

Short-range interactions: from simple ions to polyelectrolyte solutions

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Abstract

Although many properties of electrolyte solutions can be successfully described by theories at the McMillan Mayer level of approximation, there are other phenomena that cannot be explained without taking into account the explicit nature of solvent molecules. One of these that have received much attention is the Hofmeister effect that describes the influence of different types of ions on the solubility of hydrophobic molecules in water. In this work we use two simple water models, the ‘fused-spheres’ and the two-dimensional ‘Mercedes-Benz’ models to study ion solvation in water, and test suppositions about their effect on hydrophobicity. Both models give good qualitative agreement with experiment, such as Samoilov ion hydration activation energies, and Setchenow coefficients, which describe the salt concentration dependence of the solubilities of hydrophobic solutes. The results suggest that the interactions of ions with water are governed mostly by the ionic charge densities. Water structure is determined by the balance of electrostatic forces and the tendency for hydrogen bond formation. Ions with a high charge density bind water molecules very tightly and therefore exclude the hydrophobe from their first shell, leading to salting-out. The effect decreases with decreasing charge density of the ion.

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1. Introduction

Theoretical modeling of polyelectrolyte solutions is difficult, mostly due to the need to deal effectively with both solvent effects and long-range Coulomb forces. Considering the complexity of the system it is not a surprise that popular polyelectrolyte models ignore the effect of short-range interactions (for a review see [1–3]). These models consider aqueous electrolyte solutions at the McMillan Mayer level of description [5]; the solvent is treated merely as a dielectric continuum, modifying the potential of interaction between the solute ions. This approach has limited success; specific effects mediated by the solvent are observable even with strong polyelectrolytes [4,6–8]. For example, for cesium poly(styrenesulfonate) at 0 °C even the sign of the enthalpy of dilution is not predicted correctly by the popular

electrostatic theories [7]. Recent experimental results for osmotic pressure of ionene solutions with various charge on the polyions [9[•]] indicate significant deviations from electrostatic theories. The deviations seem to be present for all weakly charged polyelectrolytes in water, and are manifested in osmotic pressures, which are approximately 25% lower than predicted. Further, the enthalpies of dilutions of ionenes [10[•]] and also some other polycations in water [11] are endothermic and not exothermic, just the opposite to predictions of electrostatic theories [12]. There is no theoretical explanation for these results. The effect of short-range interactions is noticed in the temperature dependence of the degree of ion binding as obtained from transport measurements [13]. An increase of temperature should, according to electrostatic theories, decrease the fraction of free counterions. This is indeed the case for lithium but not for cesium poly(styrenesulfonate) solutions. There is no doubt that specific short-range interaction is important, and in certain situations they may overshadow the electrostatic effects [9[•],11].

The synthetic polyelectrolytes mentioned above are

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often considered as models for more complex biopolyelectrolytes. For example, poly (styrenesulfonic) acid contains charged groups of only one kind and the hydrophobic interactions are considered to be negligible. However, biological polyelectrolytes may possess both acidic and basic groups and the hydrophobicity due to non-polar groups cannot be ignored. Yet, it is quite clear that even ‘simple’ synthetic polyelectrolytes exhibit important specific effects mediated by water. The key for better understanding of polyelectrolyte solutions is understanding the mechanism of solvation of various charged groups on the polymer backbone and ions in solution, as it influences their mutual interaction.

The advent of powerful computers and their application in science yielded important developments in the theory of solutions. In particular, computer simulations become an important theoretical tool. But synthetic polyelectrolytes and even in particular biological polyelectrolytes are currently still beyond the reach of all-atom simulation studies. As an alternative we offer a simplified model of ionic solvation, which can provide important insights without using powerful computers. In this contribution we discuss to what degree ionic solvation can be explained by the concept of competition between ion–water (charge density effect) and water–water (hydrogen bonding) interactions [14[•],15^{••}].

2. Effects of ions on water

It has been known for a long time that addition of an electrolyte changes the structure of water [16]. This is shown by the viscosities of dilute solutions of alkali halide salts. Solutions of potassium fluoride in water are more viscous than pure water, while solutions of potassium iodine are less viscous than pure water. In view of these effects, ions such as fluorine are called ‘structure making’ ions, or kosmotropes, whereas ions such as iodide are called ‘structure-breaking’ or chaotropes [17].

Taking into account these experimental findings a simple model for the ion-induced structuring and disordering of water has been proposed [18[•]]. This model focuses on the charge density of an ion: high charge densities result from either high charge or small radius of the ion. For example, lithium is a small ion with high charge density, so it interacts strongly with the water dipole to strongly orient the water molecules in the ion’s first solvation shell. Larger ions having lower charge density have less tendency to orient water in the ion’s first solvation shell. Accordingly, ions with high charge density order water and are kosmotropes, while ions with low charge density only affect water ordering weakly (chaotropes). In the Collins model [18[•]], there is an asymmetry in the effects of anions and cations because the partial positive charges on water’s hydrogens are nearer the water’s surface than water’s partial negative charges on its oxygen.

The ideas discussed above can be connected to the measured viscosity of a solution using Samoilov’s model of ion hydration [19] based on the following premises. If a molecule of water is surrounded by only water molecules, then it spends some time τ_0 near a certain selected water molecule. The mean time τ_i that a molecule of water spends in the immediate vicinity of an ion before being exchanged, however, is necessarily different from τ_0 . The ions may be considered ‘positively hydrated’ if $\tau_i > \tau_0$ and ‘negatively hydrated’ if the opposite is true. We denote by E_0 the activation energy for transferring a water molecule from the first coordination shell of a second water molecule to the next coordination shell. In a similar way, E_i is the activation energy for transferring a water molecule from the immediate vicinity of an ion to the ion’s second coordination shell. In this model, the tightness of binding of a water to an ion is a predictor of the ion’s effect on the viscosity of water. The mean time τ_0 (or τ_i) may then be related to the activation energies E_0 (or E_i) of the transfer process by reaction rate theory [20^{••}]:

$$\frac{\tau_i}{\tau_0} = e^{\beta(E_i - E_0)} \quad (1)$$

As usual $\beta = 1/(k_B T)$, where k_B is Boltzmann’s constant and T absolute temperature. An important quantity is therefore the difference in activation energies $\Delta E_i = E_i - E_0$ associated with these two processes. Negative values of ΔE_i are characteristic of ‘kosmotropes’ and positive of ‘chaotropes’. Samoilov extracted this quantity from experimental data for self-diffusion coefficients and the temperature dependence of ion-mobilities in solutions [19]. It is possible, however, to ascertain ΔE_i theoretically, providing that the potential of the mean force between ions and charged sites in model water can be calculated [14[•],20^{••}].

In what follows we provide a quantitative test of these ideas. We apply the site–site integral equation of Chandler, Silbey and Ladanyi (CSL) [21,22] to obtain the potential of mean force between ions and hydrogen and oxygen sites on water molecules. The calculations were compared with the experimental data presented in [19] and with theoretical results [20^{••}] based on the state-of-art model of water.

2.1. Fused-spheres model of water

Collins suggested picturing a ‘water’ molecule as one large central hard sphere, representing the oxygen, fused to smaller hard spheres, representing the hydrogens. Cations and anions dissolved in such ‘water’ are modeled as charged spheres of various sizes. The water molecule is represented as a zwitterion of a radius of 1.78 Å for the anionic portion and 1.06 Å for the cationic portion [18[•]]. This choice is based on the

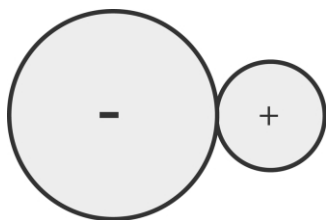


Fig. 1. The fused-spheres model of water [18*] as used in the calculation [14*]. The partial charges for the 'hydrogen' and 'oxygen' site were taken to be +0.2 and -0.2 of the elementary charge.

experimental observation that a cation and anion of these sizes do not affect the mobility of nearby water molecules. The model is schematically presented in Fig. 1.

The site-site CSL integral equation theory [21] with a hypernetted-chain closure was used to obtain the results for the potential of mean force between the ions and various sites on the model water molecule. From the potential of the mean force, we calculated the difference in activation energies ΔE_i for various ions as suggested in Ref. [20**]. Details of the calculation are explained in our previous paper [14*]. The results for $\Delta E_i = E_i - E_0$ in kcal/mol are shown in Fig. 2, where they are compared with the experimental data [19] and with recent theoretical results of Chong and Hirata [20**]. By σ_{ion} (in \AA) we denote the ionic radii used in our calculation. As seen from Fig. 2, we were able to reproduce Samoilov's classification [19] of ionic hydration as 'negative' and 'positive' and Collins's [18*] classification of the ions as 'kosmotropes' (Li^+ , Na^+ , F^-) and 'chaotropes' (K^+ , Cs^+ , Cl^- , Br^- , I^-). Our calculations are in semi-quantitative agreement with the results of Chong and Hirata [20**] obtained by the extended RISM theory with the water molecules mod-

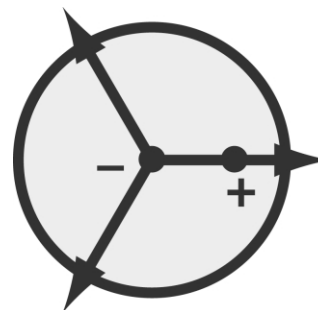


Fig. 3. The Mercedes-Benz model of water [23].

eled by the TIP3P model, and with the values of ΔE_i extracted from the experimental quantities by Samoilov [19]. In summary, the simple fused-sphere model proposed by Collins is in qualitative agreement with the experimental and theoretical data for simple monovalent ions.

2.2. Two-dimensional analogue of water

The model of water that we use here is the so-called Mercedes-Benz (MB) model, originally proposed by Ben-Naim [23]. MB 'molecules' are two-dimensional Lennard-Jones disks with three radial arms to mimic the hydrogen-bonds (HB), being arranged as shown in Fig. 3. Simulations have shown that the MB model predicts qualitatively many properties of real water, among them the density anomaly, the minimum in the isothermal compressibility as a function of temperature, and the thermodynamics of non-polar solvation [24–26*]. This model has been studied using Monte Carlo simulations [24–26*] and integral equation techniques [27,28*]. The model has recently been modified to allow studies of ionic solvation [15**]. The great advantage

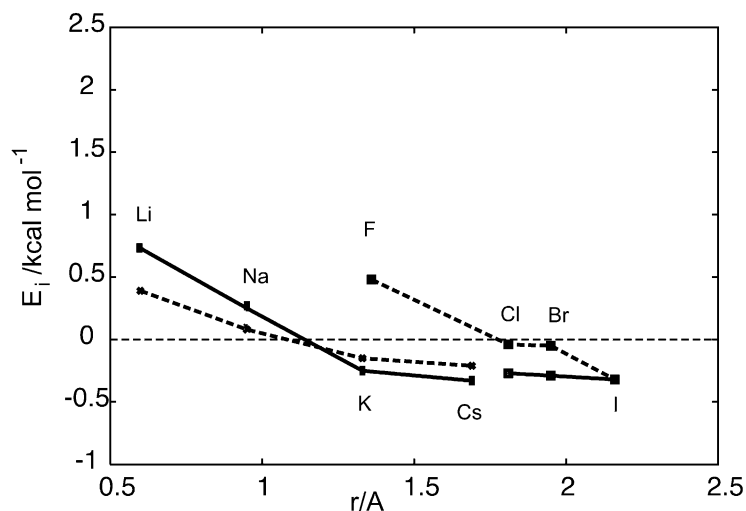


Fig. 2. Values of ΔE_i in kcal/mol for various ions as a function of the ionic radius.

of this model, compared to more realistic water models, is that well converged computer simulations of thermodynamic properties can be obtained in a reasonable amount of time.

In extensive N,P,T simulations of this model published in Ref. [15••] the authors explored the organization of ‘waters’ around ions by calculating the relevant pair correlation functions at various temperatures. They found that water orientations result from a balance between electrostatic ordering by ions and water–water HB ordering. From the potential of mean force ΔE_i 's were calculated in a similar way as for the Collins model above. The results for this quantity (see also Figure 6 of Ref. [15••]) are in semi-quantitative agreement with experiments. The MB model correctly divides monovalent ions into those, which have kosmotropic (Li^+ , Na^+ , F^- , Cl^-) and chaotropic properties (K^+ , Rb^+ , Cs^+ , Br^- , I^-). The calculations were extended to divalent ions [15••] such as magnesium, calcium and barium and again strong correlation between the charge density and ΔE_i values was observed.

3. Hofmeister effects

In 1888, Hofmeister [29] reported that salts affect the solubility of proteins in water. Certain ions precipitate proteins in water (‘salting out’) while others help solubilize them (‘salting in’). This has been interpreted as a modulation of the hydrophobic effect by salts due to the changes in the water structure brought about by ions [30,31]. The so-called Hofmeister series is a list of ions rank-ordered in terms of how strongly they affect hydrophobicity. The effect is directly proportional to the salt concentration and can be described by the Setchenow equation [32]:

$$\ln[c_i/c_i(0)] = -k_s \cdot c_s \quad (2)$$

where c_i and $c_i(0)$ are the molar solubilities of the hydrophobe in a salt solution and water, respectively, c_s is the molar concentration of the salt, and k_s is the salt's Setchenow salting-out coefficient.

The two above mentioned water models were also used to study the interpretation of the Hofmeister effect. The experimental salting-out coefficients for benzene in the presence of different salts [32] were compared with the change in the free energy of hydrophobe insertion relative to hydrophobe insertion into pure water. The results for the MB model obtained by computer simulations are in good qualitative agreement with experiment (see Figure 10 of Ref. [15••]). From these results the following conclusions could be made. Ions with high charge density bind water tightly, so the hydrophobe is excluded from the first hydration shell. The increased hydrophobe concentration in the remaining space leads to the salting-out effect. Larger ions with

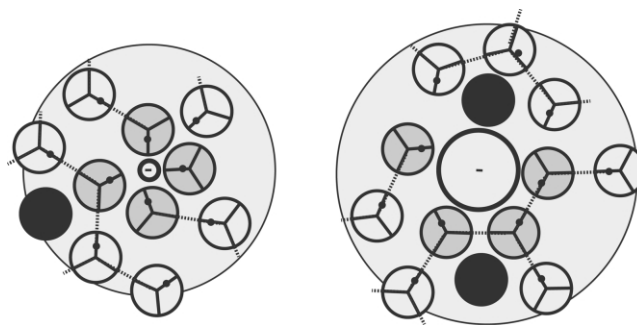


Fig. 4. Schematic representation of how water density around an ion affects the probability of solute insertion.

smaller charge density do not exclude the hydrophobe so effectively and have therefore a lesser effect on the solubility. The situation is schematically shown in Fig. 4. These results are consistent with the solvent compression volumes of the salts (cf. Table 3 of [15••]).

For the fused-sphere (Collins) model similarly good agreement was observed for the model cations but not for anions, where an opposite trend was found. We may speculate that the discrepancy is due to the approximation in the CLS theory rather than due to the simplifications of the fused-sphere model. The speculation is supported by calculations of Hirata et al. [33•,34•] who found that the site–site integral equation theory applied to the SPC/E model of water reproduces the experimental order for cations but not for anions. Clearly, computer simulations of these systems are needed to resolve this question.

4. Conclusions

Numerous experimental results show that short-range interactions play an important role even in strong polyelectrolyte solutions where the long-range Coulomb effect should be dominant. The unexplained temperature dependence of enthalpies of dilution of poly (styrene-sulfonate) solutions and endothermic effects upon dilution of cationic polyelectrolytes are two such examples. Yet synthetic polyelectrolytes are considered to be relatively simple vis-à-vis biological polyelectrolytes. The short-range interactions are mediated by water and obviously progress in understanding these solutions is only possible through increased understanding of ion–water and water–water interactions. In the present contribution two simple models of ion–water interaction were examined using numerical techniques of statistical thermodynamics. The results for the model water–ion structure reflected in measurable quantities were compared with a more sophisticated theory and with experimental findings. From this analysis we may conclude in agreement with previous findings that the charge density of ion is the most important factor in ionic

solvation. Of course, this is only the first order effect and a more exact study would need to include polarizabilities of all interacting constituents into the calculation.

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- of special interest
- of outstanding interest

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