COMMENTS

Comments on the "Osmotic Coefficients and Surface Tensions of Aqueous Electrolyte Solutions: Role of the Dispersion Forces"

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In the past decade or so, a series of papers have been published suggesting that the van der Waals interactions acting on ions near an interface can explain a plethora of phenomena, such as the ion specificity (the Hofmeister series),[1] the failure of the DLVO theory in biological systems[2] or the surface tension of electrolytes.[3] More recently, the same idea was extended to the ion specificity in bulk solutions.[4]

However, the dispersion interactions (between ions and the whole system) generate repulsive forces between the water/air interface and the highly polarizable ions (Cl⁻, Br⁻, I⁻) and attractive forces between the interface and the less polarizable ions (Na⁺, Li⁺, K⁺).[3] Some recent experimental results[5] also challenged the traditional Langmuir picture of a surface layer depleted of ions; they revealed, however, the opposite, namely that the more polarizable anions are positively adsorbed on the interface.[5] The conclusion of Hu et al.[5] was supported by the numerical simulations of Jungwirth and Tobias,[6] which demonstrated that the polarizability of halogen anions (Cl⁻, Br⁻, I⁻) is directly related to their propensity for the surface. The less-polarizable ions (Na⁺ and F⁻), however, preferred the bulk water.[6] These results are opposite to the predictions of the ion dispersion theories.[3]

The failure of the ion dispersion forces to predict even the qualitative behavior of ions near an interface is probably due to the existence of other short-ranged forces that dominate the interactions in the vicinity of the interface. We suggested that such a role might be played by the interactions of the ions with their neighboring water molecules.[7] The approach to the water/air interface is unfavorable for the structure-making ions, because they have to lose a part of their hydration shell; however, it is favorable for the structure-breaking ions because the bulk water can organize better in their absence.[7] A simple model based on short range ion-hydration forces explained fairly accurately the experiments on surface tension (namely, its increase for salt solutions but decrease for acidic solutions with increasing electrolyte concentration, its pH dependence, and the Jones-Ray effect).[7] Kunz et al. reached a similar conclusion,[4] namely, that the difficulties of the previous treatments based on ion dispersion forces were due to the fact that the incomplete hydration was not taken into account.[4]

The focus of the present Comment is on ion−ion dispersion forces, which in the opinion of Kunz et al.[4] are important in bulk electrolyte solutions. One of the questions raised by them

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is why these forces have been neglected in previous theories. They answered by suggesting that the general belief is that the Coulomb interactions dominate the van der Waals ones, and hence the latter can be neglected. Kunz et al.[4] also noted that the van der Waals interactions might be negligible at low ionic strength ($c_E < 0.02$ M), but not at high ionic strength ($c_E \sim 1$ M), for which the Coulomb interactions are screened. As a simple calculation shows, at large separations the van der Waals interactions, though larger than the screened Coulomb interactions, are much smaller than kT, and hence negligible.

To understand why the ion−ion dispersion interactions have been ignored by most theories of electrolytes, let us perform some simple calculations. The London theory provides for the ion−ion dispersion interactions:[8,9]

$$U_L(r) \cong -\frac{3}{4}\frac{h}{2\pi}\omega_0 \left(\frac{r_0}{r}\right)^6 \equiv -\frac{C_{AB}}{r^6} \qquad (1)$$

where r is the distance between the centers of two ions, h is the Planck constant, and C_{AB} is a constant dependent on ω_0 and r_0, which are given by

$$\omega_0 = \frac{4}{\pi \alpha_A^0 \alpha_B^0} \int_0^\infty \alpha_A(i\xi)\,\alpha_B(i\xi)\,d\xi \qquad (2a)$$

and

$$r_0 = \left(\frac{\alpha_A^0 \alpha_B^0}{(4\pi\epsilon_0^2)}\right)^{\frac{1}{6}} \qquad (2b)$$

where α_A is the polarizability of atom "A", α_A^0 is its zero frequency polarizability, and ϵ_0 is the vacuum permittivity. Typical values for r_0 and ω_0 are 2 Å and 10^{16} rad/s, respectively,[9] which provide a typical value of about $C_{AB} \approx 12\,000\ kT$ Å⁶.

The screened Coulomb force is given by

$$U_C(r) \cong \frac{1}{4\pi\epsilon\epsilon_0}\frac{e^2}{r}\exp\left(-\frac{r}{\lambda}\right) \qquad (3)$$

where e is the protonic charge, ϵ is the dielectric constant in water, and λ is the Debye length. The van der Waals interactions (eq 1) dominate the screened Coulomb interactions (eq 3) at both very small and very large separations. In the latter case, for a concentration of 1 M of a uni-univalent electrolyte, $\lambda \cong 3$ Å, and by employing $\epsilon = 80$, one finds that the ion−ion dispersion forces dominate the interactions only for distances larger than about 30 Å (see the inset in Figure 1). However, both interactions are negligible at those separations, being of the order of $10^{-5}\ kT$. Because the typical value provided in ref 9, $C_{AB} \approx 12\,000\ kT$ Å⁶, is rather large, it is likely that most ion−ion dispersion forces are in general negligible at large separations.

The dispersion forces play an important role only for separations less than about 5 Å. The problem is that in this region, they seem to play an enormous role (curve 1 in Figure 1). A hard-sphere repulsion (Born interaction) is typically
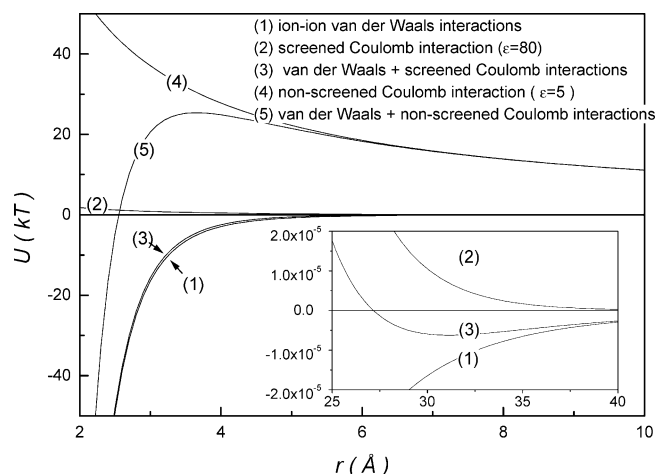
Figure 1. Ion−ion dispersion forces (curve 1) dominate the screened Coulomb interactions (curve 2, $\epsilon = 80$, $\lambda = 3$ Å) for separations smaller than about 7 Å and larger than about 30 Å (see the inset). However, the nonscreened Coulomb interactions (curve 4, $\epsilon = 5$, $\lambda = \infty$) are much larger than the ion−ion dispersion forces (1) for distances larger than about *3.5* Å.
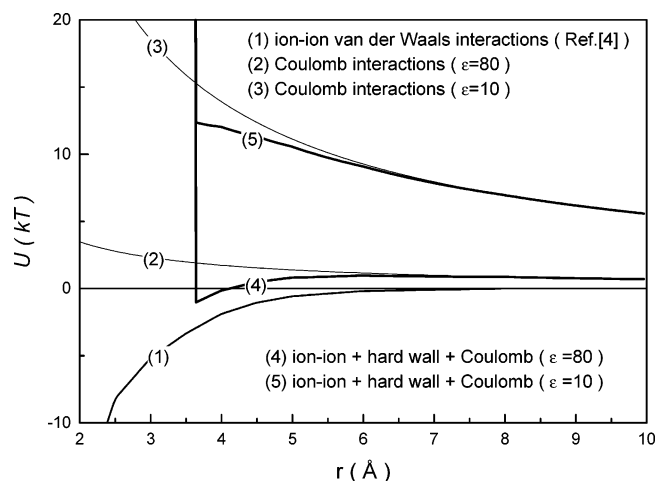

Figure 2. Ion−ion dispersion interactions (curve 1) calculated using the Lifshitz approach in ref 4 dominate at small separations the water-screened Coulomb interactions (curve 2, $\epsilon = 80$, $\lambda = \infty$); however, they are negligible compared to the nonscreened Coulomb interactions ($\epsilon = 10$, $\lambda = \infty$) (curve 3), in the presence of a hard wall repulsion at $r = 3.6$ Å.

considered to be responsible for preventing the ion−ion collapse due to their (divergently large) van der Waals attractions. If the hard sphere repulsion would start at $r_{HS} = 2$ Å, the depth of the energy minimum would be about 200 kT, and all the ions would cluster, regardless of their charge. On the other hand, if the hard sphere repulsion would start at $r_{HS} = 5$ Å, the depth of the energy minimum would be less that 1 kT and the effect of ion−ion dispersion would be much less noticeable. The effect of the ion−ion interactions (from huge to negligible) is strongly dependent on the position selected for the hard sphere repulsion. Kirkwood considered long ago[10] that a square well with a depth of the order of about 1 kT and with the width of about $(1/4)r_0$ can represent the van der Waals interactions between molecules. This choice probably influenced the conclusion that the ion−ion dispersion is not important in electrolytes, drawn by Kirkwood in his theory of strong electrolytes.[11] Later, Kirkwood and Poirier indicated a manner to include the short-ranged interactions (hard core repulsions and van der Waals attractions) and the long-ranged interactions (Coulomb force) into a unitary theory of strong electrolytes.[12] They ignored, however, the van der Waals interactions at large separations, probably for the reasons outlined above.

One might argue that the London theory for van der Waals interactions is inaccurate and the dispersion forces should be calculated using the Lifshitz approach (a macroscopic continuum theory) extrapolated to the limit of atomic distances.[1,4] Though such a theory would not predict a divergence at $r \to 0$,[4] the attractive minimum suggested by Figure 2 of ref 4 would be probably much larger than 20 kT. Even for the ion−ion dispersions potential plotted in Figure 2 of ref 4, (reproduced here for convenience in Figure 2, curve 1), the location of the hard-sphere potential strongly affects the result. Na$^+$ has a relatively low polarizability, and because $r_{HS} = 4.10$ Å, it seems that the ion−ion dispersions are not important for the Na$^+$−Na$^+$ interactions.[4] For NO$_3^-$−NO$_3^-$, $r_{HS} = 3.6$ Å, and the depth of about 2 kT of the attractive minimum generates a significant clustering of these ions.[4] In fact, the probability of the formation of NO$_3^-$−NO$_3^-$ pairs is even larger that the probability of the formation of Na$^+$−NO$_3^-$ pairs (see Figure 3 of ref 4), a surprising result. Whether the hard sphere repulsion would start at $r_{HS} \cong 2$ Å instead of $r_{HS} \cong 3.6$ Å (the r_{HS} were adjusted in ref 4 to fit the osmotic coefficients data), an attractive minimum

of over 10 kT would predict a considerable clustering of ions of the same kind. This effect (if real) would be certainly impressive.

There is, however, a more important issue. At separations of a few Ångstroms, the Coulomb interactions are hardly screened either by other ions or by the water molecules. The large dielectric constant of bulk water is due to the ability of the water molecules to reorient their permanent dipole in an electric field. However, the molecules near ions are already oriented by the strong electric fields generated by ions; therefore the local dielectric constant of water (in the vicinity of the ions) is decreased. Using a lower value $\epsilon = 5$ for the dielectric constant in the vicinity of ions, one finds only repulsive interactions between ions of the same type (curve 5 in Figure 1) for distances r larger than about 3.5 Å. Though at shorter distances divergently large attractions can be found, even in the absence of a hard-wall repulsion it is unlikely for the ions to be able to escalate a repulsive potential barrier larger than 20 kT to collapse on the attractive minimum (for $\epsilon = 1$, the repulsive barrier would exceed 150 kT). For the ion−ion dispersion forces calculated via the Lifshitz approach,[4] employing a dielectric constant $\epsilon \cong 10$ for separations distances of a few Ångstroms (curve 5 in Figure 2) instead of the bulk value $\epsilon = 78.2$ in the Coulomb interactions (curve 2 in Figure 2) would completely remove the attractive well induced by the ion−ion dispersion forces, the latter being much less important than the change in the local dielectric constant.

In conclusion, we suggest that the ion dispersion forces were ignored by most (but by no means all) electrolyte theories mainly because they are important only for separations between ions smaller than about *5* Å, and the interactions at these distances are not well-known. It is hard to believe that at these distances the interactions can be accurately described by a sum between a hard-wall repulsion, a Coulomb interaction, and a London attraction. Even if the latter would be true, a correction in the local dielectric constant (because of incomplete screening by water molecules) would render again the van der Waals interactions negligible, up to distances of the order of ion diameters.

It is true that, by adjusting the parameters of such interactions, a plethora of interesting phenomena can be predicted, such as the collapse of all the ions of the same kind of an electrolyte. We completely agree with Kunz et al.[4] that the short-range

interactions between ions are important for the behavior of the system; this was also emphasized in the work of Jungwirth and Tobias.[6] In fact, the latter work showed that the local interactions between ions and neighboring water molecules are so important, that they control the behavior of ions near interfaces. Whereas the highly polarizable ions are drawn toward the interface in their discrete, microscopic treatment,[6,7] a macroscopic, continuum van der Waals approach would predict exactly the opposite.[3]

Whether or not two ions of the same kind have an attractive minimum, possibly of many kT, when they are located at a few Ångstroms apart in water it is quite an interesting issue. But this issue has probably to be resolved by ab initio microscopic theories that include all the interactions (Coulomb, dispersion, hydrogen bonding, etc.) of a representative system. Today's computational capability (for up to about 20 water molecules) might be sufficient for such ab initio calculations.

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