

Association of Ion Pairs in Clusters of Dielectric Solvents

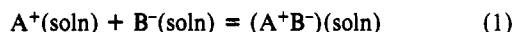
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The association of ion pairs in clusters is studied in an extended Bjerrum model using both a Coulombic potential and a potential of mean force calculated from molecular dynamics simulations. Association is found to increase rapidly as the cluster size decreases until a critical size is reached, below which the ions are in the paired state. For NaCl in water this is estimated at 12 water molecules for contact ion pairs. It is also found that the short-range details of the potential are important and that replacing them with a Coulombic assumption leads to a large overestimate of the critical size.

Introduction

Solvation of ions in clusters has been studied both experimentally¹ and theoretically² with respect to the size dependence of the solvation process and to the structure of the solvated ion. A natural extension of this interest is to consider the solvation and dissociation of a salt molecule in a dielectric cluster. In the bulk, at low concentrations of electrolyte, the molecules dissociate and the dominant picture is the Debye-Hückel (DH) model of free independent ions interacting by long-range Coulombic forces. At higher concentrations the experimentally measured behavior deviates from this simple picture, as the short-range forces become more dominant. A simple extension to the DH picture, proposed by Bjerrum³ in 1926, is based on the introduction of another chemical species into the model—the ion pair, which corresponds to two oppositely charged ions sufficiently close to each other to be strongly correlated. In the solution a dynamic equilibrium is assumed to exist between free and paired ions:



Obviously the energetic balance which enters into the classical description of ion pairs in bulk dielectric solvents changes in the finite cluster environment. In this paper we consider the evolution of this effect with cluster size and the implications of the finite size of the dielectric environment on the salt dissociation process. To get a zero-order estimate of the size effect, we do this first within the simple classic continuum dielectric theory of Bjerrum, keeping in mind that this approach needs to be improved upon in many ways. By using an extension to clusters of the simple Bjerrum picture we show that (i) association increases rapidly with decreasing cluster volume and (ii) a critical cluster volume (radius in our model) exists, below which the salt molecule is not dissociated in the sense that the ions are always "paired". Obviously this simple continuum model cannot make quantitative predictions, but these qualitative features are expected to persist in real systems. Indeed a more detailed model based on potentials derived from molecular dynamics (MD) simulations in water leads to qualitatively similar results (with a considerably different critical radius).

The existence of a critical size for ionic dissociation in clusters is intuitively expected. Indeed the dissociation of the weak acid α -naphthol in clusters of various solvents shows a critical size (>40 molecules for water) beneath which no dissociation occurs.⁴

Model

We model the ion pair in a dielectric cluster as two classical charged particles confined in a dielectric sphere of radius R and dielectric constant ϵ . The two particles are coupled to a heat bath at temperature T , which represents the internal degrees of freedom of the cluster. The solvation enthalpy is assumed to be large enough so the particles do not leave the cluster.

The potential energy, $U(\vec{r}_1, \vec{r}_2)$ is constructed^{5,6} as the sum of three terms: (a) the interaction potential between the ions in the bulk $\phi(\vec{r}_1, \vec{r}_2) = \phi(|\vec{r}_1 - \vec{r}_2|)$; (b) a correction, ΔP , to the interaction potential ϕ , which results from the reduced screening due to the finite sphere size; (c) corrections, $h(\vec{r}_1)$, to the solvation energy of a charge in the bulk due to position-dependent solvation in a finite volume.

$$U(\vec{r}_1, \vec{r}_2) = \phi(r_{12}) + \Delta P(\vec{r}_1, \vec{r}_2) + h(\vec{r}_1) + h(\vec{r}_2) \quad (2)$$

$$r_{12} = |\vec{r}_1 - \vec{r}_2|; \quad r_1, r_2 < R$$

Assuming the ions to be charged point particles allows us to obtain ΔP and h as⁷

$$\Delta P = -\frac{q_1 q_2}{\epsilon R} \sum_{n=0}^{\infty} \frac{(\epsilon - 1)(n + 1)}{\epsilon n + n + 1} \left(\frac{r_1 r_2}{R^2} \right)^n P_n(\cos \theta)$$

$$h(r_i) = \frac{q_i^2}{2\epsilon R} \sum_{n=0}^{\infty} \frac{(\epsilon - 1)(n + 1)}{\epsilon n + n + 1} \left(\frac{r_i}{R} \right)^{2n} \quad (3)$$

$$\cos \theta = \frac{\vec{r}_1 \vec{r}_2}{|\vec{r}_1| |\vec{r}_2|}$$

where q_i is the absolute charge on ion i and $P_n(\cos \theta)$ are the Legendre polynomials. Note that $U \rightarrow 0$ when $R, |\vec{r}_1 - \vec{r}_2| \rightarrow \infty$, namely, the reference state is that of isolated ions in the bulk solvent.

The probability for the two ions to be separated by a distance r_{12} is

$$p(r_{12}) = (1/Z) e^{-\beta \phi(r_{12})} f(r_{12}) \quad (4)$$

$$f(r_{12}') = \int d\vec{r}_1 \int d\vec{r}_2 e^{-\beta(\Delta P(\vec{r}_1, \vec{r}_2) + h(\vec{r}_1) + h(\vec{r}_2))} \delta(r_{12} - r_{12}')$$

$$Z = \int_0^{2R} dr_{12} e^{-\beta \phi(r_{12})} f(r_{12})$$

$\delta(x-x')$ is the Dirac delta function and Z is the classical configuration integral. Note that $f(r_{12})$ is independent of the choice of $\phi(r_{12})$.

In contrast to the bulk situation, in a cluster containing one salt molecule the ions are always paired in the sense that they are both confined in the finite cluster environment. However we may still distinguish between a "paired" state and an "unpaired" one

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(2) (a) Makov, G.; Nitzan, A.; Brus, L. E. *J. Chem. Phys.* **1988**, *88*, 5076. (b) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.*, submitted for publication. (c) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044.

(3) (a) Bjerrum, N. K. *Dan. Vidensk. Selsk.* **1926**, *7*, 9. (b) Justice, J.-C. *J. Phys. Chem.* **1975**, *79*, 454. (c) Petrucci, S. In *Ionic Interactions*; Petrucci, S., Ed.; Academic Press: New York, 1971.

(4) Knochenmuss, R.; Cheshnovsky, O.; Leutwyler, S. *Chem. Phys. Lett.* **1988**, *144*, 317.

(5) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403.

(6) Warshel, A. *Q. Rev. Biophys.* **1984**, *17*, 283.

(7) Bottcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973. Bottcher finds the potential $\phi(r_2)$ caused by a charge q_1 at r_1 , from which the terms ΔP and h in eq 3 may easily be found.

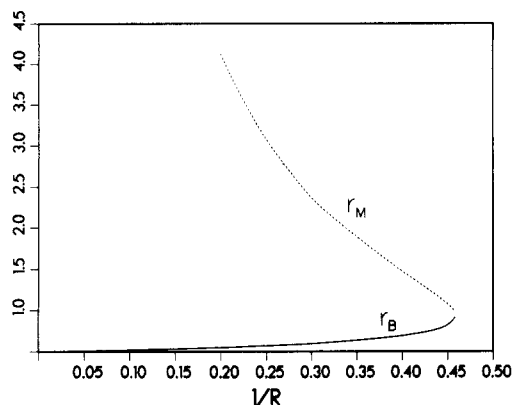


Figure 1. Locations of the minimum, r_B , and of the maximum, r_M , in $p(r_{12})$, as a function of the inverse radius (all in length units of $\epsilon k_B T/q^2$).

if a potential barrier exists as a function of the interionic distance, so that ions closer than the barrier distance are considered paired. This is the sense in which ion pairs are defined in the Bjerrum theory,³ and this is the sense adopted here. Thus the existence of two species, paired and unpaired ions, is associated in this model with the existence of a minimum in $p(r_{12})$ at $r_{12} = r_B$.³

$$\left. \frac{dp(r_{12})}{dr_{12}} \right|_{r_{12}=r_B} = 0 \quad \left. \frac{d^2p(r_{12})}{dr_{12}^2} \right|_{r_{12}=r_B} > 0 \quad (5)$$

and an ion pair is defined as two oppositely charged ions whose distance from each other is smaller than r_B (the location of the barrier peak). From this definition, in the usual notation, the associated fraction $1 - \alpha$ is

$$1 - \alpha = \int_0^{r_B} dr_{12} p(r_{12}) \quad (6)$$

Unlike the original Bjerrum theory for bulk solutions,⁸ here the probabilities are well-defined and the criticisms of Fuoss⁹ in this matter are not applicable (for this special case of two ions the Fuoss model is identical to the Bjerrum model). Thus it remains only to determine r_B . For a finite cluster $p(r_{12})$ will depend on the cluster size, so in general $r_B = r_B(R)$.

The existence of a minimum in $p(r_{12})$ can be seen qualitatively from eq 4. First, the interaction potential between oppositely charged ions has a minimum at some point r_0 ; therefore $e^{-\beta\phi}$ has a maximum at that point. Second, it can be shown that $f(r_{12})$ vanishes when $r_{12} = 0$ or $r_{12} = 2R$, so it has a maximum between them. For large clusters this occurs at $r_{12} = r_M \approx R$. Therefore, when $R \gg r_0$, $p(r_{12})$ has maxima both at $r_{12} \approx r_0$ and at $r_{12} \approx R$, which necessitates a minimum at some $r_B(R)$ between r_0 and R . This also implies that there exists a critical cluster size, of the order $R_c \sim r_0$, below which the minimum in $p(r_{12})$ does not exist. For $R \leq R_c$ no distinction can be made between "paired" and "unpaired" ions, and in the spirit of Bjerrum we may say that in this size regime only the paired species exists.

Results

A Primitive Model. First we consider a primitive model for the electrolyte analogous to the bulk model of Bjerrum. Here the ion-ion interaction potential is (for simplicity we consider only symmetrical electrolytes)

$$\phi(r_{12}) = \begin{cases} -\frac{q^2}{\epsilon r_{12}} & r_{12} > a \\ +\infty & r_{12} < a \end{cases} \quad (7)$$

q is the absolute charge on the ion and a is the DH parameter representing the distance of closest approach¹⁰ (this varies from

(8) In the Bjerrum theory³ for bulk electrolyte solutions, $p(r_{12}) \sim r_{12}^{-2} \exp(-\beta\phi(r_{12}))$. For large r_{12} , $\phi(r_{12}) \rightarrow 0$ as it should, and the probability p diverges. Bjerrum resolved the problem by considering only $a < r_{12} < R$, but this indicates the theory is incorrect as was argued by Fuoss.⁹

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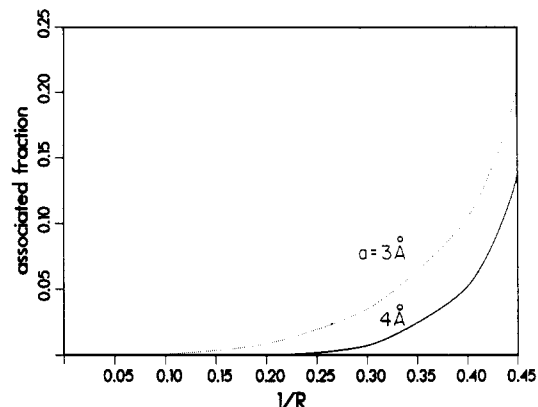


Figure 2. Associated fraction as a function of the inverse radius (in units of $q^2/\epsilon k_B T$) for two values of parameter a .

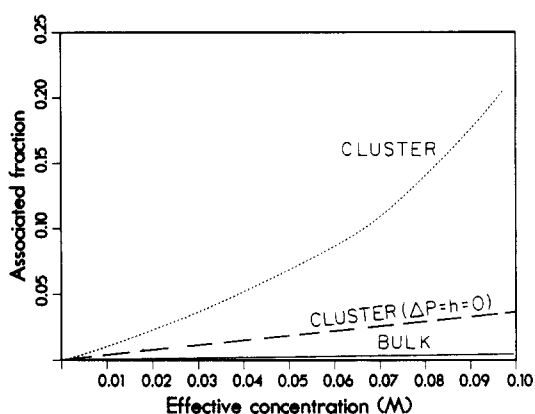


Figure 3. Comparison of the associated fraction in a cluster (dotted line) and in the bulk (full line) as a function of the molar concentration, for $a = 3 \text{ \AA}$ and $\epsilon k_B T = 2 \text{ eV}$ (e.g., $\epsilon = 80$, $T = 290 \text{ K}$). The dashed line displays the results for a cluster, taking into account only entropic (finite volume) effects (see text).

the ionic radii for large ions to the radii of the solvated ion for small ions).

In this model association, in the sense defined above, is possible only if $a < r_B(R)$. The form of $p(r_{12})$ is independent of a (which enters only as the cutoff distance and in the normalization constant) and so are the minimum at r_B and the maximum of $p(r_{12})$ at r_M . Figure 1 displays the positions, r_B and r_M , of the minimum and maximum as functions of the radius, R . The critical radius, R_c , is determined by $r_B(R_c) = r_M(R_c)$. For this model we get $R_c = 0.46(q^2/\epsilon k_B T)$ (for water at room temperature this yields $R_c \approx 15 \text{ \AA}$, corresponding to ca. 1700 water molecules in the cluster). Figure 1 also shows that $r_B(R)$ increases as the cluster size decreases, so electrolytes which Bjerrum theory predicts to be non-associating in the bulk ($a > r_B(\infty)$) will associate (in the sense discussed) in a sufficiently small cluster and will be fully associated below the critical size. This is shown in Figure 2, which displays the fraction of associated ions as a function of cluster size.

A comparison of the association probabilities in spherical clusters and in bulk solutions, when they have the same volume per ion, is shown in Figure 3 as a function of the stoichiometric salt concentration, C . We see that in the cluster environment association increases far more rapidly than in the bulk. This results from two factors: (i) the loss of solvation entropy through confinement to the cluster volume; (ii) the reduced screening in the cluster which increases the interionic attraction and reduces the solvation enthalpy.

It is interesting to consider the relative importance of these two effects. This can be done by considering only the entropic effect, i.e., setting $\Delta P = 0$ and $h(r_i) = 0$ in eq 2. This amounts to using,

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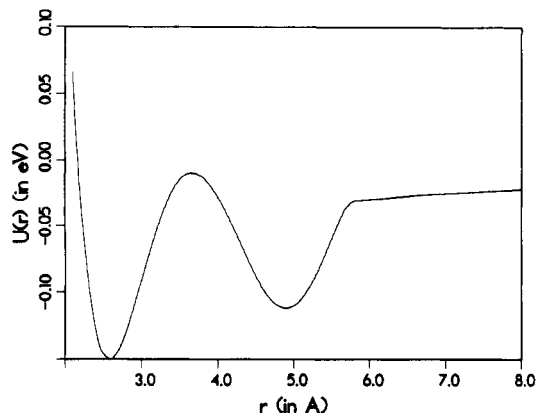


Figure 4. Hybrid potential for NaCl from the MD calculations of Berkowitz et al.⁹ extended with a Coulombic potential.

in the cluster calculation, the same electrostatic interactions as in the bulk, so the cluster size dependence results only from the finite available volume. It is seen from Figure 3 that for large clusters the entropic effect dominates, accounting for ca. 90% of the association at $C = 0.001$ M ($R \approx 72$ Å for water at room temperature). As the cluster size decreases, the loss of screening becomes more important so when $C = 0.1$ M ($R \approx 24$ Å for water), entropic effects alone account for only ca. 15% of the association.

It should be emphasized again that while the qualitative observations made here are expected to be valid, the model is too simplified to account for these features in any quantitative way. In particular the dielectric continuum approximation is not truly valid, and the assumption of a constant spherical shape of the cluster does not generally hold. For example, it is possible that surface localization of one or both ions will be dominant for small clusters. While detailed predictions can only be made within a microscopic model, we may partially compensate for the error introduced by the dielectric continuum approximation by considering a more accurate potential of mean force between the solvated ions.

NaCl in (TIP2S) Water with Dielectric Corrections. We now consider a more detailed model for the specific case of NaCl. The value of the DH parameter for NaCl is $a = 4$ Å,¹⁰ which is greater than $r_B(\infty)$ of water at room temperature (3.6 Å). Therefore NaCl in bulk water does not associate in the Bjerrum model. Experimentally the association constant of reaction 1 was reported in 1962 to be too small to be measured,¹¹ i.e. $K \leq 10^{-1}$, in accordance with the Bjerrum model.

Berkowitz et al.¹² have calculated the potential of mean force between a sodium chloride ion pair in TIP2S water at room temperature. By making a least-squares fit to their published results, and continuing them analytically with a Coulomb potential, we obtain our input potential $\phi(r_{12})$, shown in Figure 4. Note that this potential has two minima corresponding to the contact ion pair (CIP) and the solvent-separated ion pair (SSIP). This potential allows us to include in a simple manner short-range forces and an element of molecular structure. To do so we assume that the potential of mean force obtained from an MD simulation can replace $\phi(r_{12})$ in eq 2 while the finite size correction terms remain the dielectric theory expressions of eq 3. Under this assumption we repeat the calculation as before. This calculation now yields the fraction of ion pairs in each state of association (CIP and SSIP). Results of this calculation are shown in Figure 5. Comparing Figure 5a with Figure 2 for the case of $a = 4$ Å, we observe that at the critical radius of the primitive model (15 Å) two-thirds of the NaCl ion pairs are associated. Full association occurs at the smaller radius of 5 Å. The relative weight of the CIP and SSIP is equal at large clusters with the CIP gaining from $R = 15$ Å downward. At $R \approx 3$ Å (corresponding to ca. 12 water

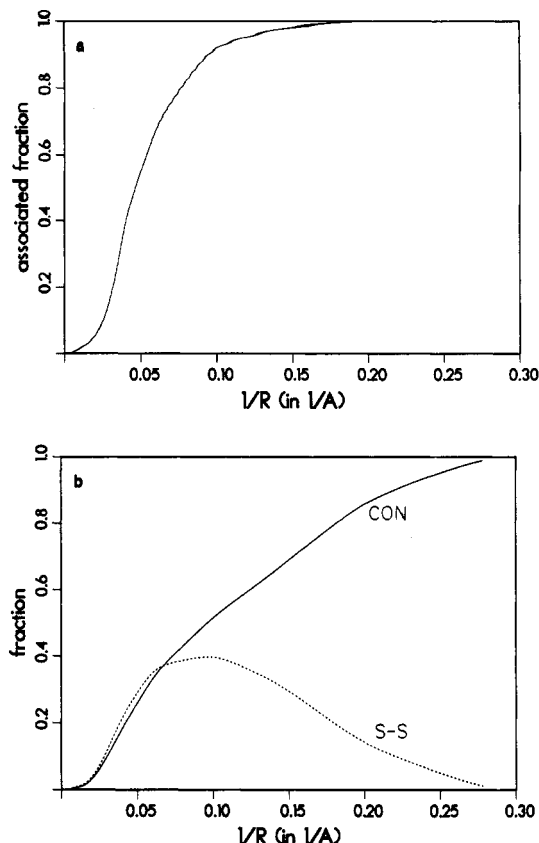


Figure 5. (a) Fraction of NaCl ion pairs as a function of the inverse radius of a water cluster at room temperature. (b) Fraction of NaCl ion pairs in the contact state (CON) and in the solvent-separated state (S-S).

molecules) all the ion pairs are in the CIP state.

Discussion and Conclusions

In this paper we have considered cluster size effects on ion association, within an extended Bjerrum model. Simple considerations lead to the conclusion that association in the Bjerrum sense is complete below a certain critical cluster size, and dissociation begins above this size. It should be emphasized that while the qualitative observations made here are expected to be generally valid, the model is too simple to account for these features in any quantitative way. We have suggested a way to reduce the error introduced by the dielectric continuum approximation, replacing the Coulombic interaction by a potential of mean force calculated in bulk simulations. However, the assumption concerning the constant spherical shape of the cluster does not generally hold, and we have also not considered the possibility of surface localization, which may be dominant for small clusters. Another surface effect not completely accounted for in the present treatment is the larger dielectric response of surface molecules relative to the bulk, because of the smaller reorganization energy at the surface.¹³ Finally, when the cluster becomes very small, the charge distribution within the ion pair may change due to the reduced solvation and this will affect the Coulombic interactions within the pair. More accurate predictions might be possible by detailed microscopic calculations.

In conclusion we have formulated a simple model for ionic association in clusters. We have shown that in this model association increases rapidly as the cluster size decrease (more rapidly than would be predicted on the basis of available volume only) and that there exists a certain critical size below which all electrolytes will be fully paired. More detailed calculations for a model of NaCl in water are in qualitative agreement with these results, and show that the primitive model overestimates the critical size considerably, owing to the neglect of short-range forces and the discrete nature of the solvent molecules.

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