

Ion association in aqueous solution



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ABSTRACT

The properties of aqueous ionic solutions are determined by strong electrostatic interactions, which are influenced by polarizability and charge transfer interactions. Potential models which include polarizability and charge transfer have been developed for water and single ion properties. Here, the ion–ion interactions are optimized so that the osmotic pressure as a function of concentration is reproduced. Using the optimized potentials, the amount of ion pairing and larger cluster formation is calculated. For NaCl, NaI, and KCl, there is a small amount of pairing, with larger clusters present as well. For KI, there is much more pairing and much larger clusters are observed. The amount of pairing is consistent with the law of matching affinities, with the pairs that show the least pairing also being the most mis-matched in terms of size or solvation free energy. The charge transferred from the anions to water is more than from is transferred from the water to cations, so the water molecules acquire a negative charge, which increases with ion concentration.

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1. Introduction

The aqueous hydration of ions involves a balance of ion–ion, ion–water interactions, and water–water interactions, in order of decreasing strength. For example, the interaction energy between a sodium and a chloride ion is -132 kcal/mol [1], the water–chloride interaction energy is -13.6 kcal/mol [2] and the water–water interaction energy is -5.0 kcal/mol [3]. This balance of large energies is indicated by the large lattice energy of salts (188 kcal/mol for NaCl) and the large solvation enthalpy (-187 kcal/mol for NaCl) adding up to give a relatively small heat of solution of about 1 kcal/mol [4]. The interplay of these interactions can determine if a salt is insoluble, completely dissociated in solution, or some intermediate point involving ion pairing. Experimental evidence for ion pairing for univalent ions below supersaturation comes from a variety of sources. Ion pairing is indicated in a variety of other approaches, including conductometry [5], potentiometry [6], ultrasonic relaxation [7], near edge X-ray absorption spectroscopy [8], dielectric relaxation spectroscopy [9], and near infrared spectroscopy [10], (see Ref. [11]), and molecular dynamics simulations [12–23]. The most direct structural indication of pairing would come from neutron diffraction or X-ray scattering but the ion–ion signal in both approaches is small relative to the signal from water–water and

water–ion correlations, and so these approaches rely on molecular dynamics simulations to determine the amount of ion pairing [24,25]. Clusters larger than pairs are found for solutions under ambient conditions at unsaturated concentrations from Raman [26] and vibrational energy transfer [27] experiments as well as molecular dynamics simulations [28–32]. The simulations revealed that alkali halide salts can form clusters of up to about five ions and while neutral aggregates are most probable, charged clusters are also found, with a preference for excess cations [30,32]. The smaller cations tend to cluster more than larger cations [30]. Experiments on alkali-thiocyanate salts reveal a different picture. The charged clusters in those solutions tend to have an excess of anions and the bigger cations tend to cluster more, suggesting that cluster formation might be driven by the matching of cation and anion types [27].

Osmotic pressure can indicate the degree of ion pairing [11]. In a concentrated solution, water–water interaction and interactions between unlike ions tend to promote phase separation into a very concentrated solution and pure water, whereas ion–water and like–ion interactions favor a single dilute solution. If ions in a concentrated solution are restrained by a semi-permeable membrane, the pressure exerted by the solution may be less than expected for an ideal solution of fully dissolved salt. Reproduction of the osmotic pressure for salt solutions has been used to parameterize potential models for ion interactions [17,21,23,33,34]. Other related methods use the activity coefficient for ion-pair potential refinement [35–37]. These efforts show that changing only the unlike ion interaction, thereby changing the amount of ion pairing, and leaving all

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other interactions unchanged has a strong effect on the osmotic pressure [21,23,34]. This method is effective because small changes in the energy can shift the balance between the contact ion pair and the fully dissociated ions. Ion pairing is believed to be largely driven by the strength of the water–ion interaction, as given by the law of matching water affinities [38]. The osmotic coefficient shows a correlation with the difference in the absolute free energy of solution between the anion and the cation (Fig. 1, data from Refs. [39–41]). This shows a similar volcano relationship (or in this case an inverted volcano) to other thermodynamic properties [38]. The salts that have the smallest osmotic coefficient are those with the closest free energies of solution. This includes large anion–large cation pairs like CsI (which has the lowest osmotic coefficient among the salts in Fig. 1) and small anion–small cation pairs like NaF. Both small anion–large cation (on the left of Fig. 1) and large anion–small cation (on the right) have larger osmotic pressures.

In this paper, we use recently developed models which include charge transfer and polarizability [42–44] to examine the formation of ion pairs and larger clusters. Models for Cl^- , I^- , Na^+ , and K^+ have been developed which reproduce the single ion free energies of solution as well as other structural, energetic, and dynamical properties [43,44]. We will adjust the interactions between unlike ion pairs to reproduce the osmotic coefficient as a function of concentration as has been done in previous studies [21,23,34]. The optimized potentials will be used for the clustering analysis of the four salt solutions, NaCl, NaI, KCl, and KI.

2. Methods

The osmotic pressure calculations. The osmotic pressure was calculated using the method of Luo and Roux [21] in which an artificial semi-permeable membrane is set up, which is permeable to water but not to ions. This method has the virtues of being exact, and so applicable to solutions of any concentration, and easy to implement. This is done by simply setting up a half-harmonic restraint which only acts on the z component of the ions according to

$$E_{\text{restraint}} = \begin{cases} 0 & z < z_r \\ \frac{1}{2}k_r(z - z_r)^2 & z \geq z_r \end{cases} \quad (1)$$

where k_r is the force constant (set equal to 10 kcal/mol/Å²) and z_r is the position of the restraining membrane (set equal to 22 Å). There are two such restraining potentials, at $\pm z_r$, which creates a

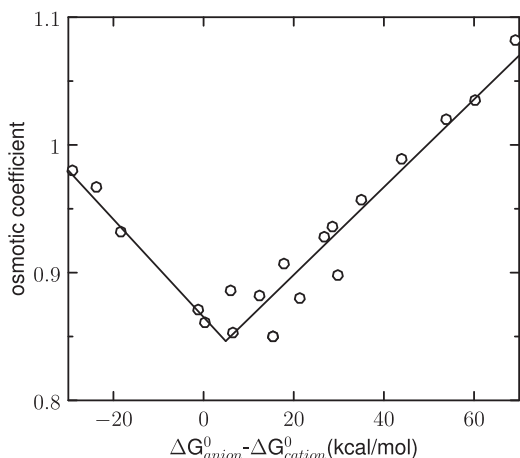


Fig. 1. The difference in the absolute single-ion solvation free energy of the anion and the cation and the osmotic coefficient at 1 m for alkali halide salts.

layer $2z_r$ thick containing the salt solution. Outside this layer is pure water. The osmotic pressure is simply the force, $-k_r(z - z_r)$, that the restraint exerts on the ion divided by the area of the periodic cell in the x and y directions. The osmotic coefficient, ϕ , is the osmotic pressure divided by the ideal solution osmotic pressure, $2c(m)RT$, where $c(m)$ is the molality of the salt solution. Notice that the factor of 2 indicates that the ideal solution limit assumes complete ion dissociation. Ion pairing would then tend to decrease the osmotic pressure by having fewer independent particles. These simulations used an orthorhombic box with side x and y side lengths equal to 44 Å. The box length in z allowed to vary so as to maintain a constant pressure. The simulations used 5680 water molecules and the appropriate number of ions to give the intended molality. This system size gives a box size in the z direction equal to about 88 Å, half of which contains the salt solution. The molality of the solution is found from the average number of ions from $-z_r$ to $+z_r$ divided by the number of water molecules in the same region. All four ion pairs were simulated at a concentration of 1 m and an additional higher concentration. The solutions NaCl and NaI were simulated at 5.0 m, KCl at 4.8 m, the saturation concentration, and KI at 4.5 m, the highest concentration for which an experimental value is available [39]. The 1 m simulations used 104 ions for the NaCl and KCl solutions, 102 ions for the KI solutions, and 100 ions for the NaI solutions. The 5.0 m NaCl solution contained 496 ions, the 4.8 m KCl solution contained 456 ions, the 5.0 m NaI solution 434 ions, and the 4.5 m KI solution contained 430 ions.

The potential model. The simulations used a recently developed model which includes both charge transfer and polarizability [42–44]. Charge transfer is treated by allowing charge to be transferred between pairs. The amount of charge transfer depends on the distance between pairs and the model has charges which change every time step, according to the local structure. The TIP4P-FQ+DCT model, which treats polarizability with the fluctuating charge method, is used for water [42]. Polarizability for the ions is treated using the Drude model, in which a charge site is placed on a spring [45,46]. The interaction between two ions i and j is given by

$$E_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij1}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij1}} \right)^6 \right] + \sum_{\alpha\beta} \frac{q_{i\alpha}q_{j\beta}}{r_{i\alpha j\beta}} S_{ij}(r_{i\alpha j\beta}) + \left(-\mu_{ij}^{CT} |q_{ij}^{CT}| + \frac{1}{2} \eta_{ij}^{CT} (q_{ij}^{CT})^2 \right) \quad (2)$$

with a Lennard-Jones interaction between the ion centers, Coulombic interactions between all sites on different ions, and a charge transfer energy term. The distance between sites α and β on ions i and j is $r_{i\alpha j\beta}$, with the first site corresponding to the ion center and the second corresponding to the Drude position. The Coulombic interactions are damped at short-range according to

$$S_{ij}(r_{i\alpha j\beta}) = 1 - \left(1 + \frac{r_{i\alpha j\beta}}{2a_{ij}} \right) e^{-r_{i\alpha j\beta}/a_{ij}} \quad (3)$$

where a_{ij} determines the amount of screening. The charge transfer between pairs is distance dependent as given by

$$q_{ij}^{CT} = \begin{cases} Q_{ij}^{CT} & \text{if } r_{ij1} < R_1^{CT}, \\ \frac{1}{2} Q_{ij}^{CT} \left[1 + \cos\left(\pi \frac{r_{ij1} - R_1^{CT}}{R_2^{CT} - R_1^{CT}}\right) \right] & \text{if } R_1^{CT} \leq r_{ij1} \leq R_2^{CT}, \\ 0 & \text{if } r_{ij1} > R_2^{CT}, \end{cases} \quad (4)$$

as characterized by a charge transfer amount, Q_{ij}^{CT} and two distances, which reduces the charge transfer to zero over the range R_1^{CT} to R_2^{CT} . The charge is transferred to the ion center and the Drude charge remains unchanged. No charge is transferred between like

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