Theoret. chim. Acta (Berl.) 17, 334—338 (1970)

An Alternative Model for Anomalous Water

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Received April 14, 1970

An alternative model for the structure of anomalous water is proposed, in which all hydrogen atoms are involved in hydrogen bonds. Such a model seems to agree well with the main experimental properties of that substance. In particular, IR and Raman spectra can be estimated in agreement with the measurements of Lippincott and coworkers.

In several previous papers [1–6] a simple model for ordinary water was developed. According to this, at temperatures not too close to freezing point water mainly consists of linear polymers of various lengths of the type schematically shown in Fig. 1.

The mean number, *L*, of molecules per polymer was deduced as a function of temperature from the viscosities of ethanol-water mixtures [2]. Independent NMR spectra and calorimetric measurements were used to support this interpretation of concentration-viscosity plots [3]. The same functional dependence of *L* on temperature was then deduced from the heats of vaporization of water, the experimental value for the latent heat of the melting of ice being assumed as known. It was also shown that with a suitable choice of the equilibrium constant for the exchange of molecules between polymers in the liquid, *L* can be calculated as a function of temperature and agrees fairly well with the preceding results. The enthalpy change of the process is found to be 0.11 eV [5]. Furthermore, it was shown that the viscosity of water can be obtained from the formula of Duncan and Flory, which holds for liquid chain polymers, when *L* is used as the chain length [6]. Finally, the model predicts a dependence of the chemical shifts of the protons of water on temperature, which agrees with the measurements of Hindman [5].

In the present paper we propose an extension of the model as an aid to the study of the molecular structure of anomalous water [7–17].

The idea is that the water molecules condense on the surface of quartz in regular arrays much longer than usual, forming linear polymers of the type shown in Fig. 1, with the distance between nearest oxygen atoms shorter than in ordinary water. Two or more such linear polymers adjacent on the quartz surface

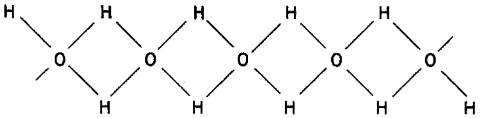

Fig. 1.

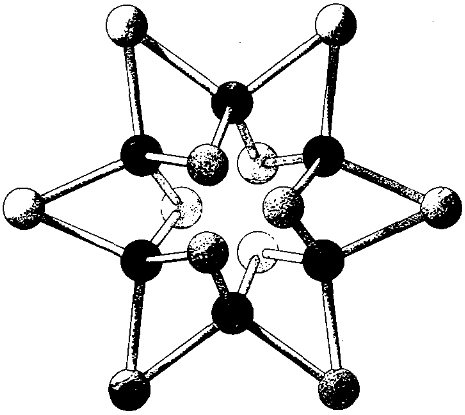

Fig. 2.

can then join their neighbouring free ends thus forming a closed chain structure, the water molecules being welded together by strong collective hydrogen bonds. These molecular aggregates have exhausted all the possibilities of hydrogen-bonding and cannot associate with other surrounding molecules. In Fig. 2 a polymer of this type made of six molecules only is represented. Here the distortion of bond lengths and directions is severe and the repulsion between the adjacent inside protons is surely so high as to make the systems unstable. As the number of molecules in the ring is increased, the distortion energy becomes less and less relevant to the stability of the system and it is not unreasonable to suppose that even with 16 to 20 molecules it would be lower than the energy set free in closing the ring. When the closed chain is sufficiently large the system is energetically stable.

More complex saturated structures of the same type are also conceivable, but in the following we shall limit ourselves to discussing this first simple example.

Let us consider now the properties to be expected for a substance consisting exclusively of such closed chain molecular aggregates of water.

First of all, it must be noted that such a liquid cannot be termodynamically stable. For statistical reasons, some H-bridges would always break spontaneously. As a consequence their rings would open and the length of the polymer be reduced by thermal collisions with a probable change of the structure into that of ordinary water, the inverse process being almost impossible in the absence of a quartz catalyst. This explains why anomalous water practically does not exist in nature and offers an interesting way of eliminating the apparent contradiction between its high stability and the fact that it is not present at the bottom of seas and lakes. The decay process at ordinary temperature, however, must be very slow, owing to the stability of the bonds caused by the peculiar structure and the closing of the rings.

The general properties of the liquid would be those of a kind of water in which hydrogen bonding between different molecular aggregates is suppressed, and the effective molecular weight highly increased.

The density must be higher than that of ordinary water, because the same number of water molecules is arranged in bigger aggregates, and the inter-

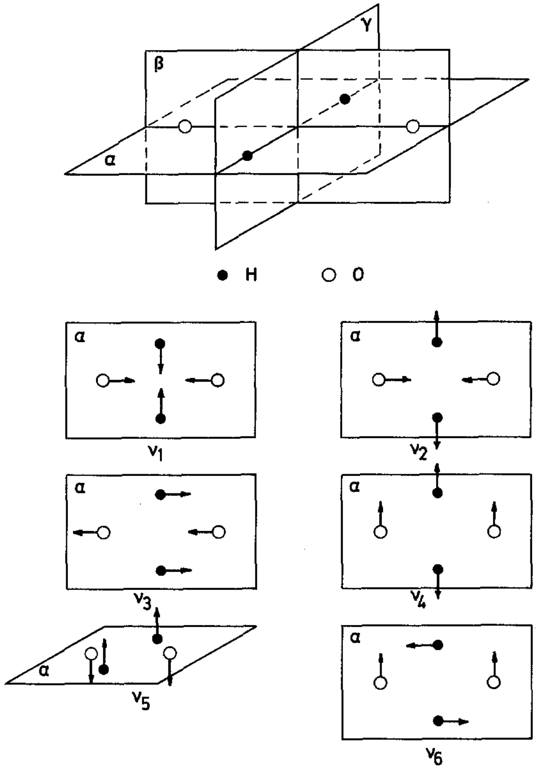

Fig. 3.

molecular distances are shorter. However, the density might also depend on the mean number of molecules per ring aggregate, i.e. on the manufacturing process and the state of the quartz surface which acts as a catalyst.

For the same reasons the present model predicts a lower vapour pressure, or higher boiling point, and a lower freezing point than ordinary water.

The solid must be amorphous, owing to the fact that no exactly repetitive unit is available. Otherwise it would be metastable and the conversion into ordinary ice would be energetically favoured.

The viscosity of the liquid must be fairly high owing to its rapid increase with the length of the linear polymers.

Only bands due to the H-bridges are expected in the IR spectrum, the stretching modes at much lower frequently than ordinary water, the bending modes much less affected.The symmetry of the protons in each two-bridge bond would prevent the presence of some of these bands in the corresponding Raman spectrum. A rough analysis might perhaps explain the experimental results obtained by Lippincott and co-workers [16].

As shown in Fig. 3, each vibrating unit of four atoms involves three mutually perpendicular symmetry planes and gives rise to six independent fundamental vibrations. Two of them, ν_1 and ν_2, retain all the symmetry elements; the following three, ν_3, ν_4 and ν_5 retain two of the three symmetry planes, and the last ν_6 retains only one of them. Dipole moment and polarizability considerations show that

Table

Frequency	IR	Raman	Lippincott
ν_1	—	weak	1865 cm^{-1}
ν_2	—	weak	1760
ν_3	weak	—	1150
ν_4	strong	—	1600
ν_5	strong	—	1400
ν_6	—	strong	620

only ν_3, ν_4, ν_5 are IR-active and only ν_1, ν_2 and ν_6 are Raman-active. Furthermore, the contribution of ν_3 to the IR spectrum must be weak, because the displacements of the atoms are along the polymer strand and, this being a closed ring, the total contribution of the entire polymer, if excited, is zero. The contribution of ν_1 and ν_2 to the Raman spectra must likewise be weak, because the vibration in adjacent loops always has opposite phases.

We can therefore tentatively propose the following relationship between the six vibrations and the peaks of the IR- and Raman spectra measured by Lippincott and co-workers (Table).

In the NMR spectrum no effect due to rapid exchange of protons between different positions in the aggregates would be seen, only one type of proton being present. Furthermore, the coupling of protons in the same aggregate, and the possibility of distortion of the long chain aggregates would cause the typical broading of the resonance peak as observed by Lippincott [17]. In ordinary water, on the contrary, rapid exchange effects prevail over the effects of coupling and the resonance peak is comparatively sharp and changes its position with temperature [18].

The solvent properties of the liquid would be typical. Electrolytes with their ions to be solvated would take molecules of water away from the ring aggregates, and tend to destroy anomalous water. For other solutes the liquid would display poor solvent properties, no hydrogen-bonding being possible between their molecules and the water aggregates. However, in this case also ring aggregates can be destroyed if the solvation enthalpy in ordinary water is sufficiently high.

An interesting test of the model may be obtained by mixing anomalous and heavy water and afterwards separating them again. Since all the hydrogen bonding possibilities are already exhausted for each aggregate of anomalous water, the model predicts that no exchange is possible (at a first approximation) between protons of anomalous water and deuterons of heavy water at ordinary temperature. Thus no protons are to be found in the heavy water, and no deuterons in the anomalous water, after their separation with the techniques described in the literature [19].

An experiment of this type could distinguish the present model from those proposed by Lippincott [16] where the external protons of the hexagonal aggregates or of the branched polymer chains must freely exchange with deuterium.

The author wishes to thank Professor L. Paoloni for his suggestions and many helpful discussions.

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