Polarizable ions at interfaces

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(Dated: April 9, 2009)

A non-perturbative theory is presented which allows to calculate the solvation free energy of polarizable ions near a water-vapor and water-oil interfaces. The theory predicts that larger halogen anions are adsorbed at the interface, while the alkali metal cations are repelled from it. The density profiles calculated theoretically are similar to the ones obtained using the molecular dynamics simulations with polarizable force fields.

PACS numbers: 61.20.Qg, 82.45.Gj, 05.20.-y

There are a number of long standing mysteries in the fields of physical chemistry and biophysics. The Hofmeister effect [1], which has now been known for over 120 years is, perhaps, one of the oldest and most puzzling ones. Hofmeister observed that different ions have very different effect on stability of protein solutions. While some electrolytes are very efficient at salting-out proteins, others lead to protein precipitation only at much larger concentrations. A related mystery, which is also very old, has to do with the surface tensions. Some hundred years ago Heydweiller [2] noted that adding a strong electrolyte to water leads to increase in the surface tension of the water-air interface. While the dependence on the type of cation is weak, there is a strong variation of the excess surface tension with the type of anion — the lighter halides lead to larger excess surface tension than the heavier ones. The sequence is precisely the reverse of the Hofmeister one. Both effects are completely unaccounted for by the current theories of electrolytes, which go back to the pioneering work of Debye and Hückel (DH) [3, 4].

Application of the DH theory to the study of interfacial properties of electrolyte solutions was initiated by Wagner [5] and continued by Onsager and Samaras (OS) [6]. These approaches were based on the observation that the image charge induced at the air-water interface repels ions from the surface, creating a depletion layer. The Gibbs adsorption isotherm then leads to the conclusion that the surface tension of aqueous electrolytes must be higher than that of pure water. Unfortunately, there is no way to account for ionic specificity within these theories. Since the hydrated size of all halide ions is nearly the same — and this is the only parameter that enters into DH theory — the OS approach predicts that the surface excess should be independent of the type of ion. Recently there have been proposed some other approaches, but none have proven completely satisfactory [7].

Some clues to the failure of the DH and the OS theories started to appeared in the 1990s when the photoelectron emission experiments [8] and molecular dynamics simulations with polarizable force fields showed that contrary to the common wisdom, there were ions present at the air-water interface [9, 10]. The simulations found that while hard alkali metal ions such as Potassium and Sodium and small halides such as Fluoride [11] are repelled from the interface, the softer more polarizable anions such as Bromide and Iodine are actually attracted to it [12]. Presence of highly reactive halogens at the air-water interface of aerosol particles might help to explain the excessive rate of ozone depletion [13].

In this paper a new class of electrolyte models will be introduced. Unlike the previous approaches, the polarizability of ions will be explicitly taken into account. The new theory is intrinsically non-perturbative — all the moments of the ionic charge distribution, and not just the dipole, are taken into account. The calculated solvation free energies are used to obtain the interaction potential of polarizable ions with an interface and to calculate the anion and cation density profiles.

Since the pioneering work of Debye and Hückel, ions have been modeled as hard spheres with a point charge located at the center [4]. While perfectly reasonable for describing bulk properties of electrolytes, this approach is bound to fail when applied to polarizable ions near a dielectric interface. The reason for this is easily understood by considering the simplest model of a perfectly polarizable ion idealized as a conducting spherical shell with a mobile surface charge. When such an ion moves across a dielectric air (oil)-water interface, the charge on its surface shifts progressively from the exposed air/oil portion to the part that still remains hydrated. For perfectly polarizable ions, energy cost of charge localization is very low and is easily compensated by the decrease in the cavitation energy [14] as the ion moves across the interface.

To make the discussion quantitative, consider a polarizable ion — modeled as a conducting sphere of radius $a$ and charge $q$, see Fig. 1 — at an air (oil)-water interface. Both half-spaces will be treated as dielectric continuums with permittivities $\varepsilon_w$ and $\varepsilon_o$ for water and air (oil), respectively. To gain insight into the problem we first consider an ion with one of its hemispheres submerged in water and the other exposed to air, $h = a$, Fig. 1. This problem can be solved exactly, yielding a purely radial
analytically. Exact solution is possible, however, when the normal component of the electric field vanishes. In this limit the electric field lines originating on the interface will be tangential to the interface, so that the normal component of the electric field vanished. Even this problem, however, is difficult to solve analytically. Exact solution is possible, however, when $h/a \ll 1$. In this limit all charge is confined to a small spherical cap located inside water. The curvature effects can be neglected, and the problem reduces to finding the solution of a mixed boundary value problem in cylindrical coordinates: $\nabla^2 \phi(z, \rho) = 0$, $\phi'(0, \rho) = 0$ for $\rho > \rho_m$, and $\phi(0, \rho) = V$ for $\rho \leq \rho_m$, where prime refers to the derivative with respect to $z$. $V$ is the electrostatic potential of the spherical cap, and $\rho_m$ is its radius, see Fig. 1. Mixed boundary value problems are notoriously difficult to study. Fortunately, this particular one can be solved analytically using the Hankel transform techniques [15]. We find

$$\phi(z, \rho) = \frac{2V}{\pi} \int_0^\infty dk \frac{\sin(k\rho_m)}{k} J_0(k\rho) e^{-kz}. \quad (4)$$

The capacitance of the spherical cap can now be calculated to be $C_c = \rho_m/\pi$. We note that this is just half the value of the capacitance of a disk of radius $\rho_m$ in vacuum. This result can be understood by considering a charged disk in front of a dielectric medium of very low permittivity. The image charge induced on the interface will then be of the same sign as on the disk, and in the limit $\epsilon_o \ll \epsilon_w$ it will also be the same in magnitude. Thus, one needs only half the charge of the disk in vacuum to have the same potential.

In view of the natural symmetry of the problem it is convenient to express $C_c$ in terms of the angle variable $\theta$, so that $C_c = a\theta/\pi$ and $f(0, h/a) = \theta/\pi$. Writing the capacitance in terms of $\theta$ extend the range of validity of $C_c$ outside the limit of completely flat disc to larger spherical caps. In particular, for a particle located half way across the interface, $h = a$, $\theta = \pi/2$, we find $f(0, 1) = 1/2$, which agrees precisely with the exact result of Eq. (1). Furthermore, comparing Eqs. (2) and (3) with Eq. (1), we see that $f_1(1) = 1/2$. We are now in position to write an approximate expression for the self energy of a perfectly polarizable ion moving across a dielectric interface,

$$U_s(h) = \frac{q^2}{2\epsilon_w C_c} \int_0^\infty \frac{d\theta}{\theta} \frac{\sin(\theta h/a)}{\theta} + \frac{\epsilon_o}{\epsilon_w}.$$

where $\theta(h) = \text{Re}[\arccos(1 - h/a)]$. The real part of $\arccos(x)$ is used in order to continue its validity into the regions $h > 2a$, where $\theta(h) = \pi$. For $h > 2a$ the electrostatic self energy reduces to $U_s \approx q^2/2\epsilon_w a$, which is the usual Born self energy of a bulk ion. In writing Eq. (5), we have approximated the scaling function $f_1(x)$ by a constant, $f_1(x) = 1/2$. This is permissible, since when the ratio $\epsilon_o/\epsilon_w \ll 1$, the prefactor of $f_1$ is very small and the precise value of $f_1(x)$ is not important — it is completely dominated by the first term of Eq. (3). We should note, however, that although Eq. (5) is very accurate for $\pi \epsilon_o/(2\epsilon_w) < \theta < 3\pi/4$, and for $h/a \gg 1$, it does not describe perfectly the crossover from the interface to the bulk regime. The reason for this is that Eq. (5) does not fully account for the image contribution to the electrostatic energy at distances $h > a$. It is possible to include this correction into the theory at the expense of more complicated expressions. In practice, however, we note
that the image contribution is screened very strongly \[6\], with the characteristic length equal to half the Debye length \(\xi_D\), \(U_{im}(z) \approx q^2 \exp(-2z/\xi_D)/(4\epsilon \nu \omega z)\). Therefore, for concentrations of electrolyte above physiological ones 150mM, the image contribution decays to zero after only a few Angstroms. For now, we shall, therefore, ignore the image effect in the crossover region.

It is important to stress the fundamental difference between Eq. (5) and a similar expression for non-polar hard ions. If a hard ion is located half way across the interface, it will have half of its charge exposed to the low dielectric environment. The electrostatic self energy cost for this is approximately \(\sim q^2/(\epsilon \nu a)\). This is almost two orders of magnitude larger than the energy cost for a polarizable ion to be at the same position! This is the reason why non-polarizable ions will not be found at the interface.

The force that drives ions towards the interface arises from the cavitation energy. Presence of ions disturbs the hydrogen bond network of water and costs energy. We can estimate this energy cost by considering a cavity which must be formed in water to accommodate an ion. For small cavities of radius \(a < 4\ \text{Å}\), which do not significantly perturb the hydrogen bonds, the energy cost scales with the volume of the void, while for larger cavities the energy cost scales with the cavity surface area \[10\]. This is, the so called, hydrophobic crossover from small to large length scales \[17\]. Small alkali metal and halogen ions are in the volumetric scaling regime. If one part of an ion leaves the aqueous environment, the cavitational energy will decrease proportionately to the volume exposed. This results in a short range cavitation potential which forces ions to move into the air (oil) phase,

\[
U_{cav}(h) = \begin{cases} 
\nu a^3 & \text{for } h \geq 2a \\
\frac{1}{4} \epsilon \nu a^3 \left(\frac{h}{a}\right)^2 \left(3 - \frac{h}{a}\right) & \text{for } 0 < h < 2a
\end{cases}
\]

From the results of bulk simulations \[13\], we calculate that \(\nu \approx 0.3k_B T/\text{Å}^3\). To account for the fact that a cavity containing an ion should be somewhat larger than the ionic crystallographic size, we will use \(\nu \approx 0.5k_B T/\text{Å}^3\). This corresponds to the cavity radius about 20% larger than the crystallographic radius.

For small non-polarizable ions, the cavitational energy is not sufficient to force ions into the low dielectric environment — the electrostatic energy cost is way too large. On the other hand, for soft polarizable ions, the electrostatic self energy cost is very small, since the ionic charge distribution can easily deform to remain mostly within the hydrated portion of the ion. The significant gain in the cavitational energy, and the low cost in electrostatic self energy, makes it energetically favorable for polarizable ions to move into the interfacial region. The amphiphilic nature of large ions, such as hexafluorophosphate \(PF_6^-\), has been known for a long time. The cavitational energy for these ions is so large, that they actually adsorb to the interface, lowering its surface tension \[18\]. What has been discovered recently is that smaller polarizable ions apparently can also have some amphiphilic activity — although not sufficiently large to lower the interfacial tension \[8,12\].

So far we have considered only perfectly polarizable ions. Real ions, however, have finite polarizability. It is not obvious how the effects of finite polarizability can be included in the the formalism developed above. In fact it is not even clear, if the concept of bulk polarizability, as a linear response to the external field, is relevant in the interfacial geometry, where a rapid variation of the dielectric constant makes all the moments of the charge distribution — not just the dipole — relevant. For perfectly polarizable ions we have avoided this difficulty by solving the full electrostatics problem for a conducting sphere. For ions of finite polarizability, to have a complete quantitative picture it might be necessary to go to full ab initio calculations. In the absence of such, we can still gain some insight into this difficult problem by considering a simple model. In the spirit of Landau, we will construct the polarization energy \(U_p\) by exploiting the symmetries of the problem.

Consider an ion of radius \(a\) and bulk polarizability \(\gamma\). We will define the relative polarizability of this ion as \(\alpha \equiv \gamma/\gamma_0\), where \(\gamma_0 = a^3\) is the polarizability of an ideal ion of the same radius, modeled as a conducting sphere. For non-ideal ions with \(0 \leq \alpha < 1\), the surface charge can not fully adjust to the external electric field. Therefore, for such ions, there is an additional non-electrostatic — quantum mechanical — energy cost for dislocating ionic charge from its position of equilibrium. Suppose that for a given ion the fraction of its total charge inside water is \(x\), then the charge exposed to air (oil) will be \((1-x)q\). For ions which are highly polarizable \(x \approx 1\), as long as \(\theta\) is not too small . There is, however, a polarization energy cost for shifting a fraction of the ionic charge (assumed to be originally uniformly distributed along the surface of the ion) from its equilibrium position in the air portion of the ion to the water part. Within our simple dielectric model \(U_p\) must be invariant under the transformation \(q \rightarrow -q\). It must also be invariant under the transformation \(\theta \rightarrow \pi - \theta\), when \(\epsilon_o \leftrightarrow \epsilon_w\), and \(x \rightarrow 1-x\). To respect these symmetries, the polarization energy must be an even function of the difference between the initial (before exposure) and the final (after exposure) amount of charge on the part of the ion exposed to air/oil. Taking all these considerations into account and recalling Eq. (5) for a perfectly conducting sphere, we arrive at the polarization energy for a non-ideal ion,

\[
\beta U_p(h; x) = \frac{\lambda_B}{2a} \left[ \frac{\pi x^2}{\theta} + \frac{\pi(1-x)^2}{\epsilon_w} \right] \\
+ g \left[ x - \frac{1 - \cos(\theta)}{2} \right] \] \tag{6}

where \(\beta = 1/k_BT\) and \(\lambda_B = q^2/\epsilon_w k_BT\) is the Bjerrum
length in water. The terms in the first square brackets of Eq. \( \Box \) are the electrostatic self energy costs of the parts of the ion exposed to the water and the air, respectively. The second brackets contain the energy cost arising from the induced inhomogeneity in the ionic surface charge distribution. The coupling constant \( g \) must be a function of the relative polarizability, \( g(\alpha) \). In the limit \( \alpha \rightarrow 1 \), ion becomes perfectly polarizable, so that \( g \rightarrow 0 \); while in the limit \( \alpha \rightarrow 0 \), ion becomes completely hard and \( g \rightarrow \infty \). To account for these, we will write \( g(\alpha) = \chi(1 - \alpha)/\alpha \), where \( \chi \) is a pure number. The precise value of \( \chi \) can only be obtained from the ab initio calculations. For now we will take it to be of order unity, \( \chi \approx 1 \). Minimizing Eq. \( \Box \) with respect to \( x \) gives the fraction of the total charge located on the hydrated part of the ion, \( x_{\text{min}}(h) \). Substituting this back into Eq. \( \Box \), yields the polarization potential that an ion feels as it moves across the interface \( U_p(h) = U_p(h; x_{\text{min}}(h)) \). For an ideal ion of \( \alpha = 1 \) located half way across the interface \( h = a \), the energy \( U_p(a) \) reduces precisely to the expression given by Eq. \( \Box \). Therefore, for this case, the formalism developed above gives the exact result. The total solvation potential felt by an ion of relative polarizability \( \alpha \) is \( U_{\text{sol}}(h; \alpha) = U_{\text{sol}}(h) + U_p(h) \). Using this potential, we can calculate the ionic density profiles inside a small water droplet of radius \( R \) by explicitly solving a modified Poisson-Boltzmann equation,

\[
\nabla^2 \phi(r) = \frac{qN}{\epsilon_w} \left( e^{\beta \phi(r) - \beta U_{\text{sol}}(h; \alpha_w)} - \frac{e^{-\beta \phi(r) - \beta U_{\text{sol}}(h; \alpha_w)}}{\int_0^R r^2 dr e^{\beta \phi(r) - \beta U_{\text{sol}}(h; \alpha_w)}} \right),
\]

where \( r \) is the distance measured from the center of the water droplet, \( h = R - r \), and \( \alpha_w \) and \( \alpha_a \) are the relative polarizabilities of cations and anions, respectively. The density profiles for electrolyte solutions of \( K^+ \), \( KBr \), and \( KCl \) are presented in Fig. 2. The polarizabilities of ions \( \gamma_K = 0.79\text{Å}^3 \), \( \gamma_I = 7.44\text{Å}^3 \), \( \gamma_{Br} = 5.07\text{Å}^3 \), \( \gamma_{Cl} = 3.77\text{Å}^3 \), where take from Ref. \( \Box \) and the ionic sizes \( a_K = 1.49\text{Å} \), \( a_I = 2.05\text{Å} \), \( a_{Br} = 1.8\text{Å} \), \( a_{Cl} = 1.64\text{Å} \), from Ref. \( \Box \). In agreement with the polarizable force field simulations, the theory predicts that Iodine is strongly adsorbed at the air-water interface. We also find that there is a significant concentration of Bromide, while Chloride, Potassium and Fluoride (not shown) are depleted from the interfacial region. The current theory, however, predicts that there is less halide ion adsorption than is found in the simulations. The difference might due to the overestimate of the net water-vapor surface potential predicted by the polarizable force field simulations to be \(-500\text{mV} \approx -20k_BT/q \). Such a huge junction potential will irreversibly drive polarizable halides toward the vapor phase, resulting in a large density build up along the interface. Recent ab initio simulations \( \Box \), however, find a much smaller contact potential, \(-18\text{mV} \approx -0.7k_BT/q \), for a water-vapor interface. This might lead to a smaller adsorption, in line with the predictions of the present theory.

There is a subtle interplay between ionic size and polarizability. Although the absolute value of polarizability for halide ions varies dramatically, the relative polarizability \( \alpha \) is practically the same for all ions \( \sim 0.85 \). On the other hand, the relative polarizability of Potassium is almost four times lower. Future work should try to optimize the parameters of the theory \( \nu \) and \( \chi \) by fitting \( U_{\text{sol}} \) to the full ab initio simulations. Unfortunately, no such calculations are available at this moment. Finally, since the surface tension of electrolyte solution is directly related to ionic adsorption in the interfacial region, the theory developed also accounts for the Hofmeister series for halogens.

I am grateful to Felipe Rizzato and Alexandre P. dos Santos for help with numerics. This work is partially supported by CNPq and by the US-AFOSR under the grant FA9550-06-1-0345.

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FIG. 2: Density profiles ($\times 10^5$) of KI, KBr and KCl, from left to right. The radius of the water drop is $R = 100\,\text{Å}$ and it contains $N_+ = N_- = 380$ ions at physiological concentration of 150mM. Solid curve is for cation (K) and the dashed ones are for anions. In all cases Potassium is depleted from the interface, but there is a formation of a double layer, where the excess of anion directly at the interface results in a build up of K in its vicinity.

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