HYDRATION OF SIMPLE IONS. EFFECT OF THE CHARGE DENSITY.#

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#Dedicated to Prof. D. Dolar on the occasion of his 80th birthday

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Abstract

Ions are often classified as 'kosmotropes' or 'chaotropes' depending on whether they order or disorder water, as determined by how much they change the viscosity of water. Collins has proposed that water ordering by an ion depends on its charge density, using a simple fused-sphere model (K. D. Collins, *Biophys. J.*, **1997**, *72*, 65-76). To make his idea more quantitative, we have applied the site-site integral equation of Chandler, Silbey and Ladanyi to obtain the potential of the mean force between ions and water molecules. From the potential of mean force curves we obtain the activation energy for transferring a water molecule from near the ion to the bulk. The results for this quantity are in semi-quantitative agreement with experimental data for alkali halides and with theoretical results based on the TIP3P model of water.

Introduction

The origins of many of the nonidealities in electrolyte solutions are well understood, and have been treated by continuum electrostatics models (see, for example,[1]). In contrast, many ion-specific effects in electrolyte solutions are not yet understood. These effects may be important even in systems where Coulombic forces are very strong, i.e. in polyelectrolyte solutions. For example, theoretical results for poly(styrenesulphonates) in water can be brought into considerably better agreement with experiment if non-coulombic forces are included in the calculations.[2,3]

It has been known since 1933, when the work of Bernal and Fowler was published,[4] that addition of ions changes the structure of water. This is shown by the viscosities of dilute solutions of alkali halide salts. Solutions of KF in water are more viscous than pure water, while solutions of KI in water are less viscous than pure water. Interestingly, the viscosity of dilute KCl solutions does not differ much from pure water. Following Bernal and Fowler,[4] ions such as fluorine are called 'structure making' ions, or kosmotropes, whereas ions such as iodine are called 'structure-breaking', or chaotropes.[5]

Collins has proposed a simple model for ion-induced structuring and disordering of water.[6] His 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 water's 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 waters in the ion's first solvation shell. The solvation model of Collins[6] predicts that ions with high charge density order waters and are kosmotropes, while ions with low charge density only affect water ordering weakly (chaotropes). In his model, there is an asymmetry in the effects of anions and cations because the partial positive charges on water's hydrogens are nearer to water's surface than water's partial negative charges on it's oxygen.[6,7]

How can we relate the ordering effects of ions to the solution viscosity? The ideas proposed by Collins[6] can be connected to viscosity using Samoilov's model of ion hydration.[8] Samoilov considered the translational motion of water molecules in a dilute electrolyte solution. 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. According to Samoilov, the ions are 'positively hydrated' if $\tau_i > \tau_0$ and 'negatively hydrated' if $\tau_i < \tau_0$. Let us 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 a water to an ion is a predictor of the ion's affect on water viscosity. 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[9]

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

As usual $\beta = 1/(k_B\mathrm{T})$, 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 for 'kosmotropes' and positive for 'chaotropes'. Samoilov extracted this quantity from experimental data for the transport coefficients of individual ions; more concretely, from self-diffusion coefficients and temperature dependence of ion-mobilities in solutions.[8] It is possible, however, to ascertain ΔE_i theoretically, providing that potential of the mean force between ions and charged sites on model water can be calculated.[9]

The purpose of this work is to provide a quantitative test of these ideas. We apply the site-site integral equation of Chandler, Silbey and Ladanyi (CSL)[10–12] to obtain the potential of mean force between ions and hydrogen and oxygen sites on water molecules. From the potential of the mean force, we calculated the difference in activation energies ΔE_i for various ions. The calculations were compared with the experimental data presented in[8] and with theoretical results based on the more realistic TIP3P model of water.[9,13]

The model and methods

We use the Collins model of water. Each water has one large central hard sphere, representing the oxygen, fused to smaller hard spheres, representing the hydrogens. Cations and anions are modelled as charged spheres of various sizes. The water molecule is represented as a zwitterion of radius 1.78 Å for the anionic portion and 1.06 Å for the cationic portion.[6] This choice is based on the experimental observation that the cation and anion of these sizes do not affect the mobility of nearby water molecules. The small ions (see Figure 3 of[6] and related references) decrease the mobility of water (kosmotropes) and the large ions increase the mobility of nearby water molecules (chaotropes). The pair interaction potential for two sites separated by distance r_{ij} is defined by

$$u_{a_ib_j}(r) = \begin{cases} -\frac{z_{a_i} z_{b_j} e^2}{4\pi\varepsilon\varepsilon_o r} & r \geq \sigma_{a_ib_j} \\ \infty & r < \sigma_{a_ib_j} \end{cases}, \tag{2}$$

where $\sigma_{a_ib_j} = (\sigma_{a_i} + \sigma_{b_j})/2$ is the contact distance between the charges $z_{a_i}e$ and $z_{b_j}e$. Further, a and b denote the particles (molecules, ions), and i and j denote the various sites on these particles. a and b therefore stand for water v and ion u, while i and j denote positively (+) or negatively (−) charged site. The ions are treated as molecules with one site. The radii of ions were taken from Reference.[6]

The site-site Chandler-Silbey-Ladanyi integral equation theory[10,11] with an HNC-like closure has been used to obtain the results for the potential of mean force between the ions and various sites on model water molecule. The theory consists of the Ornstein-Zernike-like integral equation[10–12,14]

$$\hat{\mathbf{H}}(k) = \hat{\mathbf{W}}(k)\hat{\mathbf{C}}(k)\hat{\mathbf{W}}^T(k) + \hat{\mathbf{W}}(k)\hat{\mathbf{C}}(k)\boldsymbol{\rho}\hat{\mathbf{H}}(k) \tag{3}$$

where $\hat{\mathbf{H}}$, $\hat{\mathbf{C}}$, $\hat{\mathbf{W}}$ and $\boldsymbol{\rho}$ are the matrices with the elements $\hat{\mathbf{h}}_{a_ib_j}$, $\hat{\mathbf{c}}_{a_ib_j}$, $\delta_{ab}\hat{\boldsymbol{\omega}}_{a_ia_j}$ and $\delta_{ab}\delta_{ij}\boldsymbol{\rho}_{a_i}$, which are in turn the matrices of the form:

$$\hat{\mathbf{h}}_{a_ib_j}(k), \hat{\mathbf{c}}_{a_ib_j}(k) = \begin{pmatrix} \hat{c}^{00}_{a_ib_j}(k) & \hat{c}^{01}_{a_ib_j}(k) \\ \hat{c}^{10}_{a_ib_j}(k) & \hat{c}^{11}_{a_ib_j}(k) \end{pmatrix}, \qquad \boldsymbol{\rho}_{a_i} = \begin{pmatrix} \rho_{a_i} & \rho_{a_i} \\ \rho_{a_i} & 0 \end{pmatrix}$$

$$\hat{\boldsymbol{\omega}}_{a_ia_j}(k) = \delta_{ij}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + (1-\delta_{ij})\delta_{av}\begin{pmatrix} 0 & 0 \\ \frac{\sin k\sigma_{v_iv_j}}{\sigma_{v_iv_j}} & 0 \end{pmatrix}$$

and HNC closure relations

$$g^{\alpha\beta}_{a_ib_j}(r) = e^{-\beta u_{a_ib_j}(r)+t^{00}_{a_ib_j}}\left\{\delta_{\alpha0}\delta_{\beta0} + (1-\delta_{\alpha0}\delta_{\beta0})\left[t^{\alpha\beta}_{a_ib_j}(r) + \delta_{\alpha\beta}t^{10}_{a_ib_j}(r)t^{01}_{a_ib_j}(r)\right]\right\}, \tag{4}$$

where $t^{\alpha\beta}_{a_ib_j}(r) = h^{\alpha\beta}_{a_ib_j}(r) - c^{\alpha\beta}_{a_ib_j}(r)$, and the upper indices denote the bonding state (0 for non-bonded and 1 for bonded) of the corresponding sites.[12] It is well-known that the Coulomb interaction potential requires special treatment. The renormalization procedure for the Coulomb part of the interaction potential must be applied first, before the set of equations 3 and 4 can be solved numerically. In this study we utilized the method of Ng[15] to treat the Coulomb tail of the intersite interaction.

The temperature for all calculations was $T = 298$ K and the partial charges on water and ions were assumed to be $0.3z_{a_i}e$, where e is the proton charge. This choice was dictated by problems with convergence for pure model water. The numerical solutions were obtained by the direct iteration over 1024 points using the logarithmic grid.[16] For more details concerning the integral-equation theory see Reference.[12]

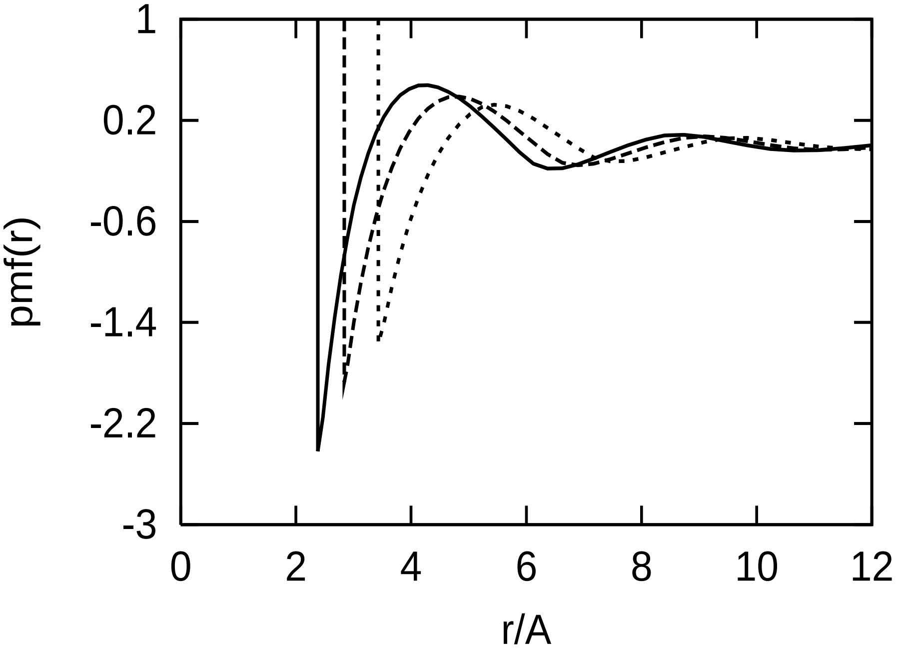

Figure 1: Ion-water (oxygen site) potential of mean force for Li^+ ion (full line), cation of the reference electrolyte (dashed line), and Cs^+ ion (dotted line) as calculated by the CSL integral equation theory.

Results and discussion

We consider first the results for the potential of the mean force, pmf(r), defined as the negative logarithm of the site-site pair distribution function $g_{a_i b_j}$(r). These results were obtained using the site-site CSL integral equation with the HNC-like closure, as briefly explained in the previous section. In order to obtain quantitative predictions for the Collins model of solvation we define the so-called reference electrolyte: the radius of the reference anion is 1.78 $\AA$ and the reference cation 1.06 $\AA$. Note, that these radii were chosen on the basis of the experimental fact that monovalent ions of this size do not affect significantly the structure and mobility of water molecules (see, for example, Fig. 1 of reference[6]).

The potentials of mean force for the cations approaching the oxygen site of water molecule are shown in Figure 1. The result for Li^+ ion is presented by full line, the result for the *cation* of the reference electrolyte by dashed line, and the potential of mean force for Cs^+ ion by dotted line. The results for potential of mean force for anions approaching the positive site of water are given in Figure 2. The

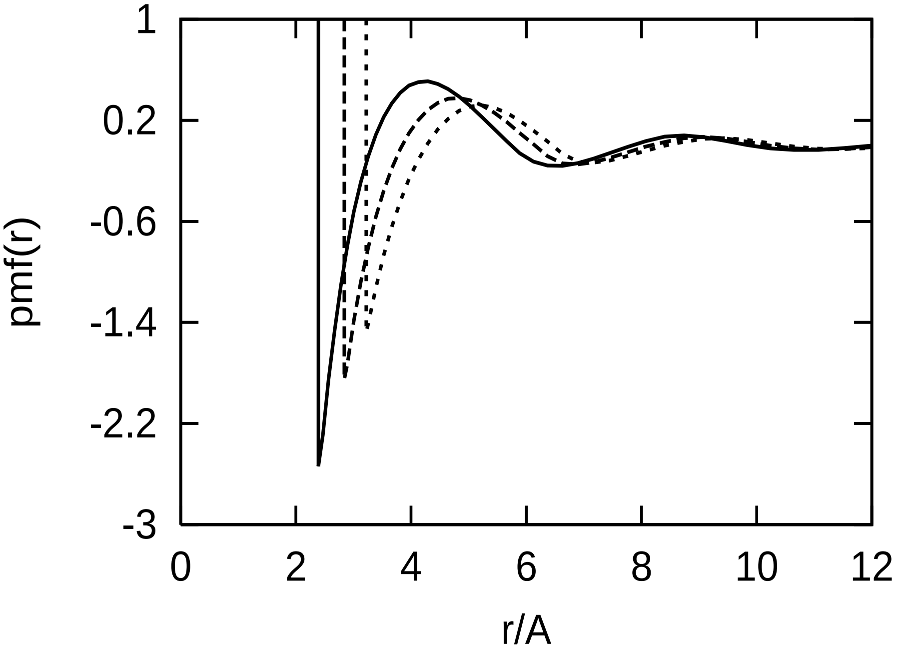

Figure 2: Ion-water (hydrogen site) potential of mean force for F^- ion (full line), anion of the reference fluid (dashed line), and I^- ion (dotted line), as calculated by the CSL integral equation theory.

potential of mean force result for F^- ion is shown by full line, the result for *anion* of the reference electrolyte by dashed line (the middle line), and the result for I^- ion approaching the hydrogen site on water by dotted line. From these and similar figures, the ΔE_i's for various ions can be calculated. Chong and Hirata[9] obtained E_i from the potential of the mean force of ion approaching oppositely charged site on the model water. They assumed that E_i is equal to the difference between the first minimum and the first maximum in the pmf(r) function. In our calculation E_0 is the corresponding difference for the site on water approaching the oppositely charged reference-electrolyte ion (dashed lines in Figures 1 and 2).

The results for $\Delta E_i = E_i - E_0$ in kcal/mol are shown in Table 1 where they are compared with the experimental data[8] and with recent theoretical results of Chong and Hirata.[9] By σ_{ion} (in Å) we denote the ionic radii[6] used in our calculation. As seen in Table 1, we were able to reproduce Samoilov's classification[8] of ionic hydration as 'negative' and 'positive' and Collins's[6] classification of the ions as 'kosmotropes' (Li^+, Na^+, F^-) and 'chaotropes' (K^+, Cs^+, Cl^-, Br^-, I^-).

Table 1:

	$\sigma_{ion}/$ Å	Experiment[8]	TIP3P/ex-RISM [9]	This paper
Li^+	0.65	0.73	1.35	0.39
Na^+	0.95	0.25	0.10	0.08
K^+	1.35	-0.25	-0.60	-0.15
Cs^+	1.35	-0.33		-0.21
F^-	1.35		2.17	0.48
Cl^-	1.80	-0.27	-0.20	-0.04
Br^-	1.95	-0.29		-0.05
I^-	2.2	-0.32		-0.32

Our calculations are in semi-quantitative agreement with the results of Chong and Hirata[9] obtained by the extended RISM theory[17] with the water molecules modelled by TIP3P model,[13] and with the values of ΔE_i extracted from the experimental quantities by Samoilov.[8] In summary, the simple solvation model proposed by Collins is in qualitative agreement with the experimental and theoretical data for simple monovalent ions.

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References

1. J. M. G. Barthel, H. Krienke, W. Kunz, *Physical chemistry of electrolyte solutions: modern aspects* (Topics in Physical Chemistry 5; ed. H. Baumgärtel, E. U. Franck, W. Grünbein), **1998**, Springer, New York.
2. D. Dolar, in *Polyelectrolytes*, ed. E. Selegny, M. Mandel and U. P. Strauss; D. Reidel, Dordrecht-Holland **1974**, Vol. *1*, pp. 97-113.
3. D. Dolar and M. Bešter, *J. Phys. Chem. B* **1995**, *99*, 4763-4767.
4. J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1933**, *1*, 515-524.
5. H. S. Frank, *Z. Phys. Chem.* **1965**, *228*, 364-372.
6. K. D. Collins, *Biophys. J.* **1997**, *72*, 65-76.
7. M. G. Cacace, E. M. Landau, and J. J. Ramsden, *Q. Rev. Biophys.* **1997**, *30*, 241-277.
8. O. Ya. Samoilov, *Discuss. Faraday Soc.* **1957**, *24*, 142-146.
9. S-H. Chong and F. Hirata, *J. Phys. Chem. B* **1997**, *101*, 3209-3220.
10. D. Chandler, R. Silbey, and B. Ladanyi, *Mol. Phys.* **1982**, *46*, 1335-1345.
11. P. J. Rossky and R. A. Chiles, *Mol. Phys* **1984**, *51*, 661-674.
12. Y. V. Kalyuzhnyi and P. T. Cummings, *J. Chem. Phys.* **1996**, *104*, 3325-3328.

13. W. L. Jorgensen, *J. Am. Chem. Soc.* **1981**, *103*, 335-340.
14. H. L. Friedman, *A Course in Statistical Mechanics*, **1985** Prentice-Hall, Inc., Englewood Cliffs, New Jersey 07632.
15. K. C. Ng, *J. Chem. Phys.* **1974**, *61*, 2680-2689.
16. J. D. Talman, *J. Comp. Phys.* **1978**, *29*, 35-48.
17. F. Hirata, P. J. Rossky, and B. M. Pettit, *J. Chem. Phys.* **1982**, *77*, 509-520.

Povzetek

V članku so predstavljeni rezultati za preprosti model hidratacije ionov, ki ga je predlagal Collins (K. D. Collins, *Biophys. J.*, **1997**, *72*, 65-76). Ioni so ponazorjeni kot toge kroglice z naboji v središčih, voda pa kot dipol, ki ga sestavljata dve spojeni nabiti togi kroglici. Ustrezno Chandler-Silbey-Ladany integralsko enačbo smo rešili numerično. Izračunali smo potenciale povprečne sile za interakcijo med vodo in nekaterimi ioni ter od tod aktivacijsko energijo za prenos vode iz prve hidratne lupine iona v drugo. Rezultati se sorazmerno dobro ujemajo z merskimi podatki in teoretičnimi rezultati, dobljenimi na osnovi bolj realističnega modela vode (model TIP3P). Naši računi potrjujejo smiselnost Collinsovega modela hidratacije, ki predpostavlja, da je gostota naboja izbranega iona tisti parameter, ki določa strukturo in gibljivost vode v njegovi okolici.