Pure Appl. Chem., Vol. 82, No. 10, pp. 1889–1899, 2010.
doi:10.1351/PAC-CON-09-07-02

Effect of ions on the structure of water*

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Abstract: Water is a highly structured liquid, as indicated by its stiffness (cohesive energy density) and being ordered (large entropy of vaporization), its three-dimensional hydrogen-bonded network being its most outstanding feature. The extent of this network depends on the definition of the hydrogen bond, and both computer simulation and thermodynamic data yield a consistent picture. The effects of ions on this network in dilute aqueous solutions have been studied from dynamic, thermodynamic, spectroscopic, and computer simulation aspects. A classification of ions from those that are highly water-structure-breaking ions through borderline cases to those that are highly water-structure-making ions results from such studies.

Keywords: aqueous salt solutions; effects of ions; hydrogen bonds; water structure.

INTRODUCTION

There are some experimental facts that need to be considered when effects of ions on the structure of water are discussed, raising some legitimate questions. One of them is the relative viscosity, η/η^*, of certain dilute aqueous solutions, where η is the dynamic viscosity of the solution and η^* that of water at the same temperature. According to Jones and Stauffer [1] $\eta/\eta^* = 0.98910$ for 0.099661 M (≡ mol dm^{-3}) of cesium iodide at 25 °C. According to Laurence and Wolfenden [2], $\eta/\eta^* = 1.0393_8$ for 0.09393 mol dm^{-3} of lithium acetate at 25 °C. In such dilute solutions, essentially complete ionic dissociation of the solute electrolyte takes place. So why do the cesium and iodide ions depress the relative viscosity of the solution, whereas lithium and acetate ions enhance it?

Another set of experimental data pertains to the transfer of salts from light to heavy water, expressed as the standard molar Gibbs energy of transfer, $\Delta_t G^\infty$ (pertaining to infinite dilution), obtainable from the solubilities of sparingly soluble salts in each kind of water. For potassium perchlorate $\Delta_t G^\infty$ = 820 J mol^{-1}, but for LiF $\Delta_t G^\infty = -270$ J mol^{-1}, both at 25 °C. (Unfortunately, the accuracy of such data, obtained indirectly as shown by Marcus [3], is only ±100 J mol^{-1}). Why, then, is the transfer of the potassium and perchlorate ions from light to heavy water disfavored, whereas that of lithium and fluoride ions is favorable?

There are many other experimental facts that point to the conclusion that ions in dilute aqueous solutions have certain effects that merit an explanation, for some ions in one direction and for some others in the opposite direction in a consistent manner, as reviewed recently by Marcus [4]. This explanation is generally given in terms of the effects of the ions on the structure of water, some enhancing it and others diminishing it. This aspect of the structure of water differs from the structure of the hydration shells of the ions (as determinable by diffraction methods at appreciable concentrations, except for

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*Paper based on a presentation at the 31st International Conference on Solution Chemistry (ICSC-31), 21–25 August 2009, Innsbruck, Austria. Other presentations are published in this issue, pp. 1855–1973.

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EXAFS which is quite short-range, and also reviewed [4]) but pertains to regions beyond them. It is, therefore, necessary to consider first what is exactly meant by *the structure of water* and how this can be expressed quantitatively with regard to the effects of ions on it.

WATER STRUCTURE

The structuredness of liquids has many aspects that transcend those of their molecular structure. The latter is determined by the total pair correlation function $g(r)$, obtained by X-ray and neutron diffraction. The molecular structure is dominated by the strong repulsion of molecules that are too closely packed together. The notion of *structuredness* [5–7] relates to more subtle interactions characterizing bulk properties of a liquid.

Water is a very stiff liquid, the *stiffness* being measured by the difference between the cohesive energy density and the internal pressure: $[\Delta_{\mathrm{vap}}H - RT]/V - [T\alpha_{\mathrm{P}}/\kappa_{\mathrm{T}} - p]$. The liquid is characterized by its molar enthalpy of vaporization $\Delta_{\mathrm{vap}}H$, molar volume V, isobaric expansibility α_{P}, isothermal compressibility κ_{T}, and vapor pressure p. Water has a stiffness value of 2129 MPa at 25 °C, much beyond other liquids [5].

Water is a highly *ordered* liquid, having $\Delta\Delta_{\mathrm{vap}}S/R = 7.94$, the criterion for order being $\Delta\Delta_{\mathrm{V}}S/R > 2$ [5,6]. This measure is the non-dimensional difference between the molar entropy of vaporization of a liquid, $\Delta_{\mathrm{vap}}S$, and an iso-skeletal alkane, deemed unordered, corrected for the corresponding non-ideality of the vapors: $\Delta\Delta_{\mathrm{V}}S/R = [\Delta_{\mathrm{V}}S_{\mathrm{liquid}} - \Delta_{\mathrm{V}}S_{\mathrm{alkane}}]/R + (P°/R)\cdot \mathrm{d}(B_{\mathrm{liquid}} - B_{\mathrm{alkane}})/\mathrm{d}T$, where B is the second virial coefficient.

The *heat capacity density* of the liquid relative to the ideal gaseous substance [5,6]: $\Delta C_{\mathrm{P}}/V = [C_{\mathrm{P}}(\mathrm{l}) - C_{\mathrm{P}}(\mathrm{i.g.})]/V(\mathrm{l})$ is a further measure of structuredness. On heating, energy is consumed by reordering the liquid molecules beyond what is going into internal degrees of freedom. Water has $(\Delta C_{\mathrm{P}}/V)/\mathrm{J\ K^{-1}\ cm^{-3}} = 2.32$, considerably larger than 0.6, the minimal value of other structured liquids.

These features mark water as an outstandingly structured liquid. Other features, though, do not support such a claim, but still include water among structured solvents.

The Kirkwood *dipole orientation correlation parameter* $g = (9k_{\mathrm{B}}\varepsilon_0/N_{\mathrm{A}})VT\mu^{-2}(\varepsilon_{\mathrm{r}} - n_{\infty}^2)(2\varepsilon_{\mathrm{r}} + n_{\infty}^2)/\varepsilon_{\mathrm{r}}(2 + n_{\infty}^2)^2$ is a measure of the structuredness of a dipolar liquid. It depends on the dipole moment, μ, the relative permittivity, ε_{r}, and the square of the infinite frequency refractive index, n_{∞}^2, of the liquid. Water has at 298.15 K the value $g = 2.57$, by no means outstandingly large, since the criterion for ordered liquids is $g > 1.7$ [5,7].

Water is a close-packed, contrary to an open, liquid, the *openness* being the fraction of free volume, $(1 - V_{\mathrm{X}}/V)$ available. The intrinsic volume [8] of water is $V_{\mathrm{X}} = 16.7\ \mathrm{cm^3\ mol^{-1}}$, and its molar volume at 25 °C is $V = 18.07\ \mathrm{cm^3}$. Hence, the openness is only 0.092, compared with most liquids, for which $(1 - V_{\mathrm{X}}/V) > 0.1$. The close-packed nature of water is also reflected by its low compressibility compared with other liquids.

All these criteria of structuredness diminish in magnitude as the temperature of the water is increased. There is general agreement that what does make water rather distinctive among liquids is the pronounced three-dimensional hydrogen bond network that characterizes it at ambient conditions. What is still controversial is the quantitative expression of the extent of this hydrogen bonding, in particular the average number of hydrogen bonds that a water molecule participates in. In order to determine this number, a definition of an intact, contrary to a broken or non-existing, hydrogen bond is required.

Definite criteria for an intact hydrogen bond in water are geometrical and energetic ones. Several such have been suggested [9,10], and for the following the angle of the O–H···O configuration is specified to be $\theta \geq 130°$, the distance to be $d_{\mathrm{O\cdots H}} \leq 0.24$ nm, and the energy to be $e_{\mathrm{HB}} < -12.9\ \mathrm{kJ\ mol^{-1}}$. It is possible to distinguish between *strong* hydrogen bonds, for which $d_{\mathrm{O\cdots H}} \leq 0.21$ nm, and *weak* ones at a longer distance. Quantum mechanical and molecular dynamics (MD) computations by Xenides et al. [9] for ambient conditions resulted in 1.81 strong and 1.29 weak, together 3.1 hydrogen bonds which each water molecule participates in on the average. This is in agreement with between 3.2 and 3.4

hydrogen bonds per water molecule from MD computations employing SPC/E water of Kumar et al. [10]. The *extent* of hydrogen bonding, that is, the number of hydrogen bonds per mole of water molecules, is $N_A/2$ times this average number, because each hydrogen bond connects two water molecules.

Over 20 years ago, the average number of hydrogen bonds per water molecule was estimated by Marcus and Ben-Naim [11] from experimental measurements involving the comparison of the properties of H_2O and D_2O. The molecular parameters of these two isotopic forms of water are very similar, but the strengths of the hydrogen bonds differ. The molar sublimation enthalpies of the ices of H_2O and D_2O to form dilute vapors (assumed to be ideal gases) correspond to complete breaking of all the hydrogen bonds. Each water molecule in ice is hydrogen-bonded to four neighboring molecules, and in each hydrogen bond two molecules are bound, so that $N_A/2$ hydrogen bonds are involved per mole of ice. Hence:

$$[\Delta_{\text{subl}}H(\text{D}_2\text{O,cr}) - \Delta_{\text{subl}}H(\text{H}_2\text{O,cr})] = (N_A/2)[e_{\text{HB}}{}^{\text{D}} - e_{\text{HB}}{}^{\text{H}}] \quad (1)$$

where superscripts D and H stand for D_2O and H_2O. 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 and the value of $\Delta^{\text{HD}}e_{\text{HB}} = e_{\text{HB}}{}^{\text{D}} - e_{\text{HB}}{}^{\text{H}}$ obtained from the ices is assumed to be valid also for liquid water.

According to statistical thermodynamic arguments [11], the difference in the molar Gibbs energy of condensation, $\Delta_{\text{cond}}G = RT\ln(p_{\text{sat}}V/RT)$, of water of each isotopic kind is proportional to the average number of hydrogen bonds per water molecule, $<\psi>^{\text{HD}}$, prevailing in liquid "mean water":

$$\Delta^{\text{HD}}\Delta_{\text{cond}}G = (N_A/2)\,\Delta^{\text{HD}}e_{\text{HB}} \cdot <\psi>^{\text{HD}} \quad (2)$$

The required quantity, $<\psi>^{\text{HD}}$, is obtained from the experimental data on combination of eqs. 1 and 2. At room temperature, 25 °C, the resulting number $<\psi>^{\text{HD}} = 1.84$ corresponds to the strong hydrogen bonds characterized by $d_{\text{O}\cdots\text{H}}/\text{nm} \le 0.21$ in the computer simulations [9]. The decreasing values of $\Delta^{\text{HD}}\Delta_{\text{cond}}G$ as the temperature is raised lead to diminishing values of the average number of hydrogen bonds per water molecule, $<\psi>^{\text{HD}}$, and the resulting extent of hydrogen bonding in liquid water.

Data for tritiated water, T_2O, permitted the evaluation [11] of the individual $<\psi>^{\text{H}}$ and $<\psi>^{\text{D}}$, the latter being 8–17 % larger than the former over the temperature range of the existence of liquid water at ambient pressures. This is in agreement with the general notion that heavy water, D_2O, is more strongly hydrogen-bonded (structured) than light water, H_2O.

EFFECTS OF IONS ON THE STRUCTURE OF WATER

Once the structure of water is expressed as the extent of hydrogen bonding, the effect of ions on the structure means the enhancement or diminution of this extent. This has been described in quantitative terms in some cases, although mostly only the trends have been reported. The following discussion is confined to such trends in dilute solutions of electrolytes in water.

Dynamic effects

As mentioned in the introduction, it was established long ago that some ions enhance and others diminish the relative viscosity of aqueous solutions, η/η^*. Cox and Wolfenden [12] were the first to mention the notion of water structure in this connection, but the terms "structure making" and "structure breaking" are attributed to Gurney [13]. The Jones–Dole B-coefficient is the quantitative measure of his effect:

$$[(\eta/\eta^*) - 1] = A_\eta c^{1/2} + B_\eta c + \cdots \quad (3)$$

The A_η coefficients can be calculated from the conductivity of the salts and the B_η values are the limiting slopes of $[(\eta/\eta^*) - 1]/c^{1/2}$ vs. the square root of the concentration, $c^{1/2}$. They thus pertain to infinite dilution, and are additive in the values for the constituent ions. They are commonly split into ionic values on the assumption that $B_\eta(K^+) = B_\eta(Cl^-)$. Local loosening of the water structure near ions with $B_\eta < 0$ (such as Cs^+ and I^-) deems them as "structure breaking" and ions tightening the hydrogen bonding having $B_\eta > 0$ (such as Li^+ and acetate) were designated as "structure making" [13]. Jenkins and Marcus [14] critically selected B_η values for over 70 aqueous ions from published data. It should be noted that the few data available for the ionic B_η values in heavy water, which is more structured than ordinary water (see above), are even more negative for structure-breaking ions than in light water.

Alas, no satisfactory theory has been developed so far to account for the observed behavior in spite of several attempts to do so. The mechanism by which the ions, given their water-structure-modifying behavior, affect the signs of B_η and dB_η/dT has not yet been established. Although positive B_η could be accounted for by, say, the Einstein relation $[(\eta/\eta^*) - 1] = 2.5v$ (v is the volume of the solute particles per unit volume of the solution), no plausible theory for negative values was proposed.

A rough consideration of the relative sizes of ions and the average sizes of void spaces in water, $(V - V_X)/N_A = 0.00227\ \text{nm}^3$, is instructive. Cavities to accommodate a moving ion need to be several times larger than the average void space. Indeed, all cations with volumes $(4\pi/3)r_{ion}^3 > 0.010\ \text{nm}^3$ have $B_\eta < 0$ and are structure breaking and those with $(4\pi/3)r_{ion}^3 < 0.007\ \text{nm}^3$ have $B_\eta > 0$ and are structure making. For anions, the magnitude of the charge also plays a role, so that the border between structure making and breaking lies at $(4\pi/3)r_{ion}^3/|z| \sim 0.02\ \text{nm}^3$. The relatively high viscosity of water is due to its hydrogen-bonded network that must be disrupted dynamically for water or the solution to flow. Ions that are too large for moving into a randomly available hole near it need to destroy some of the hydrogen-bonded structure of the water in order to create a cavity sufficiently large to move into it and thus accelerate the flow of the solution, accounting for negative B_η values. Small ions enhance the hydrogen bonding through their electric fields and therefore slow down the rate of flow.

Samoilov [15] obtained the ratio 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 ($\tau_W = 1.7$ ns), from the activation Gibbs energy of exchange of water molecules between bulk water and the hydration shells of ions, $\Delta G^\ddagger_{exch}$. This was obtained in turn from the temperature coefficients of the self-diffusion coefficient of water, D_W, and of the ion mobility, u_{ion}. Some ions, such as Li^+, Na^+, Mg^{2+}, and Ca^{2+}, have $\Delta G^\ddagger_{exch} > 0$ and $\tau_{ion} > \tau_W$ and were called "positively hydrated". For some other ions: K^+, Cs^+, Cl^-, Br^-, and I^-, $\Delta G^\ddagger_{exch} < 0$ and $\tau_{ion} < \tau_W$ and they were designated as "negatively hydrated". These terms are not in general use now, however, but the relation of the residence times to the dynamic extent of hydrogen bonding in the solution is apparent. It should be noted that the residence time of a water molecule in the vicinity of another one, 1.7 ns [15], is much longer than the mean residence time of electrons between the oxygen atom and a nearby hydrogen atom in a configuration producing a hydrogen bond (measurable in ps [9]).

Much more significant are the NMR longitudinal proton relaxation times in aqueous electrolyte solutions, T_{1ion}, in comparison with those in neat water, T_{1W}, according to Engel and Hertz [16]. An expression analogous to eq. 3 pertains to the results

$$[(1/T_{1ion})/(1/T_{1W}) - 1] = B_{nmr}c + \cdots \tag{4}$$

and the convention that $B_{nmr}(K^+) = B_{nmr}(Cl^-)$ is used to obtain the ionic values. The rotational correlation times of the water molecules are $\tau_{ion}/\tau_W = 1 + (55.51/n_{ion})B_{nmr}$, where n_{ion} is the hydration number of the ion. With ions being classified according to Samoilov's notions [15], Engel and Hertz [16] showed that $B_{nmr} > 0$ pertains to structure-making ions and $B_{nmr} < 0$ for structure-breaking ones. They also demonstrated the good correspondence between these B_{nmr} values and the ionic B_η values from the viscosities. More recently, Yoshida et al. [17] obtained B_{nmr} values from the ^{17}O NMR spin-lattice relaxation of D_2O molecules in aqueous salt solutions in good agreement both in sign and generally in magnitude with the ^1H B_{nmr} values of Engel and Hertz [16] and the viscosity B_η values [14].

The B_η and B_{nmr} values pertain to dilute solutions and are not confined to effects within the hydration shells of the ions. Other measurements were made at moderate concentrations but indicate the same trends. Dielectric relaxation spectroscopic data were analyzed by Kaatze [18], who presented the ratios of the cooperative reorientation times of water molecules near ions in 1 M solutions, τ_{Wh}, to that of pure water, $\tau_W^* = 8.27 \pm 0.02$ ps. More recently, Wachter et al. [19] obtained these reorientation times from dielectric relaxation also at lower salt concentrations, c. Values of the b-coefficient in the expression

$$\tau_{Wh}(c) = \tau_W^* + a[\exp(-bc) - 1] \tag{5}$$

are characteristic for the effects of the anions in various sodium salt solutions: 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, and Na_2SO_4 1.8. The anions range from structure makers to structure breakers, but no attempt was made to separate the cation and anion effects.

Thermodynamic data

Various thermodynamic properties of aqueous electrolyte solutions have been employed for the deduction of the effects of their ions on the structure of water. Frank and Evans [20] suggested that the entropies of hydration of ions provide an approach for deciding on their structure-making or -breaking properties. Gurney [13] demonstrated a linear relationship between the partial molar entropy of aqueous monatomic ions and their viscosity B_η coefficients. Nightingale [21] subsequently generalized this to all kinds of ions by using the entropies of hydration, $\Delta_{hydr}S^\infty$, rather than the partial molar entropies of the aqueous ions.

The effects of ions on the structure of the water were obtained by several authors [22–25] from that part of $\Delta_{hydr}S^\infty$ that remains after deducting other entropic effects of ion hydration. Krestov [22] considered that the water-structure-modifying entropic effect, ΔS_{struc}, requires the deduction from $\Delta_{hydr}S^\infty$ of the contributions of the formation of the ionic hydrate shell and, for polyatomic ions, the limitation of the ionic rotational entropy. The former corresponds to the translational entropy loss on dissolution in water of inert gas atoms isoelectronic with monatomic ions, $0.615S^\circ_{transl}$. The rotational entropy loss, however, was an unknown numerical coefficient. The low-temperature *positive* values of ΔS_{struc}, characterizing structure-breaking monatomic ions, changed sign to *negative* ones over the temperature range 15–65 °C at a definite temperature, called the limiting temperature [23]. This was explained by the decreasing inherent structure of the water as the temperature was raised so that there remains less structure to be broken.

Abraham et al. [24] obtained ΔS_{struc} by deducting the contributions of a neutral part, ΔS_n, and the bulk water dielectric effect, ΔS_{el}, from the standard molar entropy of hydration of the ions, $\Delta_{hydr}S^\infty$. The former was estimated from the $\Delta_{hydr}S^\infty$ values for nonpolar solutes having radii similar to those of the ions, r_{ion}. 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:

$$\Delta S_{el} = (N_A e^2/8\pi\varepsilon_0)z^2\,(r_{ion} + d_W)^{-1}\,\varepsilon_r^{-1}(\partial\ln\varepsilon_r/\partial T)_P \tag{6}$$

A more recent development of this concept for ΔS_{struc} that indicates the water structural effects of ions is due to Marcus [25]. It is based on a model considering the electrostricted water layer surrounding the ions where dielectric saturation takes place. The water molecules have there a volume $\pi d_W^3/6$ rather than V_W/N_A, so that Δr, the width of the electrostricted hydration shell is given by

$$(4\pi/3)[(r_{ion} + \Delta r)^3 - r_{ion}^3] = n\cdot\pi d_W^3/6 \tag{7}$$

with the hydration number $n = 0.36|z|/(r_{\text{ion}}/\text{nm})$ and $d_{\text{W}} = 0.276$ nm. Then the structural entropy is obtained from $\Delta S_{\text{struc}} = \Delta_{\text{hydr}}S^{\infty} - [\Delta S_{\text{nt}} + \Delta S_{\text{el 1}} + \Delta S_{\text{el 2}}]$, where the neutral term ΔS_{nt} takes care of the entropic effect of the creation of a cavity in the water to accommodate the ion and the compression entropy from the gaseous to the solution standard states. The electrostatic effects are

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

$$\Delta S_{\text{el 2}} = (N_{\text{A}}e^2/8\pi\varepsilon_0)z^2\,(r_{\text{ion}} + \Delta r)^{-1}\,\varepsilon_{\text{r}}^{-2}(\partial\varepsilon_{\text{r}}/\partial T)_P \tag{8b}$$

the former pertaining to the electrostricted hydration shell, where the permittivity and its temperature derivative are $\varepsilon' = n_{\text{D}}^2 = 1.776$ and $(\partial\varepsilon'/\partial T)_P = -1 \times 10^{-4}\ \text{K}^{-1}$ at 25 °C, n_{D} being the refractive index of water. This treatment was applied to aqueous cations and anions, with charges $-4 \le z \le 4$. The linear correlation with the viscosity B_{η} is

$$\Delta S_{\text{struc}}/\text{J K}^{-1}\ \text{mol}^{-1} = 20(z^2 + |z|) - 605(B_{\eta}/\text{dm}^3\ \text{mol}^{-1}) \tag{9}$$

using absolute entropies of hydration based on $S^{\infty}(\text{H}^+, \text{aq}) = -22.2\ \text{J K}^{-1}\ \text{mol}^{-1}$.

A quite different approach to obtaining the structural effect of ions from thermodynamic data considers their standard molar Gibbs energies of transfer from light to heavy water, as mentioned in the Introduction. According to Ben-Naim [26], the pair potential between the molecules in water is the sum of a term that describes both the repulsion and multipole attractive interactions and another that describes the hydrogen bonding. The latter is the product of the hydrogen bond energy e_{HB} and the geometrical factor $0 \le G_{\text{HB}} \le 1$, specifying whether a hydrogen bond exists or not. The standard chemical potential of a solute particle S introduced into light and heavy water is different, the difference, $\Delta\mu_{\text{S}}^{\infty\text{HD}} = \Delta_{\text{t}}G^{\infty}(\text{S}, \text{H}_2\text{O} \to \text{D}_2\text{O})/N_{\text{A}}$, depends solely on changes in the hydrogen bonding structure of the water caused by S:

$$\Delta\mu_{\text{S}}^{\infty\text{HD}} = \Delta^{\text{HD}}e_{\text{HB}}\cdot\Delta G_{\text{HB}} \tag{10}$$

Here $\Delta^{\text{HD}}e_{\text{HB}}$ is, as above, the difference in the strengths of the hydrogen bonds in D_2O and H_2O obtained from the sublimation enthalpies of the ices and ΔG_{HB} is the change in the average total geometrical factors over all the configurations of the water molecules of either kind caused by the introduction of a particle of S. The left-hand side of eq. 10 is an experimentally obtained quantity from measured solubilities, EMF data, etc., hence ΔG_{HB} can be determined.

This treatment was applied to ionic solutes by Marcus and Ben-Naim [11], the best description of the structure of water being in terms of the average number of hydrogen bonds per water molecule $\langle\psi\rangle^{\text{HD}}$ (see above) for expressing $\Delta G_{\text{HB}} = \Delta\mu_{\text{S}}^{\infty\text{HD}}/\Delta^{\text{HD}}e_{\text{HB}}$. The experimentally available $\Delta_{\text{t}}G^{\infty}(\text{S}, \text{H}_2\text{O} \to \text{D}_2\text{O})$ data for electrolytes are small and rather unsatisfactory, $\Delta_{\text{t}}G^{\infty}(\text{S}, \text{H}_2\text{O} \to \text{D}_2\text{O})/\text{J mol}^{-1}$ ranges from –950 for S = Bu_4N^+ to 1200 for S = Ba^{2+} at 25 °C with probable errors of ±100 [3]. Still, trends in the values for some salts are obvious, as shown in the Introduction for KClO_4 and LiF. From the sublimation enthalpies of the isotopically labeled ices, eq. 1, $\Delta^{\text{HD}}e_{\text{HB}} = -742\ \text{J mol}^{-1}$ at 25 °C. The "best" ionic values of ΔG_{HB} derived from eq. 10, based on equalizing the values for Ph_4As^+ and BPh_4^-, and incidentally also for K^+ and Cl^-, were summarized by Marcus [3]. The better-established values of ΔG_{HB} for the nine alkali metal and halide ions correlate with well-established quantities describing the water structural effects of ions, such as B_{η} and ΔS_{struc}. The resulting expressions are

$$\Delta G_{\text{HB}} = -(0.68 \pm 0.14) + (5.95 \pm 1.74)(B_{\eta}/\text{M}^{-1})/|z| \tag{11}$$

$$\Delta G_{\text{HB}} = -(0.18 \pm 0.08) - (10.22 \pm 1.26) \times 10^{-3}(\Delta S_{\text{struc}}/\text{J K}^{-1}\ \text{mol}^{-1}) \tag{12}$$

The standard errors of the fits are 0.2 to 0.3 units. Such dimensionless ΔG_{HB} values can then be generated for more ions from the known water structural effects such as the viscosity B_{η} coefficient and the structural entropy ΔS_{struc}. They do not convey more information than the latter two, but have the form suggesting the theoretical basis provided by Ben-Naim [26], in terms of the effect of the ions on the extent of hydrogen bonding in dilute electrolyte solutions.

Spectroscopy

Raman spectroscopy was employed very early to infer the effect of ions on the structure of water by Kujumzelis [27], who concluded that the hydrogen bonds between water molecules are more or less distorted by the ions. Raman spectroscopy was subsequently used by Holba [28] for the same purpose with 6 M HOD in D_2O in the presence of dissolved salts. The intensity ratios of the 6427 and 7062 cm^{-1} absorption bands for 1 M salt solutions normalized to that in the absence of salt, R_N, are the criteria for the effect: $R_N < 1$ denotes structure breaking and $R_N > 1$ structure making. The R_N values increase in the following sequence: 0.644 for $K_3Fe(CN)_6$, 0.725 for $Na_2S_2O_8$, 0.766 for $NaClO_4$, 0.877 for KSCN and NaSCN, 0.932 for KCl, 0.939 for NaN_3, 0.944 for NaCl, 1.016 for Li_2SO_4, 1.095 for Bu_4NBr, and 1.109 for $MgSO_4$, but no attempt to assign values to individual ions was made.

Raman spectroscopy was also used more recently by Li et al. [29] to study the hydrogen-bonded structure of water in the presence of sodium halide salts at various temperatures. The two higher wavenumbers for the O–H stretching vibration were assigned 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. The authors showed that at 20 °C F^- does not affect the Raman spectrum appreciably, but Cl^-, Br^-, and I^- ions do so in increasing manner, in the direction of further breaking the ice-like hydrogen bonding, as expected. However, in a very recent paper Smith, Saykally, and Geissler [30] 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 that the difference in the spectra of the salt solutions relative to water arise primarily from the electric fields rather than from rearrangement of the hydrogen bonds beyond the first hydration shell.

Choppin and Buijs [31] considered long ago a model where the near-infrared absorption bands in aqueous electrolyte solutions corresponded to water molecules with none, one, or two hydrogen bonds. They interpreted their data by assigning water-structure-making properties to La^{3+}, Mg^{2+}, H^+, Ca^{2+}, OH^-, and F^- and structure-breaking properties to K^+, Na^+, Li^+, Cs^+, Ag^+, ClO_4^-, I^-, Br^-, NO_3^-, Cl^-, and SCN^-. Recently, Nickolov and Miller [32] applied FTIR spectroscopy for analyzing the O–D stretching vibration in dilute HOD in H_2O to study the water structure effects of KF, CsF, NaI, KI, and CsCl. They inferred water structure breaking from the narrowing and shifting of the 2380 cm^{-1} band 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.

Ultrafast two-color mid-infrared spectroscopy was recently used by Bakker et al. in a series of papers [33] 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. A slow component was seen in the decay curves of some alkali metal halide solutions, increasing with the anion mass [33]. The derived hydrodynamic radii of the halide anions were found, however, to be smaller than the well-established anion-water hydrogen bond lengths, opening the results to questions.

Results specific to the O–H group hydrogen-bonded to the perchlorate anion were also obtained by Bakker et al. [34]. The orientational correlation times for bulk water molecules were deduced from the decay of the anisotropy parameter, being independent of the salt concentration and the same as for pure water. The general conclusion that "ions do not enhance or break the hydrogen bond network outside their vicinity (probably their first solvation shell)" was drawn. However, this sweeping conclusion does not explain enhanced mobilities of water molecules in solutions with structure-breaking ions nor negative B_η values.

A further difficulty with the reported conclusions [33,34] is that the solutions studied were at least 0.5 M, for which the average distance apart of the centers of the ions is ≤1.18 nm [35], there being very little free water between their hydration shells. Hence, the conclusions from the ultrafast vibrational spectroscopy cannot be readily extended to the case of dilute solutions, dealt with here.

Näslund et al. [36] applied X-ray absorption (XAS) and X-ray Raman scattering (XRS) at the oxygen K edge to water and aqueous NaCl and KCl. A significant decrease of the fraction of tetrahedrally coordinated water, with a range of hydrogen bond distances and angles, was found. These experiments, however, were not sufficiently sensitive to determine to what spatial extent the effect occurs. Recent application of these methods to water, rather than to salt solutions, was used to study the number of donor and acceptor hydrogen bonds each water molecule is engaged in. This aspect of water structure is still controversial [37,38] and requires back-up by theoretical calculations and computer simulations.

Computer simulations

Computer simulations for studying ion effects on water structure have two advantages over diffraction and spectroscopic studies: they consider individual ions and they can be applied to dilute solutions, having water-to-ion ratios up to 500:1. However, no ultimate method has yet emerged from the numerous ones employed. Classical MD has been criticized for ignoring many-body interactions, and several potential functions have been used, describing rigid and polarizable water molecules. Semi-empirical methods based on density functional theory differ with respect to the functional used, e.g., Car–Parrinello, BP86, or B3LYP. Quantum mechanical (QM) simulations have used different levels of theory and base sets, e.g., HF ab initio ones or various approximations.

Monte Carlo simulations by Bernal-Uruchurtu and Ortega-Blake [39] of Mg^{2+} at water-to-ion ratios up to 480:1 showed a well-formed second hydration shell, the water molecules being oriented not only by those in the first shell but also by those outside it. Thus, an indication of the presence of a third hydration shell was obtained, demonstrating the structure-making properties of this small doubly charged ion.

MD computer simulations have the advantage over the Monte Carlo method in that they permit the study of the dynamics of the particles in aqueous electrolyte solutions. Geiger [40] computed the mobility (self-diffusion coefficient, D_W) of water molecules around particles of the size of a xenon atom with 215 water molecules/particle with discretely varying charges: 0, +0.67, +1, +2, and –1 charge units. For lightly charged, +0.67 and +1, cations Geiger found the mobility ratios for water near the ion, $D_{W near}/D_{W\ bulk}$, 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. What is significant in the present context is that the effect persists also beyond the hydration shell. A similar effect was noted for the reorientation times of the *inter*molecular 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. This, again, indicates water-structure-breaking and -making effects of the corresponding ions.

The results of the MD simulations depend on the model potential functions employed. Thus, Geiger [40] employed ST2-water, but later workers used more sophisticated models. The average residence times of water molecules near ions, τ_{resid}/ps, were obtained with the SPC/E water model and compared with 10 ± 1 for water molecules near each other in the bulk at 25 °C. The results of Chowdhuri and Chandra [41] were: Na^+ 18.5, K^+ 7.9, and Cl^- 10, those of Guardia et al. [42] were: Li^+ 101, Na^+ 25.0, K^+ 8.2, Cs^+ 6.9, F^- 35.5, Cl^- 14.0, and I^- 8.5. It is clear that in this respect K^+ and Cl^- have little effect on the structure of water, Cs^+, and I^- break it, and Li^+, Na^+, and F^- enhance it.

For the region near an ion in dilute aqueous solution, ab initio QM methods and for regions farther away MD methods may profitably be employed, in order to reduce computation time. Recent simulations by Rode and co-workers [43] of aqueous Cs^+ solutions at a water-to-ion ratio of 499:1 and 25 °C compared three QM methods. The characteristic reorientational and rotational times of water molecules in the presence of Cs^+ are considerably smaller than for pure water. The number of water molecule exchange events per 10 ps is double than in pure water, demonstrating the structure-breaking effect of this large univalent cation. The corresponding study [44] of the dynamics near Tl^+ showed even shorter reorientation times than near Cs^+, an effect persisting beyond the first shell. Tl^+ was deemed the "best" water structure breaker of the ions examined so far, including also Rb^+ [45] and Au^+ [46].

CONCLUSIONS

The effects of ions on the structure of water have been the subject of extensive research for many decades. One wonders, therefore, that in 2003 a paper with the sweeping title "Negligible effects of ions on the hydrogen bond structure in liquid water" was published in *Science* [47]. This paper, negating ion effects on the re-orientation dynamics of water molecules outside the first hydration shell of the ions studied, has a misleading title. Only a limited aspect of the general problem of the effects of ions on the hydrogen-bonded water structure was dealt with. Several authors subsequently countered the interpretation of the experimental results [33,34,47] with data and arguments [19,36,48–50]. Anyway, only the effects of ions on the reorientation dynamics were challenged by the ultrafast spectroscopy [47], not necessarily the static amount of water structural effects. Also, when experimental determinations require relatively small water-to-ion ratios [33,34,47], the overlap of the hydration shells of the ions and counter-ions must be reckoned with, concomitant with the lack of any "bulk water" [35]. In dilute solutions, on the contrary, macroscopic water structure effects of ions are noted from dynamic, thermodynamic, and computer simulation studies that concern the water *outside* the hydration shells. Water-structure-breaking effects by some large, univalent ions demonstrated by such results cannot be explained away.

Table 1 Effects of some representative ions on the structure of water as obtained from the viscosity B_η-coefficients [14], the structural entropies of hydration, $\Delta_{\text{struc}}S$ [25], and the geometrical factor for ion transfer between light and heavy water, ΔG_{HB}.

Ion	B_η/dm^3 mol^{-1}	$\Delta_{\text{struc}}S$/J K^{-1} mol^{-1}	ΔG_{HB}
	Water-structure-breaking ions		
I^-	–0.073	117	-1.2_5
ClO_4^-	–0.058	107	-1.1_5
Cs^+	–0.047	68	–0.9
Br^-	–0.033	81	-0.9_5
SCN^-	–0.022	83	–0.9
K^+	–0.009	47	–0.7
Cl^-	–0.005	58	–0.7
NH_4^+	–0.008	5	–0.5
	Borderline cases		
SO_4^{2-}	0.206	8	0.0
Na^+	0.085	–14	–0.1
Ag^+	0.090	–15	–0.1
Ba^{2+}	0.216	–18	0.1_5
	Water-structure-making ions		
F^-	0.107	–27	0.1
OH^-	0.122	–51	0.2
Li^+	0.146	–52	0.3
CO_3^{2-}	0.294	–52	0.4_5
Ca^{2+}	0.284	–59	0.4_5
Mg^{2+}	0.385	–113	0.9
La^{3+}	0.582	–113	0.9_5
PO_4^{3-}	0.590	–131	1.0_5

In conclusion, then, ions are classified, as shown in Table 1, into groups with water structure effects ranging from strong structure breaking to strong structure making [4], as 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. It should be stressed that the effects noted in dilute homogeneous salt solutions do not bear directly on effects observed near surfaces, including those of macromolecules, such as proteins, although there is some similarity of the Hofmeister series with the classification in Table 1.

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