
**FROM CHAOS TO ORDERLINESS
AND INTELLECT!**

Anomalous Thermal Properties of Water

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Abstract—The relationships of coefficients of molecule diffusion, viscosity, thermal capacity, thermal conductivity and other properties of water as a function of temperature and pressure have been analyzed. It is shown that the main regularities of changes in water characteristics, including qualitative differences of its behavior from the rest of molecular liquids are stipulated by the peculiarities of covalent and hydrogen bonds.

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INTRODUCTION

Liquids with hydrogen bonds, especially water, possess unique properties that are essentially different from those of other molecular liquids, in which the interaction between molecules is stipulated only by the Van der Waals energy. Particularly in the case of water, the contribution of hydrogen bond to the total energy of intermolecular interactions amounts to about 70% that leads to higher melting (0°C) and boiling (100°C) temperatures as compared to the corresponding temperatures for other liquids (for example, for methane: –186 and –161°C, respectively). Naturally, with such strong impact of hydrogen bonds on melting and boiling temperatures, their role in forming other thermal characteristics must be no less essential.

The purpose of this study is to analyze thermodynamic characteristics of water, such as thermal capacity, thermal conductivity, melting heat, viscosity, coefficients of water molecule diffusion, and others, and also their dependence on covalent and hydrogen bonds [1].

VISCOSITY AND DIFFUSION COEFFICIENTS OF WATER MOLECULES

Dynamic viscosity of water (η) is substantially higher than that of the majority of liquids, of which hydrogen bonds are not characteristic, for example, at 20°C it is four times as high as the viscosity of pentane or by 30% higher than the viscosity of nitromethane. A relatively high value of η for water is stipulated by the fact the motion of its individual molecules depends on hydrogen bonds with adjacent molecules limiting their mobility. Though hydrogen bonds stipulate viscosity η of many organic liquids (alcohols, carboxylic acids, amides of carboxylic acids, and esters), their impact depends also on the structure of molecules of these liquids and on the Van der Waals forces between them. Therefore some of them are characterized by the same viscosity as the liquids without hydrogen bonds (for example, values of η for methanol and nitromethane differ by a few percent), while η for ethanol and acetic acid at 20°C are by 20% higher than η for water.

The relationships of dynamic viscosity [2, 3] and water diffusion coefficient (D) as a function of pressure (P) and temperature demonstrate anomalous behavior (Figs. 1a, 1b). Hence, with the rise of pressure leading to an increase of water density [1], its viscosity initially decreases and then rises only at very high pressures. The diffusion coefficient shows directly opposite pattern. Based on the above data, we can assume here the presence of two competing processes. At a relatively small rise of pressure, the deformation and change (weakening) of energy of hydrogen bonds take place that contributes to easier shift of molecules with respect to one another, i.e., to reduction of η and increase of D . However, with further rise of P , the water compaction increases that not only neutralizes the emerging variations of viscosity and diffusion, but also results in the opposite effect.

It should be noted that the viscosity minimum in the overcooled water (–5°C) (see Fig. 1a) is achieved at $P \sim 0.2 \times 10^9$ Pa. With the rise of temperature, this minimum shifts in the region of lower pressures and completely disappears at 50°C. This result is in good agreement with findings of paper [6] demonstrating that the minimum distance between oxygen atoms of adjacent molecules of water with simultaneous increase of the

length of hydrogen bonds are achieved at temperature 20–23°C and pressure $\sim 0.2 \times 10^9$ Pa. This implies that, on the one hand, the Coulomb repulsion of oxygen atoms is strengthened, while, on the other hand, the hydrogen bonds are weakened. Therefore, the integral attraction between the molecules weakens that contributes to their higher mobility with respect to one another, i.e., to reduction of water viscosity.

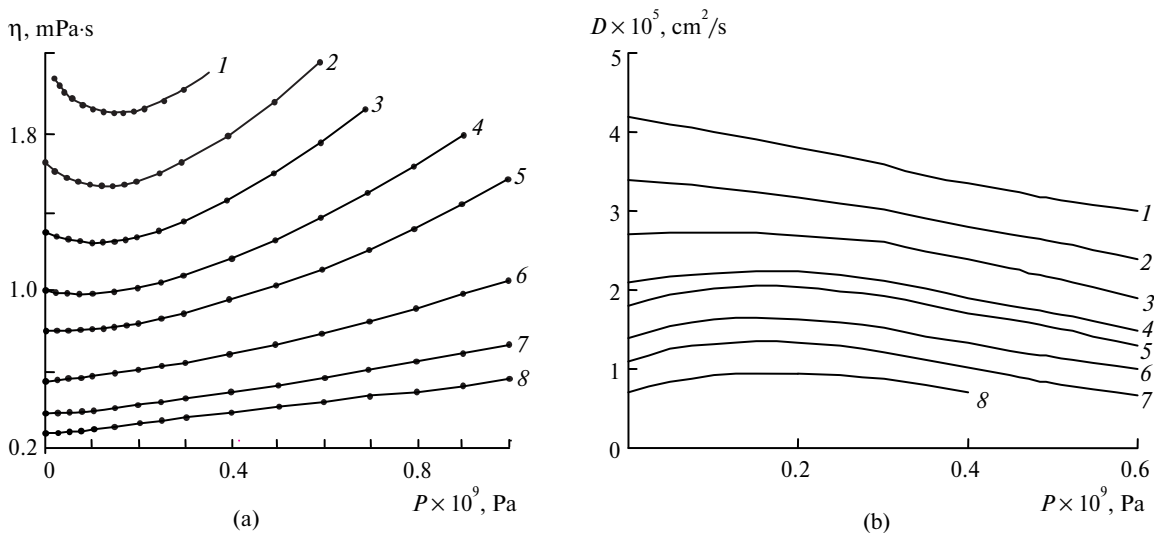


Fig. 1. The relationship of the dynamic viscosity of water (η) [2, 3] as a function of pressure (P) at temperature T , °C: -5 (1), 2.2 (2), 10 (3), 20 (4), 30 (5), 50 (6), 75 (7), 100 (8) (a) and the relationship of the water diffusion coefficient (D) [4, 5] as a function of pressure (P) at temperature T , °C: 47 (1), 37 (2), 27 (3), 17 (4), 10 (5), 4 (6), 0 (7), -10 (8) (b).

At the same time, the water spectra obtained at 52°C [7] indicate the monotonic dependence of oscillation frequency on pressure P that corresponds to the absence of extreme relationships for typical distances between atoms of water molecules. These results are in good agreement with data presented in Fig. 1a: an extremum on the water viscosity versus pressure relationship at 50°C is not observed. Hence, it follows that in the interval 23–52°C there is a change in behavior of hydrogen bond responsible for both, the substantial change of the water expansion coefficient in the neighborhood of temperature 42°C [1] and nonmonotonic change of viscosity. Thus, based on data about the water expansion coefficient (see Fig. 5 in paper [1]), the viscosity and water diffusion coefficients (see Fig. 1), we can conclude that quantitative changes of energy of hydrogen bonds and Coulomb repulsion of oxygen atoms turn into qualitative ones in the temperature interval of 30–50°C.

The detected peculiarities of η variations (see Fig. 1a) should be closely related with D . It is natural that the rise of temperature, i.e., an increase of kinetic energy of molecules kT leads to the rise of D (see Fig. 1b). In this case, the obtained experimental data [4, 5] demonstrate the pattern directly opposite to that of viscosity: with the rise of pressure P the diffusion coefficients initially increase and later decrease. The extremal D versus P relationships (see Fig. 1b) are observed in the interval from -10 to 27°C, however, at temperatures 37°C and higher, the diffusion coefficients monotonically decrease with the rise of pressure.

The inverse relationship between η and D of particles with radius a is described by the Stokes-Einstein equation:

$$D = kT/6\pi\eta a. \quad (1)$$

It is such interrelationship between η [2, 3] and D [4, 5] that is observed in comparing data presented in Figs. 1a, 1b. However, it is a question of qualitative rather than quantitative conformity. Insufficient accuracy of D versus $(1/\eta)$ relationship can be associated with the fact that formula (1) is widely used in molecular physics, it was derived for spherical particles, while the shape of practically all the molecules, including water molecules, is essentially different from sphere. In addition, the viscosity is taken into account here as a certain averaged characteristic of liquid, while the diffusion coefficient of molecules and ions depends on the local rather than averaged interaction.

The marked impact of hydrogen bonds can be also seen by comparing data for molecule diffusion of $H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$ in water and liquid without hydrogen bonds, for example in nitromethane CH_3-NO_2 . Differences between curves 1 and 2 (Fig. 2a) for molecules with different oxygen isotopes are insignificant and can be explained both by the variation of isotope composition and by conditions of specific experi-

mental investigations. We can also see insignificant differences between data obtained by different methods: using NMR (curves 1, 2) and the scattering of slow neutrons (curve 1'). It should be noted that the slope of $D(T)$ curve during the water overcooling up to -35°C actually coincides with that at $T > 0$ (curves 1, 2). This indicates the monotonic relationship of the intermolecular interaction as a function of temperature.

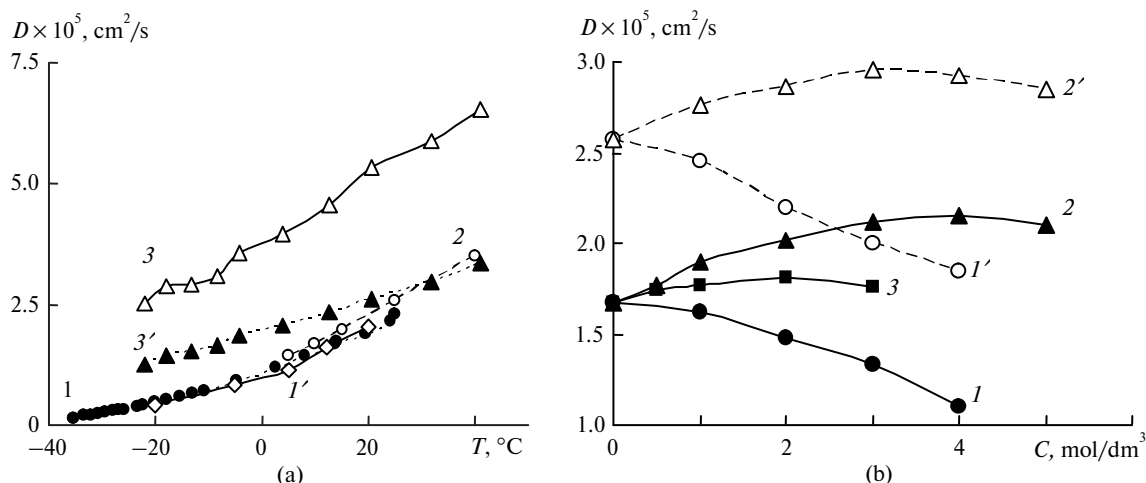


Fig. 2. The relationship of D for molecules H_2^{16}O (1, 1') and H_2^{18}O (2) in water and molecules H_2^{17}O (3) and $\text{CH}_3\text{-NO}_2$ (3') in nitromethane as a function of temperature [18–13] (a) and the concentration of salts dissolved in water: NaCl at 10 (1) and 25°C (1'), KI at 10 (2) and 25°C (2'), and KCl at 10°C (3) [14] (b).

Diffusion coefficients of water molecules and nitromethane molecules in nitromethane [13] substantially differ by their value from the diffusion coefficients of water molecules in water [8–12]. Since hydrogen bonds are absent in nitromethane, water molecules cannot form three-dimensional structures with adjacent molecules as it could be in water, i.e., their motion is freer. Therefore, the diffusion coefficient of water molecules in nitromethane (see Fig. 2a, curve 3) over the entire interval of temperatures is substantially larger than the diffusion coefficients in water (curves 1, 2). Owing to the fact that the viscosity of nitromethane due to the absence of hydrogen bonds is by 30% less than the viscosity of water, the diffusion coefficient of its molecules in the nitromethane liquid phase (curve 3') is larger than the diffusion coefficient of water molecules in water (curves 1, 1', 2). At the same time, as could be expected from formula (1), due to smaller size of water molecules as compared to the nitromethane molecule, the diffusion coefficient of its molecules in nitromethane (curve 3) is larger than the diffusion coefficient of molecules of nitromethane proper (curve 3').

The method of slow neutron scattering [8] was used to determine two components of the diffusion coefficient of molecules: unit (D_1) and collective (D_0), and the total diffusion coefficient $D_s = D_1 + D_0$ (see Fig. 2a, curve 1'). It is assumed that during a specific time (settled lifetime of molecule $\tau_0 \sim 10^{-12} - 10^{-11}$ s) each molecule oscillates around the local center of equilibrium, and then during time τ_1 ($\tau_1 \ll \tau_0$) the molecule transits continuously or stepwise into a new quasi-equilibrium state. Ratios D_0/D_1 and D_0/D_s indicate an insignificant contribution D_0 to the total diffusion coefficient D_s increasing with the reduction of temperature (Table 1). Attention is also drawn to the fast decrease of D_1 in overcooled water that indicates the strengthening of intermolecular interaction related to the reduction of thermal motion. In this case, the value of D_0 increases, however its absolute values remain practically unchanged.

The appearance of collective component is related to the existence of local strong attraction between molecules that can lead to formation of associates (clusters). The estimation of dimensions of associates using expression (1) and the value of D_s at 20°C (see Table 1) shows that their diameter amounts to about 1 nm that is ~ 10 times more than the diameter of unit molecule of water. It is such value that is presented in papers [8, 15], and it is asserted that the sizes of associates change insignificantly with the reduction of temperature. At the same time, the calculations performed on the basis of analysis of specific density of water [15] show that at temperature 0, -20 and -40°C the volume fraction of water occupied by associates amounts to 11, 31, and 41%, respectively.

The introduction of impurities into water leads to the local change of energy of water molecules that is reflected in their interaction with the nearest neighbors and, in turn, changes their diffusion mobility. Figure 2b presents the relationship of the diffusion coefficients of water in the presence of several electrolytes dissolved in water [14]. Taking into account that the used salts have different sizes of ions, degrees of their

hydration and their diffusion coefficients, they affect hydrogen bonds of the neighboring molecules in a different way: NaCl leads to reduction (curves 1, 1'), while KI leads to the rise of water diffusion coefficient (curves 2, 2'), while KCl leaves this coefficient almost unchanged (curve 3). Note that though Na⁺ ions possess lower mobility as compared to K⁺, Cl⁻ and I⁻, however, the diffusion coefficients for all specified ions are lower than for molecules of water. Hence, we could have assumed that due to the hampering of the free movement of water molecules and also fixing a part of water molecules in hydration shells, the solutions of these salts should always lead to the reduction of their diffusion coefficients that contradicts reality. Moreover, an insignificant difference in intrinsic mobility of chlorine and iodine (a few percents) leads to noticeable difference in behavior of experimental curves 2 and 3 (see Fig. 2b).

Table 1. Comparison of the total diffusion coefficient D_s and its unit D_1 and collective D_0 components [8]

$T, ^\circ\text{C}$	$D_s \times 10^5$	$D_0 \times 10^5$	$D_1 \times 10^5$	D_0/D_1	D_0/D_s	$\tau_0 \times 10^{11}, \text{s}$
	cm/s					
20	2.18	0.18	2.00	0.09	0.08	0.5
12	1.81	0.18	1.63	0.11	0.10	0.7
5	1.45	0.17	1.28	0.133	0.12	1.0
-5	1.24	0.16	1.08	0.148	0.13	1.6
-20	0.66	0.16	0.5	0.32	0.24	5.9

It was also detected that the diffusion coefficient of water molecules increased in the presence of triton X-100 [16], salts KBr, CsI, CsCl, and CsBr [17], while for a great number of solutions of other salts and acids the water diffusion coefficients decreased [18]. Unfortunately, the theoretical simulation of interaction of different solutions of electrolytes with water molecules demonstrated the reduction of water diffusion coefficient in all the cases, while the possibility of its rise was not achieved [17].

In our view, the current situation with interpretation of experimental data is determined by the complexity of taking into account simultaneously the impact of dissolved salts on electrostatic repulsion of oxygen atoms and on hydrogen bonds both between individual molecules and in nanosize clusters of water. One of the possible variants of explaining the rise of diffusion coefficients of water molecules can imply that ions of dissolved salts interact with dipole moments of water molecules and form the hydration shells by reorienting the nearest to them water molecules in such way that oxygen and hydrogen atoms are attracted to cations and anions, respectively. The degree of hydration of different ions and molecules is unequal and depends on the size of particles and the value of their charge determining the polarization of latter in the presence of dipoles of water molecules. The larger the charge and the smaller the size of ions, i.e. the higher specific density of charge, the stronger is their interaction with water molecules and, correspondingly, their hydration. Strong Coulomb attraction not only binds water molecules with salt ions in the hydration shell, but also fix them in a specific sufficiently rigid position that simultaneously changes their orientation with respect to the nearest water molecules that are not bound with ions of salts. This, in turn, leads to the local change of intermolecular interaction, i.e., to the change of orientation and interaction of water molecules with their next neighbors. Because the water molecules are arranged optimally in the absence of impurities that corresponds to minimization of their internal energy for the specified temperature and pressure, the variation of their orientation at the expense of ions of salts can lead only to weakening of bonds between unit molecules. This means a lighter sliding of molecules with respect to one another, i.e., the rise of their diffusion coefficient (see Fig. 2b).

Weakening of bonds between single molecules should also affect the formation of water clusters reducing their size that, in turn, leads to the rise of the averaged diffusion coefficient of molecules. For example, at the salt concentration of 1 mol/dm³, one molecule of this salt occupies the volume of about one cubic nanometer that corresponds to characteristic dimension of nanosize clusters of water [14]. Thus, in this case the probability of collision of salt cations and anions with clusters is very high. With due regard for the above considerations about the weakening action of hydrated ions on attraction between the nearest molecules of water, we can expect a slower formation or faster disintegration of clusters than in the absence of salts, i.e., the rise of fraction of free water molecules. Moreover, the ions of electrolyte can be incorporated into clusters changing their structure and diffusion properties. The results of analysis of X-ray and Raman water spectra in the presence of alkali metal salts [19] are a partial confirmation of the above conclusion. Here is shown that all alkali metals and iodine anion weaken hydrogen bonds, while the chlorine and bromine anions practically do not affect them. Because the weakening of hydrogen bonds, at the same time, means the rise of mobility of water molecules, it results in the difference between the curves for water diffusion coefficients in the presence of KCl

and KI (see Fig. 2b). Let us remember that sodium is more hydrated than potassium, therefore the integral diffusion coefficient of water molecules decreases at the expense of water bound with sodium. Taking into account that the properties of potassium and cesium ions are sufficiently close, data about weakening of hydrogen bonds at the expense of iodine anion, and their insignificant changes at the expense of chlorine and bromine anions bring us closer to understanding the rise of diffusion coefficient of water molecules in the presence of KBr, CsI, CsCl and CsBr [10].

The results of investigations of the dependence of diffusion coefficients of water molecules on dissolved electrolytes are in agreement with ideas that the lifetime of water molecules in the first hydration shell of ion τ_h can be both larger and smaller than the lifetime of water molecule in a specific lattice point of pure water τ_0 [20]. In particular, for ions Li^+ and Na^+ $\tau_h > \tau_0$ (positive hydration), while for ions K^+ , Cs^+ , Rb^+ , Cl^- , Br^- , I^- on the contrary we have $\tau_h < \tau_0$ (negative hydration). Table 2 presents ratios τ_h/τ_0 [21, 22], where the lifetime of water molecule in the lattice point of pure water τ_0 at atmospheric pressure and temperature 25°C fluctuates in the interval 8.32–8.36 picoseconds [22].

Table 2. Ratio τ_h/τ_0 of characteristic lifetime of water molecule in hydration shells of ions τ_h in 1 M solutions of salts and in pure water τ_0 at temperature 25°C

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-	NO_3^-
τ_h/τ_0	2.41	1.53	0.90	0.78	0.68	2.61	0.90	0.73	0.41	0.73

Double- and triple-charged ions interact stronger with dipoles of water molecules than the single-charged ones; therefore, for such ions (except certain rare-earth metals) $\tau_h > \tau_0$. It follows that the introduction of double- and triple-charged ions should slow down the diffusion of water molecules and increase its viscosity. It should be also noted that the variation of diffusion coefficients of water molecules in the presence of dissolved substances is interrelated with the variation of its activity coefficient [20]. Weakening of translational motion of water molecules, i.e., the reduction of their potential energy results in the reduction of water activity coefficient and, vice versa, the strengthening of their translational motion, i.e., the rise of potential energy, leads to an increase of this coefficient.

Since water can dissociate, it results in not only the diffusion of water molecules, as a whole, but also in diffusion of individual ions H^+ and OH^- that is especially important during the water exposure to electric field. Hydrogen ions possess the highest diffusion coefficient (which is almost 5 and 7 times as big as that of the potassium and sodium ions, respectively), and, correspondingly, the highest electromigration mobility among the single-charged ions. According to the idea proposed more than 200 years ago by T. von Grotthuss, such anomalously large diffusion coefficient of hydrogen ions is stipulated by its transfer along the chain of water molecules tied by hydrogen bonds of water molecules (relay mechanism) and is determined by the speed of their polarization. This idea, in particular, is confirmed by the method of high-speed spectroscopy of the acid and base neutralization process [23]. Diffusion coefficients of hydroxyl ions are less than those of hydrogen ions, but more than those of sodium and potassium ions. A hypothesis was proposed not long ago [24], according to which the motion of hydroxyl ions in the electric field was accompanied by hypercoordination of water molecules. The hydrated ion of hydroxyl is coordinated to four electron-acceptor molecules of water in such way that when the initial hydrogen bond is replaced with electron-donor form of hydrogen bond, the initial coordination of water molecules can be easily restored by the transfer of hydroxyl ion. The need of rearrangement of hydrogen bonds should reduce the mobility of hydroxyl ions as compared to the hydrogen ion moving by the Grotthuss mechanism that corresponds to the experimental ratio of their diffusion mobilities.

THERMAL CAPACITY AND THERMAL CONDUCTIVITY OF WATER AND ICE

Thermodynamic characteristics of water differ significantly from other liquids. First of all, its thermal capacity is several times as large as that of the majority of liquids (for example, it is twice as big as that of ethanol, 2.5 times as big as that of oil, and 30 times as big as that of mercury). In our view, these differences are explained by two factors. Firstly, due to small size of water molecules, their number in a unit volume is more than the number of molecules of other liquids; therefore, the thermal energy is spent for a larger number of molecules. Secondly, unlike the liquids without hydrogen bonds, the heating and evaporation of water or melting of ice are related to the deformation or rupture of energy intensive hydrogen bonds. The energy consumed for these processes cannot be converted into the kinetic energy of water, i.e., it cannot raise its temperature that finally results in a larger specific thermal capacity. Due to these causes, water also has larger values of specific melting heat and specific heat of evaporation. It must be emphasized that a large thermal capacity of

water prevents sharp fluctuations of temperature of both proper water and air, i.e. it is important from the viewpoint of maintaining the climate stability on the globe.

Figures 3a and 3b present the averaged curves of the relationship of isobaric thermal capacities C_p of water, electrolyte solution, steam, and ice as a function of temperature [25–27].

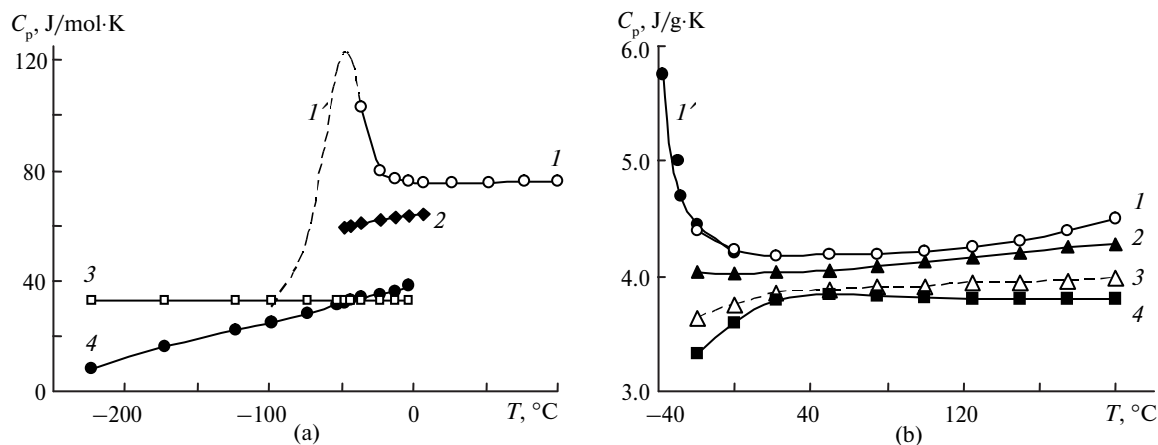


Fig. 3. The relationship of the specific isobaric thermal capacity of water (I), NaCl solution (3 mol/dm³) (2), steam (3), hexagonal ice (4), and theoretical model (I') [25–28] (a) as a function of temperature at pressure, Pa: 10^5 (I , I'), 5×10^7 (2), 2×10^8 (3), and 4×10^8 (4) [29] (b).

In vapor state the thermal capacity of water remains constant in a wide interval of temperatures (see Fig. 3a, curve 3) that is stipulated by the absence of hydrogen bonds at large distance between molecules. In the case of ice (curve 4), as its temperature drops, the length of hydrogen bonds decreases, but their energy increases; in this case, vibrations of molecules decrease that results in the reduction of thermal capacity. The introduction of NaCl into water (curve 2) also results in the reduction of thermal capacity as compared to that of pure water (curve 1) that corresponds to the reduction of mobility of water molecules (see Fig. 2a, curve 2). The variation of thermal capacity in the temperature interval from -13 to 100°C (see Fig. 3b, curve 1) is sufficiently slow with weakly pronounced minimum at 36°C . However, in case of overcooling, when the water is below -13°C (curve I'), the thermal capacity sharply rises. Figure 3a also presents relationship $C_p(T)$ [25–27] calculated for the interval of temperature from -102 to -13°C that demonstrates the presence of maximum at -48°C and the possibility of sharp reduction of thermal capacity during further overcooling of water up to approaching the thermal capacity of ice. The qualitative trend of theoretical curve I in Fig. 3a is in good agreement with data from paper [28]. This indicates that the maximum value of isobaric thermal capacity is ~ 1.5 times as high as its value at 0°C . However, in this case the maximum is located at -30°C rather than at -48°C .

It should be noted that the sharp rise of thermal capacity of overcooled water in the interval from -23 to -33°C (see Fig. 3a, curve I') is in a sufficiently good agreement with the bend of the curve for specific melting heat of ice λ (maximum $\lambda = 6.05$ kJ/mol is achieved at -17°C) [26]. In the opinion of the authors, the rise of melting heat with the reduction of temperature to -17°C is stipulated by strengthening of hydrogen bonds and reduction of vibration energy of ice as compared to the overcooled water. The change of the overcooled water structure occurs, probably, at lower temperatures that results in reduction of the heat required for transition from solid into liquid phase. With the rise of pressure (see Fig. 3b) the water thermal capacity decreases. Moreover, instead of the minimum at 36°C (curve I) and $P > 10^8$ Pa (curves 3 and 4), a maximum appears practically at the same temperature. However, with further rise of pressure, the thermal capacity of water again demonstrates anomalous behavior: after its reduction, we observe a rise (Fig. 4a, segments of curves marked by letter W).

The specified figure also presents data about isobaric thermal capacity of hexagonal (Ih), trigonal (II), tetragonal (III), monoclinic (V), tetragonal (VI), and cubic (VII) modifications of ice [30], from which we can see the anomalous behavior of water: at -33°C we observe stepwise changes of thermal capacity with the rise of pressure and transition from Ih modification of ice to modification III and from III to II and then to V.

It should be noted that the sharp reduction of thermal capacity of water during transition from the liquid state into solid one with ice modification VI at temperatures 17 and 67°C (see Fig. 4a) is not anomalous, because the transition into ice-like state leads to a rigid fixation of water molecules that reduces the possibility of thermal energy transfer to such molecules. In addition, the reduction of thermal capacity of all modifications of ice with the reduction of temperature is quite logical. If the thermal capacity of water at 17°C and ice

at -33°C in modifications Ih and II (see Fig. 4a) demonstrates a clearly defined minimum at pressure $< 5 \times 10^8$ Pa, the thermal conductivity of water up to 8×10^9 Pa at temperature $\geq 30^{\circ}\text{C}$ is a monotonic function of pressure (see Fig. 4b). Unfortunately, investigations in paper [31] were not conducted at lower temperatures and higher pressures. At the same time, according to paper [32], just at pressure 8×10^8 Pa and temperature 25°C the temperature conductivity of water $\chi = \kappa/C_p$ passes through maximum that disappears at temperature $\geq 100^{\circ}\text{C}$.

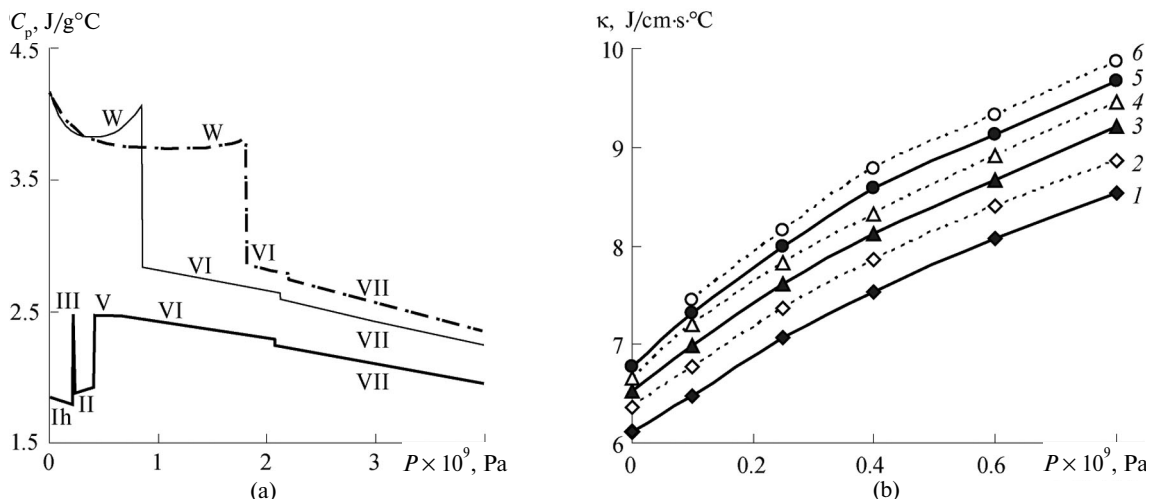


Fig. 4. The relationships of specific isobaric thermal capacity of water (W) and different modifications of ice (see Roman numerals near individual segments of curves) at temperatures, T , $^{\circ}\text{C}$: 67 (dash-and-dot line), 17 (dotted line) and -33 (solid line) [30] (a), and also the thermal conductivity of water κ at temperatures, T , $^{\circ}\text{C}$: 30 (1), 50 (2), 70 (3), 90 (4), 110 (5), 130 (6) [31] (b) as a function of pressure.

CONCLUSIONS

The presented analysis of water characteristics has demonstrated the anomaly of its behavior with variation of temperature, pressure, and the concentration of dissolved salts. However, at times the numerical data in different studies for the same parameters are distinctly different [33] that is stipulated, probably, by non-equal conditions for conducting investigations. That is why, a statistical processing of data obtained by different authors and methods needs to be performed for unequivocal assertion regarding the nonmonotonic and, therefore, anomalous changes of a specific characteristic of water. It also implies the need for simultaneous thorough analysis of test conditions, presence of impurities, isotope composition of water, experiment errors and the interpretation of findings.

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