

Chapter 2

Water Structure, Quantum Nature of Hydrogen Bonds and Diffusion of Water Molecules in Chloride Aqueous Solutions

I. I. Geru

Abstract A large variety of water properties is caused by the peculiarities of water clusters and water hydrogen bonds which are quantum mechanical in nature due to a small mass of hydrogen atoms. The concentration dependences of the diffusion coefficient D for aqueous solutions were found using the DOSY 2D NMR method. It was shown that with exception of barium chloride solution, which exhibits an anomalous concentration behavior of D in the concentration range 0–10 mg/ml, for two other solutions D decreases with increasing of the concentration. On basis of the generalized Stokes–Einstein equation the following correlation lengths for water and chloride solutions of the concentration $c = 100$ mg/ml were obtained: $\langle \xi \rangle_{H_2O} = 1.07 \text{ \AA}$, $\langle \xi \rangle_{MgCl_2} = 0.93 \text{ \AA}$, $\langle \xi \rangle_{CaCl_2} = 1.04 \text{ \AA}$ and $\langle \xi \rangle_{BaCl_2} = 0.84 \text{ \AA}$. In the model of equivalent clusters of radius R the formula for estimation of the averaged time interval τ_0 between decay and creation of the clusters $\tau_0 = \tau_1[(R - \xi_0)/(\langle \xi \rangle - \xi_0) - 1]$ was proposed (τ_1 is the cluster lifetime and ξ_0 is the correlation length of the water without clusters). It was shown that for pure water $\tau_0 \approx 10^{-8} - 10^{-7}$ s.

Keywords Water structure • Hydrogen bonds • Water diffusion • DOSY 2D NMR

2.1 Introduction

Water is one of most mysterious substance in a nature with 67 anomalies of physical and chemical properties many of which arise from the nature of hydrogen bonds [1]. It is one of the few known substances whose solid form is less dense

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than the liquid. The behavior of water is due to the properties of hydrogen bond network. There exist intermittent collective molecular motions, influences associated with the rearrangement caused by the hydrogen bonds under strong or extremely weak inner or outer interactions.

The hydrogen bond in water is part (about 90 %) electrostatic and part (about 10 %) covalent [2].

Formation of hydrogen bonds between water molecules gives rise to large energetic changes in enthalpy (becoming more negative) and entropy (becoming less positive). This enthalpy-entropy compensation is almost complete with the consequence that very small imposed enthalpic or entropic effects may exert a considerable influence on aqueous systems [1]. It is possible that hydrogen bond between para-H₂O, possessing no ground state spin, are stronger and last longer than hydrogen bonds between ortho-H₂O possessing triplet spin ground state [3].

On very short time scale (less than a picosecond), water is more like a “gel” consisting of a single, huge hydrogen-bonded cluster. On a 10^{-12} – 10^{-9} s time scale, rotations and other thermal motions cause individual hydrogen bonds to break and re-form in new configurations. The localized (H₂O)_n clusters may have a fleeting existence, and many theoretical calculations have been made showing that some combinations are more stable than other.

The lower water clusters can enlarge and to form highly symmetric icosahedral water cluster containing 280 water molecules [1]. Water is a network of icosahedral water clusters what can dynamically form continuous networks of open, low-density and condensed structures. The minimum number of possible arrangements of hydrogen bonds in the fully occupied low-density icosahedral network is more than 150-thousand. A fluctuating network of water molecules, with localized and overlapping icosahedral symmetry, was first proposed in 1998 and independently found, by X-ray diffraction, in water nanodrops on 2001 [4].

Water clusters are a considerable interest as models for the study of water structure, and many articles of them are published every year. The principal finding was that 80 % of the water molecules are bound in chain-like fashion to only two other molecules at room temperature, thus supporting the prevailing view of a dynamically-changing, disordered water structure.

The chapter is organized as follows: [Sect. 2](#) provides the water hydrogen-bonds (H-bonds). Water clusters and water H-bonds network are presented in [Sects. 3](#) and [4](#). [Section 5](#) contains short information about the quantum mechanical properties of hydrogen-bonds network such as zero-point motion, quantum delocalization and quantum tunneling.

2.2 Water Hydrogen Bonds

The water molecule is electrically neutral, but the positive and negative charges are not distributed uniformly. The negative electronic charge is concentrated at the oxygen end of the molecule and to oxygen's high positive nuclear charge which

exerts stronger attractions to the electrons. This charge displacement constitutes an electric dipole. The partially-positive hydrogen atom on the water molecule is electrostatically attracted to the partially-negative oxygen on neighboring molecules.

Each liquid water molecule is involved in about four hydrogen bonds but considerably less than covalent bonds with strength considerably greater than the natural thermal energy. More exactly, the hydrogen bonds between hydrogen and oxygen atoms belonging to different water molecules are 20 times weaker than covalent bonds and 60 times stronger than van der Waals bounds [5].

There is no standard definition for hydrogen bond energy. In liquid water, the energy of attraction between water molecules is optimal about 23.3 kJ mol^{-1} [6] and almost five times the average thermal collision fluctuations at 25°C . This is energy required for breaking and completely separating the bond, and equals about half of the enthalpy of vaporization (44 kJ mol^{-1} at 25°C). Just breaking the hydrogen bond in liquid water, leaving the molecules essentially in the same position and still retaining their electrostatic attraction, requires only about 25 % of this energy, recently estimated at 6.3 kJ mol^{-1} [7]. If the excess heat capacity of the liquid over that of steam is assumed attributable to the breaking of the bonds, the attractive energy of the hydrogen bonds is determined to be 9.8 kJ mol^{-1} [8].

This may be considered as an indication of the total extra energy caused by polarization, cooperatively and covalency of the hydrogen bond.

The Gibbs free energy change presents the balance between the increases in bond strength and consequent entropy loss on hydrogen bond formation and may be used to describe the balance between formed and broken hydrogen bonds [9]. Several estimates shown that the Gibbs free energy change needed for the formation of water's hydrogen bonds is about -2 kJ mol^{-1} at 25°C [10].

The bond lengths and angles will change as consequence of polarization shifts in different hydrogen-bonded environments. The oxygen atoms in water molecule typically passes about $0.7 e$ negative charge and the hydrogen atoms about $0.35 e$ positive charge giving rise to both an important electrostatic bonding but also the favored trans arrangement of the hydrogen atoms. The hydrogen bond strength varies with the hydrogen bond angle ($\text{O-H}\cdots\text{O}$). If the hydrogen bond is close to straight, the hydrogen bond strength depends almost linearly on its length with shorter length giving rise to stronger bending. As the hydrogen bond length on water increases with temperature increase but decreases with pressure increase, hydrogen bond strength also depends almost linearly on the temperature and pressure [11].

An important feature of hydrogen bond is that it possesses direction. This direction is that of the shorter O-H covalent bond, the O-H hydrogen atom being donated to the O -atom acceptor on another H_2O molecule. In H-NMR spectroscopy, the chemical shift of the proton involved in the hydrogen bond moves about 0.01 ppm K^{-1} upfield to lower frequency. There is also about 5.5 ppm further upfield to vapor at 100°C . That is, becomes more shielded with reducing strength of hydrogen bonding [12] as the temperature is raised.

A similar effect can be detected in water's ^{17}O -NMR, moving about 0.05 ppm K^{-1} upfield and 36–38 ppm further upfield to vapor at 100 °C [1].

The spin–lattice relaxation time ($T_1 \sim 3.6$ s, $t = 25$ °C) of the water protons is also function of the hydrogen bonding, being shorter for stronger bonding. However, the effect of solutes shows that the chemical shift and spin–lattice relaxation time are not correlated [13]. The spin–lattice relaxation time has been found to be of three times greater than the spin–spin relaxation time, suggesting the presence of supramolecular structuring in water [14]. These data were confirmed by our measurements of spin–lattice and spin–spin relaxation times for distilled water at 25 °C using the Bruker NMR relaxometer Minispec mq 20: $T_1 = 3.6 \pm 0.2$ s and $T_2 = 1.86 \pm 0.007$ s.

There is substantial cooperative strengthening of the hydrogen bonds in water, which is dependent on long-range interactions [15]. Breaking one bond generally weakens those around whereas making one bond generally strengthens those around. This leads to cluster formation where all water molecules are linked together by three of four strong hydrogen bonds. For the same average bond density, some regions consist mainly of weekly hydrogen-bonded water molecules. This variation is allowed with the water molecules at the same chemical potential as there is compensation between the bond's attractive energy and the energy required for creating the orderliness apparent in cluster formation.

2.3 Clustering of Water Molecules

When the hydrogen bonding is strong, the water network expands to accommodate these directed bonds and where the hydrogen bonding is weak, water molecules collapse into space around their neighbors. Such changes in water's clustering give rise to the so-called anomalies of water. Particularly, this leads to different behaviors of hot water which has weaker hydrogen bonding, and cold (super cooled water), which has stronger hydrogen bonding. It is the clustering of water, due to the directed characteristics of the hydrogen bonding, that is responsible for the very special properties of water that allow it to act in diverse ways under different conditions.

The water molecules form an infinite hydrogen-bonded network with localized and structured clustering. Small clusters of four water molecules may come together to form water bicycle-octamers [1]. The competition between maximizing van der Waals interactions (structure A) and maximizing hydrogen bonding (structure B) is finely balanced, easily shifted with changed physical conditions, solutes and surfaces. The potential energy barrier between these states ensures that water molecules prefer either structure A or B with little time spent on intermediate structure. An individual water molecule may be in state A with respect to some neighbors whilst being in state B with respect to others.

The bicycle-octamers may cluster further, with only themselves, to form highly symmetric 280-molecule icosahedral water clusters that are able to interlink and

tessellate throughout space. A mixture of water cyclic pentamers and tricyclodecamers can bring about the same resultant clustering [1]. As three of these small clusters are relatively stable, it is likely that their interaction will produce these large icosahedral clusters. Such clusters can dynamically form a continuous network of both open (low density) and condensed structures. The fluctuating self-replicating network of water molecules, with localized and overlapping icosahedral symmetry, was first proposed to exist in liquid water by Martin Chaplin [16].

The liquid water acts in subtly manners as circumstances change depending on variations in physical and molecular environments and occasionally acting as though it were presents more than one liquid phase. Sometimes water acts as a free flowing molecular liquid whilst at other times, in other places or under subtly different conditions, it acts more like a weak gel.

In liquid water, the balance between the directional component of hydrogen bonding and the isotropic van der Waals attractions is finely poised. Increased strength of the hydrogen bond directionality leads to ordered clustering with consequential effects on physical parameters like a glass state, whereas reducing its strength reduces the size of the cluster with the properties of the water when only the van der Waals attraction remain. Quite small percentage changes in the strength of the aqueous hydrogen bond may give rise to large percentage changes in the such physical properties as melting point, boiling point, density and viscosity.

Thus, the water can be presented as an equilibrium mixture of low-density and high-density clusters [17] and examining the consequences of hydrogen bond strength variation on the cluster equilibrium with resultant effects on physical properties. This concept has been shown to explain qualitatively and quantitatively most anomalies of liquid water.

2.4 The Hydrogen-Bonded Network

The anomalous proprieties of the water, most pronounced in the supercooled metastable state [18], can be ascribed to water's unique structure, consisting of a random and fluctuating three-dimensional network of hydrogen bonds [19]. For understanding the water anomalous properties it is necessary to have the novel experimental techniques, detailed theoretical predictions, and computer simulation methods. In particular, the development of pulse neutron sources has allowed the remarkable advance of the deep inelastic neutron scattering (DINS) technique [20–22]. DINS technique is based on measurements at high energy, $\hbar\omega$, and high momentum, $\hbar q$, transfers, thus providing a probe of both the short-time ($t \leq 10^{-15}$ s) dynamics and local ($r \leq 1$ Å) environment of the atoms in materials [20, 21]. The high energy and momentum transfers achieved allows to describe the scattering process within the framework of the impulse approximation [21, 23, 24]. The scattering cross section is the expressed in terms of the single particle momentum distribution, $n(p)$, whose variance is related to the mean kinetic energy

$\langle E_k \rangle$. In the case of water protons the $n(p)$ and $\langle E_k \rangle$ provide a richness of information about the potential surface that the proton experiences, including the effects of hydrogen bonding. These possibilities make the DINS technique unique and well established tool to investigate the hydrogen bonding of the water under various conditions [22, 25–29]. In the Ref. [22] the $n(p)$ is expressed by explanation [21]

$$n(p) = \frac{e^{-p^2/2\sigma^2}}{(\sqrt{2\pi}\sigma)^3} \sum_n C_n (-1)^n L_n^{1/2} \left(\frac{p^2}{2\sigma^2} \right), \quad (2.1)$$

where $L_n^{1/2}$ are generalized Laguerre polynomials. The coefficients C_n and σ can be determined by a least squares fitting procedure. Proton mean kinetic energy $\langle E_k \rangle$, measured in [22] with DINS experiments on water sample under different thermodynamic conditions as a function on temperature, was approximated by dependence $\langle E_k \rangle \sim (T - T_s)^\gamma$, where $T_s = 228$ K and $\gamma = 2.67$. These data are in good agreement with values found for the description of the divergence of water structural and dynamic properties at T_s [30].

To highlight the differences between the $n(p)$ measured in the supercooled states and those measured in the liquid stable phase [26], the authors of the Ref. [22] have plotted the radial proton momentum distribution, $4\pi p^2 n(p)$, for water under different thermodynamic conditions as a function of p . It has been shown that the stable liquid water ($T = 298$ K) is characterized by a main narrow peak with maximum at $p = 5.2 \text{ \AA}^{-1}$ and by a secondary peak at about $p = 17 \text{ \AA}^{-1}$, in the radial momentum distribution that indicate the quantum delocalization, or coherent interference of the protons over the two sites of a double-well potential [28, 31, 32]. In this case each water proton is shared by covalent bound oxygen and an H-bond one; the proton will be coherent over two separated sites along the H-bond direction. The similarity between the H-bond and the proton mean kinetic energies suggests that each water proton can easily break and reform hydrogen bonds with one of his two first neighboring oxygens. The resulting delocalization of the proton between the oxygen atoms of two neighboring water molecules is consistent with the finding that a proton can become strongly delocalized between two oxygen atoms if the average O–O distance is $< 2.8 \text{ \AA}$, leading to a very broad double-well potential in the energy region, corresponding to the second excited state of the O–H stretch vibration [33].

Recently, Huang et al. [29] used small-angle X-ray scattering (SAXS) over the temperature range $7\text{--}77^\circ\text{C}$, to show the existence of a shallow minimum in the structure factor, $S(Q)$, at small but finite Q which then rise to the $S(Q = 0)$ value consistent with water's isothermal compressibility at a given temperature [34]. They attribute the minimum in SAXS intensities as being connected with a difference in density between two structural species, which they analyze with a Guinier treatment usually reserved for determining the shape and size of macromolecules in a multicomponent solutions. Furthermore, they shown that a tetrahedral model of water lacks such structural signatures in the same small- Q region, concluding that representation of water as a distorted tetrahedral network is inconsistent with the new SAXS data. Instead, Huang et al. used previously reported X-ray absorption, X-ray Raman and X-ray emission spectroscopy data

[29, 35] which are in themselves controversial [36], to describe the two distinct water structural species as the hypothetical low-density liquid (LDL) and high-density liquid (HDL) that are present in the supercooled region and are observed also at ambient temperatures.

The new SAXS data on ambient liquid water obtained by using the third generation synchrotron source were analyzed in [34]. It was shown that the small-angle region measure standard number density fluctuations consistent with water's isothermal compressibility temperature trends. There is no support or need for heterogeneities in water structure at room temperature to explain the small-angle scattering data, as it is consistent with a unimodal density of the tetrahedral liquid at ambient conditions.

For a homogeneous single component liquid far from any critical region, the small- Q region of the scattering profile of a homogeneous fluid measures the length scale, l_N , over which number fluctuations

$$\lim_{Q \rightarrow 0} S(Q) = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} \quad (2.2)$$

are still observable in Q -space [37]. To determine evidence of enhanced or anomalous density fluctuations, such as that found near a critical point, one can then separate the total intensity or structure factor into normal $S^N(Q)$ and anomalous $S^A(Q)$ components [38]

$$S(Q) = S^N(Q) + S^A(Q). \quad (2.3)$$

The normal component of scattering is either assumed to be Q -independent, i.e., $S^N(Q) = S^N(O)$ over the small- Q region [39, 40], where

$$S^N(O) = k_B T \rho_N \chi_T^N. \quad (2.4)$$

In formula (2.4) k_B is Boltzmann's constant, T is temperature, ρ_N is the molecule number density and χ_T^N is the normal component of the isothermal compressibility.

The anomalous component of scattering allows for the calculation of the correlation length ξ , by fitting it to the following Lorentzian functional form

$$S^A(Q) = \frac{A(T)}{\xi^{-2} + Q^2}, \quad (2.5)$$

where $A(T)$ is the temperature specific constant [38]. For a homogeneous liquid, the correlation length derived from analysis of small-angle scattering data is interpreted to be the size of an observation window in which density fluctuations are still observable in inverse space, but is only valid when $Q \rightarrow 0$ and $S(O) \gg 1$ [34]. It is important to emphasize that far from a critical point, such as that near room temperature, the anomalous component will necessarily be small relative to the normal component.

2.5 Quantum Nature of the Hydrogen Bonds

It is known that hydrogen bonds are complex and because of the small mass of the proton it is often not appropriate to treat the proton in H-bonded system as a classical particle. The small mass of hydrogen atoms means that they are quantum mechanical in nature. Therefore the quantum nature of protons must be taken into account and issues such as zero-point motion, quantum delocalization, and quantum tunneling are relevant [41]. The relevance of quantum nuclear effects to liquid water has been demonstrated. In particular, from the first principle simulations [42, 43] and neutron Compton scattering measurements [44, 45] the impact of quantum nuclear effects on the proton's real space delocalization and water vibrational modes has been established. Upon increasing of H-bonds strength, the proton becomes more delocalized and consequently the OH stretching frequency decreases.

Quantum nuclear effects can also influence the interaction strength and consequently the structure of H-bonded systems [41, 42]. In H-bonded crystals the replacing H with deuterium (D) they causes the change of the O–O distance. The conventional effect yield on elongation of the O–O distance upon replacing H with D, although a negative effect (the shortening of the O–O distance upon replacing H with D) has also been observed [46]. In H-bonded liquids analogous effects take place. In particular, simulations for liquid water shown that the O–O radial distribution function is less sharply peaked when simulations with taking into account the quantum nuclear effects are compared to those with classical nuclei [42] suggesting the decrease in the overall H-bond strength.

Xin-Zheng Li et al. [41] investigated the impact of quantum nuclear effects on a wide range of H-bonded materials. Using state-of-the-art *ab initio* molecular dynamics and *ab initio* path integral molecular dynamics they shown that relatively weak H-bonds, such as those in water, are made weaker if quantum nuclear effects are taken into account. This correlation arises from a simple competition between the anharmonic quantum fluctuations of intramolecular covalent bond stretching (which tends to strengthen H-bonds) and intermolecular H-bond bending (which tends to weaken H-bonds). The influence of quantum nuclear effects was quantified through the ratio of the path integral molecular dynamics (PIMD) and molecular dynamics (MD) projections

$$x = (X - H'')^{PIMD} / (X - H'')^{MD}, \quad (2.6)$$

where $(X - H'')$ is the projection of the donor molecule's covalent bond along the intermolecular axis. Since $(X - H'')$ increases upon intramolecular stretching but decreases upon intermolecular bending, it allows the balance between stretching and bending to be evaluated.

The values of x greater than one indicate that quantum nuclear effects lead to more stretching than bending and values less than one indicate that quantum nuclear effects result in more bending than stretching. It was shown that for all systems where H-bond bending dominates ($x < 1$), the heavy-atom distances are

longer in PIMD than in MD. In case where, covalent bond stretching is dominant ($x > 1$), the heavy-atom distances are shorter in PIMD than in MD. With the increase of x , quantum fluctuations on the stretching mode become more dominant and quantum nuclear effects turn from weakening the H-bonds to strengthening them. Thus the overall influence of quantum nuclear effects on the H-bonding interaction quantitatively comes down to this interplay between covalent bond stretching and intermolecular bond bending [41].

2.6 Diffusion of Water Molecules in Chloride Aqueous Solutions at Ambient Conditions

Diffusion coefficients are one of the transport parameters which give substantial information about diffusion phenomenon in solutions. These parameters can be obtained using the method of open-ended conductimetric capillary cell [47], the quasi-elastic slow neutron scattering [48] and the direct measurement of diffusion coefficients using NMR field-gradient technique [49].

Below the concentration dependences of the diffusion coefficient D of water molecules in aqueous solutions of manganese, calcium and barium chlorides are presented. The experimental data were obtained on basis of DOSY 2D NMR spectra recorded by means of Bruker NMR spectrometer Avance III 400 MHz. The temperature of solutions in a resonance cavity during measurements of concentration dependences of DOSY 2D NMR spectra was fixed with the precision of ± 0.1 °C. The concentrations of aqueous solutions were changed in the limits 0–100 mg/ml. Thus, at fixed temperature the single perturbation that affect separately self-diffusing water molecules in aqueous solutions is caused by Mg^{2+} , Ca^{2+} or Ba^{2+} cations, because for all three chloride salts the anion Cl^- is the same.

For magnesium chloride the concentration dependence of the diffusion coefficient D in ambient conditions is presented in Fig. 2.1. With increasing of $MgCl_2$ concentration the diffusion coefficient D decreases in a concentration range of 0–100 mg/ml that is in agreement with the standard diffusion theory. Such concentration behavior of the diffusion coefficient is characteristic for liquids in general and therefore the diffusion of water molecules in magnesium chloride aqueous solution can be considered as a normal diffusion.

For calcium chloride aqueous solution the diffusion coefficient D of water molecules also decreases with increasing of the concentration in the same concentration range (Fig. 2.2). However, the concentration dependences for both these aqueous solutions are slightly different (Figs. 2.1, 2.2).

Figure 2.3 exhibits the situation when the diffusion coefficient of water molecules increases with increasing of aqueous solution concentration for a restricted concentration range (0–10 mg/ml) and decreases with increasing of concentration (an anomalous concentration behavior) for the remaining concentration range (10–100 mg/ml). It is the case of barium chloride aqueous solution.

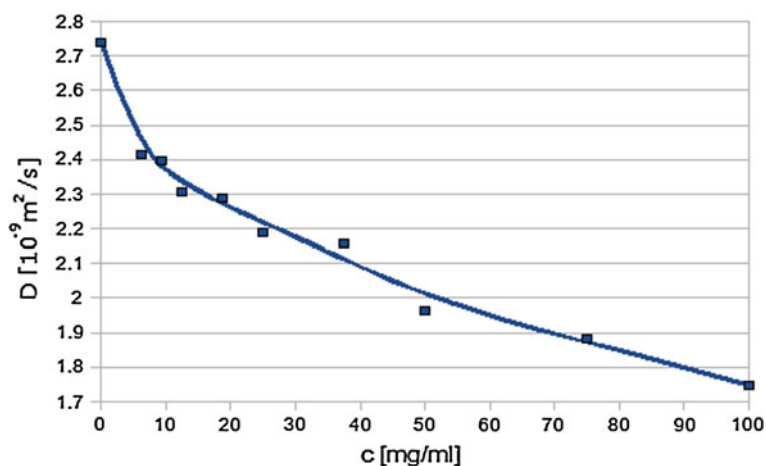


Fig. 2.1 Diffusion coefficient of water molecules versus concentration of magnesium chloride in aqueous solutions at temperature $t = 25^\circ \text{C}$

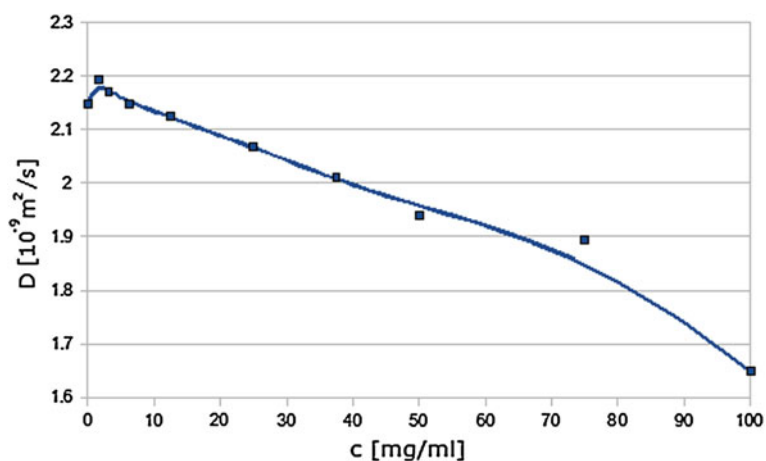


Fig. 2.2 Diffusion coefficient of water molecules versus concentration of calcium chloride in aqueous solutions at temperature $t = 25^\circ \text{C}$

The diffusion of water molecules into salt solution may be seen as the self-diffusion of water retarded by the presence of the ions in solutions. In the case of the chlorides discussed here the self-diffusion coefficient of water represents a maximum of the diffusion coefficient in the limit of extreme dilution and this tends to zero in the limit of the anhydrous salts.

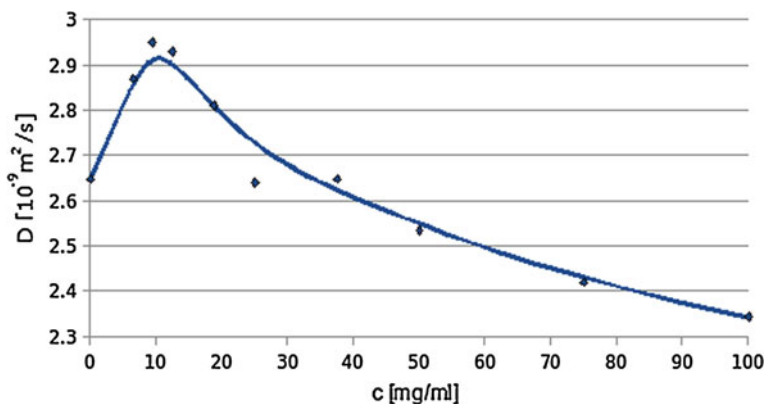


Fig. 2.3 Diffusion coefficient of water molecules versus concentration of barium chloride in aqueous solutions at temperature $t = 30^\circ\text{C}$

2.7 Discussion

Despite intense experimental and theoretical investigations more than for decades, a complete description of water properties remains elusive.

Each liquid water molecule is involved in a four hydrogen bonds between hydrogen and oxygen molecules belonging to different water molecules. The hydrogen bonds are 20 time weaker than covalent bonds and 60 times stronger than van der Waals bonds. The small mass of hydrogen atoms means that they are quantum mechanical in nature. Therefore issues such as zero-point motion, quantum delocalization and quantum tunneling of protons must be taken into account.

The water molecules form an infinite hydrogen-bonded network with localized and structured clustering. Small clusters may come to form multimolecular clusters including a highly symmetric 280-molecule icosahedral water cluster. These clusters can dynamically form a continuous network of both open (low density) and condensed (high density) structures. Therefore the water can be presented as an equilibrium mixture of low-density and high-density clusters. As consequences of hydrogen strength variation on the cluster equilibrium the resultant effects on physical properties occurs. On the basis of this concept most anomalies of liquid water can be explained qualitatively and quantitatively.

Existence of 67 anomalies of physical and physical–chemical properties of water shows the complexity of the molecular structure of water. Anomalous properties of water can be understood only on the basis of water cluster structure taking into account the quantum nature of hydrogen bonds. The short lifetimes of hydrogen bonds (1–20 ps) causes the short lifetimes of water clusters of various sizes and structures. These clusters decay with the subsequent formation of new clusters of different shapes and structures as a consequence of their short lifetime.

The lifetime of water clusters can be estimated on the basis of the data of 2D IR spectroscopy (a Fourier transfer technique that uses an excitation sequence of femtosecond IR pulses with variable time delay) [50]. However, what is the length of time since the collapse of any one cluster until the formation of another cluster in its place is not currently known.

It is well known that at sufficiently large times the motion of the individual molecules in liquids are well described in terms of ordinary diffusion. Thus, at these times the many-body problem reduces to a one-body stochastic problem in which all many body effects are hidden into a single number, the diffusion coefficient. The question is which time can be considered as sufficiently large to comfortably use the language of diffusion? The diffusion is a proper language for times larger than 2 ps [51].

The diffusion of a Brownian particle in the suspensions at intermediate and high concentration can be understood on basis of the generalized Stokes–Einstein equation [52]

$$D = k_B T / 6\pi\eta\zeta,$$

where D is the cooperative diffusion coefficient, η is the suspension dynamic viscosity, $k_B T$ is the thermal energy and ζ is “the correlation length”.

It should be noted that in case of stable particles in the suspension ζ is the radius R of the diffusing particle. If the particles (water clusters) are not stable and the time of measurement is longer than the cluster lifetime (as is in the case of DOSY 2D NMR experiments) the measured correlation length is

$$\langle \zeta \rangle = \frac{1}{n} \sum_{i=1}^n \zeta_i,$$

where n is the total number of short-lived clusters that formed during the registration of the DOSY 2D NMR spectrum.

We should expect that at investigation of water in a liquid state by means of the equipment with the time delay longer than the clusters lifetime they averaged correlation length $\langle \zeta \rangle$ should be shorter than the water cluster radius R ($\langle \zeta \rangle < R$). The value of $\langle \zeta \rangle$ should decrease with increasing of the average time interval τ_o between the collapse of the “old” and the formation of a “new” cluster compared with the average lifetime of the clusters. It can be understood on the basis of a simple model viewing an arbitrary point of the liquid and subnanometric region Ω around it. Let at $t = 0$ (the time moment corresponding to beginning of the registration of the DOSY 2D NMR spectrum) any cluster with the lifetime τ_1 arises in the region Ω . After the time $t = \tau_1$ this cluster decays and during the time τ_o the liquid in the region Ω , that is characterized by the correlation length $\zeta_o \ll R$, remains unperturbed. If $\tau_o \approx \tau_1$ and the processes of creation and decay of the clusters in the region Ω repeated n times each, then we can imagine the existence on a time axis of a finite one-dimensional lattice with the length $t_m = 2n\tau_1$. There are n time intervals during which the clusters exist in the region Ω and the other

n time intervals during which the clusters are not existing in this region. The overage correlation length in this case is $\langle \xi \rangle = (1/2)(R + \xi_0) \approx R/2$.

If during the time t_m only $n_I \ll n$ clusters arise in the region Ω and, correspondingly, during the time $t_m - n_I \tau_1$ the liquid remain unperturbed in this region with the correlation length $\xi_0 \ll R$, then $\langle \xi \rangle = (R - \xi_0)\tau_1/(\tau_0 + \tau_1) + \xi_0$.

Using the data presented on Figs. 2.1, 2.2, 2.3, the generalized Stokes–Einstein equation and taking into account the concentration dependences of the chloride aqueous solutions viscosity [53], we obtain $\langle \xi \rangle_{H_2O} = 1.07 \text{ \AA}$, $\langle \xi \rangle_{MgCl_2} = 0.93 \text{ \AA}$, $\langle \xi \rangle_{CaCl_2} = 1.04 \text{ \AA}$ and $\langle \xi \rangle_{BaCl_2} = 0.84 \text{ \AA}$ for pure water and chloride solutions at concentration $c = 100 \text{ mg/ml}$. These data are in the agreement with Ornstein–Zernike correlation lengths that for water at 25°C are included within the limits $1.2\text{--}3.1 \text{ \AA}$ [34]. Since the diffusion of water molecules into salt solutions may be considered as the self-diffusion of water retarded by the presence of the ions in solutions, we can see that at a given concentration of the most powerful influence on the processes of formation of water clusters have the Ba^{2+} ions.

On the basis of the last formula for $\langle \xi \rangle$, we can estimate the averaged time duration τ_0 between the decay of any cluster and creation in the region Ω of another cluster in the pure water and in aqueous solutions $\tau_0 = \tau_1 [(R - \xi_0)/(\langle \xi \rangle - \xi_0) - 1]$. For the parameters of a pure water in the liquid state $\tau_1 = 2 \cdot 10^{-11} \text{ s}$, $R = 3 \text{ nm}$ and $\langle \xi \rangle = 1.07 \text{ \AA}$, taking into account the inequality $\xi_0 \ll R$ and supposing that $\langle \xi \rangle - \xi_0 = 10^{-2} \langle \xi \rangle$, we obtain $\tau_0 = 5.6 \cdot 10^{-8} \text{ s}$, suggesting that τ_0 is much longer than the cluster lifetime if $R/(\langle \xi \rangle - \xi_0) \gg 1$. Water proton spin–lattice relaxation time ($T_1 = 3.6 \pm 0.2 \text{ s}$ for distilled water at 25°C) is a function of hydrogen bonding, being shorter for stronger bonding. It is approximately three times greater than the proton spin–spin relaxation time ($T_2 = 1.86 \pm 0.07 \text{ s}$), suggesting the presence of supramolecular structuring in water.

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Management of Water Quality in Moldova

Duca, G. (Ed.)

2014, VIII, 241 p. 151 illus., 67 illus. in color., Hardcover

ISBN: 978-3-319-02707-4