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ON THE STRUCTURE OF WATER

[Following is the translation of an article by G. Ya. Samoylov, Institute of General and Inorganic Chemistry imeni N. S. Kurnakova, AN USSR, Moscow, published in the Ukrainian Journal of Physics, No 4, Vol 9, 1964, pages 387-393.]

In August 1963 30 years had passed since the time of the publication of the classic work by Bernal and Fowler on the theory of water and ionic solutions [1]. This was the beginning of the contemporary stage of investigation of the structure of these liquids. In connection with the stated date it is appropriate to examine, though briefly, the contemporary state of the problem concerning the structure of water.

The most important result in the work by Bernal and Fowler lies in the establishment of the tetrahedral nature of the structure of water. Bernal and Fowler turned their attention to the following important circumstance, connected with the magnitude of the density of water. Knowing the distance between the nearest molecules in the structure of ice (2.76 Å), it can be assumed that the effective radius of a molecule of water is 1.4 Å. If water possessed the structure of the densest packing, then at that radius for a molecule the density of water would comprise 1.64 g/cm^3. For obtaining a density which is close to 1.00 g/cm^3 it is necessary to assume that either with a structure which corresponds to the densest packing there is a considerable increase in the effective radius of a molecule of water (up to a value of 1.72 Å), or the effective radius of a molecule of water during the melting of ice changes little, but the structure of water differs considerably from the densest and is open. Bernal and Fowler accepted that the effective radius of a molecule of water comprises 1.4 Å, and they calculated what would be the curve of scattering if the structure of water corresponded to a somewhat disordered densest packing - to the structure of the type ice - tridymite and of the quartz type.

A comparison of calculated curves with the then available experimental curves of scattering of X-rays by water showed that curves, similar at all to experimental, are obtained only in the hypothesis of the tetrahedral nature of the structure of water. Bernal and Fowler came to the conclusion that each molecule of water in water is surrounded on the average based on a tetrahedron by four other molecules. The properties of water which make it so different from other liquids, according to Bernal and Fowler, are conditioned by the peculiarities of a tetrahedral structure, in particular its openness, and not by the occurrence of any associates

of molecules in water. These conclusions of Bernal and Fowler were fully confirmed by subsequent investigations on the structure of water.

Already in 1934 a paper by Katzoff appeared [2] in which, based on data of the scattering of X-rays by water, a calculation was made of the curve of radial distribution of its molecules. The first maximum of the curve is located approximately at 2.9 Å, which corresponds to an effective radius of a molecule of approximately 1.4 Å, and the second - at 1.5 Å. The area under the first maximum is close to four units. Thus the tetrahedral coordination of molecules in water is confirmed.

The most complete X-ray investigation of water was carried out by Morgan and Warren [3], who determined the scattering of X-rays by water at five temperatures: 1.5, 13, 30, 62, and 83°C. The area under the first maximum of curves of distribution, and also abscissae of the first and second maximums, indicate that the structure of water (in the sense of local order) is similar to the structure of ice I. The position of the first maximum of the curve of radial distribution changes from 2.90 Å at 1.5°C to 3.05 Å at 83°C. Average coordination number of molecules according to the data of Warren and Morgan changes from 4.4 at 1.5°C to 4.6 at 83°C. The results of Morgan and Warren were later checked and verified in works by Brady and Romanow [4], and also Danford and Levy [5]. These showed the inaccuracy in the works of van Panthaleon van Eck and associates [6]. These authors came to an incorrect conclusion that local order in water corresponds to a simple cubic structure. Thus, at the present time the tetrahedral nature of local order of molecules in water is a reliably established fact.

However, water differs from other liquids not only by its open tetrahedral structure, but also by the fact that the local order of distribution of molecules which is inherent to water is expressed in it considerably stronger than the local order of distribution of particles in other liquids. In particular this statement is based on the investigation of the peculiarities of water as a solvent. Certain ions in aqueous solutions have an inherent negative hydration [7-9]. This phenomenon amounts to the fact that in the vicinity of ions molecules of water become more mobile than in pure water: the potential barrier which a molecule of water has to overcome in order to escape from the near surrounding of the ion turns out to be less than the energy of activation of self-diffusion of molecules in water. The stated potential barrier grows with an increase of the interaction of the ion with the nearest molecules of water (positive contribution) and decreases in connection with a disruption of the ionic structure of water (negative contribution). Negative hydration also takes place when negative contribution is not compensated by positive. It is clear that the more weakly expressed the mutual orderliness of molecules of a solution, then the less will be the role of negative contribution, and

negative solvation may not take place at all. According to the data of G. A. Krestov [10] in such liquids as, for example, methanol and ethanol, negative solvation is not observed.

Also connected with the disruption of the mutual orderliness of molecules of water in aqueous solutions is the phenomenon, observed under certain conditions, of soaking (increase of hydration) of the salted ion under the influence of the salting out agent [11]. In nonaqueous solutions a corresponding phenomenon is absent according to data of K. P. Mishchenko [12, 13].

It is necessary to note that in such a comparison there is an equalization of the levels of local order of molecules in water and in nonaqueous solvents at the same temperature, for example, at 25°C. The high degree of orderliness in water, in comparison with other liquids, as pointed out by N. A. Izmaylov [14] and K. P. Mishchenko [13], may be connected with the fact that the melting points which correspond to the investigated nonaqueous solvents are considerably lower than the melting point of ice (the temperature at which the comparison is made exceeds by considerably more the temperature of melting of solid bodies, corresponding to the nonaqueous solvents, than the melting point of ice).

A significant step in the investigation of the structure of water was the concept, put forth in 1946, of the occupation of the void of the tetrahedral structure [15]. According to this concept, local order, which is inherent to water, may be characterized as diffused by the thermal movement of molecules with the structure of ice I. Here the voids (cavities) of this open structure are partially filled by molecules of water. The concept of the occupation of the free spaces is based, on the one hand, on the results of Morgan and Warren, who showed that the local order of water corresponds to the structure of ice I, and the average coordination number of the molecules increases from 4.4 at 1.5°C (coordination number of molecules of ice equals four) up to 4.9 at 83°C. On the other hand, it is based on the fact that from a number of experimental facts (viscosity, infrared spectrum, ect.) there is an increase, along with a rise in temperature, in the share of broken hydrogen bonds in the water.

Thus, in water, with an increase of temperature in the presence of local order corresponding to the structure of ice I, the average coordination number of molecules increases, and at the same time there is an increase in the number of broken hydrogen bonds. This leads to the concept of the occupation of free spaces in the structure of ice by molecules of water, and the fraction of occupied free spaces increases with an increase of temperature. In actuality a molecule of water which enters the cavity of the structure turns out to be from molecules which are framing the cavity at a distance

close to the distance between the nearest neighbors in water. Correspondingly the occupation of the cavity leads to an increase in the average coordination number [17]. However, energetically this molecule is not equivalent to molecules found in positions of equilibrium of structure, and the broken hydrogen bonds do not respond to it. Therefore, energetically the quaternary coordination in water is realized only partially, and the average coordination number of molecules (in a geometric sense) is greater than in ice, and increases with an increase of temperature.

The concept of occupation of cavities of a tetrahedral structure makes it possible to understand the anomalous properties of water and, mainly, the increase in density during the melting of ice, and also the existence of a maximum of density. The anomalies of the mechanism of self-diffusion in water also become understandable: they are connected with how great is the role of the translational motion of molecules through cavities in the structure. Connected with the occupation of the cavities of a structure is the phenomenon of stabilization of the structure of water by molecules of certain nonelectrolytes. Molecules of the stabilizing admixture enter the vacancies of the structure and hinder the translational motion of the molecules of water. Correspondingly there is a lowering of "structural temperature" of water (term introduced by Bernal and Fowler); water becomes more ordered [16].

I. Z. Fisher and V. K. Prokhorenko [17] detected that a very high level of fluctuations of coordination number is inherent to water. Having in mind the comparatively strongly expressed mutual orderliness in the disposition of molecules in water, this fact should be connected with the translational motion of molecules through cavities of the structure; an increase of coordination number may be realized without breaking the "framework" of the structure of water. The assymetry of fluctuations of the coordination number of molecules in water is connected with this circumstance. It was revealed [9] that in water there is a predominance in fluctuations of coordination number in the direction of an increase in it, while in liquids with denser structures (argon, mercury) - it is in the direction of a decrease.

The double-structural model, advanced by Hall in 1965 [1], can also be connected with the concept of the occupation of the cavities in the structure of water. According to this model, in water there exists two structures - an open tetrahedral structure of ice and a denser structure. The emergence of the second, denser structure can be connected with the entry of molecules into the cavities of the tetrahedral structure of ice. On the basis of the double-structural model Hall places the concept that molecules of water in water are distributed between two conditions. This concept makes it possible to calculate the thermodynamic properties of water [5]. It is true that the approach used in the work by

Nemethy and Scheraga [21] is more extensive. In it the distribution of molecules of water between five states is examined correspondingly for the number of broken hydrogen bonds (from 0 to 4). It is necessary to note that the very model of Nemethy and Scheraga hardly corresponds to the structural peculiarities of water and, apparently, is not confirmed by X-rays.

Pauling [22] proposed a model for the structure of water which was based on the structure of hydrates of gases, methane for example. As is known, these hydrates are clathrate compounds: the molecules of gas are disposed in the cavities of the framework formed by the molecules of water. According to Pauling, the structure of water corresponds to the structure of a hydrate of gas in which the molecules of gas are substituted for molecules of water. Water, according to this model, is a clathrate "hydrate of water." A similar model, in which all the molecules of water form only mirror-symmetrical hydrogen bonds (true, somewhat distorted) was proposed by G. G. Malenkov [23, 24].

Frank and Quist [25], stemming from the position that part of the molecules of water make up the framework of the structure, and part occupy the cavities of the framework, calculated the corresponding contribution of water in thermodynamic potential, and derived at relationships describing such anomalous properties of water as, for example, the coefficient of thermal expansion. The basic result of this work by Frank and Quist may be described in the following manner.

Let f be the mole fraction of molecules of water making up the framework of the structure, and $(1-f)$ the fraction of molecules of water found in the cavities of the framework. One of the basic peculiarities of water molecules which are occupying the cavities of a framework is, according to Frank and Quist, that these molecules do not occupy volume. Then the mole volume of water

$$V_1 = f V_{fr}, \tag{1}$$

where V_{fr} - mole volume of the framework. Having differentiated (1) for temperature at a constant pressure, we obtain

$$\frac{1}{V_1}\left(\frac{\partial V_1}{\partial T}\right)_p = \frac{1}{f}\left(\frac{\partial f}{\partial T}\right)_p + \frac{1}{V_{fr}}\left(\frac{\partial V_{fr}}{\partial T}\right)_p. \tag{2}$$

The first term in the right part of relationship (2) represents the structural component of the coefficient of thermal expansion of water, and the second - the coefficient of thermal expansion of the framework. Frank and Quist showed that

$$\left(\frac{\partial f}{\partial T}\right)_p < 0,$$

i.e., that in water with a rise in temperature the average number of molecules found in the cavities of the framework increases.

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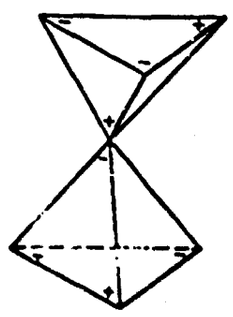
The minimum of molar volume of water is connected with the presence of positive $\frac{1}{V_{fr}}\left(\frac{\partial V_{fr}}{\partial T}\right)>0$ and negative contributions in the coefficient of thermal expansion of water. The work of Frank and Quist is in essence an investigation of those effects which the occupation of the cavities in the structure of water leads to. It is necessary to note that although Frank and Quist connect their calculation with the model of Pauling, the geometry of the framework is used by them to a minimum degree. It is significant only that the framework ensured the possibility of filling the cavities.

There is great interest in the idea of Frank and Quist that in connection with the high degree of symmetry of the field in the cavities of the framework, the molecules of water, entering into the cavities, become "nonhydrophilic," since the possibility of the formation of directing bonds (/5/, p. 307) is lessened. In other words waterproofing (true, only partially) of the molecules of water entering the cavities of the framework takes place. It is namely this circumstance which makes possible the occupation of the cavities: a molecule, entering into the cavity of the framework, interacts comparatively weakly with the molecules making up the frame of the cavity.



The most energetically favorable mutual disposition of the molecules of water forming a mirror-symmetrical bond. The tetrahedrons correspond to the molecules of water.

Of great interest in connection with the investigation of the structure of water are the results of the work by Bernal and Fowler /6/. These authors, on the basis of their X-ray investigation of water, obtained a curve of radial distribution resembling that of ice. It was accepted that the local order in water corresponds to the structure of ice I, diffused and distorted by the thermal motion of molecules, with partially filled cavities. Starting from Frank's model, with a calculation of all intermolecular distances up to 10 Å, the function of radial distribution was calculated. They found the distortions in the structure of ice and the share of occupied cavities at which the calculated curve of radial distribu-

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tion coincides with that obtained experimentally, and the calculated density coincides with the experimental value of the density of water. On the basis of the calculation conducted, Danford and Levy came to the conclusion that in water at 25°C half of all the cavities in the structure of ice are occupied and that distortions of the framework lead to an unequivalence of distances between neighboring molecules of water. In the framework each molecule of water has one neighboring molecule at a distance of 2.77 Å, and three - at a distance of 2.94 Å (on the average, according to the data of Danford and Levy, the distances between neighboring molecules of water in water at 25°C comprises 2.90 Å, which agrees with previous results).

The fact of the unequivalence of the distances between neighboring molecules in water is of great interest, since in water two molecules can form nonequivalent hydrogen bonds (stabler mirror-symmetrical and less stabler center-symmetrical). The most favorable distribution of neighboring molecules, corresponding to the mirror-symmetrical hydrogen bond, is shown in the drawing. A center- symmetrical distribution is obtained by turning one of the tetrahedrons around the direction of the bond by 60°. There is special interest in the circumstance that in ice I each molecule forms one mirror-symmetrical and three center-symmetrical hydrogen bonds. Apparently such a surrounding is also most favorable in water. Here the distance of 2.77 Å which was found by Danford and Levy corresponds to the mirror-symmetrical, and the three distances of 2.94 Å - to the center-symmetrical bonds. The stated affinity probably confirms the correctness of the model on which Danford and Levy based their work. The distribution of molecules of water in the cavities of the framework which was detected by Danford and Levy indicates the partial binding of these molecules. The model based on the structure of hydrates of gases is not supported by the results of Danford and Levy.

In essence we have examined only the problem of the distribution of atoms of oxygen in water at temperatures which are not too different from the temperature of melting of ice (~0-50°C). As regards the problem of the distribution of protons, then it is much more complex and it cannot be considered cleared up by no means. It is necessary to note that in connection with the results of Danford and Levy it is hardly possible to give a foundation to the so-called statistical or "half hydrogen" model, in which the protons are uniformly distributed between the poles of all the molecules of water.

Such is a brief characterization of the results of the investigation of the structure of water over a period of 70 years since the publication of the classical work by Bernal and Fowler.

Conclusions

1. A molecule of water in water is encircled in the center of

a tetrahedron by four other molecules. At the present time the tetrahedral nature of the structure of water is a reliably established fact. Such a nature of structure is connected with the composition of a molecule of water.

2. Local order in the distribution of molecules is expressed more strongly in water than the local order in the distribution of particles in other liquids.

3. The structure of water (in the sence of local order) corresponds to the structure of ice I which has been diffused and distorted by the thermal movement of molecules. The cavities which are inherent to this open structure are partially filled by molecules of water.

4. Distortions of structure of ice I in water are such that the distances between neighboring molecules are not the same; the distance up to one of the four molecules surrounding the selected molecule turns out to be somewhat shorter than the remaining ones. This indicates the nonequivalence of the hydrogen bonds which are formed by molecules of water with neighboring molecules. In water, apparently, just as in ice I, each molecule which is found in a position of equilibrium of structure forms one more stable mirror-symmetrical and three center-symmetrical hydrogen bonds.

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