volume of water molecules is $V_{vdW} = 12.4$ cm^3 mol^{-1}, and its McGowan intrinsic volume is $V_X = 16.7$ cm^3 mol^{-1}, both considerably smaller than its molar volume at 25 °C, $V = 18.07$ cm^3 mol^{-1}.[23] The fractions of free volume are therefore $(1 - V_{vdW}/V) = 0.314$ and $(1 - V_X/V) = 0.092$ according to these two measures. The former is less relevant because it does not take into account the exclusion volume adjacent to a given molecule where another particle cannot penetrate, which the second measure does. In this respect, water is a very close-packed, contrary to open, liquid, sharing this property with 1,2-ethanediol, glycerol, and formamide, among common solvents. These four liquids have $(1 - V_X/V) < 0.1$, in contrast with other common solvents having this quantity in the range 0.14 (DMSO) to 0.41 (nitromethane).[23]

There exists a mild positive correlation of this measure of openness with the isothermal compressibility of the liquids; for water, the latter is $\kappa_T = 0.457$ GPa^{-1} at 25 °C. Water shares this low compressibility again with the above named solvents, for which $\kappa_T < 0.5$ GPa^{-1}, whereas for other common solvents the values range from 0.524 (DMSO) to 1.706 (*n*-hexane).[23] A less pronounced correlation exists between the openness, as defined above, and the fluidity η^{-1}, the reciprocal of the dynamic viscosity, although this too is a measure of the free volume in the liquid.

The "order" existing in a liquid can be expressed in terms of the deficit of its molar entropy with respect to the same substance in the ideal gas phase. An approximate measure of this deficit is Trouton's constant, $\Delta_{vap}S(T_b) = \Delta_{vap}H(T_b)/T_b$, where T_b is the normal boiling point at atmospheric pressure (0.101325 MPa). An ordered liquid is one having $\Delta_{vap}S(T_b)/R > 12$, with the value for water being 13.15, but it shares this property with a great many other liquids that are ordered, as shown by Marcus.[19] A more refined criterion for order takes into account possible association in the vapor phase, according to Marcus[18] (rather probable at the vapor density at the boiling point), and eliminates liquids, such as normal alkanes, that are deemed to be unordered. This measure of the order is

$$\Delta\Delta_{vap}S/R = [\Delta_{vap}S_{liquid}(T,P°) - \Delta_{vap}S_{alkane}(T,P°)]/R + (P°/R)\,d(B_{liquid} - B_{alkane})/dT \qquad (3)$$

In this expression $\Delta_{vap}S(T,P°) = S(\text{vapor},T,P°) - S(\text{liquid},T,P°)$ is the molar entropy difference between the vapor and the liquid at the standard pressure $P° = 0.1$ MPa and the temperature of interest, T. The same pertains also to a saturated alkane with the same skeleton as the molecules of the liquid of interest, where noncarbon atoms (O, N, S, P, halogen, etc.) are converted to $>$CH$-$, $-$CH$_2-$, and $-$CH$_3$ groups as appropriate. The last term involves the temperature derivative of the difference between the second virial coefficients of the vapors of the liquid of interest and of the alkane, taking thereby into account association in the vapor.

Table 1. Measures of the Structuredness of Water: "Stiffness" $\delta_H{}^2 - P_i$, "Order" $\Delta\Delta_{vap}S/R$, Dipole Orientation[a] g, Heat Capacity Density $\Delta C_P/V$,[22] and Extent of Hydrogen Bonding $\langle\Psi\rangle^{HD}$

t/°C	$(\delta_H{}^2 - P_i)$/MPa	$\Delta\Delta_{vap}S/R$	g	$(\Delta C_P/V)$/J K^{-1} cm^{-3}	$\langle\Psi\rangle^{HD}$
0		8.35	2.96	2.37	1.94
10	2284	8.17	2.94	2.34	1.91
20	2179	8.01	2.91	2.32	1.88
25	2129	7.94	2.90	2.32	1.84
30	2078	7.87	2.89	2.31	1.81
40	1975	7.74	2.86	2.29	1.76
50	1877	7.63	2.83	2.28	1.72
60	1782	7.52	2.81	2.27	1.67
70	1686	7.43	2.78	2.26	1.63
80	1599	7.35	2.76	2.25	1.57
90	1508	7.28	2.73	2.24	1.53
100	1416	7.22	2.71	2.23	1.34
120	1274	7.12	2.65	2.22	1.14
140	1091	7.05	2.60	2.21	0.91
160	956	7.00	2.56	2.19	*b*
180	855	6.96	2.52	2.19	
200	772	6.93	2.48	2.20	
220	693	6.90	2.44	2.22	
240	608	6.88	2.40	2.27	

[a] The parameter g was calculated[22] as a function of the temperature by an expression modified from eq 3, employing a value of the infinite frequency refractive index differing from $1.1n_D{}^2$. [b] The extrapolation of eq 6 becomes very uncertain at $t > 150$ °C.

This criterion for the existence of "order" in a given liquid is $\Delta\Delta_{vap}S/R > 2$, and at 25 °C water has $\Delta\Delta_{vap}S/R = 7.94$, larger than most liquids deemed structured by any criterion.[23] However, this quantity is by no means larger than that for all structured liquids: for formamide it is 7.58, for 1,2-ethanediol it is 21.2, and for glycerol it is 39.5 at 25 °C. For the latter two liquids this measure decreases strongly with increasing temperature, being 13.9 and 26.4 at 60 °C (for formamide it increases slightly, to 7.68).[18]

Another measure for order in a liquid—pertaining to dipolar liquids only—is the Kirkwood dipole orientation correlation parameter g:

$$g = (9k_B\varepsilon_0/N_A)VT\mu^{-2}(\varepsilon_r - 1.1_{n_D}{}^2)(2\varepsilon_r + 1.1_{n_D}{}^2)/\varepsilon_r(2 + 11n_D{}^2)^2 \qquad (4)$$

In this expression k_B, ε_0, and N_A are Boltzmann's constant, the permittivity of vacuum, and Avogadro's constant, μ is the dipole moment of the molecules of the liquid, ε_r is the relative permittivity of the liquid, and $n_D{}^2$ is the square of its refractive index at the frequency of the sodium D-line. The coefficient before $n_D{}^2$ is empirical and serves to make $1.1n_D{}^2$ approximately equal to the infinite frequency refractive index, representative of the polarizability of the molecules of the liquid. For ordered liquids $g > 1.7$,[19] and liquids devoid of structure have, in practice, $g = 1.0 \pm 0.3$ (ideally $g = 1$). Some liquids with pronounced structure but with molecular dipoles that are aligned in an antiparallel fashion ("head to tail") have $g < 1$ (e.g., carboxylic acids), so that a fair measure of structuredness would be $|\log g|$, which would take care both of these liquids and of those having dipoles aligned in a parallel fashion ("head to head", "tail to tail"). Water has at 25 °C the value $g = 2.57$ (but see footnote to Table 1), by no means outstandingly large (cf. ethanol with $g = 2.90$, *N*-methylformamide with $g = 3.97$).[19]

A further measure of the structuredness of liquids is the heat capacity density, which was applied by Marcus[18] to a large number of them:

$$\Delta C_P/V = [C_P(\text{l}) - C_P(\text{i.g.})]/V(\text{l}) \qquad (5)$$

Here the amount of energy that must be invested to increase the temperature, i.e., the heat capacity at constant pressure of the liquid, $C_P(\text{l})$, is considered per unit volume of the liquid. This energy is consumed by reordering the liquid molecules in addition to that going into internal degrees of freedom. The latter amount of energy is taken into account by subtraction of the ideal gas quantity. Structured liquids have values of $(\Delta C_P/V)/\text{J K}^{-1}\text{ cm}^{-3} > 0.6$, with that for water being 2.32, considerably larger than the values of other structured liquids (it is 1.56 for formamide, 0.92 for 1,2-ethanediol, 1.41 for glycerol). This is due to the small molar volume of water and mainly to the extensive hydrogen bonded network that absorbs the energy. As the temperature rises, the heat capacity of liquid water increases only very moderately, the ideal gas heat capacity decreases, but its molar volume increases too.

3. Measures of the Water Structure

Some of the measures of the structuredness of water, namely the "stiffness" $\delta_H^2 - P_i$ according to eq 2, the "order" as the entropy deficit $\Delta\Delta_{\text{vap}}S/R$ according to eq 3, the dipole orientation parameter g according to eq 4, and the heat capacity density $\Delta C_P/V$ according to eq 5, are shown in Table 1 over the temperature range of the existence of water as a liquid at the standard pressure $P°$, i.e., $0 \leq t/°\text{C} \leq 100$. The structuredness of water was studied by Marcus[22] for hot water (under pressure) along the saturation line, so these measures are recorded in Table 1 also beyond the T_b of water up to 240 °C (513.15 K).

As the temperature increases, water becomes fairly rapidly less "stiff", but its "order" according to the entropy deficit and dipole orientation parameter decreases rather slowly and the heat capacity density reaches a very shallow minimum at elevated temperatures. The structuredness of water was also studied by Marcus for supercritical water,[24,25] but this aspect is not further elaborated here. Obviously, with rising temperatures (above 4 °C), water expands so the molar volume increases; hence, does also the "openness" as defined above. At $T_b = 100$ °C (373.15 K) this measure is $(1 - V_X/V) = 0.112$, compared with 0.092 at 25 °C and ambient pressure. Conversely, with rising pressures and increased densities, the water compresses and its openness diminishes. At 25 °C but under 100 bar (10 MPa) pressure, $(1 - V_X/V) = 0.072$ only, and it decreases to considerably lower values as the pressure increases. Any "free volume" practically vanishes at very high pressures (≥2.4 GPa at 25 °C).

The evaluation of the other measures of the structure of water recorded in Table 1 as a function of the pressure is less readily made, but the data can be gleaned from the Steam Tables. The hydrogen bonded structure of liquid water (see below) resembles the low-density tetrahedral arrangement in ice, but with a certain fraction of the number of water molecules being in "interstitial" positions. With increasing pressures, as the molar volume compresses, less of the water can be in low-density configurations, and this fraction must increase.

In fact, mixture models for water have been suggested over the years. These refer to at least two distinct species or domains: a low-density ice-like one, with nearly fully hydrogen bonded water molecules, and a high density domain of individual or oligomeric water molecules with few hydrogen bonds each. Röntgen[26] may have been the first to propose such a two-state model for liquid water, and Ben-Naim[27] gave such a model a detailed statistical thermodynamic basis. Later, Robinson et al.[28−31] successfully examined the volumetric properties of water at varying temperatures (−30 to +100 °C) and pressures (0.1 MPa to 0.77 GPa) in terms of an explicit two-state mixture model. Such models depend on the consideration of the hydrogen bonding in liquid water. The description of water in terms of a multicomponent mixture model, though plausible, was recently challenged. Smith, Saykally, et al.[32] contended that the spectroscopic evidence for such models, section 5.3, can equally well be explained in terms of a continuity of states with hydrogen bonds of varying strengths.

3.1. Criteria for Hydrogen Bond Formation in Water

It is generally accepted that the outstanding cause of the structuredness of water is its extended hydrogen bonded network. A quantitative measure of this extent, namely the average number of hydrogen bonds per water molecule present in the liquid, is therefore a very useful measure for the structuredness of water, in particular also as an answer to the question of how solutes (ions) affect this structure. It is recognized, of course, that the regular tetrahedral hydrogen bonded structure of ice (with four hydrogen bonds per water molecule) is destroyed on melting. Also, the average coordination number of a water molecule (number of nearest neighbors) in cold liquid water is somewhat more than 4.0, so there must be molecules not fully hydrogen bonded to others (so-called interstitial water) in addition to those that are so bonded.

An important issue in this respect is the definition of an "intact" hydrogen bond as distinct from a "broken" or nonexistent hydrogen bond, as discussed most recently by Xenides et al.[33] and by Kumar et al.[34] among others. There are several criteria to adjudicate this issue; the most definite among them are the geometrical and energetic ones. According to Xenides et al.,[33] the former criterion specifies the distance between two oxygen atoms of neighboring water molecules to be $0.25 \leq d_{\text{O-O}}/\text{nm} \leq 0.35$, the hydrogen bond distance to be $0.15 \leq d_{\text{O}\cdots\text{H}}/\text{nm} \leq 0.25$, and the angle of the O−H···O configuration to be $\theta \geq 100°$. Kumar et al.[34] suggested somewhat more restrictive geometrical criteria, $d_{\text{O}\cdots\text{H}}/\text{nm} \leq 0.241$ and $\theta \geq 130°$. They also specified the latter criterion, the interaction energy between the hydrogen bonded water molecules, to be more negative than −12.9 kJ mol^{-1}. A combination of the two criteria is probably the best yardstick to employ, but it should be realized that such criteria apply to computer simulations of water and have in fact been so applied in many studies, referenced most recently by Kumar et al.[34] but not to experimental diffraction studies.

Application of the above criteria in recent computer calculations of the numbers of hydrogen bonds per water molecule at 298−300 K yielded 2.8 from ab initio quantum mechanical and molecular dynamic computations[33] or between 3.2 and 3.4 from molecular dynamic computations employing SPC/E water.[34] "Strong" hydrogen bonds, of which there are 1.81 per water molecule, were characterized by $d_{\text{O}\cdots\text{H}}/\text{nm} \leq 0.21$, but there are added also 1.29 "weak" hydrogen bonds up to $d_{O\cdots H}/\text{nm} \approx 0.23$, to produce altogether 3.1 bonds, a number not very sensitive to θ, the O−H···O angle, according to Rode.[35]

The hydrogen bond energy dispersion, between "strong" and "weak" ones, was obtained by Walrafen[36] from the Raman intensities of the O−D stretching vibration in dilute HOD in H_2O. The energy at a given wavenumber ν_j is obtained from the intensity I_j as $E_j = -R[\partial \ln I_j/\partial(1/T)]_P$. The difference between "strong", short, and linear hydrogen bonds at $\nu_j = 2440\ \text{cm}^{-1}$ (characteristic of 1da ice at 4 K) and weak, long, and bent hydrogen bonds at ν_j 2650−2675 cm^{-1} (characteristic of supercritical HDO in H_2O at 0.9 g cm^{-3} density and 673 K) is 21.3 ± 2.1 kJ (mol hydrogen bonds)$^{-1}$. This energy difference appears to be excessive in view of the total energy of hydrogen bonding in water inferred from the sublimation energy of ice (section 3.2).

3.2. Number of Hydrogen Bonds per Water Molecule

A different approach is needed in order to ascertain from experimental measurements the mean number of hydrogen bonds in which a water molecule in liquid water is engaged. The recent development in extended X-ray absorption (XAS) at the O(1s) ionization edge and X-ray Raman scattering (XRS) spectroscopies led to studies of the structure of water in terms of the number of donor and acceptor hydrogen bonds each water molecule is engaged in. The XAS data show a pre-edge peak (∼535 eV), a main edge peak (∼538 eV), and a postedge peak (∼541 eV). The magnitudes of the absorption peaks depend on the temperature, and they correspond to signals from hydrogen bonds of various strengths. The spectroscopic results were backed-up by theoretical calculations and computer simulations. However, there arose trans-continental controversies concerning this aspect of water structure that have not been settled so far.

A research group consisting of workers from (mainly) European countries, including Wernet and Nilsson among others,[37−39] favored an interpretation of the spectroscopic results and their temperature dependence in terms of a structure predominated (∼80%) by molecules with two strong hydrogen bonds and a minority of molecules with the tetrahedral hydrogen bonding of ice ("ring and chain" model). Over the temperature range of 25−90 °C, only up to 10% of the molecules change from tetrahedral environments to the two hydrogen bond configurations.

A group based on the west coast of North America, including Saykally among others,[40,41] hold the view that the spectroscopic results and their temperature dependence should be interpreted in terms of structures with mainly tetrahedral hydrogen bonding though with long and bent hydrogen bonds included ("ice-like" model). The energy difference between the "strong" and "weak" hydrogen bonds [6.3 ± 2.1 kJ (mol hydrogen bonds)$^{-1}$] is obtained from data obtained in supercooled water at −22 °C up to water at 15 °C[40] (contrary to the much larger value reported by Walrafen;[36] see above).

The X-ray Raman scattering and absorption results, however, require support from computer simulations and theoretical calculations. The recent work of Galli et al.[42,43] on the electronic structure shows very good agreement between the first-principles density functional theory calculations and the X-ray absorption measurements applied to ice. Reasonable (though not perfect) agreement was achieved when a classical potential was applied to the tetrahedral model for liquid water at ambient conditions. This was called the "standard" model, exhibiting 3.6 hydrogen bonds per each molecule,[16] or since two molecules are involved in each hydrogen bond, there are on the average 1.8 hydrogen bonds per water molecule in liquid water at ambient conditions.

An approach based on thermodynamic data and statistical thermodynamics was provided many years ago by Marcus and Ben-Naim,[44] based on an earlier work of Ben-Naim.[21] The main idea involved the comparison of the properties of H_2O and D_2O as vapors (isolated molecules), liquids, and crystalline solids (ices). The molecular parameters of these two isotopic forms of water are very similar, except those that depend on the mass (moments of inertia): the O−H(D) bond lengths are 0.09572 and 0.09575 nm, the bond angles are 104.523 and 104.474°, the lengths of the hydrogen bond (for a couple of gaseous molecules) are 0.2765 and 0.2766 nm, the dipole moments are 1.834 and 1.84 D (1 D = 3.33564×10^{-30} C·m), and the polarizabilities are 1.456×10^{-3} and 1.536×10^{-3} nm^3, respectively, for H_2O and D_2O.[23]

However, the strengths of the hydrogen bonds in these two kinds of water differ, and this is the basis for obtaining the extent of hydrogen bonding in liquid water. When ice is sublimed, all the hydrogen bonds between the water molecules are broken. Comparison of the sublimation enthalpies of the ices formed by H_2O and D_2O pertains to the different strengths of the hydrogen bonds between the water molecules in them. Each water molecule in ice is hydrogen bonded to four neighboring molecules, and in each hydrogen bond two molecules are involved; hence, when a mole of ice sublimes to form a dilute water vapor (assumed to be an ideal gas), $2N_A$ hydrogen bonds are completely broken. In the following calculation, the energy contributions of the internal vibrations and the multipole interactions of the water molecules in the two isotopically different ices are assumed to cancel out in view of the similarities of the properties of the individual water molecules noted above. Thus, the difference between the D_2O and H_2O molar sublimation enthalpies measures the difference in the strength (energy) of the hydrogen bonds per mole of hydrogen bonds, e_{HB}, and is

$$\Delta^{HD}e_{HB} = e_{HB}(D_2O) - e_{HB}(H_2O) = -[\Delta_{subl}H(D_2O,\text{cr}) - \Delta_{subl}H(H_2O,\text{cr})]/2 = [842.3 - 4.721 \times 10^5/(T/\text{K})]\ \text{J mol}^{-1} \tag{6}$$

This numerical expression results[22] from the temperature dependence of the vapor pressures of the ices, reported by Jansco and van Hook[45] over the range $-40 \le t/°\text{C} \le 0$. It is then assumed that eq 6 can be extrapolated to higher temperatures in the range of existence of liquid water.

The next step is to note from statistical thermodynamic arguments[44] that the difference in the molar Gibbs energy of condensation of a water molecule of each isotopic kind from the vapor into its corresponding liquid is proportional to the average number of hydrogen bonds prevailing. This is given by

$$\Delta^{HD}\Delta_{cond}G = \Delta^{HD}e_{HB}\langle\Psi\rangle^{HD} \tag{7}$$

where $\langle\Psi\rangle^{HD}$ is the average number of hydrogen bonds per water molecule in "mean water", assuming $\langle\Psi\rangle^{HD} = {}^1/_2[\langle\Psi\rangle(H_2O) + \langle\Psi\rangle(D_2O)]$. The molar condensation Gibbs energy is obtained experimentally from the saturated vapor pressures p_{sat} and densities ρ of the two kinds of water, with M being their respective molar masses:

$$\Delta_{\text{cond}}G = RT \ln(p_{\text{sat}}M/RT\rho) \qquad (8)$$

The values of $\Delta_{\text{cond}}G$ from eq 8 for the two kinds of water at 5 °C steps between 5 and 100 °C (D_2O freezes at 3.81 °C) have been recorded.[44] Values of p_{sat} and ρ for the two kinds of water are also available at higher temperatures.[46] A combination of eqs 6−8 finally yields the required quantity, the average number of hydrogen bonds per water molecule for liquid "mean water", $\langle\Psi\rangle^{\text{HD}}$, as a function of the temperature, shown in Table 1. It should be noted that the values in Table 1 differ from those shown in a figure in the previous publication,[44] because, there, half of the $\langle\Psi\rangle^{\text{HD}}$ values were shown, as each hydrogen bond involves two partners and because the values of $\Delta^{\text{HD}}e_{\text{HB}}$ were fixed at that prevailing at −9 °C for reasons stated there, whereas the values in Table 1 take eq 6 to be valid also at $t > 0$ °C. At elevated temperatures, however, the extrapolation becomes uncertain, because $\Delta^{\text{HD}}e_{\text{HB}}$ eventually changes sign, although a sign reversal of $\Delta^{\text{HD}}\Delta_{\text{cond}}G$ also takes place.

A refinement, depending on additional data, those for tritiated water, T_2O, enabled the evaluation of $\langle\Psi\rangle(H_2O)$ and $\langle\Psi\rangle(D_2O)$ individually.[44] The latter is somewhat larger than the former, by 8% at 5 °C and up to by 17% at 100 °C. It is indeed generally agreed that heavy water, D_2O, is more strongly hydrogen bonded (structured) than light water, H_2O. Ignoring for the moment the differences between heavy and light water and considering the values of $\langle\Psi\rangle^{\text{HD}}$, the average number of hydrogen bonds prevailing in "mean liquid water" in Table 1, it is seen that, near the freezing point, about half of the four bonds per water molecule in ice remain intact, and this fraction decreases to near one-third at 120 °C and rapidly beyond that. Still, hydrogen bonds between water molecules persist even in supercritical water, depending on the temperature and pressure (density),[25] but their consideration is beyond the scope of this review. At room temperature, 25 °C, the number $\langle\Psi\rangle^{\text{HD}} = 1.84$ corresponds to the "strong" hydrogen bonds characterized by $d_{\text{O}\cdots\text{H}}/\text{nm} \le 0.21$ in the computer simulations.[35]

4. Structure of Ionic Hydration Shells

A detailed review concerning the structure and dynamics of hydrated ions was published by Ohtaki and Radnai some 15 years ago.[17] Subsequently, a review concerning the cations of groups I−III of the periodic table was published by Vinogradov et al.[47] Information on the structure of the hydration shells of the ions has been obtained mainly by diffraction measurements and molecular dynamics computations. The former review[16] deals with the methods available to study these topics and presents data on nearest neighbor distances and coordination numbers for oxygen atoms of the adjacent water molecules around the ions. However, whether this information concerning the first hydration shell of the ions has any bearing on their structure making or breaking properties in dilute solutions has not been settled so far.

In view of the comprehensive nature of the earlier review of Ohtaki and Radnai,[17] only studies of ion hydration published after it are to be reviewed here.

4.1. Results from Diffraction Experiments

X-ray and neutron diffraction studies are generally made on fairly concentrated salt solutions, naturally containing stoichiometric amounts of cations and anions. The evaluation of the hydration structure of individual ions is made possible by proper modeling and, experimentally, by isotope replacement (NDIS) for neutron scattering and less commonly by isomorphic substitution for X-ray scattering. Still, most of the earlier relevant diffraction studies on salt solutions have been done without these experimental devices.

4.1.1. X-ray Diffraction

For solutions used for X-ray diffraction measurements, the molar ratio of water-to-salt has generally been[17] in the range 4−40. Thus, fairly concentrated solutions were employed, with salt molalities > 1.0 m (m ≡ mol kg^{-1}) and ion molalities > 2.0 m for uniunivalent salts and even larger total ion molalities for more highly charged salts. Figure 1 shows that little "free" water exists in the solutions at these concentrations (ignoring the slight differences between the M and m scales). Even in more recent studies, such as those of Nikologorskaya et al.,[48] of Harkanyi et al.,[49] and of Bouazizi et al.[50,51] the highest water-to-salt ratios employed were 15 for KX (KX = KF, KCl, KBr, and KI),[48] 27 (2 M salt) for RbBr,[49] and 63 (0.5 m salt) in solutions of NaCl and LiCl.[50,51] According to eq 1, and ignoring the difference between molarity and molality, only the latter low concentration (0.5 m) corresponds to a mean distance apart of the ion centers of $d \sim 1.18$ nm, permitting some water molecules in between the hydration shells of the ions.

In the study on 2 and 5 mol dm^{-3} aqueous RbBr solutions (water-to-salt ratios of 26.5 and 9.0),[49] both neutron and X-ray scattering indicate considerably less hydrogen bonding in the salt solutions than there exists in neat water, so that the salt is said to be "structure breaking". This, however, is not surprising, in view of the fact that most of the water is bound in the hydration shells of the ions. The coordination number n of water molecules in the hydration shell of Rb^+ is 6−8,[47] but that of Br^- is not available[17] (that of I^- ranges from 7 to 10). This leaves indeed very little "free" water in these solutions for ascertaining from the results whether the ions affect the water structure as "making" or "breaking" it.

Again, in the X-ray diffraction study of Bouazizi et al.[50] of NaCl solutions, the distances of the first and second $\text{O}_\text{W}-\text{O}_\text{W}$ peaks do not differ (within the experimental error) between pure water and 0.5−4.0 m salt solutions. The second distance is said to be the "signature" of the tetrahedral hydrogen bonded water structure. Water molecules are, of course, bound to the ions, but effects of the salt on the pair $\text{O}_\text{W}-\text{O}_\text{W}$ correlation functions in the studies of NaCl[50] and LiCl[51] are seen only from 1.5 m onward (water-to-salt ratio of 20, little free water present), and the curves for 0.5 (water-to-salt ratio of 63) resemble closely those of pure water.

Second hydration shells have been definitely ascribed to di- and trivalent cations from X-ray diffraction measurements.[17,47] The coordination number n for water molecules is generally assumed to be 12, with the number then being corroborated by the diffraction data, although this number decreases when the anion forms a contact ion pair with the cation. Still, the measurements pertain to such concentrated solutions in which very little free water exists, so that nothing can be concluded from these results concerning the ability of the ions to affect the water structure beyond what is bound to them.

4.1.2. Neutron Diffraction

Some of the neutron diffraction studies more recent than those included in the 1993 review,[17] which are discussed briefly below, did employ also fairly dilute solutions. NDIS was applied to 1 m LiCl in D_2O (and also more concentrated solutions) by Howell and Neilson,[52] and it was concluded that the Li^+−water molecular interaction beyond the first hydration shell is not strong enough to form a well defined second hydration shell, but other measurements do suggest its formation.[47] Quasi-inelastic neutron scattering of 2.14 M LiCl and CsCl solutions measured by Novikov et al.[53] provided information on the diffusion mobility of the water molecules. This showed hampered diffusion ability in the vicinity of the Li^+ ion and enhanced mobility around the Cs^+ ions compared to the case of bulk water. Second hydration shells, beyond the four water molecules coordinated to the Li^+ cation and the eight water molecules coordinated to the Cs^+ cation, were not detected in these experiments.

Hydration of sodium and potassium cations was the subject of several neutron diffraction investigations with isotope substitution (NDIS), augmented by computer modeling, made by Soper et al.[13,54,55] The earlier study[54] of KF, KCl, KBr, and KI solutions employed for each salt water-to-salt ratio ~83, ~42, and ~21 and used computer simulation for the interpretation of the diffraction data. A second coordination shell was seen around the ions. The water structure effects were discerned only for the second O_W−O_W peak, moving from 0.44 nm in pure water to 0.40 nm, with this being pronounced only for the most concentrated solution (2.66 m) of KI. The angle distribution of O_W−O_W−O_W of adjacent water molecules outside the hydration shells differed from that in pure water mostly in the most concentrated (2.66 m) KF solution. The general conclusion was that the ions, except F^-, have a net disordering effect on water structure overall, orienting the water molecules away from the tetrahedral bonds they would otherwise adopt in bulk water.[54]

The water structure effects for the second O_W−O_W peak, moving from 0.44 nm in pure water to 0.40 nm, were subsequently[13] found also for 1.38 and 3.27 m KCl; in 3.27 m NaCl this peak moved down to ~0.34 nm, whereas the third O_W−O_W peak also moved to a lower distance than in pure water. Thus, the ion induced perturbation to the structure of water proceeds according to these results beyond the first hydration shell, an effect that persists even when the water molecules in the first shell are excluded from the calculation of the radial distribution function. The further paper by these authors[55] essentially confirms these findings, but although "high dilution" was claimed for their most dilute solutions, the salt concentration was still 0.67 m, and contact ion pairs existed in them.

An NDIS study of a 3.33 m guanidinium chloride (labeled with ^{15}N) solution by Mason et al.[56] showed that little hydration occurs, in the sense of stable hydrogen bond formation, between the cation and water molecules. The $C(NH_2)_3^+$ cation remains flat in the solution, and the tetrahedral water structure around it seems to be little affected by its presence. Similar NDIS studies, but with the solvent labeled with different H/D ratios in H_2O/ D_2O, were carried out by Turner and Soper on 0.5−8 m Me_4NCl[57,58] and on 1.4 m Pr_4NBr and 1.0 m Bu_4NBr.[59] The water-to-salt ratios in the solutions of the larger tetraalkylammonium salts were similar to those in the crystalline clathrates, corresponding to one water layer around the alkyl groups. In these studies the H_W−H_W correlations in the water surrounding the cations were explored. For the tetramethylammonium cation, hardly any changes in the hydration structure (H-bonding geometry) were found at the different concentrations, and the water in the first hydration shell did not appear to be more ordered than bulk water. For the larger cations, tetrapropyl- and tetrabutylammonium, some sharpening of the H_W−H_W structure compared to bulk water was found, i.e., a higher proportion of "ideal" hydrogen bonding angles and distances. These results were significantly different from those for Me_4N^+.

NDIS with calcium isotope substitution was applied by Badyal et al.[60] to aqueous 4.0 and 6.4 m $CaCl_2$. The first hydration shell was unaffected by these high concentrations, with a coordination number of $n = 7$ water molecules around the Ca^{2+} cation at 0.240 nm with no contact ion pairing, but the second shell was invaded by chloride anions to form solvent shared ion pairs. No conclusions regarding the effect of the ions on the structure of the water outside the hydration shells were drawn. A much more dilute, i.e., a 0.225 M solution, of $Hg(NO_3)_2$ was used by Sobolev et al.[61] in neutron scattering with isotope substitution (NDIS) measurements in D_2O (containing some DNO_3), but the results merely confirmed earlier data obtained by X-ray scattering concerning the first hydration shell, i.e., the Hg^{2+}−O_W coordination number and distance. The added information of the Hg^{2+}−D_W distance did not contribute a novel insight into the structure of the hydration shell or of the water beyond it.

Turning to the hydration of anions studied recently by neutron diffraction (i.e., not yet reviewed[17]) and beyond the halide anions referred to above, the hydration structure around nitrate, thiocyanate, formate, and acetate was studied by Kameda et al.,[62−65] who employed time-of-flight neutron diffraction, albeit in concentrated solutions with water-to-salt ratios ≤ 12.5. Another study of the hydration of the thiocyanate anion by NDIS, by Mason et al.,[56] had a water-to-salt ratio of 11.1 and found that SCN^- is only weakly hydrated. Hydrogen bonds were found between the nitrogen atom and, on the average, 1.2 hydrogen (deuterium) atoms of different water molecules at $d(N{-}D_W) = 0.21$ nm, and further hydration by 2.1 water molecules was found at $d(N{-}D_W) = 0.28$ nm. The previous study of SCN^- by Kameda et al.[63] specified 1.8 ± 2 hydrogen bonds at $d(N{-}D_W) = 0.216$ nm.

A study of the hydration of the hydroxide anion by NDIS by Botti et al.[66] in a 4.6 M NaOH solution (water-to-salt ratio ≈ 11.5) revealed a first hydration shell of 3.7 ± 0.3 water molecules in a cup-formed configuration around the oxygen atom of the OH^- anion pointing at it very short hydrogen bonds of ~0.14 nm length. One more weakly bonded further water molecule at a distance between 0.177 and 0.222 nm relates to the hydrogen atom of the OH^- anion. All these results have no bearing on the structure making/breaking properties of the anions in concentrated or dilute solutions.

4.2. Results from Computer Simulations

The computer simulations for studying ion hydration have been made either standing alone or supporting diffraction and spectroscopic studies. They have two advantages over the diffraction methods: they consider individual ions, and they can be applied to more dilute solutions (water-to-ion ratios up to 500:1 in many cases[17]). In some cases, computer simulations have been applied in conjunction with diffraction studies in order to model the structures properly, as discussed above, and need not be further treated here. The hydration structures of mostly alkali metal and alkaline earth metal cations have been studied with this approach, and fewer anions were subject to it. Studies published after the 1993 review[17] are discussed here, but *ab initio* investigations of ion hydrate clusters that are not imbedded in an aqueous solution are excluded from consideration.

It is not possible within this review to enumerate and compare the merits of the various computational methods employed. Classical molecular dynamics (MD) has been criticized for ignoring many-body interactions, and there are several potential functions for water, rigid and polarizable, that have been used. Semiempirical methods based on density functional theory also differ with respect to the functional used, e.g., Car−Parrinello, BP86, or B3LYP. The same applies to quantum mechanical simulations, where different levels of theory and base sets have been used, e.g. HF *ab initio* or various approximations. The interested reader should consult the individual papers cited.

A water-to-ion ratio of 199:1 (a nominally 0.28 m solution) was used in a quantum mechanical/molecular dynamics (QM/MD) study of the hydration of Li^+ ions by Tongraar et al.[67] This study reported an average coordination number n = 4.1 for the prevailing tetrahedral configuration and a $d(Li^+-O_W)$ distance of 0.194 nm. It also showed that molecular dynamics alone with the CF2 potential for water yielded $n = 6.0$ and the somewhat longer $d(Li^+-O_W) = 0.206$ nm. Coordination numbers n between these limits were also published in earlier studies on dilute solutions and concentrated (≥1 M) lithium halide solutions by diffraction measurements. It was concluded that the larger coordination number resulted from the neglect of many-body interactions in potentials employed for the classical MD simulations.[67] A subsequent study from the same laboratory by Loeffler and Rode[68] employed an even larger water-to-ion ratio [500:1 (0.111 m)] and confirmed the tetrahedral coordination of water molecules around the Li^+ cation but added some 20% of five-coordination. It also found the water molecules to be polarized (longer O−H bonds) and tilted away from coplanarity with the cation.

The hydration of the Na^+ and K^+ cations was also studied by QM/MD simulations at a water-to-ion ratio of 199:1 by Tongraar et al.[69] The respective distance and coordination values were $d(Na^+-O_W) = 0.233$ nm and $n = 5.6 \pm 0.3$ and $d(K^+-O_W) = 0.281$ nm and $n = 8.3 \pm 0.3$. Six-coordination for Na^+ has also been suggested by previous simulations in relatively dilute solutions and by diffraction studies at ≥0.5 M concentrations. For K^+, other simulation studies yielded somewhat smaller values of n, as did diffraction measurements for ≥2 M solutions. A quantum mechanical study by White et al.[70] describing the electronic structure by density functional theory criticized some of the QM aspects of the earlier work.[69] The average $n = 5.2 \pm 0.6$ and $d(Na^+-O_W) = 0.249$ nm were found, albeit at a lower water-to-ion ratio of 53:1 (1.05 m) and at a higher temperature (31 °C) compared to the earlier used one (25 °C). How significant these changes are is difficult to judge. Again, the necessity of including many-body interactions in MD simulations is emphasized.[70]

No consensus exists among researchers using *ab initio* quantum mechanical computer simulations on which quantum mechanical level to use. The recent simulation of Cs^+ hydration from Rode's laboratory[12] compares three QM methods at a water-to-ion ratio of 499:1 and 25 °C. The suggested $d(Cs^+-O_W) = 0.320$ nm and $n = 8.9 \pm 0.6$ represent best the result of the simulations. Comments[12] on the dynamics involved in the hydration and the structure breaking effect of Cs^+ are discussed further below.

The hydration of Tl^+ was studied by QM/MD by Vchirawongkwin et al.[71] at a water-to- ion ratio of 499:1 at 25 °C. They found an average of $n = 5.9$ water molecules coordinated in the first hydration shell at two distances (0.279 and 0.316 nm) but with very rapid exchange between these positions, as well as a second hydration shell with $n_{second} = 17.5$ at $d_{second} = 0.515$ nm. The existence of the second hydration shell enables the structure breaking effects to be extended beyond the first shell and influence a larger amount of space in the solution.

Mote Carlo simulations by Madan and Sharp[72] of an aqueous tetramethylammonium cation at 25 °C with a water-to-ion ratio of 750:1 showed small variations in the partial pair correlation functions $g(O_W-O_W)$ and $g(H_W-H_W)$ relative to pure water but a more significant change in the hydrogen bond angle O−H···O distribution. The change was toward a mean straightening of the bond, indicating a tightening of the water structure.

Marx et al.[73] used a QM/MD approach to study the hydration of Be^{2+} at room temperature with a water-to-ion ratio of 31:1. Tetrahedral coordination of the water molecules around the Be^{2+} ion was established with $d(Be^{2+}-O_W) = 0.165$ nm, and a second hydration shell extending beyond 0.35 nm from the Be^{2+} cation was indicated.

Monte Carlo simulations were also made by Bernal-Uruchurtu and Ortega-Blake[74] for the hydration of Mg^{2+} at water-to-ion ratios up to 480:1. The expected octahedral coordination in the first hydration shell was found with $d(Mg^{2+}-O_W) = 0.212$ nm and $n = 6.0$. A well formed second hydration shell with $d(Mg^{2+}-O_{W\ second}) = 0.440$ nm and $n_{second} = 12.0$ was also established, with the water molecules being oriented not only by those in the first shell, and an indication of the presence of a third hydration shell was obtained. The topic of Mg^{2+} hydration was returned to by Lighthouse et al.[75] in a QM/MD study at 27 °C with a water-to-ion ratio of only 53:1. The study confirmed the octahedral coordination of Mg^{2+} in the first hydration shell and the existence of a second shell but at $d(Mg^{2+}-O_{W\ second}) = 0.42$ nm with a not specified coordination number.

The hydration of Ca^{2+} was recently studied in several computer simulation investigations. Bernal-Uruchurtu and Ortega-Blake[74] included Ca^{2+} in the Monte Carlo study mentioned above, finding $d(Ca^{2+}-O_W) = 0.240$ nm with $n = 7.0$ and $d(Ca^{2+}-O_{W\ second}) = 0.466$ nm with $n_{second} = 20$. Water binding to the calcium is much weaker than that to the magnesium cation, and no third hydration shell could be detected for the former cations. The results from the QM/MD studies of Tongraar et al.[76] and Schwenk et al.[77] at water-to-Ca^{2+} ratios of 199:1 and 25 °C found a higher coordination number n, ranging from 7.6 to 8.3 at $d(Ca^{2+}-O_W) = 0.245$ nm, depending on the quantum mechanical method employed. The presence of a well defined second hydration shell was not confirmed in these studies. The dynamical aspects of these simulations confirmed a square antiprism eight-coordinated Ca^{2+} hydrated species with an occasional addition of a ninth water molecule that has a short residence time in the hydration shell. This structure agrees with those previously indicated by Floris et al.[78] and later by Jalilehvand et al.,[79] who employed MD simulations with 509 water molecules per 1 Ca^{2+} + 2 Cl^- ions at the highest dilution used (0.11 m), at room temperature.

Rasaiah and Lynden-Bell[80] used an MD simulation with the SPC/E point charge model of water and 215 molecules of water to study mainly the dynamic aspects of the hydration of ions. For the anions studied, they reported coordination numbers n of 6, 7, 8, and 8 for F^-, Cl^-, Br^-, and I^-, respectively. The SPC/E water model was again used for simulations of the chloride and iodide anion hydration that were made more recently by Du et al.[81] with ~125 water molecules per ion in the most dilute (0.22 M) to ~7 in the most concentrated (3.97 M) solutions. The cation accompanying the chloride anion has a profound effect on the hydration of the latter, since, in LiCl, ion pairing takes place whereas, in RbCl, the decrease in the availability of the water with increasing concentration causes a concurrent fall of n_{W-Cl} from ~7.4 to ~5.3. In the case of CsI, the coordination number of the iodide decreases from $n_{W-I} \sim 7.6$ to ~5.7 over the stated concentration range. The average number of water molecules in the first shell of a water molecule, n_{W-W}, is 4.51 at zero salt concentration, but this number rises to ~6.2 in 3.97 M LiCl and falls to ~3.8 in concentrated RbCl and CsI.

4.3. Results from Spectroscopic Measurements

Several spectroscopic methods have been employed in recent years to study the structures of hydrated ions and their aqueous environment: mainly Raman and EXAFS (X-ray absorption fine structure) as well as NMR and dielectric relaxation spectroscopic methods.

4.3.1. Vibrational Spectroscopic Measurements

Relevant recent Raman spectroscopic studies came mainly from the laboratories of Rudolph and Pye and pertain to the hydration of many cations and some anions.[82−97] The Raman frequencies and structures (coordination numbers) of the hydrated ions were generally supported by *ab initio* computations.

In dilute solutions of LiCl, LiBr, and $LiClO_4$, the tetrahedral $Li(OH_2)_4^+$ and its symmetric stretching vibration were confirmed.[82] The octahedral $Mg(OH_2)_6^{2+}$ cation was confirmed in chloride and perchlorate solutions (but an inner-sphere sulfate associate was found in sulfate solutions[84]), and a second hydration sphere was found, with water trimers hydrogen bonded to alternate faces of the octahedron.[83] In the cases of zinc[85,86] and cadmium[88−90] perchlorate solutions, the octahedral $Zn(OH_2)_6^{2+}$ and $Cd(OH_2)_6^{2+}$ cations have 12 water molecules in the second solvation shell. Seven-coordination of the cadmium cation was discounted.[89]

Of the hydrated trivalent cations, aluminum and scandium were again characterized as the octahedral $Al(OH_2)_6^{3+}$ in chloride, nitrate, and perchlorate[90] and $Sc(OH_2)_6^{3+}$ in chloride and perchlorate[91,92] solutions, with 12 water molecules in the second solvation shell. Gallium and indium in perchlorate solutions behave similarly, forming the octahedral $Ga(OH_2)_6^{3+}$[93,94] and $In(OH_2)_6^{3+}$[95] with 12 water molecules in the second solvation shell, but in nitrate solutions, a nitrate anion forms an outer sphere associated with both cations (it replaces some of the second shell hydration).

For the sulfate anion, the tetrahedral structure was confirmed by the Raman spectrum and *ab initio* calculations,[96] but nothing definite could be said concerning its hydration, though at least three but probably more than six water molecules were suggested to be hydrogen bonded to the anion. In the case of the tetrahedral phosphate anion, PO_4^{3-}, agreement of the measured Raman frequencies and those computed theoretically was best with 12 water molecules of hydration in a first shell, or with 6 in the first and 12 in a second shell of hydration.[97] The water bands in the Raman spectrum also corresponded to strong hydrogen bonds between the phosphate anion and water, and ion pairing was avoided completely in the most dilute solutions of K_3PO_4 studied (<0.005 M).

4.3.2. EXAFS Spectroscopy

Extended X-ray absorption fine structure (EXAFS) spectroscopy has been applied mainly to the hydration of trivalent cations, but a few recent studies of cations with lower valency have also been reported. The great advantage of EXAFS investigations is that they can be made in quite dilute solutions, down to 0.005 M (water-to-ion ratio of 11000!), thus avoiding ion−ion correlations. The local structure in aqueous rubidium ion solutions was studied by Kubozono et al.[98] They found $n \sim 6$ water molecules at $d(Rb-W) = 0.290$ nm, in line with data for other alkali metal cations. The hydration of Sr^{2+} was studied by Seward et al.,[99] who found $n = 8$ water molecules at $d(Sr-W) = 0.257$ nm at ambient conditions, but both the coordination number and the distance diminish with increasing temperatures. The hydration of zinc cations in dilute $Zn(NO_3)_2$ solutions was studied by Munoz-Paez et al.,[100,101] who established a first hydration shell with $n = 6$ and $d(Zn-W) = 0.205$ nm and a second one with $n_{second} = 11.6 \pm 1.6$ and $d(Zn-W_{second}) = 0.41$ nm.

Of the trivalent cations, the hydration of scandium was measured by Yamaguchi et al.,[102] but in a concentrated solution, 4.6 m $Sc(CF_3SO_3)_3$ and $n \sim 7$ at $d(Sc-W) = 0.218$ nm were found. The hydration of yttrium has been the subject of several EXAFS studies. Diaz-Moreno et al.[103] found a square antiprismatic octacoordination in dilute (down to 0.005 M) YBr_3 solutions with $d(Y-W) = 0.235$ nm. The more recent refinement by Bowron and Diaz-Moreno[104] with 1 m YCl_3 found $n = 7.4 \pm 0.5$ water molecules around the yttrium cation, but some ion pairing took place at this concentration. The octacoordination was confirmed in the study of Lindqvist-Reis et al.[105] with the distance $d(Y-W) = 0.237$ nm, and a second shell at $d(Y-W_{second}) = 0.440$ nm with $n_{second} \sim 16$ water molecules was also found.

The hydration of gallium and indium cations was studied by Lindqvist-Reis et al.[106] too, using EXAFS in dilute perchlorate and nitrate solutions, down to 0.005 M. The cations were hydrated by six water molecules at $d(Ga-W) = 0.196$ nm and $d(In-W) = 0.213$ nm, respectively, with each water molecule being hydrogen bonded to two further molecules in the second shell, with $d(Ga-W_{second}) = 0.405$ nm and $d(In-W_{second}) = 0.413$ nm, in general agreement with the earlier study of gallium hydration.[101] The more recent study by Seward et al.[107] of the hydration of indium cations confirmed hexacoordination in the first shell at $d(In-W) = 0.214$ nm, not contracting at rising temperatures. Åkesson et al.[108] quote unpublished results of J. Blixt et al. concerning an EXAFS study of thallium(III), confirming an earlier finding of hexacoordination at $d(Tl-W) = 0.223$ nm.

Trivalent chromium[100,101] and rhodium[101] were studied by Munoz-Paez et al. at 0.1 M concentrations, and hexacoordination ($n = 6.0 \pm 0.2$) was confirmed as also the presence of a second hydration shell. The distances $d(Cr-W) = 0.200$ nm in the first shell and $d(Cr-W_{second}) = 0.402$ nm were found in very dilute solutions (0.01 m).[100] A subsequent study

Table 2. Number of Irrotationally Bound Water Molecules per Ion, n_{ib}, from Dielectric Relaxation Measurements (Column A from Kaatze;[112] Column B Mostly from Buchner et al. at References Shown) and One Minus the Ratio of Irrotationally Bound Water to the Total Water Coordinated, $1 - n_{ib}/n$[113]

cation	n_{ib}(A)	n_{ib}(B)	$(1 - n_{ib})/n$	anion	n_{ib}(A)	n_{ib}(B)	$(1 - n_{ib})/n$
Li^+	3.9	7.8 ± 2.6[126]	1.00	F^-	1.2	5.0[124]	0.20
Na^+	2.6	4.5 ± 0.2[116]	0.49	Cl^-	0	0[120]	0
K^+	0	0[120]	0.06	Br^-	0		−0.02
Rb^+	0		−0.03	I^-	0		−0.06
Cs^+	0	0[120]	−0.11	OH^-		5.5 ± 0.5[115]	
Ag^+			0.06	NO_3^-			−0.07
NH_4^+			−0.10	BF_4^-			−0.05
H_3O^+			0.03	BPh_4^-			−0.05
Be^{2+}	6.5						
Mg^{2+}	7.0	~14[121]		SO_4^{2-}		10.0 ± 0.7[116]	
Ca^{2+}	6.4			oxalate		6.1 ± 1.1[119]	
Sr^{2+}	7.0			malonate		~20[122]	
Ba^{2+}	5.4			succinate		12.9 ± 0.3[122]	
Co^{2+}		~17[123]		*p*-toluenesulfonate		2−3.5[127]	
Ni^{2+}		~17[123]					
Cu^{2+}		~19[124]					
Al^{3+}	11.5	~30[125]					
Y^{3+}	12.7						
La^{3+}	13.4						
Me_4N^+		18.8[118]	−0.15				
Et_4N^+		18.8[118]	−0.12				
Pr_4N^+		18.8[118]	−0.07				
Bu_4N^+		36.3[118]	−0.06				
Pe_4N^+		44.1[118]					

by Lindqvist-Reis et al.[106] found $d(\mathrm{Cr-W}) = 0.197$ nm in the first shell and $d(\mathrm{Cr-W_{second}}) = 0.408$ nm in the second.

4.3.3. NMR Relaxation Studies

Only few pertinent NMR relaxation studies have been made after the 1993 review,[17] with an example being the study of lanthanum cation hydration by Yaita et al.[109] in nitrate and chloride solutions, but only the latter were free from ion association up to 0.6 M. However, no concrete information on the hydrated La^{3+} cation was presented. Chizhik[110] presented an ingenious method for the estimation of the hydration numbers of diamagnetic ions, based on breaks in the spin−lattice relaxation times vs concentration curves, in aqueous solutions of salts where only one of the ions is strongly hydrated. This should be the case in perchlorate solutions for cations and presumably in potassium salt solutions for anions (but this was not explicitly stated). The results for the cations merely confirm previously known coordination numbers, but for the anions, the results were subsequently refined by Chizhik et al.[111] The following hydration numbers were deduced for oxyanions: 6 for NO_3^-, 4 for $CH_3CO_2^-$, 9 for CO_3^{2-}, 8 for SO_4^{2-}, and 12 for PO_4^{3-}. These results depend, however, on breaks *read into* the curves at high concentrations from preconceived models rather than *obtained from* independent clear experimental data. Generally speaking, hydration numbers are operationally defined quantities and may but need not represent definite physical quantities.

4.3.4. Dielectric Relaxation Studies

Dielectric relaxation spectroscopy has been much more useful with respect to ion hydration studies than the recent NMR studies. The review by Kaatze[112] concerning the dielectric properties of water in its different states of interaction is a good introduction to the methodology as well as to the results obtained up to that time. The molar decrement of the static permittivity is constituted by a kinetic relaxation term that can be calculated theoretically and a dielectric saturation term for the irrotationally bound water in the hydration shell. The number of the latter per ion, n_{ib}, is shown in Table 2.[112] The ratio of these numbers to the coordination numbers obtained from diffraction measurements, n_{ib}/n, gives the fraction (percentage) of the water molecules near an ion that cannot be oriented by an external field and thereby contribute to the permittivity of the solution. Only for Li^+, Na^+, F^-, H_3O^+, K^+, and Ag^+ is $1 - n_{ib}/n$ positive; for Cl^- it is zero, whereas for other ions (large cations and anions) it is slightly negative[113] (see Table 2). This means that the small ions augment the hydrogen bonded structure of the water and large ones diminish it (see section 5.2.2). Similar considerations for the irrotationally bound water, with the slip boundary for the kinetic depolarization, have been applied by Buchner et al. in a series of papers[114−126] and also by Shikata et al.[127] The numbers of water molecules so bound, n_{ib}, based on the assignment of zero for Cl^-, are shown in Table 2 too. The discrepancies between the two sets of numbers depend on the interpretation of the kinetic relaxation contribution to the measured dielectric decrement caused by the ions.

4.4. Summary of the Structure of Ionic Hydration Shells

Table 3 provides a summary of the numerical results, obtained subsequent to the review by Ohtaki and Radnai,[17] which are discussed in the previous sections. These concern ion−water distances, $d_{\mathrm{ion-W}}$, and coordination numbers, n, in the first and, when appropriate, also the second hydration shell of ions in aqueous solutions. The new results do not necessarily supersede those in the earlier review,[17] so that they should be read in conjunction with these.

5. Effects of Ions on Properties Related to the Water Structure

The foregoing presentation pertains mainly to the hydration shell(s) of the ions, i.e., their immediate surroundings. Some

Table 3. Recent (≥1993) Numerical Results Concerning the First and Second Hydration Shells of Ions: Ion−Water Molecule Distance, *d*(ion−W), and Coordination Number, *n*[a]

ion	first shell *d*(ion−W)/nm	*n*	second shell *d*(ion−W)/nm	*n*[c]	method[b]	ref
Li^+	0.196	3.9 ± 0.5		+	n	47
Li^+		4.2		−	n	53
Li^+	0.198				x,MD	51
Li^+	<0.278[d]	4.2		−	MD	81
Li^+	0.194	4.1		+	QM/MD	67, 68
Li^+	(0.197)	4			R(QM)	82
Na^+				+	n	55
Na^+	0.233	5.6 ± 0.3			QM/MD	67
Na^+	0.249	5.2 ± 0.6			QM/MD	70
Na^+	0.234	5.3			n	55
K^+	0.265	6.0			N,MD	54
K^+	0.265		0.485	+	n	54
K^+	0.281	8.3 ± 0.3			QM/MD	67
Rb^+	<0.375[d]	7.4			n,MD	55
Rb^+		6−8			x	47
Rb^+	0.290	∼6			E	63
Cs^+	0.320	8.9 ± 0.6	∼0.52	∼18	QM/MD	12
Cs^+		8.0		−	n	53
Cs^+	<0.404[d]	9.2			MD	81
Tl^+	0.279, 0.316	5.9	0.515	17.5	QM/MD	71
$C(NH_2)_3{}^+$		−			n	56
Be^{2+}	0.165	4	>0.35		QM/MD	73
Mg^{2+}	0.212	6	0.440	12.0	MC	74
Mg^{2+}	0.213	6	0.42		QM/MD	75
Mg^{2+}	(0.209)	6	(0.435)	9	R(QM)	83
Ca^{2+}	0.240	7.0	0.466	20	MC	74
Ca^{2+}	0.245	7.6−8.3		−	QM/MD	76, 77
Ca^{2+}	0.240	7		+	E,n	60
Ca^{2+}	0.25	8.6			QM/MD	78
Sr^{2+}	0.263	8.1	0.480	∼13	x,E	*e*
Sr^{2+}	0.257	8			E	99
Sr^{2+}	0.257	8			E	99
Sr^{2+}	0.257	8			E	99
Ba^{2+}	0.281	8.1	0.480	∼13	x,E	*e*
Zn^{2+}	(0.213)	6	(0.437)	12	R(QM)	85, 86
Zn^{2+}	0.205	6	0.41	11.6 ± 1.6	E	100, 101
Cd^{2+}	(0.234)	6	(0.451)	12	R(QM)	87, 88
Hg^{2+}	0.248	6 ± 1			n	61
Al^{3+}	(0.191)	6	(0.414)	12	R(QM)	90
Sc^{3+}	(0.215)	6	(0.432)	12	R(QM)	91, 92
Sc^{3+}	0.218	∼7			x,E	102
Y^{3+}	0.235	8			E	103
Y^{3+}		7.4 ± 0.5			E	104
Y^{3+}	0.237	8	0.440	∼16	E	105
Cr^{3+}	0.200	6 ± 0.2	0.402	+	E	100, 101
Cr^{3+}	0.197	6	0.408	+	x,E	106
Rh^{3+}		6 ± 0.2		+	E	100, 101
Ga^{3+}	(0.197)	6	(0.418)	12	R(QM)	93, 94
Ga^{3+}	0.196	6	0.405	12	x,E	106
In^{3+}	(0.217)	6	(0.431)	12	R(QM)	95
In^{3+}	0.213	6	0.413	12	x,E	106
In^{3+}	0.214	6			E	108
Tl^{3+}	0.223	6			E	108
M^{2+}, M^{3+}				12	x	47
F^-		6			MD	80
F^-	0.254		0.449		n	54
Cl^-		7			MD	80
Cl^-	0.398	∼7.4			MD	81
Cl^-	0.314		0.499		n	54
Cl^-	0.316	7.0			n	55
Cl^-	0.318, 0.322				x,MD	104
Br^-		8			MD	80
Br^-	0.332		0.510		n	54
I^-		8			MD	80
I^-	0.363				n	54
I^-	0.422	∼7.6			MD	81
OH^-		3.7 ± 0.3			QM/MD	67, 68
SCN^-	0.210/0.280	1.2/2.1			n	56
SCN^-	0.216	1.8 ± 2			n	65
$ClO_4{}^-$	0.368	4.5 ± 0.7			x,E	106
X^-				+	n	55
$CH_3CO_2{}^-$	0.323	4.0			n	65
$SO_4{}^{2-}$		<6			R(QM)	96
$PO_4{}^{3-}$		12			R(QM)	97

[a] The results pertain to the most dilute solutions studied in each investigation. [b] Methods: x = X-ray diffraction, n = neutron diffraction, MC = Monte Carlo computer simulation, MD = molecular dynamics computer simulation, QM = quantum mechanical calculation, R(QM) = Raman spectroscopy in conjunction with quantum mechanical calculation, E = EXAFS spectroscopy. [c] +, presence of a second shell indicated; −, absence of a second shell indicated. [d] Distance to the first minimum in the pair correlation function. [e] Persson, I.; Sandström, M.; Yokoyama, H.; Chaudhry, M. *Z. Naturforsch. A* **1995**, *50*, 21.

of the studies summarized above, however, included also information concerning the aqueous solution beyond these shells, and this is dealt with in subsequent sections. The following discussion relates to dilute solutions of electrolytes and to the effects that the ions exert on the macroscopic properties of these solutions. The effects are eventually extrapolated to infinite dilution or expressed as the initial slope of the plots of the properties against the concentration c (or m or a simple function of it, such as $c^{1/2}$).

5.1. Viscosity *B* Coefficients

The relation of the effect of ions on the structure of water to the viscosity B coefficient and the terms "structure making" and "structure breaking" resulting from this relation are attributed to Gurney,[2] but Cox and Wolfenden[128] were the first to mention the notion of water structure in this connection. The B coefficient of the dynamic viscosity, η, of an electrolyte solution derives from the Jones–Dole[129] expression (originally expressed in terms of the fluidity $1/\eta$):

$$[(\eta/\eta^{*}) - 1] = A_{\eta}c^{1/2} + B_{\eta}c + ... \qquad (9)$$

where η^* is the viscosity of the solvent (water), A_η is a coefficient that can be calculated from the conductivity of the electrolyte according to Falkenhagen and Dole,[130] and B_η is used here to distinguish the viscosity coefficient from others that are derived from similar expressions concerning NMR or dielectric relaxation times.

It was noted much previous to Gurney[2] that some aqueous electrolytes enhance the viscosity relative to pure water. For example, NaF solutions at 25 °C have $B_\eta = 0.205\ \mathrm{M}^{-1}$.[131] Whereas, some others diminish it; for example, CsI solutions at 0 °C have $B_\eta = -0.258\ \mathrm{M}^{-1}$.[132] According to Gurney,[2] ions having the former effect, $B_\eta > 0$, were deemed to be "structure making" and the others as "structure breaking". Local loosening of the water structure near ions with $B_\eta < 0$ and a change in the local order–disorder in the hydration cosphere of the ions were the terms he used.

The B_η coefficients are the limiting slopes of plots of the left-hand side of eq 9 divided by $c^{1/2}$ against $c^{1/2}$ or of $[(\eta/\eta^*) - 1] - A_\eta c^{1/2}$ against c, using the theoretically calculated A_η values.[130,133] Hence, they pertain to infinite dilution and are additive in terms of the individual ionic contributions. Several schemes have been proposed for splitting the measured quantity into these ionic contributions.[133] Commonly used, and applicable to aqueous solutions at 25 °C, is $B_\eta(\mathrm{K}^+) = B_\eta(\mathrm{Cl}^-)$, but a slightly different way of splitting, $B_\eta(\mathrm{Rb}^+) = B_\eta(\mathrm{Br}^-)$, applicable over a wider temperature range and differing from the former by just $\pm 0.02\ \mathrm{M}^{-1}$ (+ for anions, − for cations), was suggested by Jenkins and Marcus.[133] Values for ≥70 ions were critically selected by the latter authors[133] from published data, and an even longer list of values was reported by the present author[134] and need not be repeated here.

It should be noted that the few data available from Bare and Skinner et al.,[135] Ibuki,[136] and Sacco et al.[137] for the ionic B_η values in heavy water, which is more structured than ordinary water (see section 3.2), show more negative values for structure breaking ions than they have in ordinary water, there being more structure to break. (For structure making ions, the values in heavy and ordinary water do not differ much.)

Nightingale[138,139] placed some weight on the temperature coefficient $\mathrm{d}B_\eta/\mathrm{d}T$, in addition to the sign of B_η, in relation to the structure making and breaking effects of the ions. Typical structure making ions have $B_\eta > 0$ and $\mathrm{d}B_\eta/\mathrm{d}T < 0$, and the opposite holds for typical structure breaking ions, $B_\eta < 0$ and $\mathrm{d}B_\eta/\mathrm{d}T > 0$. The latter behavior is explained by the decrease in the structure of the water as the temperature rises (Table 1, showing this according to various criteria) so that there is less structure to break at the higher temperature. There are, however, so-called anomalous structure making ions with $B_\eta > 0$ but $\mathrm{d}B_\eta/\mathrm{d}T$ also >0 and "aperipheral hydrated", i.e., essentially nonhydrated, ions with $B_\eta > 0$ and $\mathrm{d}B_\eta/\mathrm{d}T < 0$, with the latter being exemplified by the tetraalkylammonium cations.

As is seen further below, the criteria $B_\eta > 0$ for structure making ions and $B_\eta < 0$ for structure breaking ones and the relative magnitudes of these effects for series of ions correlate well with other criteria.

What is, however, not well settled so far is the mechanism by which the ions, given their water structure modifying behavior, affect the signs of B_η and $\mathrm{d}B_\eta/\mathrm{d}T$. No satisfactory theory has been developed so far to account for the observed behavior in spite of several attempts to provide such a theory, with several pathways having been followed in such attempts. One is to employ the Einstein relation $[(\eta/\eta^*) - 1] = 2.5v$,[133] where v is the total volume of the solute particles per unit volume of the solution. Taking this unit volume as 1 dm^3, then $v = cV$ for a c molar solution where V is the partial molar volume of the solute. The Einstein expression should be valid for nonelectrolytic particles having hydrodynamic diameters considerably larger than that of the solvent molecules. Skinner and Fuoss[140] applied this approach to nonelectrolytes in acetonitrile and found it to closely approximate measured values for nonpolar solutes, such as tetraphenylsilane, but they found that for polar solutes, such as nitroanilines, the (scalar) dipole field affects the viscosity.

Desnoyers and Perron[141] showed that B_η in aqueous solutions of alkali metal halides should depend on the sizes of the hydrated ions through their partial molar volumes, but they could not predict the structure making and breaking effects.

The sphere-in-continuum approach of Ibuki and Nakahara[142] presented a dielectric friction theory for the viscosity of electrolyte solutions, but it accounted only for positive values of B_η, not for negative ones nor for the effects of small ions and the changes of B_η on transfer to heavy water.[136] Similar drawbacks apply to the theory proposed by Chandra and Bagchi,[143] who directed their effort to modeling the A_η term of eq 9 but did not explain the sign and value of the B_η coefficient.

The absolute rate theory of Eyring has been applied most successfully by Feakins et al.,[144] who considered the activation Gibbs energy, $\Delta G^\ddagger$, for obtaining the transition state of the flow process. This involves the creation of suitable cavities in the solvent and the jumping of solute and solvent particles between them, severing existing bonds and creating new ones. According to this approach, and applied to (1:1) electrolytes rather than to individual ions:

$$B_{\eta} = (V^{*} - V_{\pm}^{\infty})/1000 + V^{*}(\Delta G^{\ddagger}_{\pm} - \Delta G^{\ddagger *})/1000RT \qquad (10)$$

Here V^* is the molar volume of the neat solvent, $V_\pm{}^\infty$ is that of the electrolyte (at infinite dilution), and the $\Delta G^\ddagger$ are the corresponding Gibbs energies of activation. For the solvent, the absolute rate theory yields $\Delta G^{\ddagger *} = RT\ln[0.399(\eta^*/\mathrm{mPa\cdot s})(V^*/\mathrm{cm^3\cdot mol^{-1}})]$, so that rearrangement of eq 10 leads to an expression showing $1000B_\eta + V^*\Delta G^{\ddagger *}/RT$ to be linear with V^* for various solvents (provided $V_\pm^\infty$ and $\Delta G^\ddagger_\pm$ vary only slightly with the nature of the solvent), as it indeed is.[133] However, there is no way to independently estimate $\Delta G^\ddagger_\pm$ for electrolytes and ions, although a model for it was proposed by Feakins et al.[145] A recent publication by Jiang and Sandler[146] combines the absolute rate theory for the flow process with the mean spherical approximation for ion−ion and ion−solvent interactions and four empirical parameters to model the viscosities of electrolyte solutions. However, the emphasis is on high concentrations and engineering applications and not on explaining the structure making and breaking properties of the ions in dilute solutions.

In conclusion, as stated above, there exists no satisfactory theory for the ionic B_η coefficients relating them to the ionic effects on the structure of water. What does exist is a long list of values of ionic B_η coefficients[133,134] (using a reasonable electrolyte data splitting method) and many dB_η/dT data, and a widely accepted (though not universal) interpretation of them as pertaining to the water structure making and breaking by the ions.

5.2. Effects on Solvent Dynamics

Many general aspects of the dynamics of water molecules in pure water and in electrolyte solutions have been reviewed by Ohtaki and Radnai,[17] and in the following only those pertaining more directly to the effects of ions on the water structure are discussed.

The rate of exchange of water molecules between the hydration shells of ions and bulk water was considered by Samoilov[147] to indicate the strength of the hydration. The characteristic quantity is the activation Gibbs energy of this exchange, $\Delta G^\ddagger_{\mathrm{exch}}$, obtained from the temperature coefficients of the self-diffusion coefficient of water, D_W, and of the ion mobility, u_ion, in electrolyte solutions implicitly from eq 11:

$$\mathrm{d}\ln u_\mathrm{ion}/\mathrm{d}T + T^{-1} - \mathrm{d}\ln D_\mathrm{W}/\mathrm{d}T = (\Delta G^\ddagger_\mathrm{exch}/RT^2)/[1 + 0.0655\exp(\Delta G^\ddagger_\mathrm{exch}/RT)] \quad (11)$$

According to Samoilov,[147] the ratio $\tau_\mathrm{ion}/\tau_\mathrm{W}$ of the average residence time of a water molecule near another one in the hydration shell of the ion, τ_ion, to that in the bulk ($\tau_\mathrm{W} = 1.7$ ns) equals $\exp(\Delta G^\ddagger_\mathrm{exch}/RT)$. He found that some ions (Li^+, Na^+, Mg^{2+}, and Ca^{2+}) have $\Delta G^\ddagger_\mathrm{exch} > 0$ and $\tau_\mathrm{ion} > \tau_\mathrm{W}$, and he called them "positively hydrated", whereas $\Delta G^\ddagger_\mathrm{exch} < 0$ and $\tau_\mathrm{ion} < \tau_\mathrm{W}$ for other ions (K^+, Cs^+, Cl^-, Br^-, and I^-), designated by him as "negatively hydrated". These terms have found some following but are not now in general use.

The values of τ_ion deduced from eq 11 and Samoilov's $\Delta G^\ddagger_\mathrm{exch}$ values should correspond with the unimolecular rate constants, k_r, for water release from the hydration shells of cations. Such values were obtained from ultrasound absorption and depend on the competition between water molecules and anions for sites in the coordination shell. The water release constants need to be independent of the anion in order to be valid characteristics of the cation hydration. This has, however, not been demonstrated so far, and therefore, this avenue for supporting the notion of "negative hydration" is a dead end.

Endon et al.[148] measured the self-diffusion coefficients, D_W, of water molecules in 1 m alkali halide solutions, and their extensive results for 0 °C are illuminating, as are the more recent data of Müller and Hertz[149] for 25 °C, although only entire salt results but not individual ion effects could be reported. The quantity $1 - D_\mathrm{W}/D_\mathrm{W}^*$ is negative when both cation and anion are structure breakers, according, say, to their being negatively solvated by Samoilov's criterion (KX, RbX, CsX, where X = Cl, Br, I) and is positive when at least one of the ions is strongly structure making (LiX, NaX, where X = Cl, Br, I; MF for M = K, Rb, Cs; and $M'Cl_2$ for M′ = Mg, Ca, Zn) but near zero when these tendencies are opposite and of the same magnitude (NaI). These results are complemented by the recent ones of Heil et al.[150] on 0.2−0.1 m aqueous $NaClO_4$, $LiClO_4$, and $Mg(ClO_4)_2$ at 25 °C. For these three salts, $1 - D_\mathrm{W}/D_\mathrm{W}^* < 0$, with the structure making properties of the cations predominating over those of the structure breaking perchlorate anion. As expected, the effects increase in the listed order. The self-diffusion coefficient of water in 0.94 m Bu_4NCl at room temperature was measured by Nowikow et al.,[151] using quasi-elastic neutron scattering and finding the salt to be a net structure maker ($1 - D_\mathrm{W}/D_\mathrm{W}^* > 0$), but with the water molecule residence times in the hydration shell of the cation being twice as long as those in bulk water. The D/H isotope effect of aqueous CsCl in D_2O and H_2O on the self-diffusion coefficient of the water obtained by Sacco et al.[137] is in agreement with the structure breaking properties of both ions of this salt and the more extensive ("stronger") hydrogen bonded network of the D_2O (see section 3.2).

5.2.1. NMR Signal Relaxation

Engel and Hertz[152] measured the NMR longitudinal proton relaxation times, T_1, in aqueous electrolyte solutions in comparison with those in neat water, T_1^*, mostly at 25 °C and for some salts also at 0 °C. They showed that an expression analogous to eq 9 pertains to the results:

$$[(1/T_1)/(1/T_1^*) - 1] = B_\mathrm{NMR}c + \ldots \quad (12)$$

using the convention that $B_\mathrm{NMR}(K^+) = B_\mathrm{NMR}(Cl^-)$ to obtain the ionic values. The rotational correlation times of the water molecules are similarly given by $\tau_\mathrm{ion}/\tau_\mathrm{W} = 1 + (55.51/n_\mathrm{ion})B_\mathrm{NMR}$, where, as before, the subscripts ion and W pertain to hydration and bulk water and n_ion is the hydration number of the ion. They also showed that $B_\mathrm{NMR} > 0$ for structure making ions and $B_\mathrm{NMR} < 0$ for structure breaking ones, with the ions being classified according to the signs of their $\Delta G^\ddagger_\mathrm{exch}$ values according to Samoilov.[147] Engel and Hertz[152] and Abraham et al.,[153] among others, noted the good correspondence between these B_NMR values and the ionic B_η values (section 5.1; see Table 4). The NMR measurements of longitudinal proton relaxation times, T_1, are confined to diamagnetic ions, since with paramagnetic ones (e.g., transition metal cations), other kinds of NMR measurements are required. A comprehensive discussion of the relaxation results (obtained up to 1972) is in the chapter by Hertz in Vol. 3 of Franks' treatise.[1]

Bhattacharya[154] divided the B_NMR values of electrolytes in a manner differing from that used by Engel and Hertz,[152] namely by forcing the B_NMR values to lie on a single curve against their ionic radii by using a common positive (for the alkali metal cations) and negative (for the halide anions) addend to them. This, however, disregards the different orientation of the water molecules according to the signs of the charges of the ions and loses any relation to the structure making and breaking by the ion, so that it does not provide any new insight into the problem.

Yoshida et al.[155] studied the ^{17}O NMR spin−lattice relaxation of D_2O molecules in aqueous salt solutions at five

Table 4. Comparison of Selected Ionic *B* Coefficients of NMR Relaxation and of Viscosity at 25 °C and the Sign of Their Temperature Coefficients near 25 °C

	^{1}H[152]		^{17}O[155,156]		selected[133]	
ion	B_{NMR}	dB_{NMR}/dT	B_{NMR}	dB_{NMR}/dT	B_η	dB_η/dT
Li^+	0.14	~ 0	0.120	>0	0.146	<0
Na^+	0.06	>0	0.053	~ 0	0.085	~ 0
K^+	−0.01	>0	−0.017	>0	−0.009	<0
Rb^+	−0.04	>0			−0.033	<0
Cs^+	−0.05	>0	−0.014	>0	−0.047	<0
Ag^+	0.06	~ 0			0.090	<0
NH_4^+					−0.008	~ 0
$H(D)_3O^+$	0.06	>0	0.036	>0		
Me_4N^+	0.18		0.165 (0.172)	>0	0.123	~ 0
Et_4N^+			0.444 (0.421)	<0	0.385	
Pr_4N^+			0.889 (0.868)	<0	0.916	<0
Bu_4N^+			1.33 (1.24)	<0	1.275	<0
Ph_4P^+			0.831	<0	1.072	<0
Mg^{2+}	0.50	<0			0.385	<0
Ca^{2+}	0.27	<0			0.284	<0
Sr^{2+}	0.23	>0			0.261	>0
Ba^{2+}	0.18	<0			0.216	>0
F^-	0.14	<0	0.120	<0	0.107	<0
Cl^-	−0.01	>0	−0.017	>0	−0.005	<0
Br^-	−0.04	>0	−0.026	>0	−0.033	<0
I^-	−0.08	>0	−0.055	>0	−0.073	<0
$OH(D)^-$	0.18	>0	0.083	>0	0.122	>0
CN^-	−0.04				−0.024	
SCN^-	−0.07				−0.022	
N_3^-	0.00				−0.018	
ClO_3^-	−0.08				−0.022	
BrO_3^-	−0.06	~ 0			0.009	>0
IO_3^-	0.02	>0			0.140	<0
ClO_4^-	−0.085	>0			−0.058	>0
ReO_4^-	−0.03	>0			−0.055	
NO_2^-	−0.05				−0.024	
NO_3^-	−0.05	>0			−0.043	>0
BPh_4^-			0.928	<0	1.144	
CO_3^{2-}	0.25	~ 0			0.294	
SO_3^{2-}	0.22				0.282	
SO_4^{2-}	0.12				0.206	>0

temperatures between 5 and 85 °C. They showed that splitting the salt data according to $B_{NMR}(K^+) = B_{NMR}(Cl^-)$ provides acceptable results, contrary to other methods of this splitting. These results agree well in sign and generally in magnitude with the ^{1}H B_{NMR} values of Engel and Hertz[152] and the viscosity B_η values; see Table 4 for data from all three sources at 25 °C. The signs of the temperature coefficients dB_{NMR}/dT near 25 °C for the two NMR methods (actually $\Delta B_{NMR}/\Delta T$ from 0 to 25 °C[152] and from 5 to 25 °C[155,156]) agree well but are in most of the cases of structure breaking ions opposite to those from viscosity.

The *B* coefficients obtained from viscosity and spin−lattice relaxation rates pertain to dilute solutions (they are the limiting slopes toward infinite dilution). It is thus interesting to note that, even in very concentrated solutions, where the ratio of water (D_2O) to ion is between 3.0 and 5.5, i.e., practically all the water is in hydration shells, the distinction between structure breaking and making ions persists. Deuterium spin−lattice relaxation rates were measured by Lee et al.[157] in 4.5 m KBr, RbBr, CsBr, LiCl, $CaCl_2$, and $LaCl_3$ (all diamagnetic ions) in D_2O. The deduced reorientational correlation times τ_θ are 2.65 ps for pure D_2O, 2.35, 2.31, and 2.37 ps for KBr, RbBr, and CsBr, lower than those for pure D_2O, with both cation and anion being structure breakers, and 3.58, 5.05, and 7.74 ps for LiCl, $CaCl_2$, and $LaCl_3$, where the effects of the cations are dominant and they are structure makers. Another study of concentrated aqueous solutions using NMR spin−lattice relaxation rates is that of Chizhik,[110] who reported values of relative solvent molecule reorientation times τ/τ_W* at 22 °C. The attainment of individual ionic values from those measured for electrolytes is not clear, so only the general magnitudes are shown here, with τ/τ_W* being <1 for Br^-, I^-, NH_4^+, NO_3^-, and N_3^-, ~ 1.0 for K^+, and >1 for Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, F^-, Cl^-, H_3O^+, SO_4^{2-}, and CO_3^{2-}, in more or less agreement with the signs of the B_{NMR} in dilute solutions (Table 4).

5.2.2. Dielectric Relaxation Spectroscopy

The earlier studies of the effects of ions on the water solvent dynamics by means of dielectric relaxation spectroscopy are connected with the names of Pottel and Kaatze. These authors, with Giese,[158] measured the complex permittivities as a function of the frequency in aqueous alkali halide solutions. These relaxation data and those of Wen and Kaatze[159] were subsequently reanalyzed by Kaatze,[112] who presented the ratios of the cooperative reorientation times τ_{Wh} of water molecules hydrating the ions in 1 M solutions to that, τ_W* $= 8.27 \pm 0.02$ ps, of pure water. The values as read from Figure 38 in that paper are shown in Table 5.

More recently, Buchner et al.[114,118,120,122,126,160] employed dielectric relaxation spectroscopy, mainly for studying ion association in aqueous solutions, but they also obtained results concerning the reorientation times of the water molecules. The cooperative reorientation time of bulk water decreases with increasing salt concentration, reflecting the weakening of the hydrogen bonded structure of the water. The *b* coefficient in the expression

Table 5. Ratios of Reorientation Times of Hydration Water Molecules in 1 M Salt Solutions at 25 °C, τ_{Wh}, to That in Pure Water, τ_W*, Read from a Figure[112] Based on Refs 158 and 159

ion	τ_{Wh}/τ_W^*	ion	τ_{Wh}/τ_W^*
Li^+	2.41	Pr_4N^+	2.37
Na^+	1.53	Bu_4N^+	2.80
K^+	0.90	H_3O^+	1.62
Rb^+	0.78	F^-	2.61
Cs^+	0.68	Cl^-	0.90
H_3O^+	1.62	Br^-	0.73
NH_4^+	0.72	I^-	0.41
Me_4N^+	1.59	OH^-	2.44
Et_4N^+	1.96	NO_3^-	0.73

[a] Reference 113 (at 1 m). For di- and trivalent cations, values < 1 were obtained for not properly understood reasons.

$$\tau(c) = \tau(0) + a[\exp(-bc) - 1] \qquad (13)$$

where $\tau(0) \equiv \tau_W^*$ (given variously as 8.32−8.36 ps), is characteristic for the effects of the anions in various sodium salt solutions.[160] The values of b are as follows: NaOH, 0; Na_2CO_3, 0.55; NaCl, 0.79; NaBr, 0.98; NaSCN, 0.99; NaI, 1.20; $NaNO_3$, 1.33; $NaClO_4$, 1.35; Na_2SO_4, 1.8; sodium malonate, 3.44;[122] with the anions ranging from structure makers to structure breakers. No attempt was made, however, to separate the cation and anion effects. The values of the b coefficient of eq 13 for KCl, 1.5, and CsCl, 2.1,[120] are in the same direction. A figure showing the solvent relaxation times in aqueous Et_4NCl and Bu_4NBr in a review paper by Barthel, Buchner, et al.,[161] but without the source of the data, shows that $\tau(c)$ increases in these cases with the concentration c, contrary to the behavior of inorganic salt solutions. In a subsequent paper,[118] the increases of the relaxation times of bulk water with concentration were shown for $Me_4NBr < Bu_4NBr < Et_4NBr \sim Pr_4NBr \sim Pe_4NBr < Et_4NCl$ (note the out-of-line position of Bu_4NBr), as well as that of so-called "slow water" at $\tau > 20$ ps. This was interpreted as indicating the hindered orientation of the water molecules in the ice-like cages around the hydrophobic cations. The $\tau(c)$ reported by Wachter et al. for aqueous Ph_4PCl and $NaBPh_4$[162] and for aqueous LiCl and Li_2SO_4[126] scattered too much for the extraction of meaningful b coefficients for comparison. The former two salts of hydrophobic ions have positive slopes of the $\tau(c)$ vs c curves, and the latter two salts have negative slopes. The results for LiCl and $LiSO_4$ solutions[126] suggest that the structure breaking effects of the anions predominate over the structure making effect of the cation.

The independent group of Asaki et al.[163] studied the solvent relaxation of aqueous lithium salts. Their data lead to the b coefficients of eq 13 calculated by the present author: LiCl, 0.62; Li triflate, 0.86; Li imide, 1.27. The value for LiCl is comparable but somewhat lower than that for NaCl noted above, in line with the stronger structure making properties of the lithium cation. Loginova et al.[164] studied aqueous KF and CsF in a similar fashion, and from their data, $b < 1$ for both salts is obtainable, but the data are too imprecise for the actual values to be reported.

5.2.3. Computer Simulations

Molecular dynamics computer simulations were employed in recent years by several authors to study the dynamics of the particles in aqueous electrolyte solutions. Geiger,[165] following a suggestion by Gurney,[2] computed the mobility (self-diffusion coefficient D_W) of water molecules in the first and second hydration shells around particles of the size of a xenon atom (Lennard-Jones diameter of 0.41 nm) and with discretely varying charges: 0, +0.67, +1, +2, and −1 (charge units). For lightly charged cations, +0.67 and +1 charge units, Geiger found the ratios for water in the first hydration shell, $D_{W\text{ first shell}}/D_{W\text{ bulk}}$, to be larger than unity, reaching 1.6 and 1.2, but for charges 0 (hydrophobic effect) and +2, it is smaller than unity, 0.7 and 0.5. For the anion, this ratio is 1.4. The effect persists to a smaller degree in the second hydration shell. A similar effect was noted for the reorientation times of the intermolecular H_W-H_W and O_W-H_W vectors, being shorter for the +0.67, +1, and −1 charged particles than for bulk water and longer for the uncharged and +2 charged particles.

The normalized autocorrelation functions of the water molecules in 2.2 m LiI solutions were obtained by Heinzinger.[166] The librational motions were shown separately for bulk water and the hydration water of the Li^+ and I^- ions. For the iodide anion, the frequency dependencies for bulk water and the hydration water were similar to those of pure water for all three coordinates, but for the lithium cation, those for the component in the plane of the water molecule and perpendicular to its dipole moment were strongly affected in the hydration shell.

Unfortunately, the results of these molecular dynamics simulations depend on the model potential functions employed. Thus, Geiger[165] employed ST2-water (215 water molecules/charged particle), as did Heinzinger[166] (25 water molecules/pair of charged particles), but later workers used more sophisticated models.

Balbuena et al.[167] employed the SPC/E water model (500 water molecules per ion) to study by means of semicontinuum molecular dynamics the reorientation times of water molecules over a range of temperatures including supercritical ones. At 25 °C the reorientation times in bulk water relative to those in the first hydration shell, assuming a coordination number of $n = 6$, are $\tau_{bulk}/\tau_{ion} = 0.20$, 0.47, 0.65, and 0.90 for Na^+, K^+, Rb^+, and Cl^-, respectively, showing faster reorientation as the water binding weakens. The authors were mainly interested in the results for the higher temperatures, and they did not discuss the discrepancy relative to Geiger's results.

Chowdhuri and Chandra[168] employed the same water model, SPC/E (256 water molecules per ion, as well as lower ratios at increasing concentrations), at 25 °C and reported the average residence times of water molecules near ions: Na^+, 18.5 ps; K^+, 7.9 ps; Cl^-, 10.0 ps. Characteristic residence times of the water molecules in the first hydration shells of ions were also reported by Guardia et al.:[169] Li^+, 101; Na^+, 25.0; K^+, 8.2; Cs^+, 6.9; F^-, 35.5; Cl^-, 14.0; I^-, 8.5 ps, compared with 10 ± 1 ps for water molecules in the bulk. These values result from detailed considerations of the hydrogen bond dynamics in water and near the ions using again the SPC/E model of water.

Rode et al.[12,71,77,170,171] studied the dynamics of the water molecules near calcium and cesium ions using a combination of quantum mechanics for the region near the ion and molecular dynamics for regions farther away. For cesium, the characteristic times, both τ_1 (reorientational) and τ_2 (rotational), are considerably smaller (1.1 and 0.4 ps)[12] than those for pure water (7.5 and 2.5 ps),[17]demonstrating the structure breaking effect of this large univalent cation. Furthermore, the computation resulted in a number of water molecule exchange events per 10 ps that is double (51) that in pure water (24).[12] On the contrary, near the calcium ion, only 1 exchange process per 10 ps was observed.[77] The corresponding study of the dynamics near the thallium(I) cation showed even shorter reorientation times (0.9 and 0.3 in the first shell) compared to those near cesium, an effect persisting to the second shell (1.2 and 0.5 ps for τ_1 and τ_2),[72] and Tl^+ is thus the "best" water structure breaker of the ions examined so far, including also rubidium[171] and gold(I).[170]

5.2.4. Fast Vibrational Spectroscopy

Recently, ultrafast (femtosecond) two-color mid-infrared spectroscopy was used by Bakker et al.[10,11,172,173] in a series of papers to study the effect of ions on the structure and dynamics of their aqueous solutions. The relatively long lifetimes of the O−H stretch vibration of the anion-bonded OH groups of the water permitted the selective study of such water molecules in the anion solvation shells. The method was applied[172] to 3 and 6 M solutions of KF, NaCl, NaBr, and NaI in D_2O containing <1 M HOD. A fast and a slow component were seen in the decay curves of the salt solutions (except KF); the former, at 0.8 ps, corresponds to that in pure HOD−D_2O, and the latter depends on the salt, increasing with the anion mass (2.6 ps for NaCl to 3.9 ps for NaI). These results were later affirmed,[173] where 0.1 M HOD in D_2O and down to 0.5 M salt solutions were employed.

In similar investigations,[10,11] of 3 and 6 M $Mg(ClO_4)_2$ and 0.5 to 6 M $NaClO_4$ in HOD−D_2O (with only ca. 0.25 M HOD), results specific to the O−H group hydrogen bonded to the perchlorate anion were obtained. It should be noted that these recent dynamic Raman spectroscopic results concerning the hydrated perchlorate anion are in disagreement with the static Raman results of Walrafen,[164] who concluded that the perchlorate anion is a strong water structure breaker but does not hydrate appreciably. The relaxation time of O−H stretch vibrations of perchlorate-bonded water molecules[10,11] was 7.6 ± 0.3 ps.[172,173] The orientational correlation times for bulk water molecules were deduced from the decay of the anisotropy parameter. These parameters in 0.5−6 M $NaClO_4$ as well as in 0.5 and 1 M $Mg(ClO_4)_2$ and 1 M Na_2SO_4 were independent of the salt concentration, 3.4 ± 0.1 ps, the same as that for pure water. When the O−D stretch anisotropy was studied in H_2O with 4% HOD and 1 and 3 M $Mg(ClO_4)_2$, the orientational correlation time was 2.5 ± 0.1 ps, as in pure HOD−H_2O. There was no relation of these results to the increased viscosity of the salt solutions. The conclusion was that the "ions do not enhance or break the hydrogen bond network outside their vicinity (probably their first solvation shell)."[10] Only the firmly bound water molecules in the hydration shells, leading to the bulkiness of the ions, according to the Stokes−Einstein relationship, were in the view of the authors responsible for the enhanced viscosity of the solutions (positive B_η values). However, this sweeping conclusion, negating ion effects on the structure of the water, does not explain enhanced mobilities of water molecules in solutions with structure breaking ions nor negative B_η values. Neither does it explain how could the derived hydrodynamic radii of the halide anions[163] be smaller than the well established anion−water hydrogen bond lengths.[17]

The reported conclusions[10,11,172,173] pertain to solutions that are at least 0.5 M, which for symmetrical electrolytes have an average distance apart of the centers of the ions of ≤1.18 nm (see eq 1). Thus, for the solutions examined, no more than four water molecules can be accommodated between the ions, of which two belong to their hydration shells and only up to two may be "free" water. It is difficult to see how the conclusions from the ultrafast vibrational spectroscopy for such solutions can be extended to the case of dilute solutions, where this review shows phenomena that are explained by the notion that ions have effects on the structure of water beyond their hydration shells.

5.3. Static Spectroscopic Studies

Ordinary structural investigations of water and salt solutions using neutron or X-ray scattering provide the pair correlation functions of pairs of atoms. The hydrogen bonding that takes place is inferred from the atom pair distances and the angles of the O−H...X (X = O or the anion) configurations. Specific experiments aimed at the investigation of the hydrogen bond network itself have recently been reported by Näslund et al.,[175] who applied X-ray absorption and X-ray Raman scattering at the oxygen K edge to water and 1 m aqueous NaCl and KCl. Changes in the absorption are attributed to the cations on the assumption that the chloride anion has little or no effect on the hydrogen bonding of the water.[8] Increases were noted in the fraction of single (hydrogen bond) donor water molecules, namely 2.3% for KCl and 1.6% for NaCl of the total 55.5 water molecules there are per cation, relative to the fraction that exists in pure water. The change, a decrease of the fraction of tetrahedrally coordinated water, having a range of hydrogen bond distances and angles, is thus significant. Water structure breaking by K^+ and Na^+, attributed to the first hydration spheres of these cations, is confirmed by these experiments, but they are not sufficiently sensitive to determine to what spatial extent the effect occurs.

Raman spectroscopy was employed very early by Kujumzelis[3] to infer the effect of ions on the structure of water, concluding that the hydrogen bonds between water molecules are more or less distorted by the ions. Choppin and Buijs[176] used near-infrared spectroscopy on aqueous electrolyte solutions of various concentrations at several temperatures (mostly at 4.6 m and 21−27 °C) and studied the resolved bands at 1.16, 1.20, and 1.25 μm. They considered a model where these bands corresponded to water molecules with none, one, or two hydrogen bonds. They interpreted their data by assigning water structure making properties (shifts to more hydrogen bonds per water molecule) to La^{3+}, Mg^{2+}, H^+, Ca^{2+}, OH^-, and F^- and structure breaking properties (shifts to fewer hydrogen bonds) to K^+, Na^+, Li^+, Cs^+, Ag^+, ClO_4^-, I^-, Br^-, NO_3^-, Cl^-, and SCN^-. A further study was that by Bonner and Jumper,[177] who compared the 1.15 μm infrared band of water with that of 1 M aqueous electrolyte solutions. The band consisted of two components, corresponding to bonded and nonbonded water groups. Cations were stated to increase the fraction of bonded water molecules relative to pure water at the same temperature whereas anions decreased it. It is not clear, however, how the observed changes were allocated to cations and anions. Still, for the alkali metal cations, the relative amount of free OH groups was smaller than that deduced for pure water from the temperature effect.

Raman spectroscopy was used by Holba[178] for studying the extent of hydrogen bonding of water molecules in the presence of salts. He measured the absorption intensities of the 6427 and 7062 cm^{-1} bands of 6 M HOD in D_2O in the presence of dissolved salts at 0.5−2.0 M concentration. The values of unity minus the ratios R_N of the band absorption for 1 M salt solutions normalized to that in the absence of salt are the criteria for the effect. Positive values of $1 - R_N$

denote structure breaking and negative ones structure making in the sense of decreasing and increasing the amounts of hydrogen bonded water molecules. The magnitudes indicate the extent of the effect: 0.056 for NaCl, 0.068 for KCl, 0.061 for NaN_3, 0.124 for NaSCN, 0.122 for KSCN, 0.234 for $NaClO_4$, 0.275 for $Na_2S_2O_8$, 0.356 for $K_3Fe(CN)_6$, −0.016 for Li_2SO_4, −0.095 for Bu_4NBr, and −0.109 for $MgSO_4$. No attempt to assign values to individual ions was made.

More recently, Li et al.[179] also used Raman spectroscopy to study the hydrogen bonded structure of water in the presence of sodium halide salts and at various temperatures. Although the authors mentioned the work of Omta et al.[10] (see section 5.2.4), they did not discuss it in relation to their own work. They resolved the Raman band for the O−H stretching vibration to five Gaussians at 3051, 3233, 3393, 3511, and 3628 cm^{-1} and assigned the two higher wavenumbers to water molecules with fewer than four hydrogen bonds and the three lower ones to water molecules with all four ice-like hydrogen bonds intact, mainly in view of the temperature dependence between 0 and 100 °C for pure water. They then showed that at 20 °C F^- does not affect the Raman spectrum appreciably, but Cl^-, Br^-, and I^- ions do so in an increasing manner, in the direction of further breaking the ice-like hydrogen bonding, as expected.

Nickolov and Miller[180] applied FTIR spectroscopy for analyzing the O−D stretching vibration in 8% (mass) HOD in H_2O to study the water structure effects of KF, CsF, NaI, KI, and CsCl. They did not deconvolute the 2380 cm^{-1} band but inferred water structure breaking from its narrowing and the shifting of the peak to higher wavenumbers and correspondingly structure making from the opposite trends. They required, however, appreciable concentrations of the salts in order to observe the effects, with water-to-salt ratios optimally < 20. Of the five salts, the two fluorides were deemed to be structure makers and the others structure breakers, with the effects of cation and anion possibly compensating each other to some extent.

In a very recent paper, Smith, Saykally, and Geissler[181] challenge the assumption that the frequencies of the O−H stretching Raman lines in aqueous salt solutions are related to the extent of the hydrogen bonding. They contend, based on measurements on 1 M potassium halide solutions with 14 mol % HOD in D_2O, that the difference in the spectra of the salt solutions relative to water arises primarily from the electric fields rather than from rearrangement of the hydrogen bonds beyond the first hydration shell. These conclusions are confirmed by Monte Carlo computer simulations on one halide anion and 107 rigid water molecules.

5.3.1. Structural Temperature

Bernal and Fowler[182] long ago introduced the concept of "structural temperature" of electrolyte solutions. This is that temperature, T_{str}, at which pure water would have effectively the same inner structure as the water in an electrolyte solution at the temperature T. They suggested that T_{str} could be estimated from viscosity, X-ray diffraction, Raman spectroscopy, etc., but they did not provide explicit methods and values. Leyendekkers[183] used figures reported by Luck[184] from infrared spectroscopy to calculate T_{str} values for 1 m solutions of various electrolytes at 25 °C, $T = 298.15$ K, with $\Delta T = T_{str} - T$ shown in Table 6. It is noted that ΔT is positive when the structure breaking properties dominate over the structure making ones and negative otherwise, but since no separation into the effects of the individual ions could be made, it is not possible to analyze the results further. Similar conclusions could be inferred from the recent Raman spectroscopic study of Li et al.,[179] but this was not done directly in terms of structural temperatures.

Table 6. Difference $\Delta T = T_{str} - T$ between the Structural and the Actual Temperature $T = 298.15$ K of 1 m Aqueous Electrolyte Solutions According to Leyendekkers[183]

electrolyte	ΔT/ K	electrolyte	ΔT/ K
LiCl	5	KBr	5.8
LiI	8.0	KSCN	9.6
NaCl	3.9	KNO_3	8.0
NaI	6.5	Na_2CO_3	−4.0
NaSCN	8.5	$(NH_4)_2SO_4$	−1.8
$NaClO_4$	18.9	$MgCl_2$	−3
Na_2SO_4	0.6	$MgSO_4$	−8.6
KCl	4.6	$BaCl_2$	−6

Furthermore, structural temperatures of electrolyte solutions are unfortunately only operationally defined, i.e., in terms of the method used for their determination. Thus, Bunzl,[185] also using infrared spectroscopy but concentrating on the shift of the 0.97 μm band of water, could obtain reasonable values only for the tetraalkylammonium salts, but not for salts made up of small cations. Quantitative results from Walrafen's Raman[174] measurements also differ from those from Luck's[184] infrared spectroscopy, but the NMR data (at 20 °C) of Milovidova et al.[186] and Abrosimov[187] are close to those from the latter infrared measurements.

Smith et al.[32] interpreted the temperature-dependent Raman spectra of water in terms of continuous states of various hydrogen bond strengths. This view opposes that in terms of a mixture model, as inferred, for instance, by Choppin and Buijs[176] from near-infrared spectroscopy (see above) on aqueous electrolyte solutions at several temperatures, using a model where the bands corresponded to water molecules with none, one, or two hydrogen bonds.

The concept of structural temperature has more or less been abandoned in recent years.

5.3.3. X-ray Absorption and Raman Scattering

Recent X-ray absorption and X-ray Raman scattering experiments were made by Näslund et al.[188] using the O(1s) edge in aqueous aluminum, potassium, and sodium chloride solutions. Concentrations of 1 m or higher were necessary to detect major changes, and the results are sensitive to the immediate environment of the oxygen atoms of the water molecules. These were interpreted in terms of single donor (or broken) hydrogen bonds, characterizing the prepeak (see section 3.2), being at an increased amount around potassium ions, a diminished amount of such bonds around aluminum ions, and rather indifferent effects near sodium and chloride ions. It was argued that the extent of the effects was small, a few percent of the total hydrogen bonds, and the effects pertain to the hydration shells rather than to the bulk water, with the latter still existing in the 1 m NaCl and KCl solutions but hardly in the 4 m NaCl and KCl or 2.7 m $AlCl_3$ solutions.

A different approach was taken by Cappa et al.,[189] who considered the total electron yield (TEY) on X-ray absorption of 0.8−4.0 M sodium chloride, bromide, and iodide aqueous solutions. They deconvoluted the TEY spectra into six Gaussians and plotted the difference spectra of the solutions relative to pure water. The increased intensities at the prepeak were most pronounced for the iodide solutions and hardly visible for the chloride ones, whereas the main peak showed increases and the rather wide postpeak region showed decreases in intensity for all three halides, but only a small one for the chloride.

The D_2O vs H_2O isotope effects on X-ray Raman spectra indicate according to Bergmann et al.[190] that D_2O has a structural temperature (section 5.3.3) lower by 20 K than that of H_2O at ambient conditions. This is ascribed to the inherently stronger hydrogen bonding in the heavy water.

5.4. Evidence from Thermodynamic Quantities

Various thermodynamic properties of aqueous electrolyte solutions have been employed for the deduction of the effects of their ions on the structure of water. Among the early papers may be noted that of Steward,[4] who found a striking correspondence of the rate of variation of the apparent molar volume of salts with their concentration and the alteration in the minor X-ray diffraction peak, indicating the lessening of the fraction of four-coordinated water molecules. The apparent molar volume was used for the deduction of the water structural effects of ions by Fajans and Johnson,[191] who considered that the ions of NH_4Cl at 35 °C fit into the water structure, with each ion having the same molar volume as that of a water molecule (18.1 $cm^3\ mol^{-1}$). Then the thermal expansibility of much smaller or larger ions indicates the breaking of the water structure. The adiabatic compressibility of salt solutions was studied by Corey,[7] who found a remarkable correlation with the corresponding partial molar volume of the water and concluded that water had a liquid structure that became more highly coordinated and compacted with the introduction of ions. The thermal expansion of salt solutions was similarly employed by Hepler[192] for the classification of ions as structure makers or breakers, namely from the sign of $(\partial^2 V^\infty(\text{salt})/\partial T^2)_P$. He argued that positive values of this quantity, corresponding to negative values of $-T^{-1}(\partial C_P^\infty/\partial T)_T$, are characteristic of solutions of the lower alcohols in water, known as structure makers. Conversely, however, negative values, found inter alia for aqueous LiCl, $MgCl_2$, and $CaCl_2$, should designate these salts as net structure breakers, contrary to all other accounts of their properties. Thus, this use of the expansibility appears not to have been substantiated. All these early studies, however, led to only qualitative views on the effects of individual ions on the structure of water.

In a more recent study by Chalikian,[103] the two-state model of liquid water (section 3) is applied to thermodynamic functions of ion hydration, in particular the volume and adiabatic compressibility. According to this study, the fraction of high density domains in pure liquid water at 25 °C is 0.27, whereas it is raised to between 0.80 and 0.96 in dilute solutions of the alkali halides; that is, a large amount of (tetrahedral hydrogen bonded) structure breaking takes place. Within this range, this fraction falls from sodium to cesium salts and from chloride to iodide salts for given counterions (lithium chloride is out of sequence). However, this ordering is counterintuitive and the change of the fraction of high density domains is too large for the dilute solutions considered.

Dutkiewicz and Jakubowska[194] considered the water activity in up to 2.3 m aqueous electrolyte solutions but did not go further than deducing the structural properties from a comparison of the activity coefficient of water (on the molar scale: a_W/c_W), obtained in a round-about manner from the hydration of aldehydes at fairly high concentrations, with that of pure water (1/55.51 = 0.0180). On the assumption that Cl^- anions have a negligible effect on the structure of the water, the conclusion that Na^+, NH_4^+, and Mg^{2+} are structure making and K^+ and ClO_4^- are structure breaking is not producing any new insight.

5.4.1. Structural Entropy

Frank and Evans in their classic paper[6] suggested that the entropies of hydration of ions provide an approach for deciding on their structure making or breaking properties. Even previously, Frank and Robinson[5] made a similar suggestion concerning the partial molar entropy of the water. Gurney[2] demonstrated a linear relationship between the partial molar entropy of aqueous monatomic ions and their viscosity B_η coefficients (see section 5.1). Nightingale[138] generalized this relationship to other classes of ions (polyatomic ones) by including configurational contributions to the partial molar ionic entropy, i.e., by using the entropies of hydration, $\Delta_{\text{hydr}}S^\infty$, rather than the partial molar entropies of the aqueous ions. Note that these and the following considerations, using standard molar entropies, pertain to ions at infinite dilution in water.

Krestov[195] considered that in order to yield the water structure modifying entropic effect from $\Delta_{\text{hydr}}S^\infty$, the contributions of the ionic hydrate shell formation and, for multiatomic ions, also the limitation of the ionic rotational entropy should be deducted. The remainder, ΔS_{struc} (ΔS_{II} in the notation of Krestov), then accounts for the changes in the structure of the water beyond the hydration shell:

$$\Delta S_{\text{struc}} = \Delta_{\text{hydr}}S^\infty - 0.615S^\circ_{\text{transl}} - \eta S_{\text{rot}} \qquad (14)$$

The hydrate formation was estimated from the translational entropy loss, $0.615S^\circ_{\text{transl}}$, of inert gas atoms isoelectronic with monatomic ions on dissolution in water, and for the rotational entropy loss, $0 \le \eta \le 1$ was an unknown numerical coefficient. Tables of values of ΔS_{struc} for many cations and anions, based on assigning $S^\infty(H^+,aq) = -8.8\ J\ K^{-1}\ mol^{-1}$, were shown in Krestov's book.[196] Unfortunately, there are typographical errors in this book: the signs of the values for K^+, Rb^+, Tl^+, Br^-, and At^- were erroneously shown as negative, and the value for Te^{2-} should be −33.1 instead of −433.1 $J\ K^{-1}\ mol^{-1}$. Adjustment to the more probably valid $S^\infty(H^+,aq) = -22.2\ J\ K^{-1}\ mol^{-1}$ would change the values by $-13.4z$ units, where z is the charge number of the ion. Positive values of ΔS_{struc}, noted for K^+, Rb^+, Cs^+, Tl^+, Cl^-, Br^-, I^-, and At^- among monatomic ions (also for Po^{2-}, if the adjustment noted is made), imply water structure breaking properties. Positive values are also shown[196] for many multiatomic ions (but ignoring the last term in eq 14). The linear correlation $B_\eta = 0.011 - 0.007\Delta S_{\text{struc}}$ resulted from Krestov's data.

When the positive values of ΔS_{struc} obtained at the lower temperatures were followed over the temperature range 15−65 °C,[196,197] it was noted that they changed sign from positive to negative at a characteristic temperature, called the limiting temperature. This was explained by the decreasing inherent structure of the water as the temperature was raised (section 3 and Table 1), decreasing the structure breaking effect of those ions that do so at the lower temperatures.

A somewhat different route was taken by Abraham et al.[153,198] to obtain the part of the standard molar entropy of hydration of ions that is relevant to the effects of the ions on the structure of the water, ΔS_{struc} (the notation used was $\Delta S_{\text{I,II}}$, using a two hydration layer calculation). From the standard molar entropy of hydration of the ions, $\Delta_{\text{hydr}}S^\infty$, were deducted the contributions of a neutral part, ΔS_n, and the bulk water dielectric effect ΔS_{el}. The values of the neutral part were deduced from the values for nonpolar solutes of sizes (radii) similar to those of the ions: $\Delta S_n = 5.0 + 291(r/\mathrm{nm})$ J K^{-1} mol^{-1}. The bulk water dielectric effect was calculated according to the Born expression, beyond the distance of one water molecular diameter, d_W, from the surface of the bare ion:

$$\Delta S_{el} = (N_A e^2/8\pi\varepsilon_0)z^2(r + d_W)^{-1}\varepsilon_r^{-1}(\partial \ln \varepsilon_r/\partial T)_P \tag{15}$$

Values of S_{struc} for the alkali metal and halide ions as well as Ag^+ and ClO_4^- were reported[153] on the unusual mole fraction scale for the solution, with $S^\infty(H^+,aq) = -68.2$ J K^{-1} mol^{-1} on this scale, causing K^+ to appear as a structure making ion. Adjustment to the molar scale with $S^\infty(H^+,aq) = -22.2$ J K^{-1} mol^{-1} corrects this unacceptable result. Abraham et al.[153] noted the usual linear correlation of their ΔS_{struc} with the viscosity B_η coefficients as well with the B_{NMR} coefficients (see section 5.2.1) and also with the ionic partial molar volumes or their electrostricted volumes. Bhattacharya[199] inverted the correlations of ΔS_{struc} with B_η and B_{NMR}, with ionic values for the latter two parameters obtained according to his method of splitting electrolyte data into ionic contributions (section 5.2.1), to calculate ionic entropies of hydration, but they did not discuss the effects of the ions on the water structure from the resulting values.

Marcus and Loewenschuss[200] and Marcus[201] suggested yet another model for obtaining ΔS_{struc} values from $\Delta_{hydr}S^\infty$ ones, pointing out that $\Delta_{hydr}S^\infty$, with the standard state of 0.1 MPa for the ideal gaseous ions and 1 mol dm^{-3} for the aqueous ones, includes an irrelevant entropy of compression of $\Delta_{comp}S = -26.7$ J K^{-1} mol^{-1} that ought to be removed from the absolute $\Delta_{hydr}S^\infty$ values (based on $S^\infty(H^+,aq) = -22.2$ J K^{-1} mol^{-1}). The electrostatic effect beyond the first hydration shell was obtained as above, $\Delta S_{el} = (N_A e^2/8\pi\varepsilon_0)z^2(r + d_W)^{-1}\varepsilon_r^{-1}(\partial \ln \varepsilon_r/\partial T)_P$, from the Born expression. However, within this hydration shell the n water molecules are translationally immobilized, having to move together with the ion X^z, with a concomitant reduction of their entropy. This contribution

$$\Delta_{tr\,im}S(X^z) = 1.5R \ln[M(X(H_2O)_n/M(X)]\text{-}26.0n \tag{16}$$

where the first term denotes the change of translational entropy due to the larger mass (M) of the hydrated ion and 26.0 is the molar translational entropy of water in its liquid form, does not pertain to the water structural effects either.[201] The value of $n = A|z|/(r/\mathrm{nm})$ with $A = 0.355$ was obtained empirically, so as to yield

$$\Delta S_{struc}(Na^+) = \Delta_{hydr}S^\infty(Na^+) - \Delta_{comp}S - \Delta S_{el}(Na^+) - \Delta_{tr\,im}S(Na^+) = 0 \tag{17}$$

on the supposition that sodium ions are indifferent with respect to the water structure making and breaking. In view of the cumulative errors incurred in such calculations, only values of $\Delta S_{struc}(X^z)$/J K^{-1} mol^{-1} > 6 were construed as indicating the ion X^z to be definitely water structure breaking, values < −6 were construed as indicating it to be structure making, and in between values were construed to be borderline cases, including those for Na^+, Ag^+, and Cl^-. The assignments[201] of ions to such classes generally conformed to assignments by other methods, such as the signs of B_η and B_{NMR}.

Other models and approaches for obtaining the water structural effects of ions from the entropies of hydration, such as those of Uhlich,[202] Ryabukhin,[203] and Friedman and Krishnan,[204] were briefly reviewed by Marcus and Loewenschuss[200] and need not be detailed here.

A final development of this concept for ΔS_{struc} that indicates the water structural effects of ions is due to Marcus,[205] resembling more that of Abraham et al.[153] than his own previous one.[201] It is based on a model common for various thermodynamic functions of ion hydration,[206] with the key quantity being Δr, the width of the electrostricted hydration shell, where the water molecules have a volume $\pi d_W^3/6$ rather than V_W/N_A. Thus, Δr is obtained from the volume of the hydration shell with n water molecules:

$$(4\pi/3)[(r + \Delta r)^3 - r^3] = n\pi d_W^3/6 \tag{18}$$

with $n = A|z|/(r/\mathrm{nm})$ as before, $A = 0.36$ being slightly different, and $d_W = 0.276$ nm. Then the structural entropy is obtained from

$$\Delta S_{struc} = \Delta_{hydr}S^\infty - [\Delta S_{nt} + \Delta S_{el\,1} + \Delta S_{el\,2}] \tag{19}$$

Here the term ΔS_{nt} takes care of the entropic effect of the creation of a cavity in the water to accommodate the ion ΔS_n[153] as well as the compression term $\Delta_{comp}S$[201] of the previous models. It is evaluated from the entropies of hydration of small neutral molecules or rare gas atoms, interpolated for a radius r the same as that of the ion: $\Delta S_{nt} = -3 - 600(r/\mathrm{nm})$ J K^{-1} mol^{-1}. In analogy with eq 15, the electrostatic effects are

$$\Delta S_{el\,1} = (N_A e^2/8\pi\varepsilon_0)z^2[\Delta r(r + \Delta r)^{-1}]\varepsilon'^{-2}(\partial\varepsilon'/\partial T)_P \tag{20a}$$

$$\Delta S_{el\,2} = (N_A e^2/8\pi\varepsilon_0)z^2(r + \Delta r)^{-1}\varepsilon_r^{-2}(\partial\varepsilon_r/\partial T)_P \tag{20b}$$

The former of these two expressions (eq 20a) pertains to the electrostricted hydration shell, where the permittivity and its temperature derivative are assumed to have the infinitely large field value of $\varepsilon' = n_D^2 = 1.776$ and $(\partial\varepsilon'/\partial T)_P = 2(\partial n_D/\partial T)_P = -1 \times 10^{-4}$ K^{-1} at 25 °C, where n_D is the refractive index of water at the sodium D line. This treatment could be applied to nearly 150 aqueous cations and anions, monatomic and polyatomic, with charges $-4 \leq z \leq 4$. Sodium and silver cations now reverted to the structure making category and chloride to the structure breaking one, but the borderline region is widened to ±20 J K^{-1} mol^{-1}. The linear correlation with the viscosity B_η (except for tetraalkylammonium cations) is

$$\Delta S_{struc}/\mathrm{J\,K^{-1}\,mol^{-1}} = 20(z^2 + |z|) - 605(B_\eta/\mathrm{dm^3\,mol^{-1}}) \tag{21}$$

Values of ΔS_{struc} of representative ions obtained according to the treatments of Krestov[193] as reported in ref 196 and by Abraham et al.[153] and Marcus[205] are shown in Table 7, adjusted where applicable to the M scale for the entropies of hydration and based on their absolute values with $S^\infty(H^+,aq) = -22.2$ J K^{-1} mol^{-1}.

A treatment based on the same model,[206] but dealing with the structural heat capacity, $\Delta C_{P\,struct}$, contribution of the effects of ions on the water structure was also repotted by Marcus.[191] Here C_P replaced S in eqs 19 and 20a, $\Delta C_{P\,nt} = -48 + 1380(r/\mathrm{nm})$ J K^{-1} mol^{-1}, and $T(\partial^2\varepsilon'/\partial T^2)_P$ and $T(\partial^2\varepsilon_r/\partial T^2)_P$ replaced the corresponding factors in eqs 20a and 20b.

Table 7. Water Structural Entropy ΔS_{struct}/J K^{-1} mol^{-1} and Heat Capacity $\Delta C_{P\ struct}$/J K^{-1} mol^{-1} Effects of Representative Ions According to Three Treatments

	Krestov[196]	Abraham[153]	Marcus[205]	
ion	ΔS_{struct}	ΔS_{struct}	ΔS_{struct}	$\Delta C_{P\ struct}$
Li^+	−69	−81	−52	147
Na^+	−19	−27	−14	83
K^+	21	40	47	0
Rb^+	39	50	52	−38
Cs^+	46	76	68	−83
Ag^+	−13	−20	−15	47
NH_4^+	−8[a]		5	28
Me_4N^+			41	−30
Ca^{2+}	−159		−59	215
La^{3+}	−300		−113	355
F^-	−57	−87	−27	20
Cl^-	20	−2	58	−62
Br^-	41	21	81	−88
I^-	68	52	117	−113
NO_3^-	23		66	−59
SCN^-			83	−33
ClO_4^-	44[a]	68	107	−87
CO_3^{2-}	−160[a]		−52	68
SO_4^{2-}	−100[a]		8	−14
PO_4^{3-}	−319[a]		−131	103

[a] The contribution from hindered rotation could not be explicitly included in the ΔS_{struct} of the polyatomic ions.

A negative bias occurred in $\Delta C_{P\ struct}$ calculated in this manner, due to the choice of $C_P^\infty(H^+,aq) = -71$ J K^{-1} mol^{-1}, and in order to show the structure making and breaking properties of the ions, $175z$ J K^{-1} mol^{-1} are added here, to yield the values shown in Table 7, with positive values for structure making ions and negative ones for structure breaking ones, but allowing for a wide borderline region of ±60 J K^{-1} mol^{-1}.

5.4.2. Transfer from Light to Heavy Water

Ben-Naim[21] laid the foundation for the estimation of the effects of ions on the structure of water in terms of the changes in the average number of hydrogen bonds that characterized this structure (section 3.2). The pair potential between water molecules is written as a sum of two terms: one that describes both the short-range (repulsion) and long-range (multipole) interactions and another that describes the hydrogen bonding as the product of the hydrogen bond energy e_{HB} and the geometrical factor $0 \le G_{HB} \le 1$, specifying whether a hydrogen bond exists or not (section 3.1). The introduction of a solute particle S into H_2O and into D_2O is associated with a difference in its standard chemical potentials in these two kinds of water, $\Delta\mu_S^{\infty\ HD}$, that depends solely on changes in the hydrogen bonding structure of the water, in view of the very similar properties of molecules of these two kinds of water with respect to solute−solvent interactions (section 3.2). Therefore, this difference can be written as

$$\Delta\mu_S^{\infty HD} = \Delta^{HD}e_{HB}\Delta G_{HB} \qquad (22)$$

Here $\Delta^{HD}e_{HB}$ is the difference in the strengths of the hydrogen bonds in D_2O and H_2O obtained from the sublimation enthalpies of the ices (eq 6) and ΔG_{HB} is the change in the average total geometrical factors over all the configurations of the *N* water molecules of either kind caused by the introduction of a particle of S:

$$\Delta G_{HB} = (2/N)[\langle\Sigma_N G_{HB}\rangle_S - \langle\Sigma_N G_{HB}\rangle_0] \qquad (23)$$

The left-hand side of eq 22 is an experimentally measurable quantity (from solubilities, EMF data, etc.); hence, ΔG_{HB}, the effect of the solute *S* on the (hydrogen bonded) structure of water, can be determined. Nonionic solutes, such as argon or methane, are known from several approaches to enhance the structure of water and have positive values of ΔG_{HB}, diminishing with increasing temperatures, as is expected (section 3, Table 1).[21]

Application of this treatment to ionic solutes was also tentatively made by Ben-Naim[21] and was subsequently taken up by Marcus and Ben-Naim.[44] The most satisfactory description of the structure of water appears to be in terms of the average number of hydrogen bonds per water molecule existing in it (section 3). It is, therefore, deplorable that the data for $\Delta\mu_S^{\infty\ HD}$ of electrolytes are rather unsatisfactory, not to speak of the lack of definite data for ascribing $\Delta\mu_S^{\infty\ HD}$ to individual ions. The values of $\Delta\mu_S^{\infty\ HD}$ that have been measured for various electrolytes are small, and even in a recent electrochemical study,[193] they are of the same order as their uncertainties. The "best" values available were summarized by Marcus,[208] ranging from $\Delta\mu_S^{\infty\ HD}$/J mol^{-1} = −950 for Bu_4N^+ to 1200 for Ba^{2+}, at 25 °C with probable errors of ±100. According to eq 6, $\Delta^{HD}e_{HB} = -742$ J mol^{-1} at 25 °C, but the value of −929 J mol^{-1} was previously employed.[201,205,208] The better established values of $\Delta\mu_S^{\infty HD}$ for the nine alkali metal and halide ions, based on equalizing the values for Ph_4As^+ and BPh_4^-, and incidentally also for K^+ and Cl^-, should be taken for correlations with well established quantities describing the water structural effects of ions, such as B_η and ΔS_{struc}. The resulting expressions, calculated with $\Delta^{HD}e_{HB} = -742$ J mol^{-1} in eq 22, are

$$\Delta G_{HB} = -(0.68 \pm 0.14) + (5.95 \pm 1.74)(B_\eta/\mathrm{M}^{-1}) \qquad (24)$$

with a standard error of the fit of 0.3 units and

$$\Delta G_{HB} = -(0.18 \pm 0.08) - (10.22 \pm 1.26) \times 10^{-3} \quad (\Delta S_{struc}/\mathrm{J\ K^{-1}\ mol^{-1}}) \qquad (25)$$

with a standard error of the fit of 0.2 units. In this manner, values of ΔG_{HB} can be generated for a large number of ions. These dimensionless values, of course, do not describe the ionic water structural effects any better than the viscosity B_η coefficient and the structural entropy $\Delta S_{struc,}$ themselves, but they have the form suggesting the theoretical basis provided by Ben-Naim in terms of the effect of the ions on the extent of hydrogen bonding in dilute electrolyte solutions.[21]

6. Biochemical Significance of Ion Effects on Water Structure

The notion that liquid water differs from so-called "normal liquids" by having a pronounced three-dimensional structure due to the extensive network of hydrogen bonds is discussed in sections 2 and 3. This structure is affected by the presence of solutes, as was inferred by a great variety of methods, as shown in sections 4 and 5. Despite some sweeping claims to the contrary (reported in section 5.2.4), the results of substantially all these studies are that in *dilute* solutions certain ions enhance and others diminish the structure of the water. Collins and Washabaugh[8] introduced the concepts of kosmotropic and chaotropic solutes (water structure makers and breakers) used extensively by the biochemical and biophysical communities. The question remains of what significance these notions have concerning the behavior and use of electrolyte solutions in biological environments.

Table 8. Ions Arranged According to Their Effects on the Structure of Water, Following Marcus[205] but with an Adjusted Value of $\Delta^{HD}e_{HB}$ (See the Text)

ions	ΔG_{HB}
Structure Breaking Ions	
I^-, I_3^-, ClO_4^-, BrO_4^-, IO_4^-, MnO_4^-, TcO_4^-, ReO_4^-, $AuCl_4^-$, $Ag(CN)_2^-$, $Au(CN)_2^-$, $S_2O_8^{2-}$, $S_4O_6^{2-}$, $Cr_2O_7^{2-}$, $PdCl_6^{2-}$, $PtCl_6^{2-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	≤ -1.1
Br^-, Br_3^-, SCN^-, BF_4^-, SiF_6^{2-}	-1.1 to -0.9
K^+, Rb^+, Cs^+, Tl^+, Cl^-, SH^-, CN^-, N_3^-, OCN^-, NO_2^-, NO_3^-, ClO_3^-, $Al(OH)_4^-$, S^{2-}, Se^{2-}, $S_2O_6^{2-}$	-0.9 to -0.7
$CH_3NH_3^+$, $(CH_3)_4N^+$, Ra^{2+}, SH^-, HF_2^-, ClO_2^-, BrO_3^-, HCO_2^-, HSO_3^-, HSO_4^-, SeO_4^{2-}, CrO_4^{2-}, $S_2O_3^{2-}$, $S_2O_4^{2-}$, $P_2O_7^{4-}$	-0.7 to -0.4
NH_4^+, $B(OH)_4^-$, SO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, $C_2O_4^{2-}$	-0.4 to -0.1
Borderline Ions	
Na^+, Ag^+, $(C_2H_5)_4N^+$, Ba^{2+}, Pb^{2+}, F^-, IO_3^-, HCO_3^-, $H_2PO_4^-$	-0.1 to 0.1
Structure Making Ions	
Li^+, Cu^+, Au^+, $(C_6H_5)_4As^+$, Sr^{2+}, Sn^{2+}, Al^{3+}, Cr^{3+}, Bi^{3+}, OH^-, $CH_3CO_2^-$, $B(C_6H_5)_4^-$, CO_3^{2-}, SO_3^{2-}	0.1−0.4
Ca^{2+}, Eu^{2+}, Hg_2^{2+}, Sc^{3+}, Co^{3+}, Tl^{3+}, Pu^{4+}, HPO_4^{2-}	0.4−0.7
$(C_3H_7)_4N^+$, V^{2+}, Cr^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, Sm^{2+}, Yb^{2+}, Gd^{3+}, V^{3+}, Fe^{3+}, Ga^{3+}, Rh^{3+}, U^{3+}, Pu^{3+}, AsO_4^{3-}	0.7−0.9
Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Y^{3+}, La^{3+} to Eu^{3+}, Tb^{3+} to Lu^{3+}, Th^{4+}, U^{4+}, PO_4^{3-}	0.9−1.1
$(C_4H_9)_4N^+$, Fe^{2+}, UO_2^{2+}	≥ 1.1

On the whole, however, other aspects of ion hydration than their water-structural effects appear to play the major role in their biological effects. Thus, the relative ease of hydration and dehydration of sodium and potassium ions plays an important role in their passage through membrane channels. As some examples, Collins et al.[209] discussed in a recent review the forces that control chemical processes and biological structure in electrolyte solutions. They cited biological evidence for the short-range nature of the dominant forces generated by ions in water. The main argument, however, does not consider the water structure affecting properties of the ions but the strength of their water binding properties in competition with that of ionic groups in the proteins. Jungwirth et al.[210] considered the contact ion pairing of anions with Na^+ and K^+ to play a key role in biological discrimination between them. The ordering of the anions does not differ much from that involved in their water structure modifying effects (section 7) or of the Hofmeister series (section 6.1), so no far reaching conclusions can be drawn from the results. The effects of guanidinium and thiocyanate ions on proteins were explained by Neilson et al.[56] on the basis of their very weak hydration, found by neutron diffraction (section 4.1.2). These ions are pushed to the positively charged sites of the protein chains by the stronger water−water interactions of the structured water, resulting in protein folding. The water structure, in terms of the two-state model of Robinson et al.[211] is capable of explaining the denaturation of proteins by temperature and pressure effects even in the absence of ions. Effects of anions on the pH of buffers used in biochemical studies have been indirectly cited as due to their hydration properties and being partly responsible for enzymatic effects.[212,213] Such results cast some doubt on whether the ionic water structure effects (of kosmotropic and chaotropic ions) play a dominant role in biological processes or whether other causes (direct hydration and dehydration, ion pairing, hydrophobic interactions) are, in fact, more important.

6.1. Hofmeister Series

The empirical Hofmeister series[14,15] relates to the minimal concentrations of various salts required to precipitate a given protein from aqueous solution. The effectiveness of salts is dominated by the properties of the anions and is manifested typically at approximately one molar concentrations but may be seen in some cases at as low a concentration as 0.01 M. For a given cation, the series is generally written as

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > OH^- > F^- > HCO_2^- > CH_3CO_2^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^- \qquad (26)$$

In the sequence in eq 26, carbonate anions are the most kosmotropic, i.e., effective in the precipitation of proteins, whereas thiocyanate anions are the most chaotropic, i.e., the least effective, and in some cases even salt the protein in, that is, enhance its solubility. There are some small variations in the sequence noted when various related phenomena are used in order to define it.[212,214,215] In particular, reversals of the order of the items $H_2PO_4^-$ and SO_4^{2-} and ClO_4^- and SCN^- have been noted,[212,216] among others.

A less well developed series exists among cations for a given anion:[15,217]

$$(CH_3)_4N^+ > (CH_3)_2NH_2^+ > K^+ \sim Na^+ > Cs^+ > Li^+ > NH_4^+ > Mg^{2+} > Ca^{2+} \gg C(NH_2)_3^+ \qquad (27)$$

Again, there are some reversals (e.g., NH_4^+ and K^+) in reports from different authors. These two series of ions resemble to a certain extent those defined by their structure making and breaking effects as listed in Tables 4−7 and 8. A thorough treatment of the Hofmeister series is outside the scope of this review, but the relevance of the water structural effects of the ions to the phenomena covered by this series is briefly discussed here.

In spite of the partial resemblance of the Hofmeister series to the effects noted for ions at infinite dilution on the water structure, no well established correlation exists between protein stability and such water structural effects. The main point to note is that the Hofmeister series pertains to ions near a *surface*: that of a macromolecule (a protein or some other polymer)[214,217] or of glass[218] or of a solution of a surfactant[219] or a monolayer of it.[220] This conclusion of the absence of a definite correlation was based[218] also on a two-state model of water[30,167] that may but need not represent its actual structure (section 3) nor the effects of ions on it.

Interfacial water molecules are already ordered nonisotropically by the surface at which they reside, so that the effects of ions on them cannot be directly compared with the effects in isotropic dilute aqueous solutions. The interfacial water structure was directly monitored spectroscopically[220] for an octadecylamine monolayer on D_2O, as affected by various sodium salts, and the degree of ordering of the monolayer followed the Hofmeister series of the anions. The same should be true for macromolecules in aqueous solutions, with the surrounding water molecules having already some structure forced on them by the presence of the macromolecule, so that the ion effects described by the Hofmeister series should differ from those in homogeneous isotropic dilute solutions discussed in this review. Partition coefficients of individual ions between the air/solution interface and the bulk solution were deduced from the surface tension increment, $d\sigma/dm$, of these ions[217] and were shown to follow qualitatively the Hofmeister sequences for the anions and the cations. This conclusion concerning the surface tension effects is in line with that of Collins and Washabaugh.[8] Other surface effects, such as at the glass/solution interface, have been shown to be responsible for the specific effects of salts on the pH of the solution measured with a conventional glass electrode, both in the absence[219] and in the presence of a protein.[213]

On the other hand, the salting out of small hydrophobic molecules (methane and neopentane) through their hydrophobic self-association correlates well with the bulk water structure affecting properties of the salts. This was concluded by Thomas and Elcock[221] from molecular dynamics calculation of the relative number of hydrogen bonds per water molecule (sections 3.1 and 3.2) in the salt solutions. The relative effects of the anions SO_4^{2-}, F^-, Cl^-, I^-, and ClO_4^- on the salting out of 1-propanol studied by Miki et al.[222] are well explainable by their water structure affecting abilities discussed in this review and, hence, have no relation to surface effects and are in fact unrelated to the Hofmeister series, contrary to what was stated in the title of their paper. It appears from such results that where small, though hydrophobic, solutes are concerned, the water around them is not as strongly structured as near more extensive interfaces (polymers, macroscopic air/solution surface). The water structure affecting properties of ions can then be manifested more clearly.

7. Classification of Ions as Structure Makers/Breakers

The results summarized in section 5 and its subsections (except section 5.2.4, dealing with ultrafast vibrational spectroscopy), obtained from a great variety of methods involving both static and dynamic properties of *dilute* ionic solutions, point toward the modification of the structure of the water by the presence of ions beyond their hydration shells. Whether the ions are called structure makers and breakers or kosmotropic and chaotropic, the extent of the hydrogen bonding in the solution per water molecule in the surroundings of an ion (and not necessarily in its hydration shell) differs from that in pure water at the same temperature and pressure. It is the extent of hydrogen bonding in water (not its strength or its dynamics) that is meant in this review as describing the structure of the water and the effects of ions on it. This extent was given a numerical value, ΔG_{HB}, by noting the change in the ionic standard chemical potential on transfer from H_2O to D_2O, a change that correlates well with other measures of the structure modifying properties of the water (section 5.4.2).

A table of such values was reported by the present author[205] in steps of 0.2 units, ranging from < -0.9 to $> +0.9$, with values of $-0.1 \leq \Delta G_{HB} \leq +0.1$ constituting borderline cases. This table is reproduced here as Table 8, but in view of the less negative value of $\Delta^{HD}e_{HB}$ used now for 25 °C, all the former[205] values were multiplied by 1.25. It should still be noted that the boundaries between the groups of ions having neighboring ΔG_{HB} values in Table 8 are diffuse, and the assignment of values according to eqs 24 and 25 is apt to be uncertain by as much as 0.2 units. For instance, fluoride ions are, according to both the viscosity and entropy criteria, structure making, but the correlations make it a borderline ion in terms of ΔG_{HB}.

8. Discussion and Conclusions

Although the effects of ions on the structure of water have been the subject of extensive research for many decades, they were not the subject of comprehensive reviews or generalized considerations except in a few instances in recent years,[223−225] with some partial discussions of the relevant problems. The present review intends to fill this gap, although it necessarily cannot claim to have included all of the relevant research in its considerations.

The year 2003 may be regarded as somewhat of a watershed concerning the question of the effect of ions on the structure of water. In that year, the paper by Omta, Bakker, et al.[10] "Negligible effects of ions on the hydrogen bond structure in liquid water" was published in *Science*, a high-impact journal. This conclusion, pertaining to the reorientation dynamics of water molecules outside the first hydration shell of the ions studied, based on femtosecond pump−probe spectroscopy, was confirmed by other papers from that research group.[11,172,173] It is obvious that the sweeping title of the paper in *Science*[10] is misleading, since only a limited aspect of the general problem of the effects of ions on the water structure was dealt with. Several authors subsequently just ignored these results (e.g., refs [12,47,50,55,122,218])—some of whom were not concerned with the dynamic aspects of ions affecting the water structure—but others countered them with data and arguments,[54,55,160,175] partly based on highly sophisticated computer simulations.[13,169,221]

Nevertheless, that the water molecules in the first hydration shells of ions (ref 17 and Table 3) do not have average hydrogen bonding, in terms of the extent, geometry, and dynamics that exist in pure water, is beyond controversy. The problem lies in the water outside the hydration shell, and even there, only the effects of ions on the reorientation dynamics have been challenged by ultrafast spectroscopy,[10] not necessarily the static amount of structure, whatever its measure. Again, when experimental determinations require small water-to-ion ratios (as was the case with some of the ultrafast spectroscopy measurements), the overlap of the hydration shells of the ions and counterions must be reckoned with, concomitant with the lack of any "bulk water", as demonstrated in Figure 1.

The macroscopic water structure effects of ions noted in dilute solutions, from dynamic studies (viscosity, NMR relaxation, diffusion) and thermodynamic ones (entropy of hydration, transfer between light and heavy water), pertain to infinite dilution and, hence, concern the water *outside* the hydration shells. Water structure breaking by some (large, univalent) ions demonstrated by such results cannot be explained away. The very recent paper by Vchirawongkwin et al.,[71] employing quantum mechanical/molecular mechanical simulation with 499 water molecules per Tl^+ ion, demonstrates that water structure breaking is a very real process in dilute aqueous solutions. Both structural and dynamical effects beyond the hydration shell were considered in this work and “a far reaching influence on the solvent structure” was deduced. On the other hand, geometry-based simulation of the build-up of hydration shells around sulfate and phosphate anions[226] showed them to be structure-makers, whereas guanidinium cations do not build any hydrate structures around them, as concluded above[56] (section 4.1.2).

The classification of ions into groups with water structure effects varying from strong structure breakers to strong structure makers in Table 8 should be a guide to the effects of ions observed by macroscopic measurements in dilute solutions. Whatever consequences this classification may have on chemical reactivity and biochemical responses must be deduced from further studies.

9. References

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