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# Internal structure of water around cations

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ABSTRACT

In the present paper, we use statistical mechanics to probe into the changes induced by cations ($Al^{3+}$, $Mg^{2+}$, $Ca^{2+}$, $Li^{+}$, $Na^{+}$, $K^{+}$, $Rb^{+}$, $Cs^{+}$) on the structure of water. The theory aims to find the minimum free energy state, taking into account the hydrogen bonding interactions between water molecules, electrostatic interactions between water and the ion, and thermal energy. Water molecules in the first shell of $Na^{+}$ ions are found to largely retain their structure; the average number of H-bonds ($<n^{HB}>$) and the average dipolar alignment ($<\theta>$) of a water molecule are only marginally different from the corresponding values of bulk water. This is made possible by the "caging" of the $Na^{+}$ ions by water molecules. The magnitudes of $<n^{HB}>$ and $<\theta>$ are, however, found to decrease for ions on either side of $Na^{+}$ ions in the Hofmeister Series. Water molecules around small ions with high charge density (e.g. $Al^{3+}$) are found to strongly align their dipoles in the direction of field, despite the reduction in the number of H-bonds per molecule. Those around large ions with low charge density (e.g. $Cs^{+}$) are oriented such that one of their H-bond axes involving a lone pair of electrons is directly facing the ion, thereby maximizing their H-bond interactions at the other three bonding sites. Beyond the first shell of all the ions studied, the degree of hydrogen bonding is similar to that of bulk water molecules. Changes in the molecular orientation and non-linear polarization effects, however, persist up to ~3–4 hydration shells in the case of salting-in ions, and ~7–9 shells in the case of salting-out ions.

## 1. Introduction

The Hofmeister series is an arrangement of ions in the order of their ability to alter the solubility of various proteins in water. It is generally thought to be related to the ability of ions to alter the structure of water. Gurney [1], for example, considered the effect of ions on the viscosity of water. The Jones–Dole equation [2] for the viscosity of aqueous salt solutions (up to concentrations of 1 M) states that $(\eta - \eta_o)/\eta_o = A\sqrt{c} + Bc$. Where $c$ is the concentration of ion, $\eta$ is the viscosity of the solution, $\eta_o$ is the viscosity of pure water, and A and B are constants. The two terms on the right side are attributed to the ion–ion interactions and the influence of ions on the H-bond network of water, respectively. "Structure-breakers" have large B coefficients, while "structure-makers" have negative B coefficients. This is in line with the expectation that structured water should be more viscous than unstructured water. The lower mobilities of small ions with high charge densities, as compared to large ions with low charge densities, are also attributed to the ability of ions to either "make" or "break" the structure of water. Studies on the vibrational spectra of solutions containing high charge density ions have reported a slight red-shift, indicative of enhanced hydrogen bonding [3]. Employing classical molecular dynamics simulation techniques, Chandra [4] found a reduction in the number of H-bonds with increasing concentration of ions (NaCl and KCl), indicating that water molecules are significantly influenced by the presence of ions. Chandra et al. [5] further deduced that in the presence of ions, pressure had a weaker influence on the number of H-bonds per water molecule and the strength of H-bond.

The above view has, however, been recently challenged. Gurau et al. [6] concluded, based on their studies using vibrational sum frequency spectroscopy, that the Hofmeister effect is primarily due to the ions' ability to penetrate the head-group region of surfactant monolayers thereby disrupting the hydrocarbon packing, and not due to any long-range changes in the water structure. Batchelor et al. [7] used a new technique, pressure perturbation calorimetry, and found no correlation between the solute's impact on water structure and its effect on protein stability. Kropman and Bakker [8] probed the structure of water using femtosecond pump–probe spectroscopy, and found that the presence of ions (both salting-out and salting-in) does not lead to an enhancement or a breakdown of the hydrogen bond network outside nearest vicinity (first shell). Naslund et al. [9] showed that the H-bond network in bulk water, in terms of forming and breaking H-bonds as detected by XAS/XRS, remains unchanged, and only water molecules in the close vicinity to the ions are affected. Cappa et al. [10] found, using XA spectroscopy, that monovalent cations induce no long-range changes to the H-bond network of water.

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Obst and Bradaczek [11] performed MD simulations and found no significant differences between H-bond structure of water molecules beyond the second hydration shell of various cations.

One explanation for the apparent contradictions of the above experiments and the conventional view that the influence of ions is not just restricted to the first hydration shell is that the H-bonds near ions may be distorted, but not necessarily broken (analogous to what happens to pure water in high pressure); however, ions may perturb the orientational ordering of neighboring water molecules, and that this perturbation could have a knock-down effect on water molecules in the second and subsequent hydration shells [12,13]. This explanation has also been supported by Monte Carlo simulations with revised ab initio based potential [14]; the reference value of the energy of water molecules in bulk was found to be recovered only at a distance of 10 Å away from the cations.

The present study aims to remove some of the above-mentioned contradictions using statistical mechanics. The approach we follow is similar to the one described earlier in the context of water molecules near a planar electrode surface [15], except that curvature effects due to the small size of the ions are additionally accounted for.

## 2. Theory

### 2.1. Statistical mechanics

The theory presented here is an extension of that proposed earlier for bulk water [16] (hereafter referred to as Paper-I), and for water near charged electrode surfaces [15] (hereafter referred to as Paper-II).

Each water molecule is assumed to be spherical in shape, and is assigned two proton donor sites (referred to as *d*-sites) and two proton acceptor (lone pair of electrons) sites (referred to as *e*-sites). Diameter of a water molecule was taken to be the same as reported in Refs. [17,18]. Ionic radii were taken from the literature [19]. The tetrahedral arrangement of the donor and acceptor sites, the H-bond, and the permanent dipole moment of a water molecule is schematically shown in Fig. 1. The energy of a water molecule near an ion is assumed to depend on two angles: the dipolar angle ($\theta$) w.r.t the E-field axis, and the angle of rotation ($\Phi$) of the molecule about the dipole moment axis (see Fig. 1). The former angle governs the torque experienced by the molecule due to E-field, and hence determines the dipole energy. The later angle, at a given $\theta$, governs the angular orientation of the four H-bonding axis of the molecule w.r.t the E-field axis, and hence governs its H-bond interaction. Our goal now is to evaluate the number distribution of water molecules $\{N_{(\theta,\Phi,r)}\}$ in orientation ($\theta$, $\Phi$), and with its center at a distance $r$ from the center of the ion.

The key assumptions related to H-bonds are: a) they can form only between a donor and an acceptor site belonging to neighboring molecules, b) they are not permanent; they continually break and form under the influence of thermal energy, c) the O-*d* and *e*-O axes of the two molecules must be nearly collinear (within a deviation of ~0.5°), d) formation of a H-bond is accompanied by the release of energy (exothermic), and e) bonding at any site on a given water molecule is independent of whether other sites on the same molecule are bonded or not.

The system under consideration comprises $N^{\circ}$ water molecules near an ion. The free energy ($F$) of this system, in excess of that containing non-polar, water-like hard-spheres, is written as:

$$F = U - TS = U - kT.\ln(\Omega) \tag{1}$$

where $U$, $S$, $T$ and $\Omega$ are the internal energy, entropy, temperature and the number of distinguishable ways of arranging molecules in the system. $U$ is assumed to be composed of three terms: a) H-bond interactions between water molecules, b) electrostatic interactions between water molecules and the ion, and c) all other non-specific intermolecular interactions (e.g. dispersion) other than electrostatics and H-bonding. They are termed as "physical" interactions.

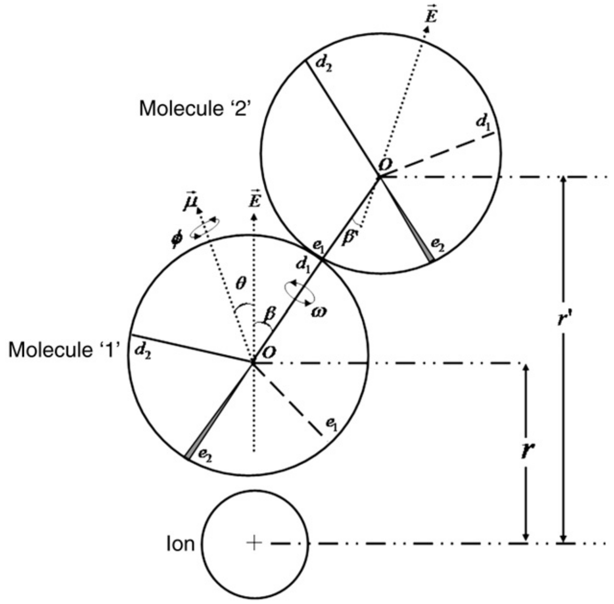

**Fig. 1.** Our model for water. $d_1$ and $d_2$ denote the two donor sites (protons). $e_1$ and $e_2$ denote the two acceptor sites (lone pairs of electrons). $\vec{\mu}$ and $\vec{E}$ are vectors corresponding to the dipole moment of water and electric field due to the ion. $\theta$ is the angle made by the dipole moment of water and the electric field due to ion. $\Phi$ is the angle of rotation of the molecule about the dipole moment axis. $\omega$ is the angle of rotation of the molecule about the H-bond axis.

$$U = U_{hb} + U_{el} + U_{ph} \tag{2}$$

Similarly, the term $\Omega$ in Eq. (1) is assumed to be composed of two terms: a) Electrostatic interactions between water molecules and the ion, and b) H-bond interactions between water molecules:

$$\Omega = \Omega_{el} \cdot \Omega_{hb}. \tag{3}$$

The "physical" interactions do not contribute to $\Omega$ as they are assumed to be independent of molecular orientations. Combining Eqs. (1)–(3), we obtain:

$$F = \{U_{el} - kT\ln(\Omega_{el})\} + \{U_{hb} - kT\ln(\Omega_{hb})\} + U_{ph}. \tag{4}$$

We will now derive expressions for each term of the Eq. (4), using statistical mechanics, and find the minimum energy state of the system.

We first consider the electrostatic term, $U_{el}$, of Eq. (4). Our expression is the same as that derived earlier by Onsager [20]:

$$U_{el} = -\sum_{r=(d_{ion}+)/2}^{\infty} \cdot \sum_{\Phi=0}^{2\pi} \cdot \sum_{\theta=0}^{\pi} \left[E_r \cdot \mu_r^{eff} \cdot N_{(\theta,\Phi,r)} \cdot \cos(\theta)\right], \text{ where } \mu_r^{eff} = \frac{\varepsilon_r \cdot \left(R^2+2\right)}{\left(2\varepsilon_r + R^2\right)} \cdot \mu \tag{5}$$

where $d_{ion}$ is the diameter of the ion, $\sigma$ is the diameter of water molecule, $R$ and $\varepsilon_r$ are the refractive index and dielectric constant of liquid water, $\mu$ is the permanent dipole moment of a water molecule in vapor phase, and $\mu_r^{eff}$ is the "effective" dipole moment of a water molecule in the liquid phase. $\varepsilon_r$ and $\mu_r^{eff}$ depend on the radial position ($r$) of the water molecule (w.r.t the center of the ion) because they include contributions from dipole moments induced by the cavity and