

Where do ions solvate?

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Abstract. We study a simple model of ionic solvation inside a water cluster. The cluster is modeled as a spherical dielectric continuum. It is found that unpolarizable ions always prefer the bulk solvation. On the other hand, for polarizable ions, there exists a critical value of polarization above which surface solvation becomes energetically favorable *for large enough* water clusters.

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1. Introduction

It has been accepted for almost a century that there are no ions in the interfacial region separating water from air. A simple argument for this conclusion is based on the fact that the variation of the dielectric constant ϵ across the liquid–air interface is fast, going from $\epsilon \approx 80$ in the bulk water, to $\epsilon \approx 1$ in the bulk air. Therefore, an ion near an interface will see an image charge of the same sign as its own. The ion will then be repelled from the interface and driven towards the bulk [1–4]. From the Gibbs equation [5,6], the negative ionic adsorption, leads to an increase of the air–water interfacial tension as has, indeed, been observed in the experiments [7]. The story would have ended here, but for the fact that recent molecular dynamics (MD) simulations find that contrary to this simple theoretical picture, ions *are* present at the air–water interface [8–10]. In particular, the MD simulations show a propensity of large halogen anions to preferentially adsorb to the surface of small water clusters [11]. If this adsorption persists up to mesoscopic scales, aqueous salt aerosols can provide a source of reactive halogens and play an important part in the heterogeneous atmospheric chemistry.

2. Ionic solvation

In this contribution we will explore a simple model of ionic solvation. We shall model a cluster of water molecules as a sphere of radius R and dielectric constant

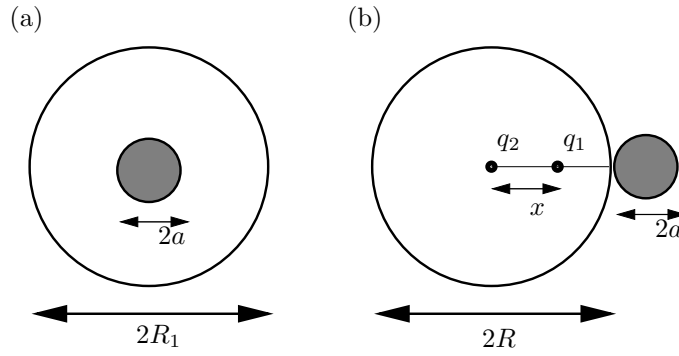


Figure 1. (a) Ion inside the water cluster. (b) Ion outside the water cluster. The dielectric constant inside the water cluster is $\epsilon = 80$, outside is $\epsilon_0 = 1$, and inside the ion $\epsilon_0 = 1$.

$\epsilon = 80$. An ion of charge q and polarizability α will then be idealized as a rigid sphere of radius a . The question that we would like to answer is what is the preferred location for the ionic solvation, the bulk of the water cluster or its surface? To see which one of these two possibilities is realized we compare the free energies of the two states: (1) the ion located at the center of the cluster and (2) the ion located at the surface of the water cluster, see figure 1.

We shall first consider the energy of an ion solvated at the center of the water cluster. The electrostatic potential can be easily determined from the solution of the Laplace equation. We find

$$\varphi(r) = \frac{q}{\epsilon_0 r} + \left(\frac{q}{a} - \frac{q}{R_1} \right) \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right) \quad \text{for } r < a, \quad (1)$$

$$\varphi(r) = \frac{q}{\epsilon r} - \frac{q}{R_1} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right) \quad \text{for } a \leq r \leq R_1, \quad (2)$$

$$\varphi(r) = \frac{q}{\epsilon_0 r} \quad \text{for } r > R_1, \quad (3)$$

where $R_1^3 = a^3 + R^3$.

The potential appearing in eq. (1) consists of two terms. First is the potential produced by the central ion, while the second term is the induced potential

$$\phi = q \left(\frac{1}{a} - \frac{1}{R_1} \right) \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right) \quad (4)$$

that the ion feels as a result of polarization of the water cluster (the dielectric). The energy of solvation can be obtained using the charging process

$$F = q \int_0^1 \phi(\lambda q) d\lambda. \quad (5)$$

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Substituting eq. (4) into eq. (5) and noting that $1/\epsilon$ is quite small, the energy of solvation of an ion inside a spherical water drop is

$$F_i = -\frac{q^2}{2\epsilon_0} \left(\frac{1}{a} - \frac{1}{R_1} \right). \quad (6)$$

In the limit $R \rightarrow \infty$, eq. (6) reduces to the classical Born solvation energy of an ion inside the bulk water [12]. Because of the spherical symmetry, the polarizability of the ion does not contribute to F_i .

We next consider the solvation energy for an ion on the surface of a water cluster, figure 1b. Since $\epsilon \gg \epsilon_0$, to leading order in $1/\epsilon$ we may approximate $\epsilon \approx \infty$. In this case the dielectric becomes a conductor and the electrostatic potential can be easily calculated by the method of images. There are two image charges: $q_1 = -Rq/(R+a)$ located at $x = R^2/(R+a)$; and $q_2 = Rq/(R+a)$ located at $x = 0$, see figure 1b. Using the charging process, eq. (5), the electrostatic energy of an ion due to water cluster (dielectric) polarization is

$$W_1 = -\frac{q^2}{2\epsilon_0} \left(\frac{R}{2Ra+a^2} - \frac{R}{(R+a)^2} \right). \quad (7)$$

Furthermore, the induced charges inside the dielectric produce an electric field E at the position of the ion,

$$\begin{aligned} E &= \frac{q_1}{\epsilon_0(R-x+a)^2} + \frac{q_2}{\epsilon_0(R+a)^2} \\ &= -\frac{Rq}{\epsilon_0(R+a)} \left[\frac{(R+a)^2}{(2Ra+a^2)^2} - \frac{1}{(R+a)^2} \right] \end{aligned} \quad (8)$$

which will polarize the ion, inducing a dipole moment $p = \alpha E$. The electrostatic energy due to ionic polarization can, once again, be obtained using the charging process [13]

$$W_2 = -\int_0^1 p(\lambda q)E(\lambda q) \frac{d\lambda}{\lambda} = -\frac{1}{2}\alpha E^2. \quad (9)$$

The total energy for an ion solvated at the surface of a water cluster is then $F_o = W_1 + W_2$. The ionic position is then determined by

$$\Delta F = F_i - F_o. \quad (10)$$

If $\Delta F < 0$ the ion will solvate in the interior of the water cluster. On the other hand, if $\Delta F > 0$ the surface solvation will be energetically favored. In figure 2 we have plotted the value of ΔF as a function of the water cluster size R for different values of the reduced ionic polarizability $\alpha^* = \alpha/a^3$. We find that for $\alpha^* > 8$ there exists a critical cluster size R_c , such that for $R > R_c$, $\Delta F > 0$ and the surface solvation becomes energetically favorable. In the limit $\alpha^* \rightarrow 8^+$, the critical cluster size diverges as

$$R_c \approx \frac{4a}{\alpha^* - 8}. \quad (11)$$

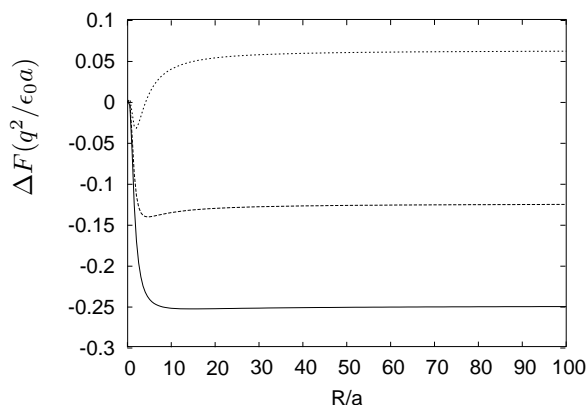


Figure 2. ΔF as a function of R/a for: $\alpha^* = 0$, the solid curve; $\alpha^* = 4$, the dashed curve; and $\alpha^* = 10$, the dotted curve. Note that in this case surface solvation becomes energetically favorable for $R/a > 4.5$.

3. Conclusions

We have studied a simple model of ionic solvation. A water cluster is modeled as a spherical dielectric continuum. It is found that unpolarizable ions always prefer the bulk solvation. On the other hand for polarizable ions there exists a critical value of polarization above which surface solvation becomes energetically favorable, *for large enough* water clusters. The critical polarization required to produce a surface solvation is quite large, $\alpha_c^* = 8$. This means that for ions of $a \approx 1 \text{ \AA}$, the polarization must be at least 8 \AA^3 , before the surface solvation can occur. This value is higher than the characteristic polarizabilities of real ions. We note, however, that our model does not take into account a number of important effects. It overestimates the modulus of the bulk solvation energy by not taking into account the fact that bulk solvation disturbs the hydrogen bond network. Furthermore, the theory presented above was constructed only for one isolated ion. In practice, a water cluster will contain many ions. Since a cation, such as Na^+ , is only weakly polarizable, it will prefer the bulk solvation. The conservation of water molecules, therefore, suggest that presence of non-polarizable cations will lead to further expulsion of polarizable anions towards the interface. We shall address both these effects in the future work.

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