

## Solvent Role in the Formation of Electric Double Layers with Surface Charge Regulation: A Bystander or a Key Participant?

Mark E. Fleharty,<sup>1</sup> Frank van Swol,<sup>1,2,\*</sup> and Dimiter N. Petsev<sup>1,†</sup>

<sup>1</sup>*Department of Chemical and Biological Engineering, and Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, New Mexico 87131, USA*

<sup>2</sup>*Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

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The charge formation at interfaces involving electrolyte solutions is due to the chemical equilibrium between the surface reactive groups and the potential determining ions in the solution (i.e., charge regulation). In this Letter we report our findings that this equilibrium is strongly coupled to the precise molecular structure of the solution near the charged interface. The neutral solvent molecules dominate this structure due to their overwhelmingly large number. Treating the solvent as a structureless continuum leads to a fundamentally inadequate physical picture of charged interfaces. We show that a proper account of the solvent effect leads to an unexpected and complex system behavior that is affected by the molecular and ionic excluded volumes and van der Waals interactions.

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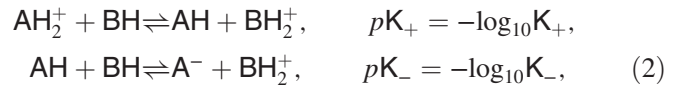
Interfaces involving polar liquids are often charged. The charging is due to ionic dissociation, adsorption, or both at the interface [1,2]. This leads to a bulk potential and charge redistribution in the vicinity forming an electric double layer (EDL). Understanding the EDL is of key importance to the theory of electrolytes, colloid science, soft-matter systems, rheology and dynamics of complex fluids, corrosion, and material science. As the solvent is typically uncharged, it is only considered to be less important than the ions. Hence, it is often ignored or is considered only to provide molecular interpretation for the dielectric permittivity [3–11]. We demonstrate that the solvent role is much more important than that. It provides a structural framework for the solution, which has a strong effect on the surface charge formation. Surprisingly it is the nonelectrostatic interactions (e.g., excluded volume, van der Waals) that determine the properties of charged interfaces.

An early analysis of an EDL was offered by Gouy [12,13] and Chapman [14], which was based on the continuum Poisson-Boltzmann equation [15]

$$\nabla^2 \Psi = -\frac{1}{\epsilon \epsilon_0} \sum_i \rho_i^0 q_i \exp\left(\frac{-q_i \Psi}{k_B T}\right), \quad (1)$$

where  $\Psi$  is the electrostatic potential,  $q_i$  is the charge of ion species “ $i$ ” (in units of the elementary charge  $e$ ),  $k_B T$  is the thermal energy,  $\rho_i^0$  is the bulk number density of charged species  $i$ , and  $\epsilon$  and  $\epsilon_0$  are the medium dielectric permittivity and the dielectric constant of vacuum. The problem was solved by fixing the value of the surface potential  $\Psi = \Psi_s$ . Alternatively, the potential derivative (i.e., the surface charge  $\sigma$ ) can be specified to a known value, or  $\epsilon \epsilon_0 (\nabla \Psi)_s = \sigma$ . Both conditions are well defined and very popular. However they are not physically justified. This

was first recognized by Ninham and Parsegian [16] who argued that the surface charge and potential should be determined from the thermodynamic equilibrium between the surface groups and the dissolved species that chemically interact with them. The ionic species that attach to or detach from the surface determine the charge and potential at the interface. They are called potential determining ions (PDIs). This mechanism is called surface charge regulation and it is the condition that provides a physically correct description [17–25]. While the surface charge regulation may involve multiple chemical reactions [20], a reasonable model was suggested by Chan *et al.* [17], based on the equilibria



where  $K_+$  and  $K_-$  are the equilibrium constants, and  $\text{AH}$  is a surface chemical group that can either bind or release a hydrogen ion depending on local densities  $\rho_{\text{BH}_2^+}$ ,  $\rho_{\text{BH}}$  of species  $\text{BH}_2^+$  and  $\text{BH}$  in the solution. The species  $\text{BH}$  can lose another proton in the reaction  $2\text{BH} \rightleftharpoons \text{B}^- + \text{BH}_2^+$  and become negative. Alternatively it may bind one and become positive. The latter species is the PDI. Its concentration is defined in the subsurface layer at the interface. This model translates into the following relationship [17,26]:

$$\sigma = e\Gamma \frac{\rho_{\text{AH}_2^+}^s - \rho_{\text{A}^-}^s}{\rho_{\text{AH}}^s + \rho_{\text{AH}_2^+}^s + \rho_{\text{A}^-}^s}. \quad (3)$$

$\Gamma$  is the number of ionizable groups per unit area at the surface and  $\rho_i^s$  ( $i = \text{AH}, \text{AH}_2^+, \text{A}^-$ ) are the surface densities

of the various charged and uncharged groups attached at the boundary of the EDL. Equation (3) provides a physically consistent boundary condition to Eq. (1). The second boundary condition requires charge neutrality away from the surface.

The continuum model is incomplete since it does not take into account the structure of the solution. A better theoretical framework is offered by more modern statistical mechanical approaches [3–9,11,27]. However, these models are often simplified by representing the solvent as a structureless continuum and account explicitly only for interactions between the ionic species. Such models are defined as “primitive.” In contrast, models that take into account the interactions between all species including the solvent fall under the “civilized” category [11]. The primitive model for dilute electrolyte solutions is equivalent to the continuum theory based on equation (1) [28]. For high electrolyte concentrations primitive models may produce structural peaks in the density profiles, which are due to ion-ion correlations but the effect of the solvent molecular contribution is still absent.

Recently Heinen *et al.* [9] incorporated a surface charge regulation condition into a primitive model for describing charged colloidal suspensions using an integral equation approach [29]. This work presents a step forward but it is incomplete because it neglects the solvent effect on the structure.

We argue that the physically adequate analysis of an EDL should include charge regulation at the interface in conjunction with a full account of the solvent contribution to the solution structure. Such an analysis is not an incremental improvement but reveals a number of new effects that were yet unknown. This is because the surface charge regulation [see Eqs. (2) and (3)] is extremely sensitive to the local structure and ionic density in the vicinity of the reaction surface. While the PDIs are very important, their local density is dominated by the solvent due to its overwhelmingly high concentration. The solvent structure determines that of the PDIs and hence, couples with the charge regulation [see Eq. (2)]. The factors governing the coupling are the excluded volume and long-ranged attractive interactions between all species.

Our analysis of the EDL is based on classical density functional theory (DFT) [3,30–34] starting with a grand thermodynamic potential that has the form

$$\begin{aligned} \Omega[\{\rho_i(z)\}] = & k_B T \sum_{i=1}^N \int dz \rho_i(z) \{ \ln [\lambda_i^3 \rho_i(z)] - 1 \} \\ & + F_{\text{HS}}^{\text{ex}}[\{\rho_i(z)\}] + F_{\text{long}}^{\text{ex}}[\{\rho_i(z)\}] \\ & + \sum_{i=1}^N \int dz \rho_i(z) [V_{\text{ext}}(z) - \mu_i], \end{aligned} \quad (4)$$

where  $\lambda = \sqrt{h^2/(2\pi m_i k_B T)}$  is the thermal de Broglie wavelength,  $h$  being the Planck’s constant,  $m_i$  is the mass of species “ $i$ ,” and  $\rho_i(z)$  is the local density ( $z$  being the coordinate normal to the interface) of component “ $i$ .”  $V_{\text{ext}}(z)$  is the external field due to the charged interface.  $F_{\text{HS}}^{\text{ex}}[\{\rho_i(z)\}]$  and  $F_{\text{long}}^{\text{ex}}[\{\rho_i(z)\}]$  account for the hard sphere (excluded volume) and all long-range interactions, respectively. The hard sphere (HS) interactions are implemented using the theory of Rosenfeld [35], while the long range interactions are expressed by Lennard-Jones (LJ) and Coulombic electrostatic (EL) contributions. The grand potential defined by Eq. (4) corresponds to an open system in contact with infinite reservoir for all species to ensure constant chemical potentials  $\mu_i$ .

The electrolyte is dissolved in a hard core-LJ solvent. The bulk LJ contribution between species with diameters  $d_j$  and  $d_j$ , separated by distance  $r_{ij}$ , is given by

$$\Phi_{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{d_{ij}}{r_{ij}} \right)^{12} - \left( \frac{d_{ij}}{r_{ij}} \right)^6 \right], \quad r_{ij} > d_{ij} \quad (5)$$

where  $d_{ij} = (d_i + d_j)/2$ . The LJ interaction of a molecule (or ion) of type “ $i$ ” with a wall is

$$\Phi_{\text{LJ}}(z) = \epsilon_i \left[ \frac{2}{15} \left( \frac{d_i}{z} \right)^9 - \left( \frac{d_i}{z} \right)^3 \right], \quad z > d_i/2, \quad (6)$$

where  $\epsilon_{ij}$  and  $\epsilon_i$  determine the magnitudes of the LJ energy. All charged species experience electrostatic interactions in the bulk

$$\Phi_{\text{el}}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon\epsilon_0 r_{ij}}, \quad r_{ij} > d_{ij}, \quad (7)$$

as well as with the charged wall

$$\Phi_{\text{el}}(z) = \frac{q_i \sigma z}{2\epsilon\epsilon_0}, \quad z > d_i/2. \quad (8)$$

The interaction energy is infinite for separations less than the cutoff distances  $d_{ij} = (d_i + d_j)/2$  and  $d_i/2$  [see Eqs. (5) to (8)]. A LJ fluid with isotropic interactions cannot provide a molecular interpretation of the dielectric solvent properties. They are accounted for by the introduction of a bulk dielectric permittivity as a parameter to scale the electrostatic terms [Eqs. (7) and (8)] to physically correct magnitudes. Such an approach is justified for moderately concentrated solutions [11,27]. The solution consists of (i) solvent molecules, (ii) PDIs ( $\text{BH}_2^+$ ), (iii) background ions with the same charge as the PDIs that do not chemically bind to the EDL interface, and (iv) negative counterions ( $\text{B}^-$ ) that are common to the PDIs and the background ions. The LJ energy parameters are assumed to be the same for all possible interactions:  $\epsilon_{ij} = \epsilon_i = \epsilon$ . While this is a rather simplified model, it captures two

very important physical characteristics of the solution: the excluded volume of all species, and the long-range interactions such as Coulombic and nonelectrostatic attractions between all species as well as with the surface. The model is civilized as the solvent is explicitly taken into account. The focus of the analysis is on the effect of the solvent structure on the surface charge regulation given by Eq. (2).

The grand thermodynamic potential Eq. (4) is minimized with respect to the density distribution of each component,  $\delta\Omega[\rho_i(z)]/\delta\rho_i(z) = 0$ , using the Tramonto code [36]. The latter was modified to include the surface charge regulation boundary condition Eq. (3). This procedure gives the spatial distribution of all species in the EDL. The surface charge  $\sigma$  is obtained from balancing it against the bulk excess charge to achieve global electroneutrality.

Figure 1 shows the dependence of the surface charge  $\sigma$  on the size of the solvent molecules. All ionic species have the same molecular diameter equal to  $d$ . The latter is adjusted to  $d = 0.288$  nm so that for overall density  $\rho d^3 = 0.8$  and solvent diameter  $d_s = d$ , the total molarity of all species is 55.5 M. All ions are monovalent and the ionic strength is 10 mM, which includes both PDIs (with concentration 0.1 mM) and non-PDIs, both sharing the same counterion. This corresponds to a Debye wavelength  $\kappa^{-1} = 3.04$  nm, or  $(\kappa d)^{-1} = 10.56$ . The density of surface ionizable groups [see Eq. (2)] is  $8 \times 10^{18} \text{ m}^{-2}$ , or 0.66 per  $d^2$ . The parameters for the surface reaction are  $pK_+ = -2$  and  $pK_- = 6$  (see [26]). In the limit  $d_s \rightarrow 0$ , the solution becomes primitive and all curves coalesce into a single point,  $\sigma d^2/e = -2.94 \times 10^3$ . However, the physical reality is represented by the far right region of the figure, where the solvent size is comparable to that of the ions. This illustrates the importance of the neutral solvent molecules and their interactions for understanding charged interfaces.

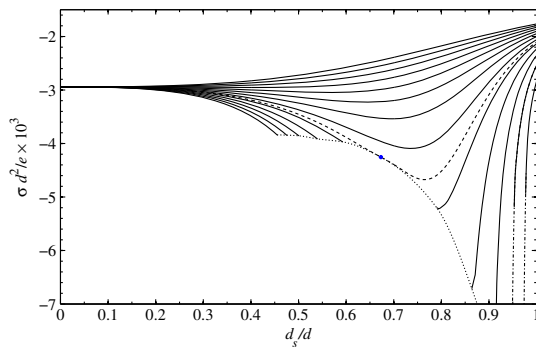


FIG. 1. Surface charge of an EDL as a function of the solvent molecular diameter. The different curves are for different values of the LJ parameter  $\epsilon$ , which starts at zero (top curve) and increases by increments of  $0.1 k_B T$ , with the exception of the dashed curve, which is for  $\epsilon/k_B T = 0.76$  (see the text). The dot corresponds to the critical point. The curves for  $\epsilon/k_B T = 1.1$  and  $\epsilon/k_B T = 1.2$  are extrapolated (dot-dashed parts) since in that region the surface charge is so sensitive to  $d_s/d$  that exact computation becomes extremely difficult.

The top curve in Fig. 1 illustrates the effect of purely excluded volume interactions on the surface charge  $\sigma$ . It shows that the magnitude of the surface charge starts to appreciably change after the solvent diameter exceeds  $\sim 0.17$ . Including attraction between the species (including the solvent) has a dramatic effect on the system behavior. As the LJ parameter  $\epsilon$  increases (in steps of  $0.1 k_B T$ ) the charge vs solvent diameter curves gradually become non-monotonic and above  $\epsilon/k_B T = 0.3$  start exhibiting a minimum. The dependence of the charge on the solvent diameter becomes very strong as the latter approaches values comparable to the ions. Note that in a real electrolyte solution, the ionic dimensions are similar to that of the solvent species [37]. The strong effect of the solvent size on the surface charge is driven by the competition between the excluded volume effects and the attraction between the ions and the solvent molecules. As the solvent molecules “grow” the ions (most importantly the PDIs) have less space available and are expelled towards the surface. At the same time the attractive interactions lead to solvation of the ions and their transfer from the interface into the bulk. The greater the LJ parameter, the stronger the solvation effect. The LJ interactions with the wall for all species also become stronger with the increase of  $\epsilon$  but nevertheless the solvent-ion interactions prevail. This may not be the case if different values for the LJ parameters for bulk and wall interactions are selected. Our approach allows us to analyze electrolyte properties and interpret experimental observations that go beyond simple electrostatics [38–43]. Accounting for the solvent contribution alone will still be insufficient if the proper surface chemistry is replaced by a constant charge or potential condition at the interface.

In the primitive limit only the ions are involved and the actual density is much less than the one for liquid states,  $\rho d^3 \approx 0.8$ . The solution is then represented by a plasmalike gas. Its structure also remains gaslike and that is problematic when a surface charge regulation condition is enforced. As the solvent diameter increases so does the overall solution density and in the presence of attractive interactions the system undergoes a phase transition as indicated by the interruption of the charge vs solvent diameter curves in Fig. 1. The region under the dotted curve corresponds to the spinodal domain in the phase diagram of the solution. The dot represents the surface charge at the critical point and the dashed curve that passes through that point is for  $\epsilon/k_B T = 0.76$ . The position of the spinodal has been compared to results for decomposition in LJ fluids [26,31]. This formal phase separation again indicates that the primitive models are not working when applied to a charge regulating EDL. These models miss very important physical effects because they are gaslike, and yet applied to the liquid density domain. The situation is similar to applying the ideal gas equation to dense liquids. The surface charge density is greatly affected by that inconsistency.

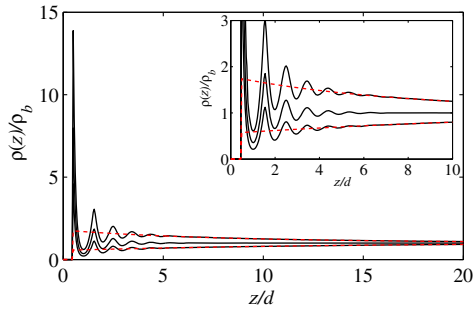


FIG. 2. Density profiles for the counterions (top curves), co-ions (bottom curves), and neutral solvent (middle curves). The full curves were calculated using DFT while the dashed ones correspond to the “primitive” Poisson-Boltzmann limit. The distributions for PDIs and background counterions are indistinguishable. The LJ parameter is  $\epsilon/k_B T = 0.0$ ; all other parameters are described in the text.

Figure 2 shows the density distribution of all solution components in the EDL for  $\epsilon/k_B T = 0.0$  and  $d_s/d = 1$ . The dashed lines present results obtained using the primitive model, while the full curves are results from a computation that includes the solvent. The relative increase in density of the PDIs and non-PDIs (the two curves overlap) in the subsurface layer next to the interface is less than 20%. In contrast, if the solvent molecules are taken into account, the increase of the PDIs and non-PDIs in the subsurface layer is about seven times the bulk value. The solvent dominates the structure by creating a matrix where the only option for an ion (positive or negative) is to move into a vacancy that is not occupied by a solvent molecule. The excluded volume effect alone is so strong that even the surface co-ions peak near the interface. The background (non-PDI) counterions always follow the same density distribution shape as the PDIs because of the same charge. This implies that both ionic species respond to the electrostatic potential in exactly the same way. However, the surface charge regulation chemical equilibria (2) involve only the PDIs. Therefore, they regulate the charge, while all other ionic species are affected only by the electrostatics. More details are outlined in the Supplemental Material [26].

As the distance from the solid interface increases this structure decays as seen from Fig. 2. The rate of decay can be quantitatively assessed by observing the peak height position with distance as suggested by Martynov [44]. According to that analysis we expect that the peak heights for each component will decrease exponentially with the distance. For the charged ions, that implies first subtracting the continuum electrostatic component characterized by the Debye wavelength  $\kappa^{-1}$ . After such subtraction and normalizing the distributions with the respective bulk values we find that all curves collapse onto a single curve (see Fig. 3). The peak heights of that curve exponentially decrease with a characteristic decay length  $(\beta d)^{-1} = 1.3$ . The solution structure dominates the properties near the charged surface,

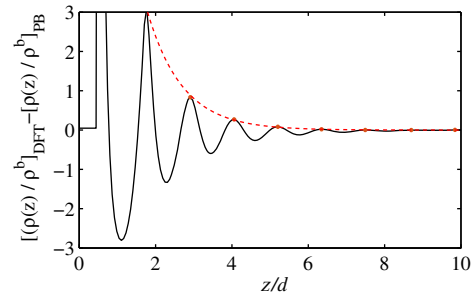


FIG. 3. Structure decay with distance. The LJ parameter is  $\epsilon/k_B T = 0.0$ . See also the text for details.

but its effect decreases with distance more rapidly than that due to pure electrostatics characterized by the Debye wavelength. It is near the surface, however, where the structure is crucial for the surface charge.

The charge formation at the boundary of an EDL is governed by the chemical equilibrium between the surface ionizable groups and the PDIs in the subsurface layer. It is very sensitive to the precise solution structure in the vicinity of the interface. The structure couples to the surface chemistry leading to a complex dependence of the surface charge density on the solvent molecular size. This complexity would be missed unless the solvent molecular effect and the surface charge regulation are *both* taken into account. The civilized analysis reveals that there are two characteristic length scales associated with (i) the electrostatic long-range screening,  $\kappa^{-1}$ , and (ii) structure,  $\beta^{-1}$ , which determines the solution-wall interactions at close proximity, but rapidly decreases with distance. In effect the neutral solvent governs the magnitude of the surface charge. It is also valid to state that a civilized model alone is inadequate if a constant charge or potential is enforced at the EDL interface as an external condition.

Our approach allows further investigation of properties of the EDL that are beyond the electrostatic interactions [38–43] such as solvation of the ions in the bulk and at the wall, and interactions and structure of large charged molecules (proteins, polyelectrolytes) near charged walls. It can be generalized to address nonequilibrium situations like surface reaction kinetics and solution transport [31,45]. A better understanding of the EDL properties at the molecular level will lead to new insights in many areas of physical sciences.

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\*vanswol@unm.edu

†dimiter@unm.edu

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