Water

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Specific Ion Effects on Water Structure and Dynamics beyond the First Hydration Shell**

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Dedicated to Professor Manfred Zeidler on the occasion of his 75th birthday

Our ongoing interest in the puzzling physical properties of liquid water arises from water's presence in daily life, and its importance in technical, chemical, and biological processes. As water is already interesting alone, the addition of solutes considerably broadens the spectrum of observed phenomena. For this reason the structure and dynamics of water in the vicinity of solutes have been studied for decades. One of the most challenging phenomena in this respect is the so-called Hofmeister effect, first reported by Franz Hofmeister in 1888.[1,2] He made the observation that different salts have different efficiencies in salting-out proteins, while some salts have no effect. Most importantly, the effectiveness of the anions and cations seems to assume a particular specific order. Moreover, these specific ion effects are ubiquitous in chemistry and biology, and similar ordering of the ions is observed for numerous macroscopic properties including surface tension, chromatographic selectivity, colloid stability, and protein-denaturation temperatures.[3–7] The best approach to understanding these ion effects is to focus on the simple solvation of the ions. Consequently, the Hofmeister series has been speculated to reflect different ordering powers of ions, usually anions, on the surrounding water molecules. Hence the ionic sequence has been thought as ranging from stabilizing "kosmotropes" to disruptive "chaotropes". The structure-making (kosmotrope) and structure-breaking (chaotrope) influence of ions on the hydration water has been basically understood as arising from a balance between the water–water and ion–water interactions, which vary considerably with the charge density on the solute surface. However, the challenge is to obtain a detailed understanding of those phenomenological observations by direct experimental microscopic examination of what the different ions do to water. In particular, it seems to be important to understand whether the alteration of the water structure extends beyond the first hydration shell (Figure 1).[8,9]

In two very recent studies new types of spectroscopy (along with computer simulations) provide valuable new insight into the rotational and translational motion of water molecules in solution.[10,11] These studies set out to challenge the notion that the Hofmeister effect can be explained solely by direct ion interactions and that salts affect the structure of water molecules only in their immediate surroundings. Tielrooij et al. studied the effect of ions on water by means of femtosecond time-resolved infrared (fs-IR) spectroscopy and terahertz dielectric relaxation (DS) spectroscopy.[10] The two techniques proved to be complementary. The rotational dynamics of water molecules were measured with polarization-resolved anisotropy decay, while the low-frequency spectroscopy in the terahertz regime monitored intermolecular vibrations. Tielrooij et al. studied dissolved salts consisting of various combinations of ions that have different charge densities and water affinities such as LiCl, CsCl, $MgCl_2$, Cs_2SO_4, $Mg(ClO_4)_2$, and $MgSO_4$. In the DS experiments they found that ions with a larger charge density affect the dynamics of a larger number of water molecules than ions with a lower charge density. Obviously, small and multivalent ions give higher hydration numbers. From the fs-IR measurements Tielrooij et al. showed that only $MgSO_4$ gives a very large reorientation component, whereas the individual ions

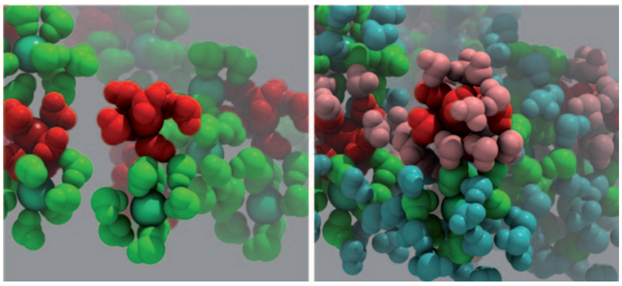

Figure 1. Water molecules in the first (left) and beyond the first (right) hydration shells of cations (Na^+, red) and anions (Cl^-, green) in an aqueous sodium chloride solution as taken from a snapshot of molecular dynamics simulations. New experiments show that the structure and dynamics of these water molecules is ion specific and different from bulk water.

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Mg^{2+} and SO_4^{2-}, in combination with ClO_4^-, and Cs^+ do not. Based on this result they concluded that the effects of ions on water dynamics can be nonadditive. If this is true, a reasonable interpretation would be that for specific combinations of cations and anions, water dynamics are affected well beyond the first hydration shell.

A somewhat different approach was used by O'Brien et al.[11] They studied the hydration patterns of $SO_4^{2-}(H_2O)_n$ clusters in the gas phase by infrared photodissociation (IRPD) spectroscopy. Here the environment of the hydrated ions is probed directly by means of vibrational resonances. This method is especially suited for investigating ion effects on the water structure at long distances. The OH stretching frequencies of the water molecules are highly sensitive to the hydrogen-bonding environment. The broad features in the OH frequency range between 3100 and 3700 cm^{-1} can be assigned to hydrogen-bonded OH groups. For smaller clusters $SO_4^{2-}(H_2O)_n$ with $n < 43$ the maximum of the OH vibrational band is blue-shifted from that of bulk water. Apparently, less optimal water–water binding arises because of the strong organization of the first hydration shell by the ion. No contributions of free OH groups could be observed, indicating that each surface molecule forms two hydrogen bonds. That such a large number of water molecules show this pattern indicates ion-specific effects beyond the first hydration shell (including approximately 12 water molecules).[12] For larger clusters $SO_4^{2-}(H_2O)_n$ with $n > 43$ the broad feature increasingly resembles that of bulk water, and a new band appears above 3700 cm^{-1} which can be assigned to the free OH groups of water molecules like those at the surface. Interestingly this contribution increases with increasing cluster size. O'Brien et al. explain the appearance of the free OH band by intrinsic water–water interactions which begin to dominate the ion-induced structure prominent for smaller clusters. This effect occurs for clusters with $n > 43$ only indicating that these water molecules belong to the third or higher solvation shells of the sulfate anion. In conclusion, long-range structural effects beyond the first hydration shell can be observed. As SO_4^{2-} is at the "structure-making" end of the Hofmeister series for the anions it will be interesting to also study the hydration shells of perchlorate ClO_4^-, which is a typical "structure-breaking" ion.

The present studies suggest that the structural change in the solvent is more than just the change associated with the water molecules in the hydration sphere of the ions, if one considers the longer-ranged nature of the ion-induced perturbation. However, there was also previous evidence that even monovalent ions can exert long-range effects. Mancinelli et al. concluded from neutron-scattering data that the structural perturbation generated by monovalent ions in aqueous solutions of NaCl and KCl exists beyond the first hydration shell.[13] Their study emphasizes longer-ranged ion-induced perturbation and related shrinkage of the second and third coordination shells of the water molecules, while the first hydration shell is largely unchanged. The overall observed structural changes are found to be similar to the effect of high pressure. Moreover, by using molecular dynamics (MD) simulations of aqueous salt (NaCl) solutions, Holzmann et al. predict that this structural feature is also significantly temperature dependent and strongly pronounced at supercooled temperatures.[14] Their MD simulations suggest that the structure and dynamics of water well beyond the first hydration shells are significantly affected by the presence of the ions and that these hydration shells are even fluidized and more mobile than bulk water under cold conditions. Thus it will be highly desirable to have experimental data for those lower temperatures as well.

In conclusion, there is ample evidence supporting the importance of hydration effects beyond the first hydration shell. The structure and dynamics of water molecules are different from those in the bulk and exhibit specific ion effects. This has been observed in particular for stronger hydrating multivalent ions such as Mg^{2+} and SO_4^{2-}. Such cooperative effects on the structure and dynamics of water support the view that water-mediated interactions must be taken into account for understanding the Hofmeister series. However, important questions still remain. How does the solvation of the ions affect their capability to bind to molecular interfaces, supposedly an important driving force for protein stabilization/destabilization?[7] Is the anion or the cation mostly responsible for the long-range effects? How important is whether the ions are mono- or multivalently charged? What is the specific role of the counterions? Are these ion-specific effects more pronounced at lower temperatures? Exciting progress for understanding specific ion effects at the molecular level is reported. But it seems that we are still away from understanding the phenomena of the Hofmeister effect.

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