



Activation energy of water structural transitions

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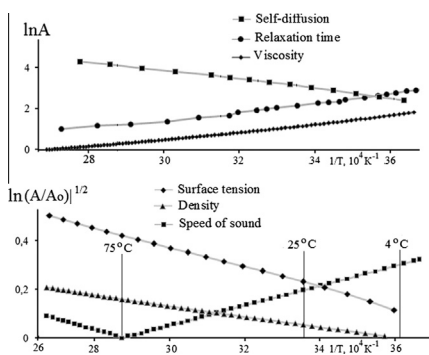
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HIGHLIGHTS

- Temperature dependencies of water properties have different activation energies.
- Break of hydrogen bonds limits diffusion and electric relaxation in water.
- Rotation of water clusters limits the thermodynamics of its static properties.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the nature of molecular motions that dominate in the thermodynamics of anomalies of liquid water properties in the range of 0–100 °C has been studied. Temperature dependencies of water properties have been approximated by exponential functions and the activation energies for water structure transitions have been evaluated. The activation energy values were compared with the energy spectra of characteristic vibrations and with those of cooperative molecular motion in the lattice-type structure of hydrogen bonds. It has been found that it is the reaction of hydrogen bond breaking that mainly limits the abnormal dynamics of water viscosity, self-diffusion, dielectric relaxation time and electric conductivity. It has been assumed that the thermodynamics of cooperative motion and resonance phenomena in water clusters form a basis for the differentiation mechanism of extrema points in temperature dependencies of water density, isobaric heat capacity, sound velocity, surface tension coefficient and compressibility.

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Introduction

The anomalies of water properties are defined by its specific molecular structure, hydrogen bonds (HB) dynamics and disassociation of water molecules resulting in proton and hydroxyl group formation. The earliest life forms first appeared in water and they consist of mainly water. That is why, in the course of phylogenesis, the anomalies of water have, in one form or another, found their development in physical–chemical metabolism mechanisms and the ability of biological systems for adaptation to various

environments, and there is every reason to suppose that water participated actively in the genesis of bilateral and chiral biosphere asymmetry [1,2]. Among the anomalies of water in the liquid phase are, first of all its extremal temperature dependences (TD) of density (ρ), heat capacity at constant pressure (C_p), compressibility (γ) and sound velocity (V). The extrema points of these TD s are 4 °C, 35 °C, 45 °C and 75 °C, respectively.

The thermodynamic mechanism of extrema points (T_e) differentiation, as well as that of TD shape, are not yet perfectly clear [3]. Generally, T_e can be compared with the critical points of second-order phase transition where only system restructuring takes place without intrinsic energy change (constant-energy transitions)

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[2–5]. Water restructuring mechanisms of this type in T_e points are realizable because water is a kind of cooperative quantum system composed of molecules linked by means of HBs into a three-dimensional lattice [6]. The data related to the water polymorphic properties proves the existence of such systems [7]. The tetrahedral structure of the lattice is defined by sp^3 -hybridization of oxygen atom orbitals and the ability of water molecule to form two donor-type and two acceptor-type HBs. The thermodynamics of the lattice structure depends on the energy and lifetime of HBs, as well as on the lattice integrity degree i.e. on the number of defects interfering with its tetrahedral structure and consistency. Defects may appear due to rotation–translation reorientation of molecule or due to the change of its HBs number.

The quantum origin of intermolecular interactions in lattice-type water structures can be detected, for example, in the dependence of HB formation reaction on the nuclear mechanical moment of water molecule [8,9]. In the course of HB formation, rotationally excited para-molecule returns into its ground state where its rotation energy equals to zero. The value of the quantum number for an ortho-molecule in its ground state is unity. Firstly, it prevents the HB formation, secondly, it increases the probability of lattice structure deformation or breakage during the transition of para-molecule into ortho-molecule. In accordance with the spin theory [9], the rate of thermally-induced transitions between para- and ortho- states increases drastically when quanta of rotational transitions of ortho- and para-water isomers come into resonance with thermal energy quanta (kT_e) at T_e . The growth of ortho-isomer concentration leads to the restructuring of HB lattice resulting in the change of water property's TD with its extrema at T_e .

The fluctuation-type HB concept [10,11] also correlates with the critical phenomena mechanism at T_e . Calculations in the frames of this concept have shown that due to the donor-type HB asymmetry within one water molecule, the difference of O–H group oscillation energy for the majority of molecules varies in the range of 0.6 kJ/mol to 1.8 kJ/mol and attains its maximum at $\sim 33^\circ\text{C}$, i.e. close to T_e for heat capacity at constant pressure [10]. At the same time, a “shoulder” appears on the TD curve for radial distribution function for the nearest neighboring atoms, at temperatures above 45°C . It is associated with the growth of the share of very weak HBs and deformation of tetrahedral cell due to the displacement of central water molecule towards a neighboring one resulting in formation of single HB with optimal geometry instead of four HBs [11].

The results of computer simulation of water molecular dynamics at 24°C show that 98% of molecules in their distribution have more than one HB while only 1% of them have one HB, and there is no molecule without, at least one HB [12]. The investigations of water molecular dynamics in the condensed phase have proved the existence of two fractions in it: one with low (**A**) and the other with high (**B**) density [13,14]. Clusters with tetrahedral, ice-like, structure form **A**-fraction while clusters with denser packing of water molecules and greater number of strained HBs belong to **B**-fraction [9,15]. In a number of works [14,16] transitions between **A** and **B** fractions are involved to explain abnormal water properties' behavior, first of all, that of volumetric density.

In work [17], the **A**-type “flickering cluster” model [19] was applied to approximate the experimental TD of C_p [18]. “Flickering” refers to the reversible dissociation of cluster as a result of cooperative process that starts with the exit of one water molecule from the HB lattice. In accordance with this model, the authors of [17] made a polynomial approximation of TD for C_p comprising three power functions of temperature. They evaluated the enthalpy of reversible transformation of **A**-type flickering cluster.

In paper [20], a theoretical substantiation of cluster formation in the tetrahedral HD lattice has been made. Clusters are associated

with each other into spiral chains consisting of tetrahedrons. This theory says that the coherent oscillation frequency for n protons in a chain can be calculated using the following formula:

$$\nu_n = 22n^{-1}(n-1)^{1/2} \text{ (THz)}.$$

For example, ν_n amounts to 6.6 THz for $n = 10$ while the oscillation energy is ~ 2.6 kJ/mol [20]. It is clear that an external electromagnetic radiation acting in resonance with the proton oscillation frequency ν_n would stimulate spiral clusters formation. Water spiral clusters may probably be involved in the metabolism processes in life forms and, therefore, could have contributed to the chiral biosphere genesis.

In this work, the difference in thermodynamics of TD s for abnormal water properties has been studied and the average values of temperature gradients, as well as those of activation energy for structural reforming that determines both the TD behavior and T_e for each water property, have been estimated. For this purpose, the linear approximation method was applied [21] to the published data related to the TD s of water properties.

Methods and results

The experimental TD s of ρ [24], C_p [16,22], γ [25], ν [26], as well as those of dynamic viscosity (η) [27], surface tension coefficient (σ) [23], specific conductivity (λ) [28], self-diffusion coefficient (D) [29] and dielectric relaxation time (τ) [12] were taken from reference books and other information sources. The numeric values of parameters along with the corresponding references are given in Annex. Normally, the TD s of water properties are approximated by complex power polynomials. For example, for the ρ and C_p TD s the following expressions are often used:

$$\rho = (a_0 + a_1t + a_2t^2 + \dots + a_5t^5)(1 + bt)^{-1} \quad [19],$$

$$C_{p(T_e)} / C_{p(15^\circ\text{C})} = 0.99618 + 0.0002874(1 + t/100)^{5.26} + 0.01116010^{-0.036t} \quad [22],$$

Calculations of σ are usually done using formula [23]: $\sigma = 235.5(T/T_0)^{1.256}[1 - 0.625(T/T_0)]$.

Approximations like these are rather helpful for technical and technological applications but their complexity may completely obscure the abnormal TD behavior and T_e position. In [21], to approximate TD s of ρ , ν , C_p , γ and σ functions of the following form were used:

$$A = A_e \pm B(1/T - 1/T_e)^2, \quad (1)$$

where A are experimental values of water properties, A_e are their extremal values for T_e and B is a constant. Approximations (1) were linear for the corresponding anamorphoses and temperature ranges, being subject to kinking at T_e . Values 0, T_e and 100°C were the limits of temperature ranges.

Generally, two types of water cluster cell restructuring mechanisms are possible. The first type (I-type) includes structure transitions associated with HB breaking and those of water molecule withdrawal from the cell. Effective activation energy (E_{ef}) of this type structure transition will be of the same order of magnitude as that of HB (E_H) which equals, in average, to ~ 19 kJ/mol [19]. The second type of structure modification (II-type) belongs to the transformation of HB lattice structure configuration [19]. Values of E_{ef} for II-type structure transitions will be of the same order of magnitude as E_H of weak HBs, as well as the energy of rotation–translation motion of single molecules and cooperative molecular systems. Since, in accordance with Arrhenius equation, the water molecular restructuring kinetics is proportional to $\exp(\pm E_{ef}/RT)$ it

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