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# Hydrogen Bond Interactions Between Water Molecules in Bulk Liquid, Near Electrode Surfaces and Around Ions

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## 1. Introduction

Recently, a panel of experts, nominated by IUPAC, proposed the following tentative definition for the hydrogen bond: "The hydrogen bond is an attractive interaction between a group X-H and an atom or group of atoms Y in the same or different molecule(s), where there is evidence of bond formation" (Arunan, 2007). The energy of H-bond (~5 Kcal/mole of H-bonds) is intermediate between those of Van der Waals interaction (~0.3 Kcal/mole) and covalent (~100 Kcal/mole) chemical bonds (Stillinger, 1980). Since the energy of H-bond is of the order of a few KTs, thermal energy constantly acts to disrupt H-bonds. One can thus consider the energetics to drive formation of H-bonds, and entropic factors arising from thermal energy to break H-bonds. The result is a time-varying distribution of H-bonds among the different donor-acceptor pairs in the system. Combination of femtosecond 2D IR spectroscopy and molecular dynamics simulations demonstrated that the vast majority of average numbers of H-bonds are part of a H-bonded well of attraction and virtually all molecules return to a H-bonding partner within 200 fs (Eaves et al., 2005). Despite this continuous dynamics, fluctuation in the total number of H-bonds in a system containing a large number of molecules is quite small. Most simulation models suggest that a given H atom in water is H-bonded for 85-90% of the time (Bakker & Skinner, 2010).

H-bonds have been a subject of intense research over several decades owing to the enormous role they play on several physico-chemical properties of interest. As quoted by Buckingham et al., "The concept of the H-bond is a century old but youthful because of its vital role in so many branches of science and because of continued advances in experiment, theory and simulation" (Buckingham et al., 2008). The significance of H-bonds can be best understood by comparing the physical state of water and methane, both of similar size; at room temperature, while methane is supercritical, water exists in liquid state, making it possible for life to sustain on earth. The anomalous expansion of water at 4°C makes it possible for marine life to exist. The high dielectric constant of water opens up the entire field of electrochemistry. The internal structure of water is largely responsible for self-assembly of surfactants, leading to a wide array of liquid crystalline phases. H-bonds are largely responsible for preserving the structure/conformation of several life-supporting biological molecules such as DNA, RNA and proteins in aqueous solutions.

Despite the vast advances made in the recent past, H-bonding in liquid water continues to be one of the most challenging topics to understand. Each water molecule possesses two proton donors and two proton acceptors (lone pairs of electrons). X-ray and neutron diffraction studies reveal a three-dimensional network of H-bonds with a local preference for tetrahedral geometry (Narten & Levy, 1971). *Ab initio* calculations on the water dimer (Morokuma & Pedersen, 1968; Morokuma & Winick, 1970; Yamabe & Morokuma, 1975) reveal the important contribution of electrostatic interactions on H-bonding. Xenides et al (Xenides et al., 2006) have suggested the following parameters for H-bonded water molecules: distance between two oxygen atoms lies between 0.25-0.35 nm, H-bond distance lies between 0.15-0.25 nm, and the angle of the O-H... O configuration  $\theta \geq 100^\circ$ . It is, however, important to note that there is no consensus in the literature on the precise values of these parameters; for example, Kumar et al. suggest that  $\theta \geq 130^\circ$  (Kumar et al., 2007).

In the absence of a universally agreed mathematical definition for the H-bond, it is not surprising to note that H-bonding between water molecules under the influence of an external field is an even less understood topic. This is nevertheless an extremely important topic given that we commonly observe water being subject to external fields such as that imposed by an uncharged solid wall, a liquid-liquid interface, an electrode surface, a nanopore or an ion. In-fact, a detailed understanding of this topic probably holds the key in resolving some of the most difficult problems in Chemical Physics, such as: What is the origin of Hofmeister Series? What is the mechanism of gating of ion channels in biological membranes? What is the role played by interfacial water on electrochemical reaction pathways?

The present Chapter aims to elucidate our current understanding of H-bonding in liquid water, and is organized as follows. We start with a description of H-bonding in liquid water in the absence of any external field (Section 2), and then proceed to understand the influence of external fields generated near an electrode surface (Section 3) and around an ion (Section 4).

## 2. Structure of bulk water

We start with a qualitative discussion on the internal structure of water, followed by a compilation of literature data on a specific quantitative feature of the H-bond, namely the average number of H-bonds per water molecule.

Bernal and Fowler (Bernal & Fowler, 1933) suggested that molecules in liquid water are arranged in a tetrahedral manner, with each water molecule forming approximately four H-bonds with its nearest neighbors. Wall and Horing (Wall & Hornig, 1965) observed the Raman-scattering motions of the HDO molecules in H<sub>2</sub>O or D<sub>2</sub>O and concluded that liquid water does not have any significant fraction of unbonded molecules. Narten and Levy (Narten & Levy, 1969) supported the viewpoint that water molecules in liquid state are arranged in a predominantly tetrahedral geometry based on the observation that the mean separation between nearest neighbor molecules in ice and water are only marginally different. Stillinger and Rahman (Stillinger & Rahman, 1974) also suggested a similar structure for liquid water and additionally concluded that it contained a large proportion of broken H-bonds. Narten et al. (Narten et al., 1982) showed that most water molecules are connected to their nearest neighbors through nearly straight H-bonds. Gorbaty and Demianets (Gorbaty & Demianets, 1983) and Hoffmann and Conradi (Hoffmann & Conradi, 1997) showed, through independent studies, that the disorder in H-bond structure in liquid

water increases with increasing temperature. Schwegler et al. (Schwegler et al., 2000) showed that the application of external pressure on pure water weakens H-bonds. Lee and Tuckerman (Lee & Tuckerman, 2006) studied the structural property of liquid water using a Car-Parrinello ab initio molecular dynamics (CPAIMD) simulations combined with Kohn-Sham density functional theory and BLYP exchange correlation functional for electronic structure, and found that more than 50% of water molecules are bonded in a tetrahedral geometry. Leetmaa et al. (Leetmaa et al., 2008) confirmed the tetrahedral arrangement with 74% double H-bond donors (DD) and 21% single donors (SD). Lehmann et al. (Lehmann et al., 2009) used quantum cluster theory and found dominance (75%) of two-bonded water molecules at room temperature.

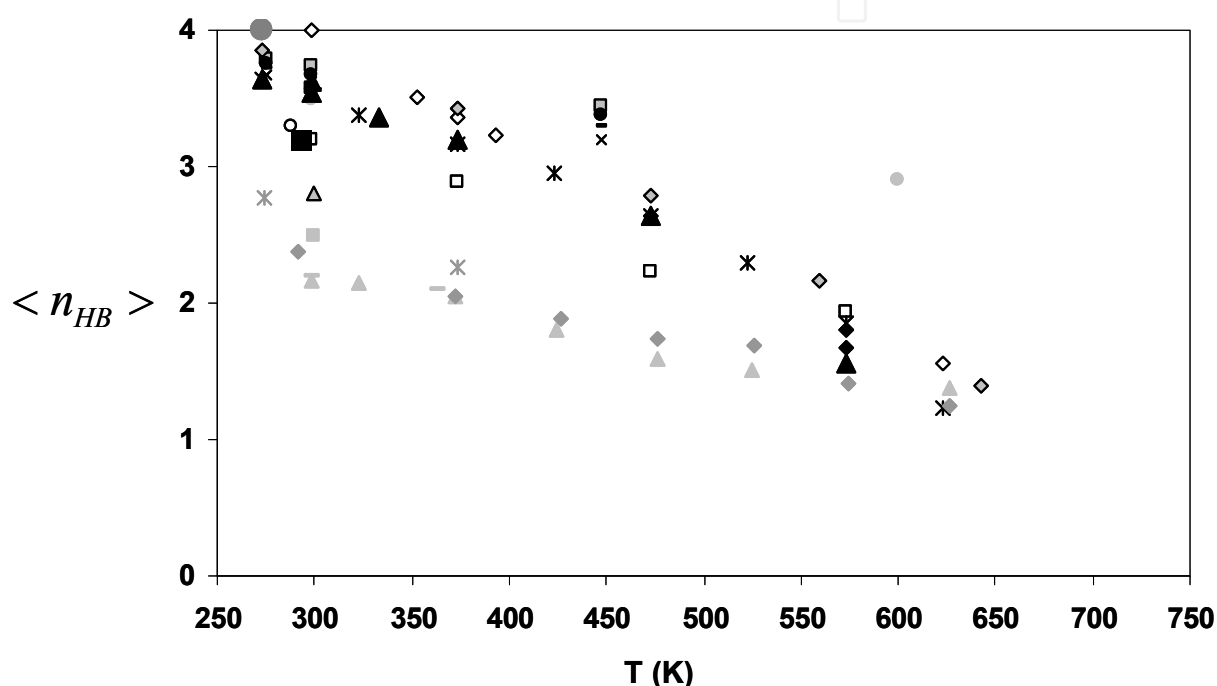


Fig. 1. Average number of H bonds per water molecule at various temperatures, as extracted using different techniques in the past.  $\blacktriangle$  X ray diffraction study at 100 MPa (Gorbaty & Demianets, 1983);  $\diamond$  NMR (Hoffmann & Conradi, 1997);  $\bullet$  Water electronic study (Schwegler et al., 2000);  $\nabla$  Quantum cluster equilibrium method (Lehmann et al., 2009);  $\Delta$  TIP4P (Prendergast & Galli, 2006);  $+$  CPAIMD (Lee & Tuckerman, 2006);  $\blacklozenge$  Neutron diffraction (Soper et al., 1997);  $\times$  IR (Luck, 1967);  $\circ$  TEY-NEXAFS (Smith et al., 2004);  $\triangle$  SXEER (Myneni et al. 2002);  $\blacklozenge$  IR at 250 atm (Bondarenko & Gorbaty, 1991);  $\blacktriangle$  Latent Heat (Haggis et al., 1952);  $\blacklozenge$  Statistical mechanics (Suresh et al., 2000);  $\blacksquare$  Electronic structure study (He et al. 2007);  $-$  TIP4P (Nieto-Draghi, 2003);  $\times$  TIP5P (Nieto-Draghi et al., 2003);  $\square$  SPC/E (Nieto-Draghi et al., 2003);  $\bullet$  DEC (Nieto-Draghi et al., 2003);  $\square$  Monte Carlo (Kalinichev & Bass, 1997);  $\blacksquare$  *Ab initio* (Kuo & Mundy, 2004);  $\blacksquare$  FPMD (Hetenyi et al., 2004);  $-$  X-ray absorption (Wernet et al., 2004).

Figure 1 shows the temperature variation of the average number of H-bonds per water molecule,  $\langle n_{HB} \rangle$ . Two points are worth noting. One, irrespective of the source of literature,  $\langle n_{HB} \rangle$  is seen to decrease with increasing temperature. Two, there is a large scatter in data points; for example,  $\langle n_{HB} \rangle$  at room temperature varies from 2 to 4. This

scatter can be attributed to a number of factors, such as differences in the definition of the H-bond, limitations in experimental/simulation techniques, and ambiguities in the interpretation of experimental data in relation to H-bond stoichiometry. Such an in-depth analysis of the factors involved is not within the scope of the present Section. However, in order to provide an appreciation of the ongoing debate in this area of research, we will bring out the key features of two landmark papers published in *Science*, one suggesting that  $\langle n_{\text{HB}} \rangle \sim 3.3$  and the other suggesting a different value of 2.

We first start with a discussion on the paper published by Smith et al. (Smith et al., 2004) which concluded that  $\langle n_{\text{HB}} \rangle \sim 3.3$ . The authors used oxygen K-edge X-ray absorption technique, wherein a core electron was excited to an unoccupied electronic state. The electronic character of the unoccupied states is known to be sensitive to the local geometric structure. The authors recorded area-normalized spectra of water at 254 K and 288 K. The intensity of pre-edge region ( $\sim 535$  eV), which is a signature of distorted H-bonds configurations, increased with increasing temperature. On the other hand, the intensity of post-edge region ( $\sim 541$  eV), which is a signature of stronger and fully coordinated ice-like bonds, decreased. The authors assumed the relative populations of post-edge ( $I_{\text{post}}$ ) and pre-edge ( $I_{\text{pre}}$ ) intensities to be a function of absolute temperature only, and proposed that a plot of  $\ln(I_{\text{post}}/I_{\text{pre}})$  versus  $1/T$  would yield a straight line with a slope that is proportional to the average difference in energy between the two classes, and determined the rearrangement energy between two classes of H-bonding distributions to be  $1.5 \pm 0.5$  kcal/mol. This small energy difference indicates that molecules contributing to pre-edge intensity are only slightly distorted compared to those contributing to post-edge intensity. The average energy of a fully formed ice-like H bond is known to be  $\sim 5.5$  kcal/mol (Kuo & Mundy, 2004; Stillinger, 1980). Therefore, the authors attributed the difference in energy (1.5 kcal/mol) between the two H-bonding distributions to a loss of  $27 \pm 9\%$  of average H-bond energy. Later, Nilsson et al. (Nilsson et al., 2005) questioned the quality of the temperature dependent X-ray spectra presented by Smith et al. (Smith et al., 2004). They pointed that three different sets of measurements displayed an energy difference of approximately 1.2, 1.5 and 1.8 kcal/mol between the two different species, and attributed this lack of reproducibility to energy dependent nonlinear effects in X-ray absorption spectrum measurements. In response to Nilsson comments, Smith et al. (Smith et al., 2005) showed that under constant conditions (e.g., jet size, collection geometry), the X-ray absorption spectrum is highly reproducible.

We now focus our attention on another paper which suggested a different value for  $\langle n_{\text{HB}} \rangle$ . Wernet et al. (Wernet et al., 2004) employed X-ray absorption (XAS) and X-ray Raman (XRS) spectroscopic techniques to understand the H-bond configurations in bulk ice, ice surface,  $\text{NH}_3$  terminated ice surface and bulk liquid water. The spectra were divided into three regions: pre-edge ( $\sim 535$  eV), main edge (537-538 eV), and post-edge (540-541 eV). The bulk ice spectrum was dominated by the intensity in post-edge region and showed a weak main edge structure. Both the surface ice and liquid water spectra had a peak in the pre-edge region, a dominant main edge, and lesser intensity compared with bulk ice in the post-edge region. Termination of ice surface with  $\text{NH}_3$  entails a coordination of free O-H groups and caused the pre-edge peak to vanish. It was observed that liquid water spectra closely resembles that of ice surface, which consists of one strong and one non-bonded or weakly-



bonded O-H group, but is very different from that of bulk ice. On the basis of these findings, the authors concluded that liquid water consists of two structural species, one with two H-bonded (at one acceptor and one donor site) and another tetrahedrally coordinated. A theoretical analysis of XAS and XRS spectra, based on density functional theory (DFT) with a small model cluster of 11 molecules, revealed that each molecule has on average  $2.2 \pm 0.5$  H-bonds at 25°C and  $2.1 \pm 0.5$  at 90°C temperature.

### 3. Structure of water near electrode surfaces

Structure and orientation of water molecules adjacent to charged surfaces play an important role in surface science, electrochemistry, geochemistry and biology (Thiel & Madey, 1987; Henderson, 2002; Guidelli & Schmickler, 2000). Several force fields are operational in such situations. Molecular dynamic simulations (Segura et al., 1997) reveal entropy driven piling-up effect near even an uncharged wall. Additional presence of charge on surface polarizes water molecules. The presence of ions ( $H^+$ ,  $OH^-$ ) in the liquid phase further induces formation of an electrical double layer within which the electric field decays with distance from the surface. Advanced experimental and molecular simulation techniques are just beginning to shed light on the influence of a charged electrode surface on the various aspects of the internal structure of water, such as H-bonding, density and dipolar alignment. It is the purpose of this Section to discuss the current understanding of this topic. More specifically, we focus on studies revealing two opposing viewpoints; one suggesting that the H-bond structure of water near a charged surface is significantly disrupted, and the other concluding the opposite, namely that the H-bond network near the surface is largely intact. Toney et al. (Toney et al., 1994) studied the distribution of water molecules perpendicular to a charged silver (111) electrode interface in NaF solution using X-ray scattering technique. An interface at a single crystal creates additional scattering to the Bragg peaks of crystal, which permits the determination of surface structure and water distribution. Figure 2 shows the distribution of oxygen atoms with distance from the electrode surface. Using Gaussian functions to fit the oxygen distribution function, the first layer density was calculated to be 1.1 and 1.8 water molecules per Ag atom, corresponding to an applied voltage of -0.23 V and +0.52 V, respectively. In contrast, bulk water had a density of  $\sim 0.8$  water molecules per Ag atom. The conclusion that water density is significantly altered near a charged electrode was confirmed by Danielewicz-Ferchmin (Danielewicz-Ferchmin & Ferchmin, 1996) as well, albeit using a different approach. A simulation study (Zhu & Robinson, 1991) with SPC-FP water model (simple point charge model with flexible bonds and polarization) also showed that water density near a charged surface is higher than that in bulk and increases with field intensity. Moreover, they found that the length of O-H bond (of water) near the electrode surface is smaller than in bulk, indicating weaker H-bonds. Suresh (Suresh, 2007) arrived at a similar conclusion using a statistical thermodynamic model, and showed that the average number of H-bond per molecule near the charged surface decreases from 2.8 at zero electric field to 2 at  $E = 2 \times 10^9$  V/m.

We now focus our attention on another set of papers (Schweighofer et al., 1996; Torrie et al., 1988; Yeh & Berkowitz, 2000) that reached a different conclusion, namely that the H-bond structure of water near a charged electrode surface is largely intact. Schweighofer et al. (Schweighofer et al., 1996) performed molecular simulations with SPC/E water molecules

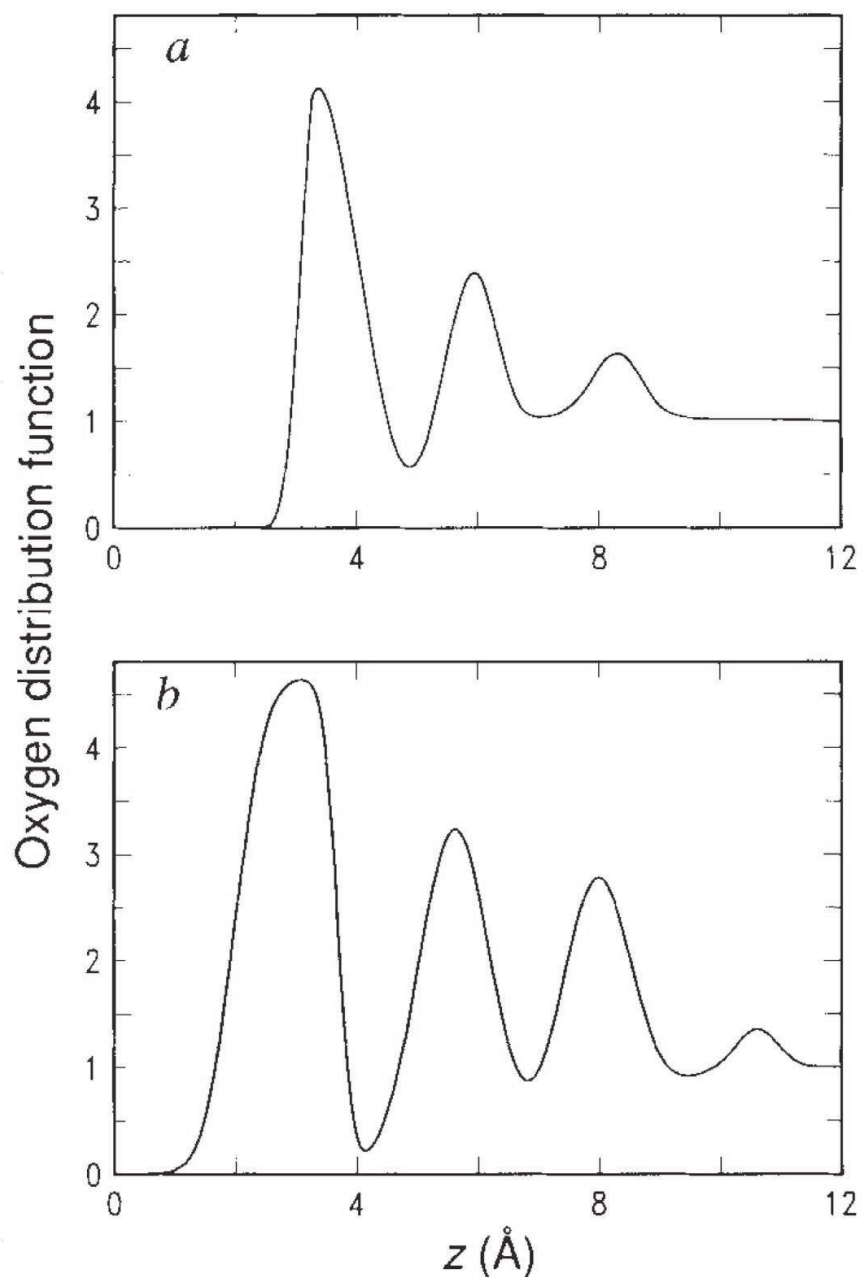


Fig. 2. Oxygen distribution functions of water molecules near silver Ag (111) electrode with potentials of (a)  $-0.23$  V of the p.z.c. and (b)  $+0.52$  V of the p.z.c. Reproduced with permission from Toney, M. F. et al., *Nature*, 1994, 368, 444. © 1994 Nature Publishing Group.

contained between two parallel Ag(111) surfaces with charge densities fixed at  $0.0$ ,  $8.85$ , and  $26.55$   $\mu\text{C}/\text{cm}^2$ . They did not observe increase in water density near the electrode even with the highest charge density ( $+26.5$   $\mu\text{C}/\text{cm}^2$ ); rather, it was found to decrease. Authors explained this observation to strong polarization of water molecules due to the applied electric field resulting in some of the oxygen atoms associated with water molecules to desorb from the surface and move into subsequent layers in order to keep intact the H-bond network. Torrie et al. (Torrie et al., 1988) showed that the H-bond structure near the electrode is resistant to surface charges as high as  $17.5$   $\mu\text{C}/\text{cm}^2$ , apparently because such a

strong field can not compete with the stronger intermolecular forces of water-like models. Yeh (Yeh & Berkowitz, 2000) studied water density near a charged silver electrode surface using polarizable point charge model and found that water density near the surface was not affected by surface charge. Xia and Berkowitz (Xia & Berkowitz, 1995) performed molecular simulations with SPC/E modeled water lamina embedded between two Pt (100) walls, charged with 0, 8.85, 26.55 and 35.40  $\mu\text{C}/\text{cm}^2$  on the left wall and values opposite in sign on the right wall. Figure 3 shows the density profile of O and H atoms of water as varying from positively charged electrode to negatively charged electrode.

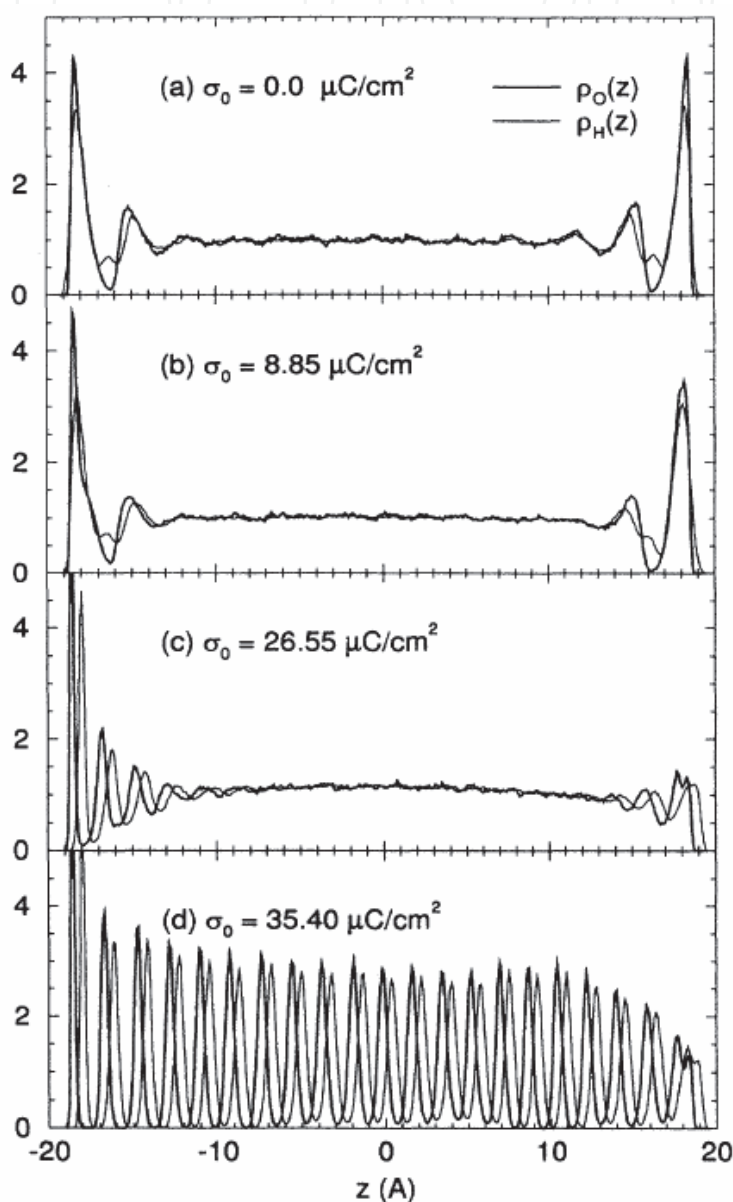


Fig. 3. Density profile of oxygen  $\rho_o$  and hydrogen  $\rho_H$  atoms for systems with (a) no surface charge density on Pt surface, (b) surface charge density of 8.85  $\mu\text{C}/\text{cm}^2$ , (c) 26.55  $\mu\text{C}/\text{cm}^2$ , and (d) 35.40  $\mu\text{C}/\text{cm}^2$ . The positively charged surface is on the left, the negatively charged surface is on the right. Reproduced with permission from Xia, X.; et al. *Physical Review Letters*, 1995, 74, 3193. © 1995 The American Physical Society.



There was no significant change in density profile up to  $8.85 \mu\text{C}/\text{cm}^2$  surface charge. When the surface charge density was increased to  $26.66 \mu\text{C}/\text{cm}^2$ , which is close to the surface charge density in experiments performed by Toney et al. (Toney et al., 1994) four distinct water layers were observed near the positively charged surface. When the charge density on electrode was increased to  $35.4 \mu\text{C}/\text{cm}^2$ , water restructured itself in order to adapt to the new environment and eventually crystallized into domains of cubic ice. In other words, the H-bond network not only survives in electric field, but is also responsible for the observed structural changes. Otani et al. (Otani et al., 2008) performed *ab initio* molecular dynamics simulations on water/Pt interface with a negative bias up to  $-0.81 \text{ V}$ . They observed only a small increase in interfacial water density and found that for bias and unbiased conditions, the average number of H-bonds per water molecule in bulk region as well as in contact layer was almost equal. This implied that water molecules rotate their molecular axes in response to the external electric field, but retain their tetrahedral configuration by rearranging the H-bond network. Compared to bulk, however, near the charged interface, the average number of H-bonds per water molecule was lesser.

#### 4. Structure of water near ions

Hofmeister first established that different ions have different efficiency at salting-out egg-white protein (Hofmeister, 1888). The sequence of ions, based on their effectiveness towards enhancing or diminishing the solubility of proteins, is termed as Hofmeister series. This series is generally written as (Marcus, 2009).

Anions:

Kosmotrope (Structure maker)

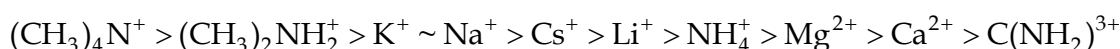
Chaotrope (Structure breaker)



Cations:

Kosmotrope (Structure maker)

Chaotrope (Structure breaker)



The molecular origin of salting-out or salting-in effects is not fully understood. But broadly, the current view is that addition of salts alters the internal structure and hence the solubility power of water. In this context, ions are classified in two groups, namely “structure makers” and “structure breakers” (Cox & Wolfenden, 1934). Implicit in this conjecture is that ions influence the long-range structure of water. Whether this conjecture is indeed borne out in experiments is one of the topics of debate in the literature. In this Section, we discuss key aspects of papers on both sides of this debate.

Leberman and Soper (Leberman & Soper, 1995) showed that ions can induce a change in water structure equivalent to that caused by the application of high pressure, and that the extent of this effect is ion-specific. Based on neutron diffraction patterns, the authors determined distribution distances  $\Delta g_{\text{HH}}(r)$  between water protons in aqueous solutions of salts ( $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaCl}$ ), and in pure water at high pressure. Figure 4 shows that the  $\Delta g_{\text{HH}}(r)$  in all these cases are of qualitatively similar shape. The general trend is a negative region near  $r = 2 \text{ \AA}$ , a positive region near  $r = 3.2 \text{ \AA}$  and a set of oscillations with a period of  $\sim 3 \text{ \AA}$ . Under ambient conditions, the intermolecular HH pair correlation function for pure water consists of two peaks, one at  $\sim 2 \text{ \AA}$  and another at  $\sim 3.8 \text{ \AA}$ ,

with a minimum between them at  $r = 3.0 \text{ \AA}$ . In ionic solutions under normal pressure and pure water at high pressure, peaks at  $\sim 2.4 \text{ \AA}$  and  $3.8 \text{ \AA}$  are apparently diminished and a minimum at  $\sim 3.0 \text{ \AA}$  fills in. These results strongly suggest that ions disrupt the water structure comparable in extent to that caused by the application of high pressure to pure water. The possibility of pressure and salt leading to similar effects on the structure of water has also been investigated using molecular simulation techniques. Holzmann et al. performed molecular dynamics simulations of aqueous NaCl solutions, and arrived at three broad conclusions (Holzmann et al., 2007). One, the H-bond network is modified well beyond the first hydration shell. Two, an analysis of free water distribution showed that the effect of salt and pressure might be considered as "two sides of the same coin". Three, the authors cautioned against using the pressure/salt equivalence as a sole factor influencing solubility of biomolecules; adsorption/desorption of ions might also have to be accounted for.

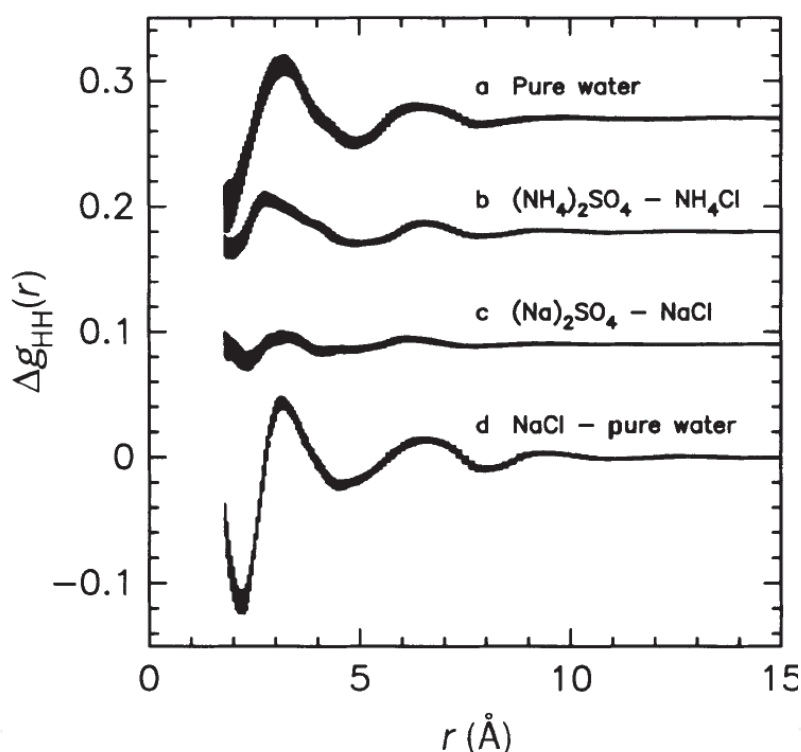


Fig. 4. Changes in the HH pair correlation function: curve a, for pure water for an applied density increase of  $0.0017 \text{ molecules per \AA}^3$  above ambient density ( $0.0334 \text{ molecules per \AA}^3$ ); curve b, between a  $2 \text{ m}$  aqueous solution of  $\text{Na}_2\text{SO}_4$  and a  $4 \text{ M}$  solution of  $\text{NH}_4\text{Cl}$ ; curve c between  $2 \text{ M}$  aqueous solution of  $\text{Na}_2\text{SO}_4$  and  $4 \text{ m}$  solution of  $\text{NaCl}$ ; and curve d, between a  $4 \text{ m}$  solution of  $\text{NaCl}$  and pure water. Reproduced with permission from Leberman, R. et al.; *Nature*. 1995, 378, 364. © 1995 Nature Publishing Group.

Chandra (Chandra, 2000) investigated the specific role of ions on H-bonds between water molecules using molecular dynamics. The systems chosen were NaCl and KCl in water at various concentrations (from  $0 \text{ M}$  to  $3.35 \text{ M}$ ). Water molecules were modeled by the extended simple point charge (SPC/E) potential and ions were modeled as charged Lennard-Jones particles. For analyzing the hydrogen bond breaking dynamics, the author calculated the time correlation functions  $S_{\text{HB}}(t)$  and  $S^{(d)}_{\text{HB}}(t)$ .  $S_{\text{HB}}(t)$  describes the probability that an initially

hydrogen-bonded pair remains bonded at all times up to time  $t$ , and  $S^{(d)}_{\text{HB}}(t)$  describes the dynamics of hydrogen-bond breaking due to translational diffusion. Figure 5A represents the decay of  $S_{\text{HB}}(t)$  and  $S^{(d)}_{\text{HB}}(t)$  for the various solutions studied. Decay of both  $S_{\text{HB}}(t)$  and  $S^{(d)}_{\text{HB}}(t)$  is found to accelerate with increase in ion concentration. This indicates that the H-bonded water pair in ionic solutions is less strongly held compared to that in pure water. The author also calculated the oxygen-oxygen and oxygen-hydrogen potentials of mean force (pmf) between two neighboring water molecules (figure 5B). The well depth of the pmf decreases with increasing ion concentration, suggesting weakening of the effective strength of water-water hydrogen bonds. This effect is more pronounced in case of NaCl solutions because of smaller size and stronger hydration of sodium ions compared to that of potassium ions.

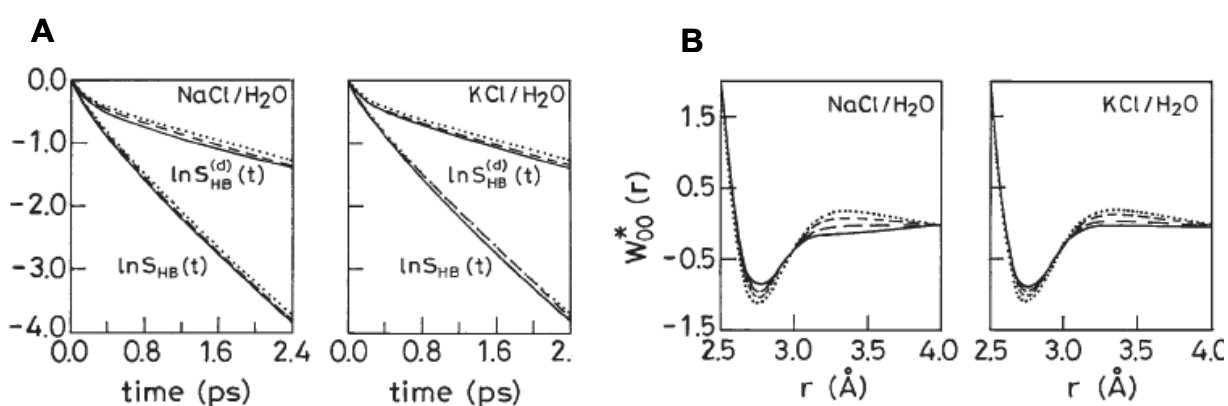


Fig. 5. (A) The time dependence of the logarithm of  $S_{\text{HB}}(t)$  and  $S^{(d)}_{\text{HB}}(t)$  for NaCl and KCl solutions. The dotted, dashed, and solid curves are for 0.0M, 2.2M, and 3.35M solutions. (B) The distance dependence of the oxygen-oxygen potential of mean force between two neighboring water molecules in NaCl and KCl solutions [ $W_{\text{OO}}^*(r) = W_{\text{OO}}(r)/k_B T$ ]. The dotted, short-dashed, long-dashed, and the solid curves are for 0.0M, 0.88M, 2.2M, and 3.35M solutions. Reproduced with permission from Chandra, A., *Physical Review Letter*. 2000, 85, 768. © 2000 The American Physical Society.

Hribar et al. (Hribar et al., 2002) employed a two-dimensional MB model, in which each water molecule was represented as a two-dimensional disk that interacted with other water molecules through a Lennard-Jones (LJ) interaction and an orientation-dependent H-bond interaction. Figure 6A shows that the average number of H-bonds per water molecule around the first shell of smaller cations such as  $\text{Li}^+$  and  $\text{Na}^+$  (kosmotropes) is lesser than that in bulk water, while the corresponding number for molecules around larger ions such as  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  are higher. The molecular picture giving rise to this conclusion is shown in Figure 6B. The number of H-bonds per water molecule in the first shell around an ion is governed by two competing ordering effects, one induced by electrostatic interaction with the ion and the other by water-water H-bond interaction. For small ions, the former effect dominates, while for large ions the later effect dominates.

We now turn our attention to papers that concluded the opposite, namely that the presence of ions do not lead to an enhancement or a breakdown of H-bond network in liquid water. This viewpoint, which was originally initiated by Omta et al. (Omta et al., 2003), has profound implications, one of which is that the conjecture of ions being classified as being “structure-makers” and “structure breakers” does not have a molecular basis. The authors

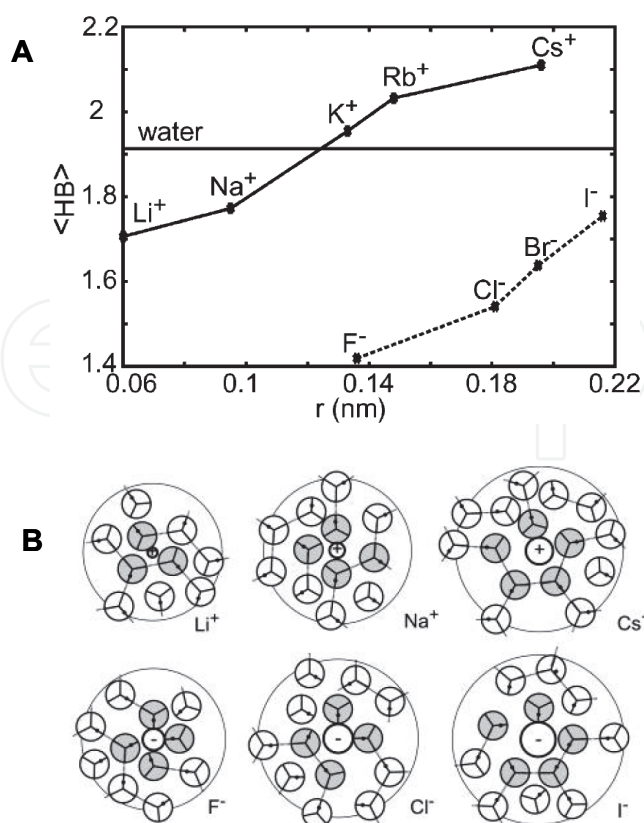


Fig. 6. (A) The average number of the hydrogen bonds per water molecule in the first shell around various ions. (B) Snapshots of waters in the first (shaded) and second shell (white) around an ion (black). Reproduced with permission from Hribar, B. et al., *J. Am. Chem. Soc.* 2002, 124, 12302. © 2002 American Chemical Society.

measured the orientational correlation time of water molecules in  $\text{Mg}(\text{ClO}_4)_2$  solution by using femtosecond pump-probe spectroscopy. The technique was based on measuring the anisotropy parameter ( $R$ ), which was defined as  $[(\Delta\alpha_{\parallel}(\tau) - \Delta\alpha_{\perp}(\tau)) / (\Delta\alpha_{\parallel}(\tau) + 2\Delta\alpha_{\perp}(\tau))]$ , wherein  $(\Delta\alpha_{\parallel})$  and  $(\Delta\alpha_{\perp})$  are absorption changes measured parallel and perpendicular to the pump polarization, and  $\tau$  is the time delay between pump and probe pulses. To measure  $R$ , OH groups in the liquid were anisotropically excited by a linearly polarized pump pulse. The decay time of  $R$  represents the orientational correlation time of water molecules, a measure for the stiffness of the H-bond network. The decay of  $R$  turns out to be independent of the salt concentration (0 M, 1 M, and 3 M  $\text{Mg}(\text{ClO}_4)_2$  in HDO:H<sub>2</sub>O solutions), which means the orientational correlation time ( $\tau$ ) for the water-bonded OD groups is not affected by the presence of  $\text{Mg}^{2+}$  and  $\text{ClO}_4^-$  ions. Moreover, the authors found that the orientational correlation time for salt solutions ( $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{NaClO}_4$  and  $\text{Na}_2\text{SO}_4$ ) and pure water are not very different, based on which the authors concluded that H-bond interactions between water molecules outside the nearest solvation shell are largely intact.

We now mention two other recent studies whose conclusions are broadly in line with those of Omta et al. (Omta et al., 2003). Guardia et al. (Guardia et al., 2006) carried out extensive molecular dynamics simulations of aqueous alkali metal and halides at ambient and supercritical conditions to explore the effects of ions on the intermolecular connectivity of water in the close vicinity of solutes. From a dynamical perspective, the most relevant feature was that the lifetimes of hydrogen bond do not seem to be affected in an appreciable manner by the presence of ions. More recently, in 2007, Smith et al. (Smith et al., 2007)

compared experimental Raman spectral measurements with classical Monte Carlo simulations and concluded that the change in vibrational spectrum of water by the addition of potassium halides is a direct result of the electric fields that anions exert on adjacent H atoms, and that the halide ions induce only minor HB distortions beyond the adjacent shell of coordinating OH groups.

## 5. Summary

Given the ongoing debates in our current understanding of liquid structure of water even in the absence of external fields, it is not surprising that there is lack of consensus in the literature on even some of the fundamental aspects of H-bond interactions in the presence of an external field. For example, it is not yet clear whether the H-bond structure near a charged electrode surface is disrupted or not. Similarly, E-fields are generally considered to align water dipoles in the direction of the field; however, a recent study (Suresh et al., 2006) has reported the additional presence of H-bond stabilized water molecules with their dipoles lying perpendicular to that of field. The fraction of such molecules is relatively small; for every thousand molecules with their dipoles aligned in the direction of field, roughly one was found aligned perpendicular to that of the field. Nevertheless, the role of these “defects” on the transport or solvation properties of water remains to be investigated. Whether ions induce long-range changes in the structure of water is still an open question (Bakker, 2008). The study of confined water molecules is equally, if not more interesting. The thermodynamic properties of confined water are generally considered to be different from those of bulk water; however, what gives rise to these differences is still an open question. A recent study (Han et al., 2009) showed reduced extent of H-bonding in a quasi-two-dimensional hydrophobic nanopore slit as compared to that in bulk water, partly due to geometric constraints imposed by confined geometries on the tetrahedral bonding patterns in water; however, the characteristics of H-bond dynamics, such as the Arrhenius dependence of the average H-bond lifetime, have been reported to be largely preserved. In the above context, it is clear that the structure of water in external fields is a topic that requires much more detailed investigations before unambiguous conclusions can be reached. While this endeavor would require the development of advanced techniques, it is equally if not more important that the scientific community agrees on a single mathematical definition of what constitutes a H-bond. It is hoped that this clarity will help in reducing the confusion prevailing today in relation to design, implementation and interpretation of experimental/simulation data related to the internal structure of water.

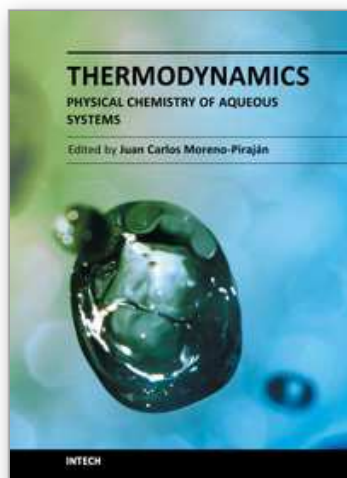
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