WATER

Planets, Plants and People

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WATER — A UNIQUE LIQUID

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Introduction

From the point of view of mankind, water is certainly the most important simple substance in the world. It is a very general and powerful solvent so that the oceans, which account for more than 99 percent of Earth's water, have a large solute content. At the same time Earth's ice caps contain something like 30 million cubic kilometres of ice with an impurity content measured in parts per million. The Earth's weather and the erosive processes which determine its surface topography both arise from the fact that phase changes between the solid, liquid, and vapour states of water can readily occur. And finally, most biological processes take place in a cellular environment of which liquid water is the main constituent.

It is of course possible to take the view that water plays this ubiquitous role simply because of the astronomical chance which made it the only abundantly occurring liquid on Earth's surface. On the other hand so many geophysical and biological processes depend so critically upon the unique properties of water that the substitution of any other liquid would either prevent them occurring or at least modify them almost beyond recognition.

My object in this symposium is to discuss some of the unique properties of water, to show how they derive from the structure of the water molecule, and thus to set the stage for the detailed discussions that follow on the role of water in geophysical, biological, and social systems.

The Water Molecule

The water molecule, H_2O, is relatively simple, with only three nuclei and ten electrons, but all the properties of ice and water and all the special attributes which make water unique are implicit in its structure. A hydrogen atom, of course, has only one electron so that we can write its electronic stucture as H(1s) while an oxygen atom with its eight electrons in a state ready for chemical bonding, can be described as

$$\mathrm{O}\ (1s)^2\ (2s)^2\ (2p_x)^2\ (2p_y)\ (2p_z).$$

The orbitals containing two electrons are already filled and the energy of the whole system is minimized, forming a stable molecule, if one hydrogen atom lies on the y-axis, and the other on the z-axis, forming electron-pair bonds like

$$\psi_{I} = H_{I}(1s) + \lambda O(2p_y)$$
$$\psi_{II} = H_{II}(1s) + \lambda O(2p_z),$$

where the constant λ determines the polarity of the bond. Each of the orbitals ψ_I and ψ_{II} accommodates two electrons of opposite spin.

This picture, which is oversimplified, suggests a triangular molecule with an H—O—H angle of 90° and a "lone-pair" of electrons $(2p_x)^2$ contributing an extra negative charge density along the $\pm x$ axis. In fact because the O—H bonds are somewhat polar in the direction O^-H^+, they repel each other and open out the H—O—H bond angle to about 104°. At the same time this distortion of the electron cloud pushes the lone-pairs towards the "back" of the molecule, mixing in the 2s electrons and giving the molecule a nearly tetrahedral electrical structure with two positive and two negative vertices, as shown in Figure 1(a). Despite this electrical polarity, the electron distribution in the molecule is not very far from spherical with a radius of about 1.4 Å, as shown in Figure 1(b).

The tetrahedral four-charge model of a water molecule is very useful when thinking about interactions between water molecules. For other purposes it is sometimes easier to picture the molecule as having a dipole moment of 1.84 Debyes (6.1×10^{-30}C m) — a moderately large but not unusual value for a small molecule — supplemented by quadrupole and higher moments to allow for deviations from a simple dipole.

Water Molecule Interactions

When water molecules interact, the electrical forces between vertices of opposite electrical polarity completely dominate the behaviour. A water molecule in a condensed phase is therefore almost always surrounded by

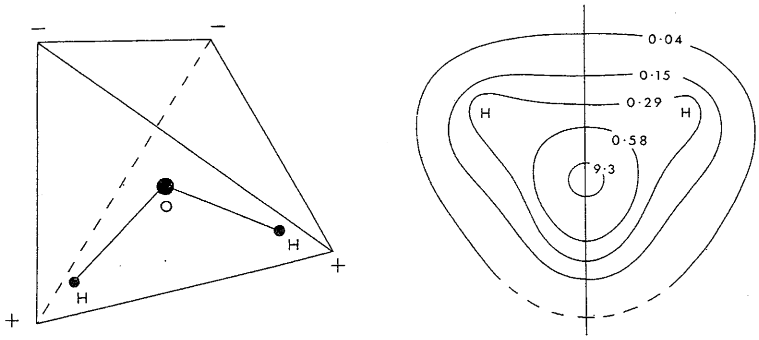

FIGURE. 1 (a) An idealized tetrahedral model for the water molecule. Protons are near the positive vertices and lone pairs near the negative vertices. (b) A more realistic map of electron density in the plane of the nuclei in the water molecule. (The numerical values are in atomic units e/a_0^3).

four nearest-neighbour water molecules making positive to negative vertex bonds. These bonds are drawn as O—H · · · O, where the dots represent the lone pair electrons on the second molecule, and are called hydrogen bonds. Because the hydrogen is stripped of much of its electron cloud it is effectively very small and the O—O distance is only about 2.8 Å. The bonds are cooperative in the sense that a two-bonded molecule is held more than twice as strongly as a one-bonded molecule, so that full four-fold bonding is much the most stable arrangement.

Ordinary ice, as shown in Figure 2, is a good example of the sort of structure that results from this four-fold tetrahedral bonding. The structure, which is related to that of the mineral wurtzite, is the hexagonal

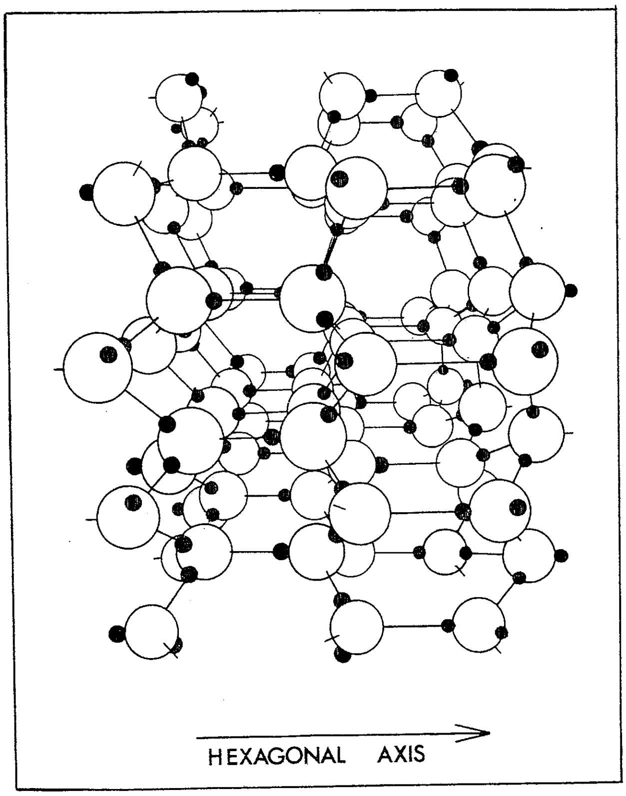

FIGURE 2 The crystal structure of ordinary ice. White spheres represent oxygens and black spheres protons. Each water molecule has four bonds and there is one proton on each bond, but their configuration is disordered. Note the prevalence of six-fold rings and the crinkled molecular layers normal to the hexagonal axis.

analogue of the cubic structure of diamond, silicon, or germanium. It is a very open structure with large cavities and low density compared with a typical rare gas crystal in which the number of nearest neighbours is twelve rather than four. Note the crinkled hexagonal rings that are a feature of the normal ice structure. Each molecule participates in twelve such rings and in none of smaller size. Note also the crinkled layers of molecules normal to the hexagonal axis of the crystal. It is the slow sliding of these layers over one another that is largely responsible for the creep of ice crystals under mechanical stress, and hence for the motion of glaciers.

Because of its open structure, ice tends to collapse under the influence of pressure. For moderate pressures this simply lowers the melting point by about 1 degree per 100 atmospheres but for pressures above 200 atmospheres new and denser crystalline ice phases are produced. Altogether ten crystalline forms of ice are known, including the highest-pressure form which has a melting temperature of 440°C at 200 kbar. Nowhere on Earth, incidentally, even under the Antarctic ice cap, is the pressure large enough to lead to formation of one of these higher ices, though they can be made easily in the laboratory. The important thing is that all these ices maintain complete four-fold hydrogen bonding — the bonds may distort and rearrange but they do not remain broken. We shall see presently that this bonding property is the key to the understanding of the behaviour of liquid water.

A Model for Liquid Water

A liquid does not have a structure in the same sense as does a crystal, for the liquid molecules continually rearrange to new configurations. Typically, however, a molecule in a liquid will make about 100 vibrations of frequency 10^{13} per second before making a diffusional jump to a new configuration. It is therefore possible to speak of a "structure" for the liquid if we confine our attention to a time span of 10^{-12}–10^{-11} s. The new structure formed at a later time will have the same general characteristics but will differ in detailed configuration.

Because of the persistence that the four-fold coordination of water molecules in ice exhibits under quite extreme conditions of temperature and pressure, it is natural to expect that water should maintain a large component of four-fold bonding. However, since water is about 10 percent more dense than ice — an important feature in the freezing of lakes and oceans — then either the cavities in the structure must be reduced in size or else their number must be decreased.

Two extreme models take up these two possibilities. The first supposes that in water very few of the bonds are broken but all of them are distorted to produce non-ice-like structures such as five-fold molecular rings which

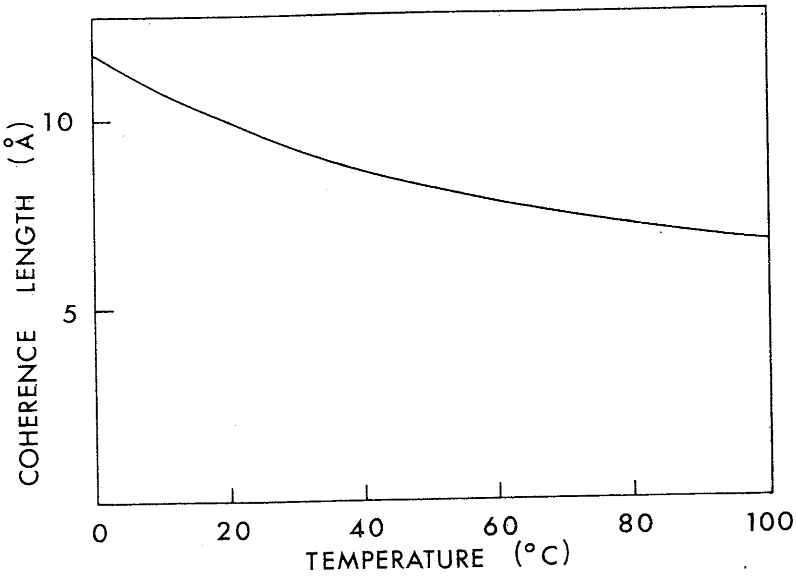

FIGURE 3 Approximate variation of the bonding coherence length in water with increasing temperature, as deduced from various model theories.

effectively reduce the cavity sizes as in the high pressure ices. The second model supposes that some reasonable fraction of the molecules is essentially unbonded, producing a relatively dense simple liquid in which are dispersed more or less ice-like clusters of four-bonded molecules. In each case the detailed bonding geometry changes on a short time scale and the second class of model is aptly described as involving "flickering clusters"

Of course the real picture lies somewhere in between these two extremes. A large fraction of the water molecules maintains four-fold bonding but the bonds are distorted giving non-ice-like structures. At the same time some of the bonds are so distorted that the molecule involved is free to reorient itself and is quite likely to occupy a cavity in the bonded structure.

It is not really correct to talk either of strictly ice-like clusters or simply of bond distortions but it does make sense to introduce a coherence length — that is, the distance over which, on the average, tetrahedral coordination is maintained. This length is about 10 Å near 0°C, corresponding to an effective cluster size of about fifty molecules, and decreases with rising temperature as shown in Figure 3.

These models also account for the peculiar fact — again important in the freezing of lakes and oceans — that water has its maximum density at

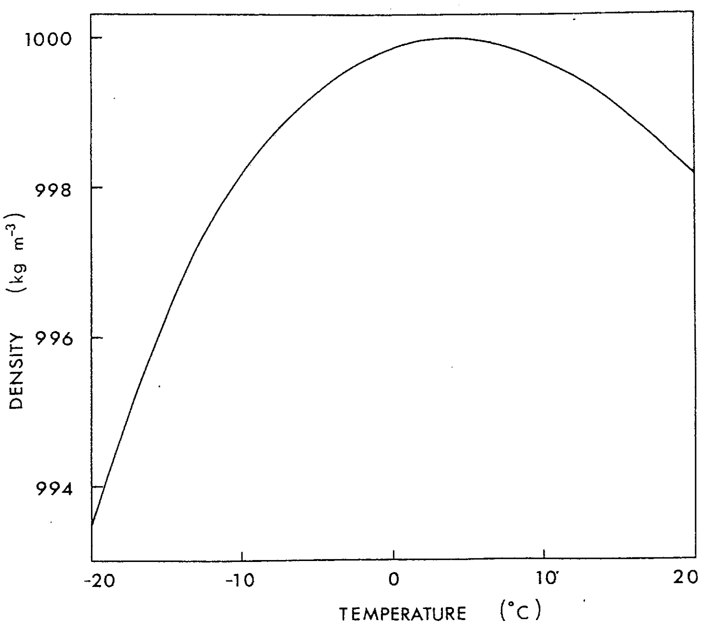

FIGURE 4 Density of water, as a function of temperature, at normal atmospheric pressure. Note the density maximum near 4°C.

a temperature of +4°C, as shown in Figure 4. As water is heated so the extent and symmetry of the tetrahedral coordination decreases and the structure collapses gradually towards a more dense closely-packed arrangement. At the same time the increased vigour of thermal agitation leads to expansion of the whole structure and it so happens that these two effects balance at 4°C under normal atmospheric pressure, giving a density maximum.

Thermal Properties

From a physical point of view the liquid state of water is remarkably stable — and all on account of the extended four-fold bonds that are made possible by the geometry of the water molecule. Figure 5 shows the melting point, the normal boiling point, and the critical temperature for the group of ten-electron hydride molecules Ne, HF, H_2O, NH_3, and CH_4, all of which have nearly the same molecular weight. Clearly the condensed phases of water are much more stable to thermal disruption than are any of the other substances.

Similarly Figure 6 shows the critical pressures of this same group of materials. In fact if we extend the comparison to other materials we find

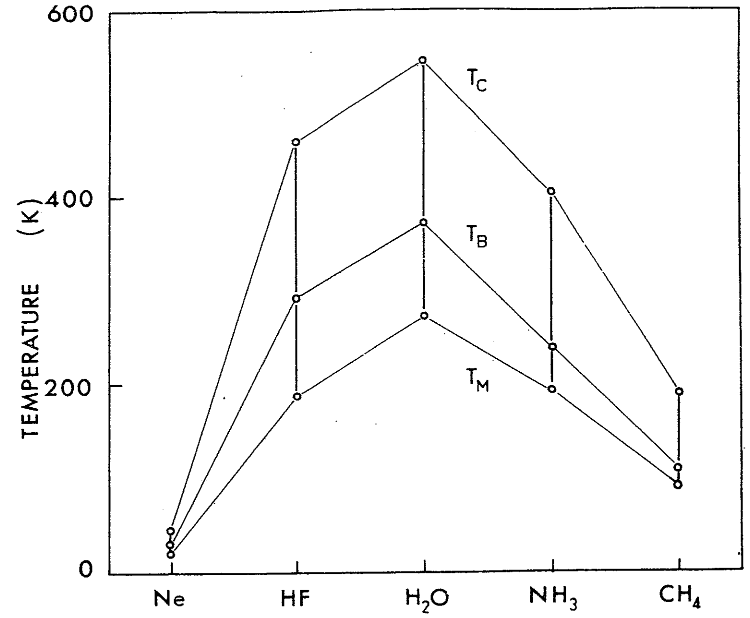

FIGURE 5 The melting temperature T_M, normal boiling temperature T_B, and critical temperature T_C for the simple ten-electron molecules. Note how the four-fold bonding network possible for water extends the range of stability of both solid and liquid phases.

that the critical pressure for water (218 atm) is about twice as large as its nearest rivals iodine (116 atm) and ammonia (112 atm) and three to five times as large as the critical pressure of most other liquids. Again this reflects the stability conferred on the liquid by extensive four-fold bonding even at temperatures near the critical point.

The heat capacity of water is also anomalously large — indeed the specific heat of water (4.2 J deg^{-1} g^{-1}) is exceeded only by that of ammonia (4.6–6.2 J deg^{-1} g^{-1}) at temperatures 0–100°C. Part of this large value is accounted for simply by the small molecular weight and density of the material involved, since all solids have comparable heat capacity per unit volume, but in addition the specific heats of water and liquid ammonia are each nearly twice that of the corresponding solid at its melting point. This unusual circumstance is brought about, in the case of water, by a continual decrease in the extent of four-fold coordination in the liquid as the temperature is raised. This progressive "structural melting" in the liquid accounts for nearly half of its heat capacity with normal vibration energy contributing the other half, as shown in Figure 7.

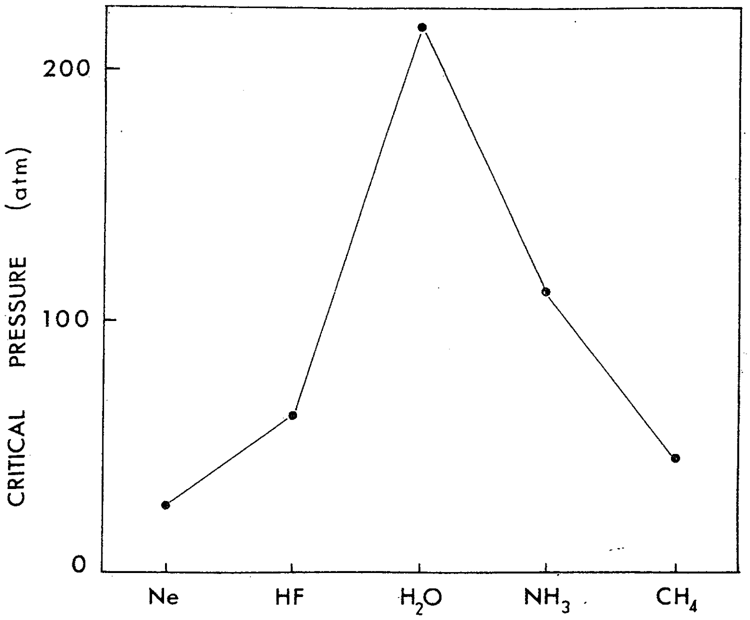

FIGURE 6 Critical pressures for the simple ten-electron molecules. Note the stability of liquid water.

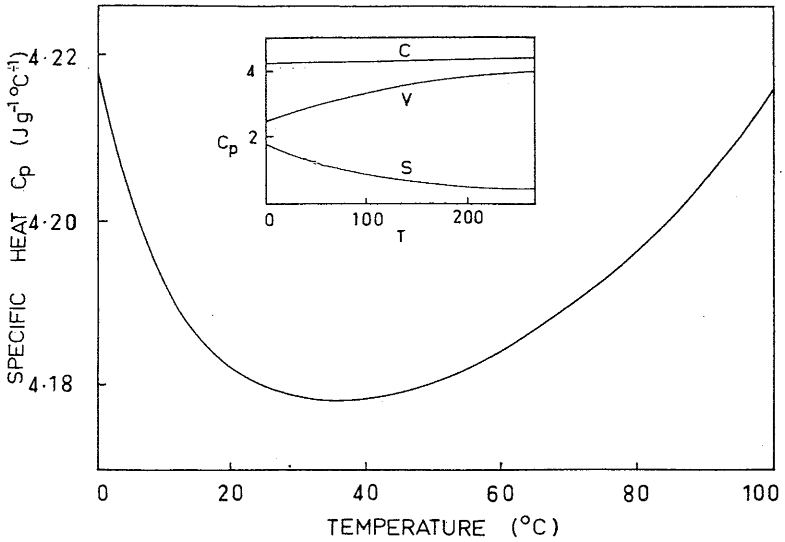

FIGURE 7 Temperature variation of the specific heat of water at constant pressure. The inset shows approximately how the total specific heat *C* is made up from a normal vibrational component *V* and a structural-melting component *S*.

Mechanical Properties

Despite the extensive cooperative bonding in liquid water, the rearrangement of bonding patterns is so rapid ($\approx 10^{-11}$ s) that the viscosity of water (10^{-3} Pa s at 20°C) is very similar to that of other simple liquids. The viscosity of water increases by about 30 percent for a 10°C fall in temperature but there is no approach to a glassy state at low temperatures (though vitreous ice can be made by condensing water vapour below –100°C).

Small quantities of pure clean water can in fact be supercooled well below the equilibrium freezing point before a sufficiently large cluster of molecules finds itself by chance in an exactly ice-like configuration and nucleates the freezing process. The limit to this supercooling has been found to be at a temperature of –41°C or about 0.85 of the absolute melting temperature. This is a value not very different from that characteristic of other simple liquids.

The viscosity of water is, of course, greatly influenced by the presence of solutes like sugar and these solutions can often be supercooled to glasses. I return to discuss solutions later.

Surface tension is another mechanical property of water that is important, particularly in biological systems. The surface tension or surface free energy of water (0.076 J m^{-2} at 0°C) is two or three times larger than that of most common liquids, though ten to one hundred times smaller than the surface tension of liquid metals (where free electrons make a major contribution). The surface tension of water decreases with rising temperature to vanish at the critical point and its large value is associated with bonding in the liquid which means that many bonds must be effectively broken at the surface.

Electrical Properties

Because the water molecule has a large dipole moment (1.84 Debye) it is natural to expect water to have a large dielectric constant. The actual value (88 at 0°C) is, however, surprisingly large and is exceeded among common liquids only by hydrocyanic acid HCN (158 at 0°C) and formamide CH_3NO (109 at 20°C). The explanation is that in water, as in these few other materials, there is substantial hydrogen bonding between neighbouring molecules in the liquid. Thus when one molecule is oriented by an electric field it imposes part of this orientation upon a whole cluster of neighbours as shown in Figure 8, and greatly magnifies the dielectric effect. It is worth noting that the same thing happens to an even greater extent in ice, which has a dielectric constant of 100 at 0°C. Like most orientation effects, these dielectric constants vary approximately inversely with absolute temperature.

Because the bonding pattern and hence the polarization in water can

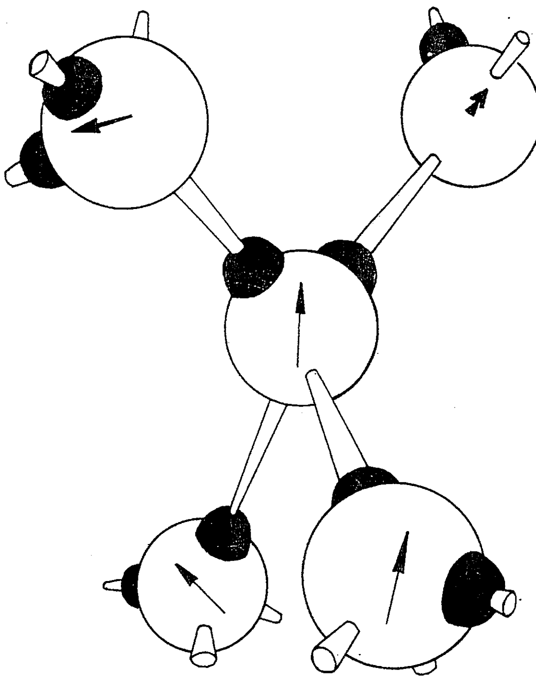

FIGURE 8 A cluster of water molecules showing how the direction of the electric dipole moment of the central molecule influences the directions of nearest-neighbour dipoles through normal bonding requirements.

change in a time of order 10^{-11} s, the dielectric polarization in water can follow an applied electric field at frequencies up to about $10^{11}/2\pi \approx 10^{10}$ Hz, which lies in the 3 cm microwave range. Measurement of this frequency serves to check some aspects of the liquid water model.

The high dielectric constant of water shields any ions which may be in solution and so reduces ionization energy. The self-ions H^+ and OH^- are present in concentrations of about 10^{14} per cubic centimetre at room temperature. Actually H^+ does not exist as an independent entity but combines with one of the lone pairs of a water molecule to give a tetrahedral ion H_3O^+ with one negative and three positive vertices.

The way in which these self-ions move through the liquid is particularly interesting, as is shown in Figure 9. It is not so much an ion that moves as an "ion state," each proton making only a single jump before handing on the role of charge carrier to one of its neighbours. Clearly any broken or badly distorted bond will interrupt the proton transfer process and it is the time delay involved in the fluctuating remaking of these bonds

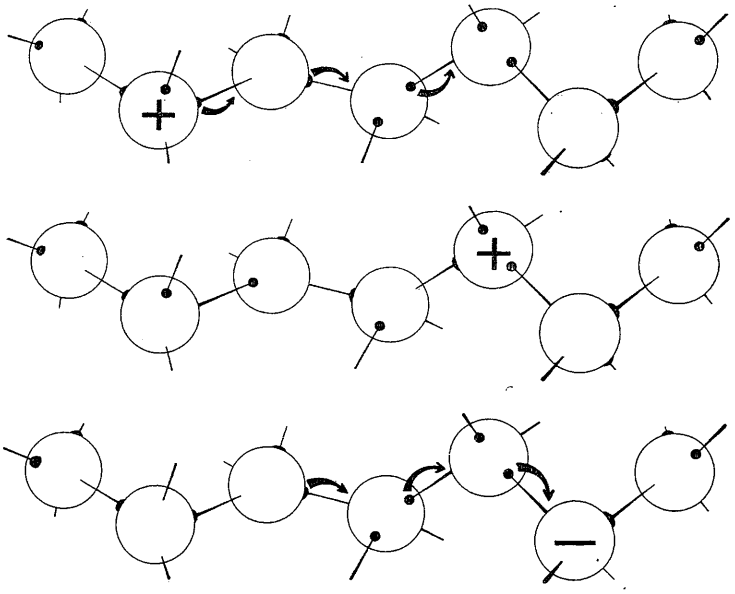

FIGURE 9 Ion state motion in water or in ice. (a) A positive ion state H_30^+ and the sequence of proton jumps by which it can move through the liquid. (b) The new configuration after proton jumps have occurred. (c) A similar sequence of proton jumps for motion of a negative ion state $0H^-$

that determines the self-ion mobility. Modification of water structure at surfaces or interfaces will clearly affect this mobility.

Essentially all the electrical conductivity of water arises from the motion of self-ions, OH^- and H_3O^+, or of ions from foreign solutes. The electronic conductivity is nearly zero because of the tight binding of electrons within the molecules which results in an electronic band gap of about 7 eV, if I may speak of it in this way. The peculiar transport mechanism for OH^- and H_3O^+ ion states, however, gives these an unusually large mobility (2×10^{-7} and 4×10^{-7} m^2 V^{-1} s^{-1} respectively at 25°C, compared with values nearly ten times smaller for solute ions). In ice the contrast is even greater. For some purposes it is thus appropriate to think of ice and liquid water as being "protonic semiconductors" with the self-ion states playing roles similar to those of electrons and holes in electronic semiconductors. The protonic band gap for creation of (OH^-, H_3O^+) pairs is about 1 eV.

Solutions

Water acts as a vehicle for countless important chemical and biochemical processes in solution, and the properties of ordinary and of colloidal aqueous solutions depend so much on the properties of water that they must always be kept in mind. We have already mentioned the high dielectric constant of water which promotes the dissolution of ionic solids by reducing the energy penalty involved in separating the ions. This is of course an over-simplification because, on a molecular scale, water is not a homogeneous dielectric. Thus each ion in solution is surrounded by a sheath of tightly bound and strongly oriented water molecules in a configuration which depends on the ion charge and ion radius but which will generally differ considerably from the normal near-tetrahedral water structure.

The presence of an ionic solute obviously has an immense effect on the electrical conductivity of an aqueous solution and also affects, in a smaller way, many of its other properties. The different structural effects that ions have on water can be seen from the influence of alkali halides on viscosity. As shown in Figure 10, NaCl simply increases the viscosity of

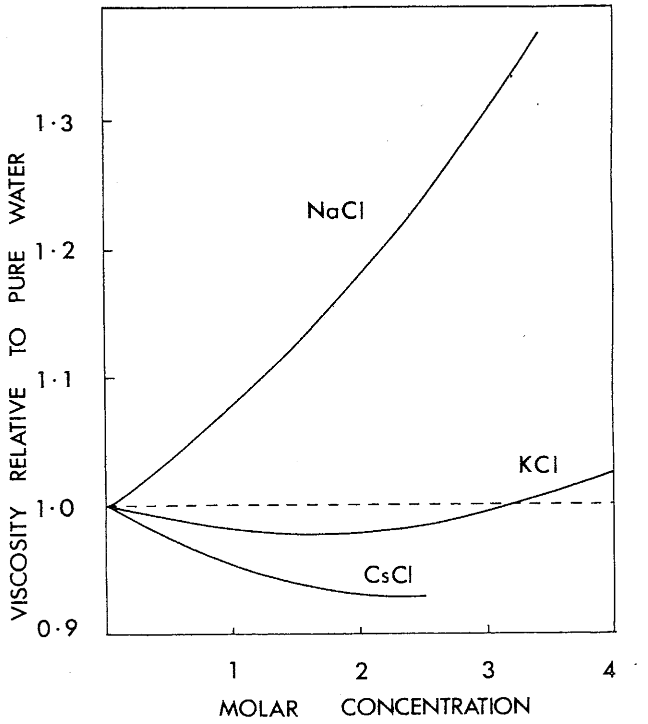

FIGURE 10 Influence of small quantities of alkali halide solute on the viscosity of water. The differences in behaviour suggest structural differences in the hydration shell of different cations.

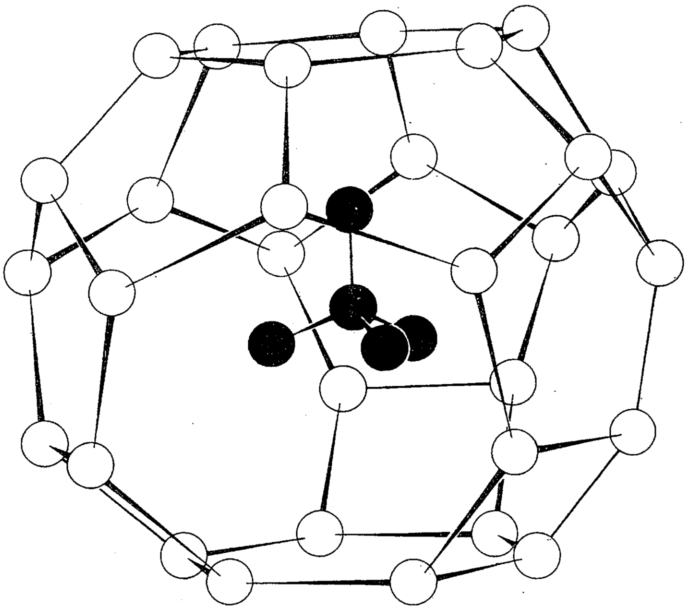

FIGURE 11 A single clathrate cage of the type formed by water molecules, in this case around a molecule of tert-butylamine, $(CH_3)_3CNH_2$

the solution as its concentration is increased, while KCl and CsCl first lower the viscosity then raise it slightly.

Non-ionic solutes sometimes show even more extreme structural effects and many small molecules like Ar, Kr, Xe, Cl_2, SO_2, CH_4, form crystalline hydrates which are stable to temperatures approaching (and sometimes even above) 0°C. In these clathrate materials the foreign atoms or molecules are confined in bonded cages of water molecules, as shown in Figure 11. These cages then bond together to form an ice-like crystalline structure, though with very different geometry from that of ice.

In liquid water solution these non-ionic molecules, and the larger molecules characteristic of biological systems, undoubtedly have an influence on the average structure of the water that surrounds them, though this influence will relax over a distance comparable with the 10 Å coherence length characteristic of water. Structural effects will be felt in viscosity, electrical conductivity, and ionic transport as well as in other phenomena.

Surfaces and Interfaces

Finally we must expect structural effects in water at surfaces and interfaces that will extend for roughly a coherence length, or about three molecular layers, into the bulk liquid. This is quite apart from any layer of adsorbed ions, which may be much more extended.

Colloid suspensions, emulsions, and foams are all examples of the importance of interfaces and of the electrical forces that may be associated with them, and it is hard to imagine biological processes proceeding in their absence. Similar processes are also important in soil behaviour in which the swelling of clay soils depends on the build-up of structural water layers between the crystalline sheets of mica-like minerals.

Conclusion

Water is a liquid that exhibits a whole range of unusual and extreme properties deriving from the peculiar geometry of the water molecule. In addition, of course, it also shows most of those normal properties possessed by essentially all liquids. From the viewpoint of mankind some of the peculiarities of water are probably merely interesting, but some of them are intimately bound up with the forces that have shaped the Earth's surface and with the detailed biochemistry and biophysics of the living organisms that have developed on it. Life in the universe is perhaps not limited solely to aqueous environments, but the unusual properties of water seem uniquely suitable for such a development.

References

The literature on water is immense and for that reason I have simply listed a selection of works that review the field and give detailed references to the research literature.

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