A new uniformist model of water

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A simple uniformist model is proposed for the structure of liquid water which consists of a puckered hexagonal ring of six oxygen atoms with six hydrogen-bonded hydrogen atoms within the ring and six non-bonded non-cyclic hydrogen atoms. This model differs from previous ones in that it postulates that of the two hydrogen bonds one oxygen can form with two hydrogen atoms, one is stronger than the other. Both exist in ice. The weaker hydrogen bond (5.9 kJmol⁻¹ at 0°C) breaks when ice melts while the stronger one (37.7 kJmol⁻¹ at 100°C) persists in water and breaks only when water boils. The stronger bond also breaks during sublimation of ice. This explains why the heat of melting, due to breaking of the weak H-bond, is only 13% of the sublimation energy of the solid. The puckered six-membered ring of the H₂O molecule is enclosed in a hexagonal cell, the volume of which is controlled by the oxygen-oxygen distance and the bond angles. The hexagonal cell in water is thinner than that in ice. This uniformist model is in good agreement with the distances of nearest neighbours as obtained from X-ray diffraction data for both water and ice-I. It also offers an explanation of not only why the number of nearest neighbours increases from 4.0 to 4.4 when ice melts but also why there is a neighbour at 0.35 nm in water but not in ice. Due to breaking of the weak hydrogen bonds on melting, the hexagonal cells can approach one another closer than they can in ice which explains the density increases on melting. On the basis of an empirical equation for the thickness of the hexagonal cells in water the predicted bond angle is 112°. Based on the distances of the nearest neighbours in water, it is calculated that the O-O-O bond angle is 106° at 0°C.

All previous models for the structure of liquid water are based on the following assumption: the two hydrogen bonds that one oxygen atom can form are both equal and have a value of 20.9 kJmol⁻¹ (ref. 2). So it is unexpected that liquid water has a higher critical temperature (374.15°C) than that of hydrogen fluoride (230.0°C) which has a hydrogen bond strength of 28.0 kJmol⁻¹ (ref. 3). All the theories agree that the hydrogen bonds in ice are fully satisfied. The differences arise regarding the state of these bonds when ice melts to form water. Buijjs and Choppin⁶ estimated that 46% of the hydrogen bonds are broken when ice melts. Scherer et al.⁶ have reported that an appreciable number of room temperature water molecules have one hydrogen strongly bonded and the other comparatively free. They have also proposed the existence, in water, of strong and weak hydrogen bonds as well as regular ones. In this paper a new uniformist model is proposed for the structure of water which is based on an analogous behaviour of some polymeric systems.

Discussion

A new uniformist model

In a study on the swelling of nitrile rubber by various liquids, it was discovered that alcohols, such as n-butanol and n-pentanol, behave as associated clusters containing six alcohol molecules. The association in alcohols has been proposed to be a cyclic structure (Fig. 1) by Pauling. As pointed out by Frank, bonds in rings are always more stable than those in the most stable open chains of the same polymer number.

Replacement of the alkyl groups by hydrogen atoms would lead to a cyclic structure (Fig. 2) which is the same as that proposed for water by Pennycook in 1928. However, the Pennycook model does not explain why some hydrogen atoms are involved in hydrogen-bonding while others are not. It may be proposed that the two hydrogen bonds an oxygen atom can form are not equal, with one being stronger than the other. Several studies have supported this proposal. For example, Jean and Volatron observed that the two lone pair electron groups on an oxygen are not of equal energy. Laing also questions the conventional assumptions about the bonds in water. It follows that of the two types of hydrogen bonds existing in ice, the weak bonds break when ice melts and the strong bonds persist in water and break only when water boils.
The strengths of the hydrogen bonds can be calculated from the latent heats of fusion and boiling. The weaker one, of 5.9 kJmol⁻¹ at 0°C, is broken when ice melts. The stronger one, of 37.7 kJmol⁻¹ at 100°C, breaks when water boils. According to Stillinger, the heat of melting is only 13% of the sublimation energy of the solid. This is because the latter involves breaking of the stronger bond while the former is due to breakage of the weaker bond. From this information it is calculated that the value of the stronger hydrogen bond is 45.4 kJmol⁻¹ at 0°C. Ideally, the presence of hydrogen-bonded and non-bonded OH groups in water should be detected by infra-red and Raman spectroscopy. However, the intensity of the O-H stretching bond is increased by a factor of 10 when the O-H group forms a hydrogen bond. Thus, non-bonded O-H groups are more difficult to detect by IR methods than the hydrogen-bonded O-H groups.

Bjerrum postulated that ice is a plastic substance. This plasticity is analogous to the thermoplastic behaviour of zinc oxide-carboxyl polymers where the thermoplasticity arises due to the breakage and reformation of labile ionic cross-links formed through zinc oxide-carboxyl group interactions. These ionic bonds are weaker than the covalent bonds which form the backbone of the polymer and may be considered analogous to the weaker hydrogen bonds in ice.

According to the new uniformist model, the non-cyclic hydrogen atoms are unable to form hydrogen bonds with oxygen atoms in other water molecules because the weaker sites on the oxygen atom are not able to form hydrogen bonds. However, these hydrogen atoms can form hydrogen bonds with other molecules, such as benzene. In this uniformist model the oxygen atoms are in a puckered ring in a manner similar to the carbon atoms in cyclohexane.

When the vapour condenses into liquid water, six H₂O molecules polymerize through the strong hydrogen bonds into a cyclic structure analogous to the Diels-Alder reaction of 1,4-butadiene to form vinyl cyclohexene. At the freezing point the cyclic oligomer further polymerizes through the weak hydrogen bonds, in a manner similar to the polymerization of phenol-formaldehyde resins, to give a three-dimensional structure. Thus, ice can be considered to be a polymer of water in the same way that polystyrene is a polymer of styrene. The structure of ice is shown in Fig. 3 in which the cyclic oligomers are shown in hexagonal cells containing six H₂O molecules.
Volume of a hexagonal cell

The density of ice-I can be calculated by enclosing each six-membered ring in a cell such that the boundaries of this cell are the intersections of the oxygen-oxygen distances with the neighbouring cells and that there is no free space between the cells. The upper and lower surfaces of each cell are regular hexagons as shown in Fig. 3.

The volume of the hexagonal cell is controlled by two variables, the oxygen-oxygen distance and the bond angle. Mathematically, it is possible to isolate a single cell to show the effect of the two variables. The volume $V$ of the hexagonal cell is given by:

$$V = \frac{1}{6} \left[ 1 + 4 \sin^2 (\theta/3) \right] \sin (\theta/2) a^3$$

(1)

where $a$ is the oxygen-oxygen distance, and $\theta$ is the intra-cell O - O - O bond angle.

When the bond angle is the tetrahedral angle the volume of the hexagonal cell is:

$$V = 16 a^2 (3)^{1/3}$$

(2)

Since the O - O distance in ice-I is 0.277 nm, the volume of the hexagonal cell is 0.1963 nm$^3$. (H$_2$O)$_6$ has been reported to have a mass of 179.724 x 10$^{-24}$ g. Hence, the calculated density of ice is 0.915 g/cm$^3$ which is comparable to the experimental value for the density of ice-I (0.916 g/cm$^3$).

Figure 4 shows the effect of varying the intra-cell bond angle when the oxygen-oxygen distance is constant at the value for ice. Curve A shows that the tetrahedral angle gives the minimum density and any change from this value results in a higher density.

At the melting point, the oxygen-oxygen distance increases from 0.277 nm in ice-I to 0.282 nm in water so that if the bond angle remains at the tetrahedral angle value the calculated density is less than that of ice and much less than that of water. This is shown by curve B in Fig. 4. A continuum model with few, if any, broken hydrogen bonds must obey this curve if all the intra-cell bond angles are the same. Fig. 4 also shows that to obtain the density of water the bond angle should be either 88° or 119.5° which are probably not viable structures. Therefore, there must be a range of bond angles to obtain the required density.

An acceptable model for the structure of liquid water has to satisfy a wide range of properties, not only those of water but also those of ice. In particular, it has also to explain several anomalies:

1) When ice melts, the number of nearest neighbors of oxygen atoms increases from 4.0 to 4.4. The proposed model explains observation (1) as in ice the hexagonal cells are rigidly connected to one another so that there are only four nearest neighbours for a given oxygen atom, e.g. oxygen atom C* in Fig. 4. However, in the liquid form one cell can also rotate with respect to the one above or below it. C* moves from the position in Fig. 5 to that in Fig. 6 such that BC* = CC*. When this occurs there are five oxygen atoms as nearest neighbours. The average of four and five, 4.5, is comparable to the experimental value of 4.4 and it indicates that the
four position is statistically preferred over the five position.

(2) Ice-I shares with diamond, silicon and germanium of the unusual property of floating on its melt, i.e., the solid, unlike most other substances, is less dense than the liquid. Explanation of observation (2) is as follows:

When ice melts there is an increase in density from 0.916 g/cm³ for ice to 0.999 g/cm³ for water despite the fact that the oxygen-oxygen distance increases from 0.277 nm in ice to 0.282 nm in water at 0°C. This increase in density must arise from a combination of the following: a change in the bond angle and a decrease in the thickness of the cell due to the ability of the cells to approach each other more closely than they can in ice.

The position of C* in Fig. 6 indicates that the thickness of the cell in water is less than that in ice (in Fig. 5). When the bond angle is 120° all the oxygen atoms are in the same plane and the thickness of the cell is the height of an equilateral triangle of sides a, i.e., \((3^{0.5})a\). This is the minimum thickness of the cell.

Since the thickness of the cell in ice-I is \((a + p)\), a modified equation for the thickness of the cell in water is proposed:

\[ h' = a \cdot \sin(\theta/2) + p \]  \hspace{1cm} (3)

where \(h'\) is the thickness of the water cell and \(p\) is the distance between the plane of BDF and the plane of ACE in Fig. 5.

\[ p = 1 - 4 \cdot (\sin(\theta/2)/3)^{0.5} \cdot a \]  \hspace{1cm} (4)

Note that when the bond angle is 120°, \(p = 0\) and \(h' = a \cdot \sin(120/2) - (3^{0.5})a/2\) as noted above.

An empirical equation for the volume of the hexagonal cell for water is a modification of Eq. 1 with the initial 1 replaced by \(\sin(\theta/2)\):

\[ V' = (\sin(\theta/2) + 1 - 4(\sin(\theta/2)/3)^{0.5}) \times (6(3)^{0.5}\sin(\theta/2) \cdot a) \]  \hspace{1cm} (5)

Based on the above equation, curve C in Fig. 4 demonstrates the principle that the increase in density must arise from a combination of a change in the bond angle and a decrease in the thickness of the cell. This equation suggests that the bond angle in water is 112°.

If the nearest oxygen-oxygen distance is \(a\), then the next nearest neighbour distance \(b\) is:

\[ b = 2a \cdot \sin(\theta/2) \]  \hspace{1cm} (6)

The second nearest neighbour is the diagonal \(c\) of sides of a rectangle of length \(a\) and \(b\), is given by

\[ c = (a^2 + b^2)^{0.5} \]  \hspace{1cm} (7)

From Eqs (6) and (7) above, the bond angle which gives the experimental values of the nearest neighbour oxygen atoms for water is found to be 106°. Thus, Eq. 4 needs to be modified to give the correct answer. It is of interest to note that 106° is intermediate between the tetrahedral angle and the H - O - H angle in the vapor of 104.5°.

(3) Various isotopic forms of water, \(H_2O, D_2O, T_2O\), etc., are unique in that for each there is a point of maximum density above and close to the freezing point. Starting with liquid at the freezing point the maximum density can be obtained by either increasing the temperature by a few degrees or by increasing the pressure. Also, up to about 40°C the application of pressure can make water more fluid.

As the temperature is increased from 0 to 4°C the bond angle increases even more to give a maximum density at 4°C. A similar effect is noticed when the pressure is increased. At temperatures greater than 4°C the dominant effect is the increase in O-O distance which leads to a larger volume of the hexagonal cell and, thus, a lower density.
It is reported that up to 40°C the application of pressure can make water more fluid. This suggests that the bond angle can be further increased by increase in pressure with the corresponding reduction in the thickness of the cell.

(4) For the oxygen atoms in Ice-I there is a high concentration of neighbours at distances of 0.277 nm, 0.45 to 0.53 nm and 0.64 to 0.78 nm, but no neighbours between 0.276 and 0.45 nm or between 0.53 and 0.64 nm. Similar results are obtained with liquid water with the difference that extra neighbours appear at 0.35 nm.

It was noted above that there is nearest neighbour in water at 0.35 nm which is not present in ice-I. This probably arises from the distance AC* in Fig. 6. While the length of AC* will vary with the bond angle there does not appear to be any simple equation relating one to the other. In the special case when C* is equidistant from A, B and C, such that AC* = \(a\), we have \(p = a/2\). Substituting in Eq.4 we get a value of \(\theta = 97.18^\circ\) which is the minimum value of the bond angle. At the other extreme when \(\theta = 120^\circ\) when the ring is no longer puckered, the value of AC* will be 1.6a. Thus, a value of 0.35 nm is not unreasonable for AC*.

The uniformist model proposed here is a special case of the continuum model such that \(n = 1\) in the formula \([\text{H}_2\text{O}_8]\). Therefore, it is possible that much of the analysis and discussion applied to the continuum model could also be applied to this model. Recently, Clary, using computer simulations, predicts that the basic structure of water is a hexamer.

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**References**