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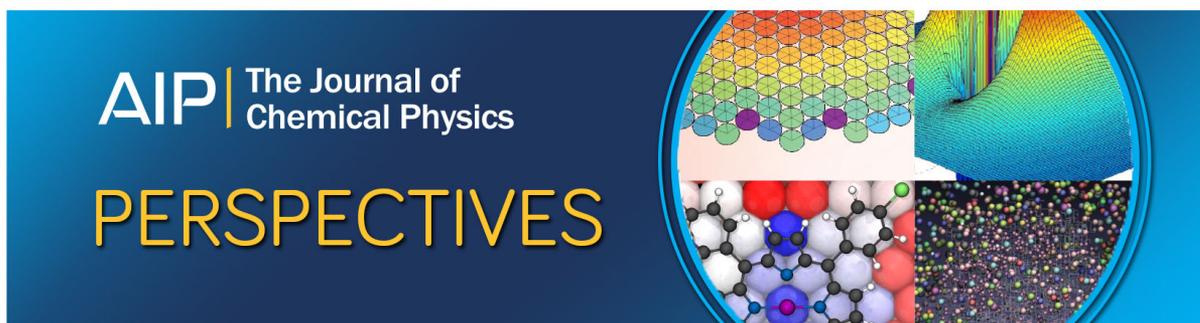
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Ionic solvation and solvent-solvent interaction effects on the charge and potential distributions in electric double layers

R. Vangara, F. van Swol,^{a)} and D. N. Petsev^{b)}

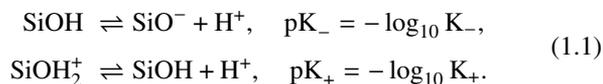
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Electric double layers are complex systems that involve a wide variety of interactions between the different components of the electrolyte solutions and with the charged interface. While the role of all Coulombic types of interactions is clear, that of the non-Coulombic forces is less obvious. The focus in the present study is on the effect of bulk solvation interactions on the properties of the electric double layer. The analysis is based on classical density functional theory. This approach allows us to account for the correlations between all charged (ionic) and uncharged (solvent) species in the solution. The surface charge at the boundary of the electric double layer is derived from the surface chemistry pertinent to the system. The surface is sensitive to the concentration of potential determining ions, which in turn depends on the correlations and activities of all remaining components. The analysis shows that the solvation forces have a profound effect on the charge and potential distributions in an electric double layer. This is true not just for the solvation of the potential determining ions, but for all species. Even varying the solvent-solvent interaction has a significant impact on the charge and potential distributions in the electric double layer. *Published by AIP Publishing.*
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I. INTRODUCTION

All matter of substances, when brought in contact with water or any electrolyte, spontaneously ionize. A very familiar example is NaCl, which readily falls apart, splitting into Na⁺ and Cl⁻. Indeed, even the so-called pure water by itself will see a small fraction of water molecules split into H₃O⁺ and OH⁻, thus giving rise to the concept of pH, and providing for a small electrical conductivity. Similarly, when a large molecule such as a protein or a solid surface such as silica is contacted by water, it will acquire a charge as a consequence of ionizable groups splitting off an ion. A relevant example is silica, SiO₂, which has terminating hydroxyls, SiOH, which can split off a proton and leave a negative charge on the surface. Naturally, the chemical equilibrium is characterized by a change in the Gibbs free energy or, equivalently, by an equilibrium constant, K. Often there exist multiple ways of leaving the surface charged. For example, the hydroxyl, SiOH, may also bind an available proton to pick up a positive charge, i.e.,



Surfaces that can split off positive ions as well as bind positive ions are referred to as amphoteric surfaces. They can end up charged negatively or positively depending on the electrolyte conditions. Specifically, the final equilibrium

charge depends on both equilibrium constants and the local concentration of the ions involved in the reactions, here H⁺ (or H₃O⁺). The ions participating in the surface chemical reaction(s) are referred to as potential determining ion(s) or PDIs.

In the example above, the final surface charge (as well as the final electric surface potential) depends on the constants K₊ and K₋, temperature, T, the pH, and the concentration of any added salt. The added salt, NaCl, say, does not directly participate in the chemical surface reactions. However, the presence of added salt does, indirectly, affect the surface concentration of H⁺ (or H₃O⁺), and hence it will shift the equilibria. The way the ions of the added salt affect the local proton concentration is through the local electric potential inside the so-called electric double layer (EDL).

In other words, changing the PDI concentration (here pH) will directly change the surface charge (and surface potential) because it changes the surface concentration. However, spectator species such as non-PDIs (i.e., added salt) can also shift the surface equilibria by their effect on the EDL.

To put this in more general terms then, the surface charge (or surface potential) depends on the shift in equilibrium due to the environmental parameters (e.g., hydration and composition). For instance, in an experiment or in a modeling approach, these parameters can be varied by the manipulation of the solvent. Doing so changes the reaction free energy through changes of the dissociated state of the PDIs and the ionized surface group on the one side of the reaction and the non dissociated surface group on the other.

Anything that changes the free energy difference between the reactants and products will potentially lead to a change

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in the surface quantities (i.e., charge or potential). Heterogeneous regions such as interfaces and EDLs are prime examples of this phenomenon. As we have shown in a series of papers on EDL phenomena, classical Density Functional Theory (cDFT) is uniquely suited for an investigation of this sort. cDFT minimizes a free energy functional and is firmly anchored in statistical mechanics and, at equilibrium, provides direct access to the free energy. In addition, our cDFT calculations explicitly represent the solvent as atoms. Given that the number of solvent atoms greatly exceeds that of the ions, the solvent structure dictates the short-range structure of the EDL.¹⁻⁸ Interestingly, even though the density profile of the net local charge distribution is strongly oscillatory, the electric potential Ψ is not. The Poisson equation⁹

$$\nabla^2 \Psi = -\frac{\rho_e}{\epsilon \epsilon_0} \quad (1.2)$$

is, of course, satisfied, guaranteeing that the second spatial derivative of Ψ is proportional to the net local charge profile. But this does not preclude a monotonic Ψ , similar to what is found in a simple Poisson-Boltzmann approach¹⁰⁻¹² where

$$\rho_e = \sum_i \rho_i^0 q_i \exp\left(\frac{-q_i \Psi}{k_B T}\right), \quad (1.3)$$

where ρ_i^0 is the density of ionic species i infinitely far from the interface, q_i is the ion charge, and $k_B T$ is the thermal energy. Other parameters include the dielectric constant of vacuum ϵ_0 and the relative dielectric permittivity of the solvent phase ϵ .

In this paper, we explore the role of the solvation (hydration) interactions. We do this by varying the strength of the non-Coulombic interactions within the solvent as well as between the solvent and the ionic species. We examine the detailed charge and potential distribution in the bulk in the vicinity of charged interface. This includes the so-called Stern layer¹³ and beyond, where the charge distribution is mostly diffuse.

The paper is organized as follows. In Sec. II, we describe the details of the cDFT parameters and calculations. The results are presented in Sec. III, and we conclude with Sec. IV.

II. THEORY

A. Density functional theory for electrolyte solutions at charged interfaces

The system under consideration represents a charged interface in contact with an electrolyte solution. All species are assumed to have the same size.^{7,8} To put this into perspective, for molecular/ionic diameter of 0.288 nm, 55.56M of solvent would occupy a liter. This is useful to bear in mind when discussing moles and mole fractions below. Thus, the overall ionic strength in all computations was set to 0.01M. Such moderate ionic concentration allows us to demonstrate many important physical effects and is still in agreement with the use of the bulk dielectric permittivity in all Coulombic expressions.^{7,8}

The theoretical approach we use is based on cDFT.^{7,8,14-16} The model fluid consists of four components: solvent, potential

determining ions (PDIs), and binary 1:1 background electrolyte. The background electrolyte ions are chemically inert with respect to the surface, as opposed to the PDIs, which participate in a charge regulating reaction. The functional describing the systems is given by

$$\begin{aligned} \Omega[\{\rho_i(z)\}] = & k_B T \sum_{i=1}^M \int dz \rho_i(z) \left\{ \ln \left[\lambda_i^3 \rho_i(z) \right] - 1 \right\} \\ & + F_{HS}^{ex}[\{\rho_i(z)\}] + F_{long}^{ex}[\{\rho_i(z)\}] \\ & + \sum_{i=1}^M \int dz \rho_i(z) \left[V_i^{ext}(z) - \mu_i \right], \quad (2.1) \end{aligned}$$

where $\lambda = \sqrt{h^2/(2\pi m_i k_B T)}$ is the thermal de Broglie wavelength, h is the Planck's constant, m_i is the mass of species " i ," and $\rho_i(z)$ is the local density of component " i ." The latter is a function of z , which is the coordinate normal to the interface. $V_i^{ext}(z)$ is the external potential energy for species " i " due to interactions with the wall and μ_i are the chemical potentials of all species. M is the total number of components: ions and solvent. The functional $\Omega[\{\rho_i(z)\}]$ is then minimized following the Euler-Lagrange procedure¹⁷

$$\frac{\delta \Omega[\{\rho_i(z)\}]}{\delta \rho_i(z)} = 0 \quad (2.2)$$

to obtain the densities for each species $\rho_i(z)$ (charged ions or neutral solvent molecules).

The interactions between the solutions' species are determined by the excess free energy terms $F_{HS}^{ex}[\{\rho_i(z)\}]$ and $F_{long}^{ex}[\{\rho_i(z)\}]$. The former takes into account the excluded volume effects according to the fundamental measure theory.^{18,19} The latter term accounts for all long-range interactions. In our analysis below, we consider a Lennard-Jones²⁰ type of electrolyte solution where the long-range interactions are given by

$$\Phi_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{d_{ij}}{r_{ij}} \right)^{12} - \left(\frac{d_{ij}}{r_{ij}} \right)^6 \right], \quad r_{ij} > d_{ij}, \quad (2.3)$$

where $d_{ij} = (d_i + d_j)/2$, d_i is the diameter of component " i ." All non-Coulombic interactions of a molecule (or ion) of type " i " with the interface are assumed to be of the "hard wall" type, i.e., only the excluded volume effects are taken into account. Long-range non-electrostatic interactions with the wall are not included in the present analysis.

All charged species also exhibit Coulombic electrostatic (el) interactions (in addition to the LJ). In the bulk, this energy is defined by

$$\Phi_{el}(r_{ij}) = \frac{q_i q_j e^2}{4\pi \epsilon \epsilon_0 r_{ij}}, \quad r_{ij} > d_{ij}, \quad (2.4)$$

while the electrostatic interaction with the interface is

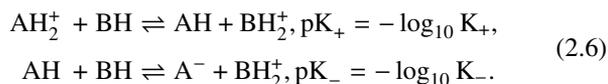
$$\Phi_{el}(z) = \frac{q_i \sigma z}{2\epsilon \epsilon_0}, \quad z > d_i/2. \quad (2.5)$$

Using a solution model based on a combination of Coulombic and LJ interactions is clearly an approximation when polar solvents such as water are involved. Still, it captures the main effects that are present in electrolyte solutions such as attractive and repulsive interactions between all

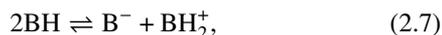
solution components.⁷ This approximation is reasonable for low to moderate ionic concentrations.^{2,8,21} In such cases, the average distance between the charged species is sufficiently large so that any ion-induced local perturbation is relaxed to the bulk solvent state before reaching another ion.²²

B. Charge regulation and charge formation at the electric double layer interface

The surface charge is a result of the thermodynamic equilibrium between the reactive groups at the interface and the PDIs in the solution. The particular chemistry may vary depending on the specific system under consideration.²³ In the present analysis, we adopt a model first proposed by Chan *et al.*²⁴ It considers the surface reaction equilibria [see Eq. (1.1)]



and a bulk reaction



where K_+ and K_- are the equilibrium constants and AH represents a surface chemical group that can either bind or release a proton depending on local densities $\rho_{\text{BH}_2^+}$ and ρ_{BH} of species BH_2^+ (PDIs) and BH in the solution. The model also allows for the presence of ions that are not involved in the chemical reactions (2.6) and (2.7). They still have a significant effect on the properties of the EDL through their interaction with the rest of the solution components as well as with the surface.

The densities of all ions in the immediate vicinity of the charged interfaces are given by^{7,8}

$$\rho_i^s = \frac{\int_0^{d_i/2} dz \rho_i(z)}{\int_0^{d_i/2} dz}. \quad (2.8)$$

The surface charge is²⁴

$$\begin{aligned} \sigma &= e\Gamma \frac{\rho_{\text{AH}_2^+}^s - \rho_{\text{A}^-}^s}{\rho_{\text{AH}}^s + \rho_{\text{AH}_2^+}^s + \rho_{\text{A}^-}^s} \\ &= e\Gamma \frac{\delta \sinh[e(\Psi_N - \Psi_s)/k_B T]}{1 + \delta \cosh[e(\Psi_N - \Psi_s)/k_B T]}, \end{aligned} \quad (2.9)$$

where $\delta = 2\sqrt{K_-/K_+}$, Γ is the surface concentration of ionizable groups, and Ψ_s is the surface potential. The quantity $\Psi_N = [\ln(10)k_B T/e] (\text{pI} - \text{pH}_b)$ is the Nernst potential where $\text{pI} = (\text{pK}_- + \text{pK}_+)/2$ is the surface isoelectric point and pH_b is the pH value in the bulk solution, far from the charged interface. The relationship (2.9) corresponds to the charge at the physical interface between the substrate and the electrolyte solution, also known as the inner Helmholtz plane (IHP).²⁵ The charge of the Stern layer is located at the outer Helmholtz plane (OHP).

Finding the density distributions of all ionic species in the solution allows for determining the overall charge density distribution,

$$\rho_e(z) = \sum_{i=1}^M q_i \rho_i(z), \quad (2.10)$$

more accurately than using the approximate Eq. (1.3). The charge density can be then introduced in Eq. (1.2) to find the electrostatic potential distribution in the solution and at the surface.

The surface charge is also equal (and opposite in sign) to the net bulk charge or

$$\sigma = - \sum_{i=1}^M \int_0^\infty q_i \rho_i(z) dz, \quad (2.11)$$

where M is the total number of components in the solution. Since the solvent is neutral, it is formally treated as a component with zero charge ($q_s = 0$).

Equations (1.2) and (2.9)–(2.11) are then iteratively solved to obtain the surface charges and potentials as well as the corresponding distributions in the fluid phase.

The computations are performed using the free-ware Tramoto code²⁶ to minimize the grand thermodynamic potential [see Eq. (2.2)]. The parameters governing the surface chemistry are $\Gamma d^2/e = 0.66$, $\text{pH} = 4$, $\text{pK}_- = 6$, and $\text{pK}_+ = -2$.^{7,8,27} The ionic strength is 0.01M. The solvation energy was varied between 0 and $1.2k_B T$ to avoid numerical stability problems when approaching the triple point for the LJ fluid, which is around $\sim 1.4k_B T$.²⁸

The boundary condition for the surface charge is given by Eq. (2.9). The densities far away from the interface are equal to their fixed bulk values. More details are provided elsewhere.^{7,8}

III. RESULTS AND DISCUSSION

A. Composition of the Stern layer

The layer in the immediate vicinity of the interface (the boundary of the EDL) is known as the Stern layer. Stern's model¹³ considers the finite size and specific interactions with the wall exhibited by the ionic species in this layer, but the rest of the EDL is still regarded as a continuum. cDFT is a major improvement in comparison with Stern's approach because it takes into account molecular and ionic correlations everywhere in the system. Still, the Stern layer defines an important sub-domain of the EDL. It is the layer, which is primarily involved in any chemical interactions with the surface. These could be instances of electrochemical charge transfer, or reactions that establish the surface charge such as Eq. (2.6). The physical dimensions of the Stern layer are also related to the position of the shear plane in electrokinetic phenomena.^{29–33} Therefore, it deserves a more rigorous analysis.

The mole fraction of a component is calculated from the density profiles. If ρ_i^{st} is the density of a component in the Stern layer, L is the thickness of the Stern layer, which is taken after the first peak of the charge density profiles (see below)

$$\rho_i^{st} = \int_0^L dz \rho_i(z) / L. \quad (3.1)$$

The mole fraction x_i of component i is given by

$$x_i = \frac{\rho_i^{st}}{\sum_{i=1}^M \rho_i^{st}}. \quad (3.2)$$

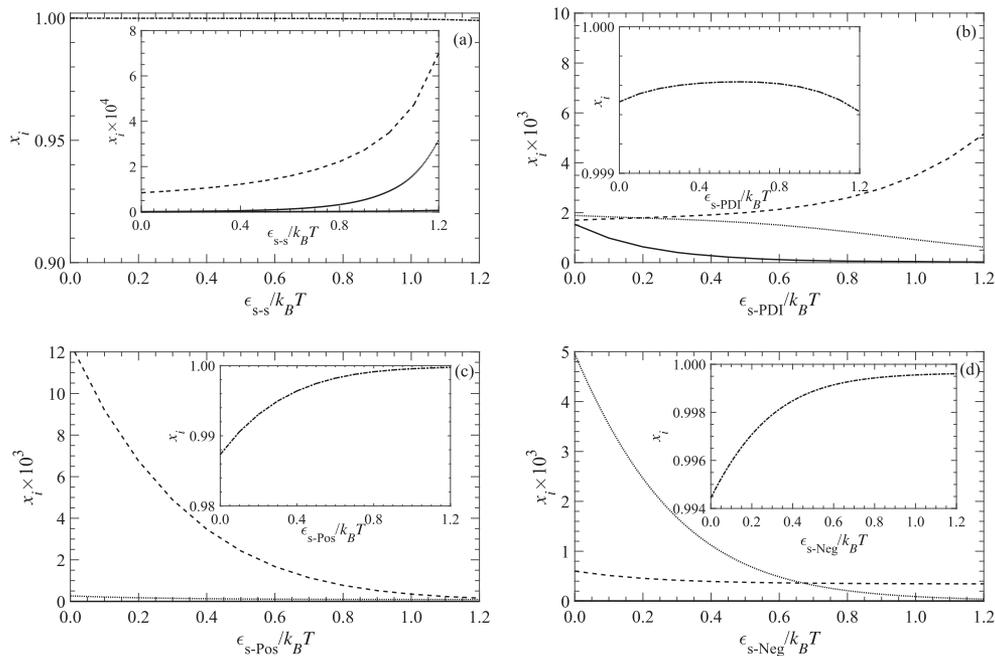


FIG. 1. Mole fraction of solution components as a function of the solvation interaction of various species. The different lines correspond to PDIs (solid line), positive non-PDIs (dashed line), negative ions (dotted line), and solvent (dotted-dashed line). (a) Solvent-solvent; (b) Solvent-PDIs; (c) Solvent-positive non-PDIs; and (d) Solvent-negative non-PDIs.

Figure 1 demonstrates the mole composition in the Stern layer as a function of the solvation interaction for the different solution species. The solvation interactions are separately varied for the solvent, PDIs, and positive and negative ions by varying the respective LJ energy [i.e., the parameter ϵ_{ij} in Eq. (2.3)]. While the LJ parameter for a given component and the solvent is varied, the rest of the LJ interactions are maintained at $1k_B T$.

It is immediately obvious the solvent is the dominant species in all cases. Also, the mole fraction of PDIs is consistently low. This is because the overall concentration of PDIs at pH = 4 is low in comparison with the rest of the species. Figure 1(a) shows the effect of the solvent-solvent molecular, non-Coulombic LJ interactions on the properties of the EDL. The relative change in the mole fraction of solvent with the LJ parameter ϵ_{s-s} is rather insignificant. The effects on the ions, however, are more noticeable. As the solvent molecules become more attracted to each other, they are less involved in solvation interactions with the ions. Hence, all ionic species tend to move from the bulk of the solution towards the interface and in the Stern layer. The mole fraction of positive non-PDIs exceeds that of the negative. This is due to the negative surface charge, which attracts the positive ions and repels the negative ions. The amount of PDIs also increases, which reduces the surface charge [see Eq. (2.6)].

Figure 1(b) depicts the effect of the solvation interactions for the PDIs. As the PDI become more solvated (ϵ_{s-PDI} increases), their concentration in the Stern layer decreases. The reduction of the PDI number in the Stern layer leads to an increase in the surface charge because of a shift in the chemical equilibrium (2.6). The effect of the PDI solvation on the mole fraction of the positive and negative non-PDIs is primarily driven by the electrostatic interactions with the interface. As the charge increases, the positive ions are attracted into the

Stern layer, while the negative are repelled. The mole fraction of the solvent still dominates the composition of the Stern layer. Interestingly it passes through a slight maximum as the solvation interaction for the PDIs varies. This is most likely an excluded volume effect that stems from a competition with the positive and negative ionic species.

Figure 1(c) shows the effect of the positive non-PDIs solvation on the composition of the Stern layer. The greater solvation energy of the positive ions, ϵ_{s-Pos} , reduces their number in the Stern layer. This leads to an increase in the concentration of PDIs, which have less competition (in terms both excluded volume and Coulombic repulsion) to accumulate in the Stern layer. Their increase again affects the surface equilibrium (2.6). Some of the negative ions also transfer into the bulk to ensure overall bulk neutrality together with the positive ones.

Figure 1(d) shows the effect of the solvation interactions for the negative ions. Following a trend, similar to the rest of the solution species, the negative ions tend to leave the Stern layer with the increased solvation energy, ϵ_{s-Neg} . The presence of negative ions in the Stern layer increases the overall negative charge and attracts positive counterions (both PDIs and non-PDIs). Therefore, as the number of negative ions decreases with the solvation, so does the number of PDIs and non-PDIs as indicated in the figure. The positive ions are being replaced by solvent molecules.

B. Charge and potential distribution

1. Solvent-solvent interactions

The charge density distribution, for different values of the solvent-solvent LJ interaction parameter ϵ_{s-s} , is shown in Fig. 2(a). The plot exhibits well-defined oscillations near the wall, which are due to excluded volume effects as well as

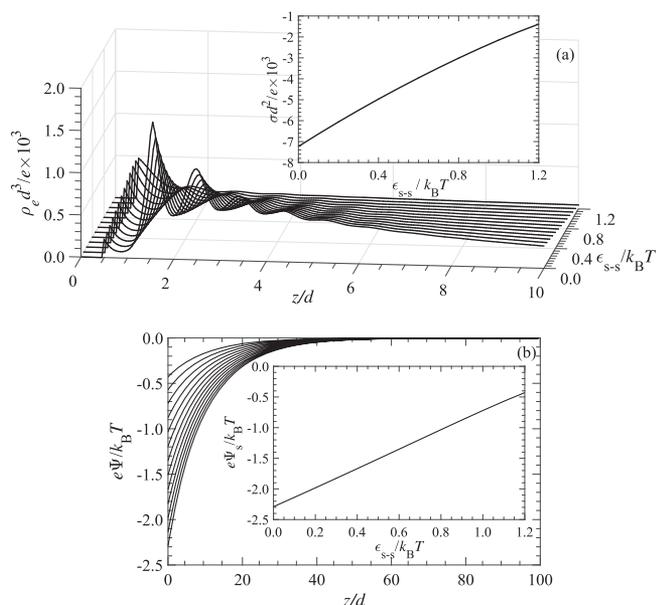


FIG. 2. Charge and potential in an EDL for variable solvent-solvent LJ interactions ϵ_{s-s} . (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.

longer-ranged correlation between the solution species and excluded volume effects with the interface. The curves are very different from the charge density distributions that correspond to the Boltzmann distribution (1.3), which describes a monotonic function. For low LJ attractions between the solvent molecules (starting with $\epsilon_{s-s} = 0$), the first peak in the charge density distribution is much lower than the rest. This means that the charge density in the Stern layer is lower. This is due to excluded volume competition from the large number of solvent molecules. These molecules displace ions from the Stern layer and thus deplete it of charges. As the solvent attractive energy (i.e., ϵ_{s-s}) increases, the solvent molecules are less driven to accumulate near the surface or interact with the ions. Hence, the height of the first peak increases allowing for (predominantly positive) ions to accumulate in the Stern layer. This in turn leads to less charge in the region right next to the Stern layer [the second set of peaks in Fig. 2(a)]. The rest of the peaks decrease in height both with the distance from the surface and with ϵ_{s-s} . At about $\epsilon_{s-s} = 0.8$, the first and second peaks have similar height and the trend reverses. Above $\epsilon_{s-s} = 0.8$, the first peaks are the highest, indicating that the Stern layer has the greatest bulk charge density compared to the next layers of the solution.

The resultant potential distribution, however, is monotonic, see Fig. 2(b). Each curve corresponds to a different value of the solvent-solvent interaction parameter ϵ_{s-s} . The potential is most negative in the complete absence of any LJ attractions ($\epsilon_{s-s}/k_B T = 0$). As the parameter ϵ_{s-s} increases (in steps of $0.1k_B T$), the magnitude of the potential decreases. The top curve corresponds to $\epsilon_{s-s}/k_B T = 1.2$. These results demonstrate that even non-Coulombic interactions between neutral molecules have a strong effect on the electrostatics of charged interfaces. All components in a solution are involved in interactions with each other as dictated by thermodynamics, therefore changing the attraction between the solvent

molecules inevitably affects their interactions with the ionic species. Among the ionic species are the PDIs, and perturbing their density in the Stern layer (see above) shifts the surface equilibrium (2.6), the interfacial charge, and, consequently, the bulk charge and potential distributions.

The spatial potential distributions are reasonably well described by exponential curves. While the potential magnitudes exceed the Debye and Huckel regime,³⁴ they are still moderate, which contributes to such behavior. The Debye screening length for the computations is determined by the total ionic strength (0.01M) and is given by $\kappa^{-1} = 10.56d$.

Interestingly, the surface potential Ψ_s becomes less negative in a linear proportion to the bulk solvent LJ interactions or the parameter ϵ_{s-s} [see the inset in Fig. 2(b)].

2. Solvation of the potential determining ions

The PDI solvation effect on the charge and potential distributions in EDLs is illustrated in Fig. 3. Since the PDIs determine the surface charge, their solvation should have a significant effect on the surface charge and the overall properties of the EDL. The solvation interactions of the PDIs compete with the electrostatic interactions with the interface and with the chemical reaction (2.6).

The spatial charge density distributions are depicted in Fig. 3(a). In this case, the domain with greatest charge density is the Stern layer, which is demonstrated by the highest first peaks. The heights of these peaks, however, exhibit a minimum as ϵ_{s-PDI} varies from 0 to $1.2k_B T$. This behavior is related to the solvation of the PDIs. At low values of ϵ_{s-PDI} , the PDIs interact very weakly (or not at all) with the solvent, and hence, they accumulate in the Stern layer. For example, for $\epsilon_{s-PDI} = 0$, the density of PDIs in the Stern layer is $\rho_{PDI} \sim 6.1 \times 10^{-4}$. The positive non-PDIs in the Stern layer have a density $\rho_{Pos} \sim 3.1 \times 10^{-4}$. Note that the PDIs have a 100 times

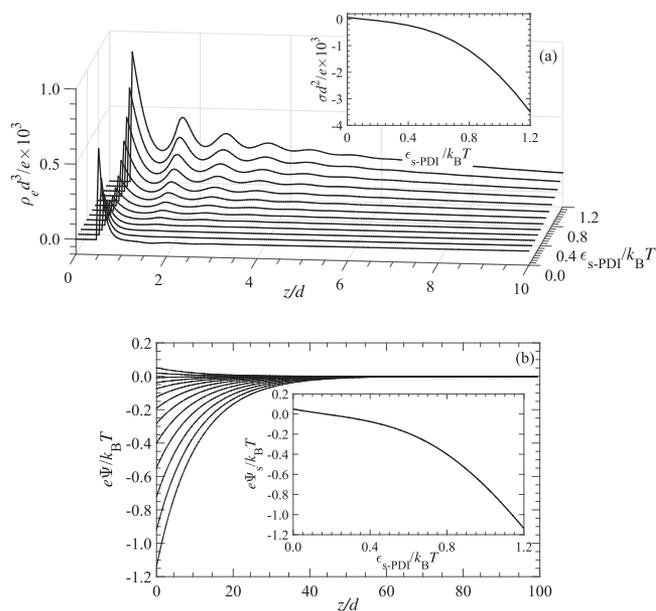


FIG. 3. Charge and potential in an EDL for variable solvent-PDI interactions ϵ_{s-PDI} . (a) Bulk charge density distributions at different solvent-PDI LJ parameter values. Inset: surface charge. (b) Electrostatic potential. Inset: surface potential.

lower density in the bulk compared to the non-PDIs. However, the latter ions are solvated, while the PDIs are not. These are the factors that lead to the particular density values. For $\epsilon_{s\text{-PDI}} = 1.2k_B T$, the respective density values for the two positive ionic species are $\rho_{\text{PDI}} \sim 3.4 \times 10^{-6}$ and $\rho_{\text{Pos}} \sim 9.7 \times 10^{-4}$. Hence, as the solvation of the PDIs increases, they are removed from the Stern layer into the bulk, which decreases the total amount of positive charge. This, however, leads to an increase of the negative surface charge, which in turn attracts positive counterions. Hence the number of positive non-PDIs, which also are in much greater number in the solution, populates the Stern layer thus making it again more positive.

The potential distributions are shown in Fig. 3(b). In this, the stronger the PDIs solvation, the more negative is the surface charge. For very weak solvent-PDI attraction $\epsilon_{s\text{-PDI}} \approx 0.2k_B T$ and below, the PDIs are present in large numbers in the Stern layer and turn the surface positive according to (2.6). The shape of the potential distribution curves is still very close to exponential. The surface potential, however, is not a linear function of the solvation energy parameter, in this case $\epsilon_{s\text{-PDI}}$. The surface potential Ψ_s becomes more negative with the solvation of the PDIs because they are effectively removed from the surface into the bulk and the reaction equilibrium (2.6) is shifted in the direction of greater dissociation.

3. Solvation of the positive non-potential determining ions

The effect of the positive non-PDIs solvation is illustrated in Fig. 4. The charge density distribution curves at different values of $\epsilon_{s\text{-Pos}}$ [Fig. 4(a)] exhibit noticeable peaks that correspond to the accumulated positive charge in the Stern layer. These peaks are much higher than those further away from the surface, which while present are hard to detect at this scale. The Stern peaks, corresponding to various positive ion

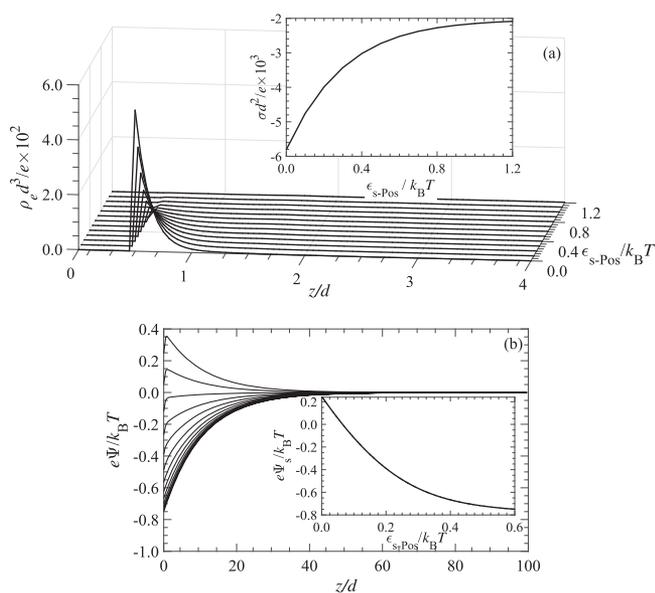


FIG. 4. Charge and potential in an EDL for variable solvent-positive ion interactions $\epsilon_{s\text{-Pos}}$. (a) Bulk charge density distributions at different solvent-positive ions LJ parameter values. Inset: surface charge. (b) Electrostatic potential. Inset: surface potential.

solvation, are also more pronounced than the peaks that correspond to the solvent-solvent and solvent-PDI interaction cases discussed above. This indicates that the positive non-PDI tend to accumulate in great numbers in the Stern layer, particularly when not strongly solvated. The peak height rapidly drops as the LJ interaction $\epsilon_{s\text{-Pos}}$ increases. The bulk concentration of the positive non-PDIs is also high (0.01M) relative to that of the PDIs (10^{-4} M). This certainly facilitates the population of the Stern layer with positive ions, which while not involved in any surface chemical reaction are still subject to Coulombic interactions (with the rest of the ions and the charged interface), and solvation forces (with the solvent molecules).

The potential distribution in the EDL is displayed in Fig. 4(b). Low solvation of the positive ions leads to their accumulation near the interface. As we have established earlier,⁸ the large number of positive ions in the Stern layer creates an exclusion volume and electrostatic barrier for the PDIs to reach and chemically react with the surface. Hence, the interface tends to be more negatively charged. Note that despite the positive surface potential for low solvation interactions ($\epsilon_{s\text{-Pos}} \lesssim 0.2k_B T$), the surface charge is still very negative since $\sigma = -\epsilon\epsilon_0(\nabla\Psi)_s$. The steep change in the potential very near the charged interface corresponds to the capacitance effect of the Stern layer.³⁵ The potential distribution beyond the Stern layer is very close to exponential. The surface potential changes from weakly positive to moderately negative as $\epsilon_{s\text{-Pos}}$ varies from 0 to $1.2k_B T$ and shows a trend to leveling off at large values of the LJ interactions.

4. Solvation of the negative non-potential determining ions

Figure 5 shows the effect of negative ion solvation on the charge and potential distribution in an EDL. The charge distribution is depicted in Fig. 5(a), and it shows a very different behavior compared to all cases discussed above. The

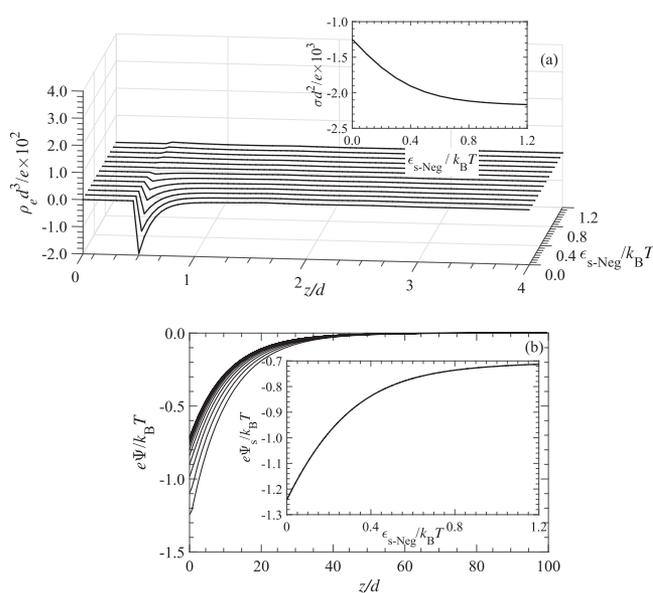


FIG. 5. Charge and potential in an EDL for variable solvent-negative ion interactions $\epsilon_{s\text{-Neg}}$. (a) Bulk charge density distributions at different solvent-negative ions LJ parameter values. Inset: surface charge. (b) Electrostatic potential. Inset: surface potential.

reason is that the negative ions have a sign opposite to the PDIs and the rest of the positive ions. Hence, when poorly solvated (or not at all), they tend to accumulate near the surface forming a Stern layer with predominantly negative charge. This is most pronounced for $\epsilon_{s\text{-Neg}} = 0$ and increases with the LJ attraction between the negative ions and the solvent molecules. This negative charge is effectively added to that of the surface. At about $\epsilon_{s\text{-Neg}} \gtrsim 0.7k_B T$, the charge in the Stern layer changes from negative to positive, which is due to the removal of negative ions into the bulk with the increased solvation.

The potential distribution curves become less negative as the LJ parameter $\epsilon_{s\text{-Neg}}$, characterizing the solvation interactions increases. The effect levels off at greater solvation interactions. This trend is also seen in the plot for the surface potential.

IV. CONCLUSIONS

The electric double layer is a central concept in research fields such as fundamental electrochemistry, colloid science, biophysics, material science, corrosion, and many others. The approach outlined in this study can be directly applied to problems in these areas. For example, the replacement of A with AlO^- and B with OH^- in Eq. (2.6) represents a corroding aluminum interface in contact with water.

The properties of electric double layers are determined by the electrolyte solution thermodynamics in the presence of a charged and chemically reactive interface. This implies that all components play a role, including those that are not charged and therefore, insusceptible to Coulombic type of interactions. An example for such a component is the solvent. Typically, the solvent is present in amounts that strongly exceed those of the dissolved ionic species. The solvent molecules interact among themselves and with the rest of the components through non-Coulombic interactions due to van der Waals molecular forces. These are known as solvation interactions and, despite their non-electrostatic origin, have a strong impact on the properties of electric double layers. The solvation interactions essentially compete with the interactions with the charged interface. Hence, they affect the distribution of solutes in the system, including in the Stern layer. A particularly important component of the Stern layer is the potential determining ion. These ions chemically interact with the surface ionizable groups and therefore, their local concentration is directly related to the dissociation-association equilibrium that determines the actual surface charge. Obviously, the surface charge is an important factor that sets the distribution of all charged species in the solution.

The solvent-solvent interactions do not directly involve the charged species, and yet, their effect is significant. The solvent molecules occupy a considerable fraction of the Stern layer and hence, determine its overall charge. A linear relationship between the surface potential and the energy parameter for the Lennard-Jones solvent attraction is observed.

The solvation of the potential determining ions also affects the properties of the electric double layers. The main factor that plays a role in this case is the surface reaction. In the presence of additional and chemically inert ionic species,

the charge density in the Stern layer exhibits a minimum with the variation of the potential determining ions solvation strength.

The positive non-potential determining ions interaction with the solvent also has an effect on the properties of the electric double layer. Depending on the strength of the solvation interactions, these ions accumulate in different quantities in the Stern layer and thus determine its charge. The positive ions, while chemically inert with respect to the surface, may serve as an excluded volume/electrostatic barrier for the potential determining ions and hinder their access to the interface. Hence, the positive ion solvation can indirectly affect the surface charge.

The solvation of the negative ions may have a dramatic effect on the electric double layer. When poorly solvated, these ions accumulate in the Stern layer and add more negative charge to an already negative surface. A strong solvation of the negative ions, however, eliminates this effect.

Charged interfaces involving electrolytes are complex systems. Their properties depend on many factors, some of which are unrelated to electrostatic interactions. This observation is in accord with the great number of experimental data showing that the properties of electric double layers may differ when different types of ions having the same charge are involved.

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