

Inversion of the Electric Field at the Electrified Liquid–Liquid Interface

Guillermo Iván Guerrero-García[†] and Mónica Olvera de la Cruz^{*,†,‡,§}

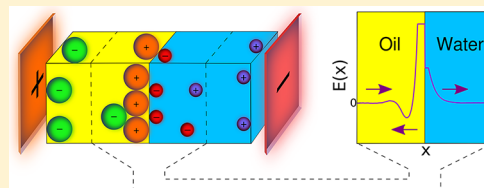
[†]Department of Materials Science, Northwestern University, Evanston, Illinois 60208, United States

[‡]Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208, United States

[§]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

S Supporting Information

ABSTRACT: The thermodynamics of the general system of two immiscible electrolytes in the presence of an electric field depends strongly on the distribution of ions near the liquid interface. Here, we calculate the corresponding electrostatic potential difference, excess surface tension, and differential capacity *via* Monte Carlo simulations, which include ion correlations and polarization effects, and *via* a modified nonlinear Poisson–Boltzmann theory. Macroscopically, we find good agreement between our results and experimental data without needing any fitting parameter. At higher salt concentrations, charge overcompensation in the lower-permittivity region is observed, which results in a local inversion of the electric field accompanied by charge inversion near the interface. We find that these interesting phenomena are mainly driven by the excluded-volume effects associated with large organic ions in the oil phase, although polarization effects and between-layer ion correlations have a significant impact in the adsorption of ions close to the liquid interface. In addition, our Monte Carlo simulations predict that the differential capacity is maximal at the point of zero charge, in contrast with the classical Poisson–Boltzmann theory results.



Immiscible liquids usually have very different dielectric properties that result in fascinating and important interfacial phenomena. In particular, the dielectric heterogeneity at the interface between two immiscible electrolyte solutions (ITIES) leads to the partitioning of the ionic components^{1–4} near the interface. Ion partitioning results in an excess surface charge or the so-called electrical double layer. Technological applications relying on the precise knowledge of the electrical double layer at the ITIES, including ion transfer, electro-extraction, label-free detection, and drug delivery, have increased significantly in recent years.^{5,6} The ITIES also constitutes a very simple model of the biomembranes typically found in living organisms.^{5,7}

Large differences in the dielectric properties of the ITIES may produce notable polarization effects analogous to those observed in typical colloidal suspensions.^{8–14} These effects modify the bare $1/r$ Coulombic interactions between charged particles in a single continuum solvent. In the most simple instance, polarization effects are responsible for the attraction (repulsion) of a single charged particle toward a macroscopic sharp interface limiting another medium with higher (lower) dielectric constant. In planar geometry, such behavior can be easily understood in terms of image charges.¹⁵ For arbitrary shapes of the dielectric interface, this approach is no longer useful, and more sophisticated variational formulations of electrostatics are indeed required.¹⁶

Another important ingredient in a theoretical description of charged systems is ion correlations (including excluded-volume effects),^{17–29} which are not accounted for by the classical Poisson–Boltzmann equation. Excluded-volume effects play a

key role in the appearance of charge inversion,¹⁷ which is the inversion of the role of counterions and co-ions near a strongly charged surface leading to the overcompensation of the bare colloidal charge by counterions. These effects are important in biology and materials fabrication and depend on the size ratio of the counterions and co-ions.^{30–32} In addition, charge inversion has been experimentally detected by the reversal of the electrophoretic mobility^{33–37} in the presence of multivalent ions.

Polarization and ion correlations at the ITIES were studied by Torrie and Valleau³⁸ via numerical simulations. They show that (i) image forces make the diffuse electrical double layer thinner in the lower dielectric liquid medium and thicker in the higher dielectric medium and that (ii) ion correlations within the layers have the overall effect of thinning both layers as well as reducing the potential drop across an ITIES. However, explicit calculations of experimental measurable quantities typical of the ITIES (such as the excess surface charge density, surface tension, and differential capacity) have not been analyzed including consistently the above effects. In this work, we perform Monte Carlo (MC) simulations focusing on the behavior of such thermodynamic properties, as a function of both the strength of the electric field and the electrolyte concentration. In particular, we explore their behaviors in relation to the corresponding microscopic ionic structure near the dielectric discontinuity, by considering a

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realistic size for the organic ions submerged in the lower-dielectric solvent without necessitating any fitting parameter.

When an electric field is applied, an accumulation of charge is observed near the ITIES, as shown in the schematic representation of Figure 1. This case has been widely studied

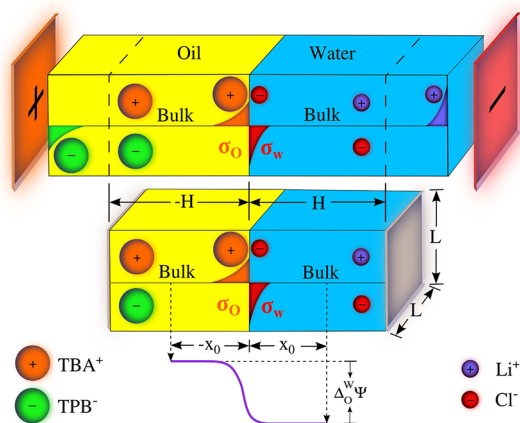


Figure 1. Schematic representations of (top) the experimental system, (middle) the Monte Carlo setup for the numerical simulations, and (bottom) the Galvani potential.

using a simplified approach,³⁹ which assumes a liquid–liquid electrolyte interface forming two independent back-to-back electrical double layers meeting at a common sharp surface. In this approach, polarization and correlations between ions, whether within the same layer (within-layer ion correlations) or across the different layers (between-layer ion correlations), are completely neglected (see Figure 2). The corresponding ionic

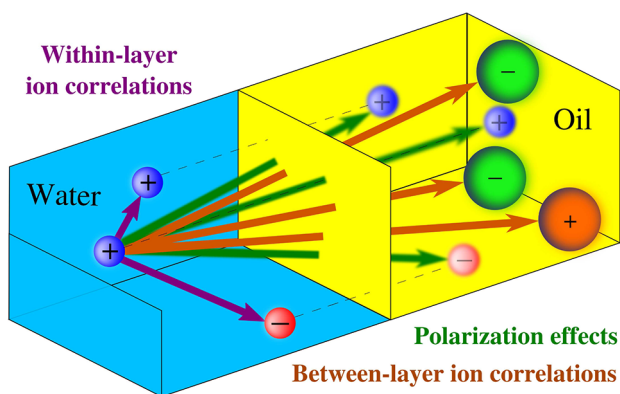


Figure 2. Schematic representation of within-layer ion correlations, between-layer ion correlations, and polarization effects included in our Monte Carlo simulations. These effects are completely neglected in the classical Poisson–Boltzmann theory.

profiles can be calculated by solving the nonlinear Poisson–Boltzmann (NLPB) theory under appropriate boundary conditions,⁴⁰ which is based on the classical Gouy–Chapman theory. A modified version including an additional *inner layer* has also been proposed.^{41,42} This inner layer has been related to the existence of a compact ion-free layer of oriented solvent molecules (characterized by a dipolar electrostatic potential)⁴³ or to the presence of a mixed solvent–ion layer at the interface.⁴⁴ However, in systems consisting of highly immiscible liquids, such as oil and water, the physical properties of the resulting sharp interface are not known, and the properties of

the inner layer cannot be clearly established as a result. We implement here a modified nonlinear Poisson–Boltzmann (MNLPB) theory, in which ion-size effects are partially considered via a closest approach distance (analogous to a Stern layer), and we compare the results with our Monte Carlo simulations. Despite the improvement of the MNLPB over the classical NLPB theory, ion correlations and polarization effects are still significant.

In typical experiments, where an electric field is applied via two electrodes as shown in Figure 1, an excess of charge is expected to be adsorbed at the electrodes and at the liquid interface. In the absence of ion transfer, each electrolyte is electroneutral in the phase in which it resides (oil or water). As a result, the adsorbed excess of charge on one side of the liquid interface has the same magnitude but opposite sign of that adsorbed at the electrode placed in the same phase (see Figure 1). Far away from the liquid interface, in the regions located between the dielectric discontinuity and the electrodes, the electrolytes reach their corresponding bulk values in equilibrium. Then, far away from the dielectric interface, the limiting values of the mean electrostatic potential and the electric field can be defined as $\Psi_\infty^O = 0$ and $\vec{E}_\infty^O = 0$ in oil and $\Psi_\infty^W = \Delta_0^W \Psi$ and $\vec{E}_\infty^W = 0$ in water. These are the mathematical boundary conditions of our ITIES. The difference in the electrostatic potential in the bulk phases of both immiscible electrolytes, $\Psi_\infty^W - \Psi_\infty^O = \Delta_0^W \Psi$, is the so-called Galvani potential in electrochemistry⁴⁰ (see Figure 1). Let σ_O and σ_W be the total net charge per unit area around the ITIES in the oil and aqueous phases, respectively. Without a loss of generality, in order to describe experimental results,⁴⁵ we impose an excess of anions or cations in the aqueous and in the oil phase in our simulations (e.g., $\sigma_W < 0$ and $\sigma_O > 0$) depending on the direction of the electric field, satisfying the electroneutrality condition $\sigma_W + \sigma_O = 0$. Under these conditions, it is possible to relate the difference in the electrostatic potential to the charge distribution around the ITIES using the Gauss law, as will be shown below. As a result, the explicit knowledge of the applied electric field is no longer required. In standard electrochemistry experiments, macroscopic measurable quantities (as the excess surface charge density in one of the phases, the surface tension, and the differential capacity at the ITIES) are usually reported as a function of the Galvani potential.

Monte Carlo simulations are performed in the canonical ensemble in order to efficiently access concentrated electrolyte solutions. In this approach, the simulation box must be large enough to mimic a bulk electrolyte reservoir (see the Supporting Information document for further details). We have monitored this condition, obtaining the desired bulk electrolyte concentration with an error of less than 1%. In our simulations, the ions are represented by the primitive model (i.e., hard spheres with point charges in their centers), and the solvent is modeled as a continuum, characterized by a uniform dielectric constant, which can capture some ion-specific effects at the surfaces by modifying ion sizes.⁴⁶ The immiscible liquids in contact are nitrobenzene and water, with dielectric constants $\epsilon_O = 34.8$ and $\epsilon_W = 78.4$, respectively. The two electrolytes studied at room temperature, $T = 298$ K, are the LiCl inorganic ions of diameter 4.25 Å in water and the tetrabutylammonium tetraphenylborate (TBATPB) organic ions of diameter 8.5 Å in nitrobenzene, unless otherwise stated. A simulation box of volume $2HL^2$, with periodic boundary conditions imposed along the y and z directions and a finite length of $2H$ along the x axis, is considered (see Figure 1). The dielectric interface is

modeled as an uncharged hard wall at the center of the simulation box at $x = 0$ with the assumption that there is no ion transfer between the two phases. In addition, two uncharged hard walls are located at $x = -H$ and $x = H$. In the absence of ionic transfer, the formed liquid–liquid interface is the so-called ideally polarizable ITIES in electrochemistry.^{6,41,42} A mean field calculation suggests that the ion transfer should be negligible for weak/moderate Galvani potentials if we take into account the experimental values of the standard Gibbs energy of transfer of Li^+ , Cl^- , TBA^+ , and TPB^- from water to nitrobenzene (see the Supporting Information document for further details). For high Galvani potentials, this hypothesis should still hold if the nitrobenzene is replaced by another solvent with higher standard Gibbs energies of transfer for the organic ions from oil to water, and for the inorganic ions from water to oil.

In the primitive model, the interionic potential can be separated into two contributions: one-body and two-body interactions. Each contribution can also be further split into an electrostatic and a hard sphere contribution. The two-body contribution for hard spheres is given by $S_{ij}(r_{ij}) = 0$ if particles i (at position $\vec{r}_i = (x_i, y_i, z_i)$) and j (at position $\vec{r}_j = (x_j, y_j, z_j)$) do not overlap and $S_{ij}(r_{ij}) = \infty$ otherwise. In this expression, the distance between the particles is $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}$. Let $\alpha = O, W$ and $\beta = O, W$ represent the solvents with dielectric constant ϵ_α and ϵ_β in which particles i and j reside, respectively. The two-body electrostatic interaction between particles i (with valence v_i) and j (with valence v_j) can be written as $U_{ij}^{\alpha\beta}(\vec{r}_{ij}) = l_{\alpha\beta}[(v_i v_j)/r_{ij}] + \delta_{\alpha\beta} l_{\alpha\beta}[(\epsilon_\alpha - \epsilon_\beta)/(\epsilon_\alpha + \epsilon_\beta)] [(v_i v_j)/r_{ij}]$, where α' is the complementary solvent to α , $\delta_{\alpha\beta}$ is the Kronecker delta, $l_{\alpha\beta} = e^2/([4\pi\epsilon_0(\epsilon_\alpha + \epsilon_\beta)]/2)$, e is the protonic charge, ϵ_0 is the vacuum permittivity, and $\vec{r}_{ij} = (-x_{ij}, y_{ij}, z_{ij})$ if the origin of the system is placed at the liquid interface according to the method of images.¹⁵

The hard sphere one-body contribution can be written as $S_i^\alpha(\vec{r}_i) = 0$, if the inorganic ions are in water and the organic ions are in nitrobenzene, respectively, and there is no overlapping between the ions and the hard planes located at $x = -H$, $x = 0$, and $x = H$. Otherwise, $S_i(\vec{r}_i) = \infty$. This definition constrains each electrolyte to be in only one solvent phase. The one-body electrostatic interaction corresponds to the self-image electrostatic energy defined as $U_i^\alpha(\vec{r}_i) = (l_{\alpha\alpha}/2)[(\epsilon_\alpha - \epsilon_{\alpha'})/(\epsilon_\alpha + \epsilon_{\alpha'})](v_i^2/r_{ii})$, where $\alpha = O, W$ is the medium in which ion i is located and α' is the complementary solvent.^{15,38} The one-body and two-body interactions can be written as $H_i^{\text{one-body}}(\vec{r}_i) = S_i^\alpha(\vec{r}_i) + U_i^\alpha(\vec{r}_i)$ and $H_{ij}^{\text{two-body}}(\vec{r}_{ij}) = S_{ij}(r_{ij}) + U_{ij}^{\alpha\beta}(\vec{r}_{ij})$. Thus, the total energy of the system can be defined as $H_T = \sum_{i=1}^N H_i^{\text{one-body}}(\vec{r}_i) + (1/2) \sum_{i=1}^N \sum_{j=1}^N H_{ij}^{\text{two-body}}(\vec{r}_{ij})$, where $i \neq j$, and N is the total number of particles. Electrostatics were properly included via Torrie and Valleau's charged-sheets method⁴⁷ with Boda et al.'s modification.⁴⁸

Let us consider that x_0 is a distance far enough away from the dielectric discontinuity, at which the electrolyte can be considered in its bulk state, but which is shorter than half of the length of the simulation box, H , in its finite dimension (see schematic representation in Figure 1). The excess surface charge density in the nitrobenzene can be then defined as $\sigma_O = \int_{-x_0}^0 \sum_{i=\text{TBA}^+, \text{TPB}^-} \rho_i(x) e z_i dx$, where $\rho_i(x)$ is the density of ions per volume unit of species i . This value is exactly the opposite of the excess surface charge density in water, $\sigma_W = \int_0^{x_0} \sum_{i=\text{Li}^+, \text{Cl}^-} \rho_i(x) e z_i dx = -\sigma_O$, due to the electroneutrality condition. As such, the excess surface charge densities in both liquid media can be controlled in simulations by varying only σ_W (or σ_O). If

the electrical double layer is determined in both phases from simulations or theory, it is possible to calculate the corresponding electric field near the ITIES and the Galvani potential. With this in mind, let us define the integrated excess surface charge density as $\sigma(x) = \int_{-x_0}^x \sum_i \rho_i(x) e z_i dx$, for $i = \text{TBA}^+$, TPB^- , Li^+ , Cl^- and $x \leq x_0$. Some particular cases of this expression are $\sigma(0) = \sigma_O$ and $\sigma(-x_0) = \sigma(x_0) = 0$. Applying the Gauss law, it can be shown that the electric field (perpendicular to the dielectric discontinuity) can be written as $E(x) = \sigma(x)/(\epsilon(x)\epsilon_0)$, where $\epsilon(x) = \epsilon_O$ if $x < 0$ and $\epsilon(x) = \epsilon_W$ if $x > 0$. Notice that from this definition, the continuity of the perpendicular electric displacement $D_O^\perp = D_W^\perp = \lim_{x \rightarrow 0^-} \epsilon_O E(x) = \lim_{x \rightarrow 0^+} \epsilon_W E(x)$ is fulfilled, in agreement with the Maxwell equations.^{15,38} The mean electrostatic potential difference (or Galvani potential) can be then calculated from the electric field as $\Delta_O^W \Psi = -\int_{-x_0}^{x_0} E(x) dx$, where a zero value in the bulk of nitrobenzene has been taken as a reference.

If the relationship between the excess surface charge density and the Galvani potential is known, it is possible to calculate experimental properties typical of these charged systems, such as the interfacial surface tension, γ , by using the Lippmann equation, $\sigma_W = -(\partial\gamma)/(\partial\Delta_O^W \Psi)$, or the differential capacity, $C_d = (\partial\sigma_W)/(\partial\Delta_O^W \Psi)$.⁴⁰

In Figure 3, we show experimental results of the excess surface charge density between two immiscible monovalent

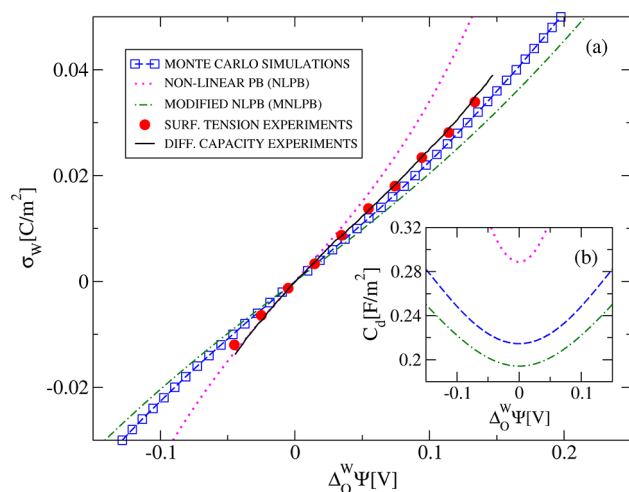


Figure 3. Excess surface charge density, σ_W (a), and differential capacity, C_d (b), as a function of the difference of the bulk electrostatic potential, $\Delta_O^W \Psi$. In nitrobenzene, the concentration of TBATPB is 0.1 M. In water, the concentration of LiCl is 0.1 M. The filled circles and solid line correspond to σ_W values obtained from experimental measurements of interfacial surface tension and differential capacity, respectively.⁴⁵ Empty squares and dashed lines correspond to MC results. Dotted and dotted-dashed lines are associated with the nonlinear Poisson–Boltzmann and the modified nonlinear Poisson–Boltzmann theories, respectively.

electrolytes.⁴⁵ In this system, the TBATPB electrolyte at a 0.1 M concentration in nitrobenzene and 0.1 M LiCl salt in water have been placed in contact as well as under the influence of an electric field. As a further consistency test, the excess surface charge density as a function of the Galvani potential obtained from the interfacial surface tension data was collated with that obtained from experimental polarographic differential capacitance measurements.⁴⁵ Both experimental approaches display an excellent agreement with each other, as shown in Figure 3.

Our MC simulation results, including polarization and ion correlations, show good agreement with the experimental results at the level of excess surface charge density and interfacial surface tension (not shown). In contrast, the classical NLPB theory predicts reasonable values only for small values of the Galvani potential, deviating significantly for larger electric fields. Interestingly, the MNLPB theory predicts reasonable values of excess surface charge density, interfacial surface tension (not shown), and differential capacity (see Figure 3b) for the same range of Galvani potential.

Despite the apparent similarity of the thermodynamic properties resulting from MC simulations and the MNLPB theory with experimental results, noticeable differences at the level of ionic density can be observed near the dielectric discontinuity, as is shown in Figure 4. Here, we observe that for

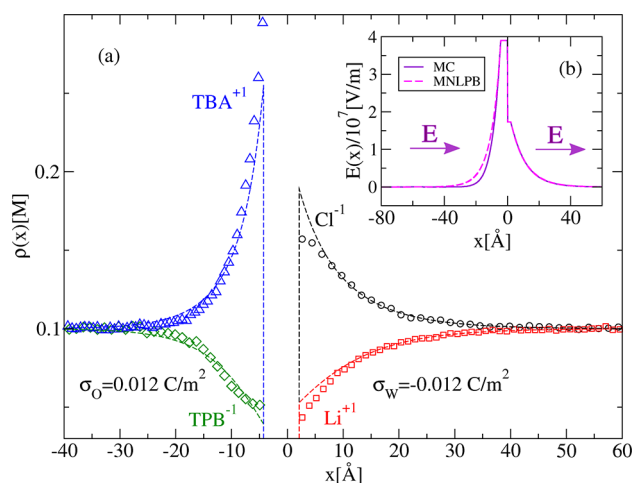


Figure 4. Ion density profiles (a) and electric field (b) as a function of the distance to the dielectric discontinuity for TBATPB 0.1 M in nitrobenzene ($x < 0$) and LiCl 0.1 M in water ($x > 0$). The excess surface charge density in water is $\sigma_w = -0.012 \text{ C/m}^2$. In the main figure, empty symbols correspond to MC simulations, and the dashed lines denote results from the modified nonlinear Poisson–Boltzmann theory (MNLPB). In the inset, the solid and dashed lines correspond to MC and MNLPB results, respectively. Here, and in the rest of the figures, the interface between nitrobenzene and water is located at $x = 0$.

an excess surface charge density $\sigma_w = -0.012 \text{ C/m}^2$ in water, the most significant difference occurs in the contact values for all ionic species. In particular, MC simulations demonstrate greater absorption of TBA^{+1} in nitrobenzene than expected from the MNLPB theoretical calculations. As a result, a larger electrostatic screening of the aqueous negative excess surface charge density, $\sigma_w < 0$, occurs in the nitrobenzene phase. This is observed in Figure 4b, where MC simulations display a lower electric field for negative distances to the dielectric discontinuity. The enhanced attraction of TBA^{+1} and TPB^{-1} is a consequence of ion correlations and polarization effects that are completely neglected in the MNLPB theory.

Given that the dielectric constant of nitrobenzene is less than half that of water at room temperature, and that the size of organic ions is approximately twice the size of the inorganic ones, it would be possible to expect strong polarization and ion correlation effects near the dielectric discontinuity at higher electrostatic coupling, even in the case of monovalent ions. This is indeed illustrated in Figure 5, in which the bulk ion concentration of the system discussed in Figure 4 has been

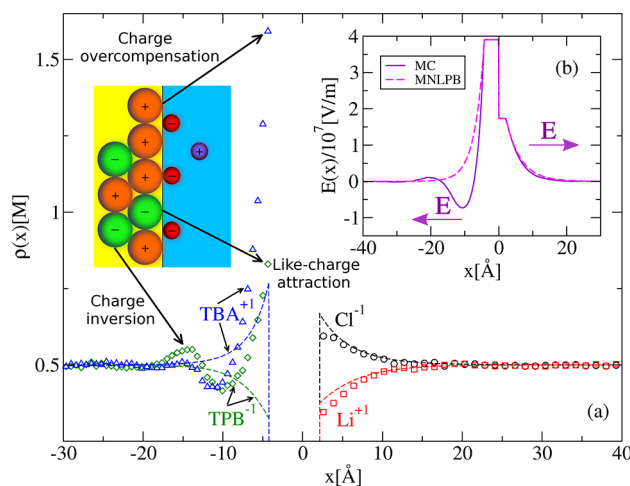


Figure 5. The same as in Figure 4 but for a 0.5 M TBATPB electrolyte in nitrobenzene and a 0.5 M LiCl electrolyte in water.

augmented 5-fold. The discrepancies previously observed between the contact values predicted by MC simulations and the MNLPB theory for all ionic species still persist and are remarkably magnified in the nitrobenzene phase. For example, it is seen in this case that TBA^{+1} ions are significantly more strongly attracted to the dielectric discontinuity than the predicted values by the MNLPB theory in nitrobenzene. Even more remarkable is the like-charge attractive behavior displayed by TPB^{-1} ions, which are significantly adsorbed to the dielectric interface, despite the fact that they have the same sign as the negative excess surface charge density in the aqueous phase, $\sigma_w < 0$. In both instances, ionic layering is displayed by the organic ions. Furthermore, there exists a region in which the local ionic density of organic anions (co-ions of $\sigma_w < 0$) is larger than that of the organic cations (counterions of $\sigma_w < 0$). This inversion of the roles between counterions and co-ions in the electrical double layer is precisely the so-called charge inversion. In addition, a significant inversion of the electric field in the nitrobenzene phase (approximately one-fifth of the magnitude of the electric field at the interface for the current conditions) can be seen in the Figure 5b.

The significant deviations from the classical Poisson–Boltzmann picture can be attributed to the polarization effects and ion correlations (including excluded-volume effects) consistently included in our MC simulations. The relevance of excluded-volume effects to the appearance of charge overcompensation has been well established in the absence of polarization effects for colloidal systems.^{17,20–22,25} Nevertheless, at the ITIES, the enhanced adsorption of organic ions to the liquid interface can also be promoted by polarization effects and electrostatic between-layer ion correlations. The former are caused by image charges in the aqueous solvent, while the latter are due to the interaction between organic ions in nitrobenzene with inorganic ions in water. Excluded-volume effects and electrostatic coulomb interactions are usually coupled in a nontrivial manner, even in the absence of polarization effects, as has been discussed elsewhere.^{17,20–22,25} Thus, two additional independent MC simulations are performed at room temperature, $T = 298 \text{ K}$, to determine how the charge overcompensation in the oil phase is impacted by the ionic excluded volume, polarization effects, and electrostatic between-layer ion correlations. In the first simulation, a 0.5 M equal-sized LiCl electrolyte of diameter 4.25 Å in water is

placed in contact with an infinite, positively charged plate of surface charge density $\sigma_{\text{wall}} = 0.012 \text{ C/m}^2$. In the second simulation, a 0.5 M equal-sized TBATPB electrolyte of diameter 8.5 Å in nitrobenzene is placed in contact with an infinite, negatively charged plate of surface charge density $\sigma_{\text{wall}} = -0.012 \text{ C/m}^2$. A fixed number of counterions is added to each independent system to satisfy the electroneutrality condition (see the corresponding graphical representation in Figure 6). Notice that excluded-volume effects are included

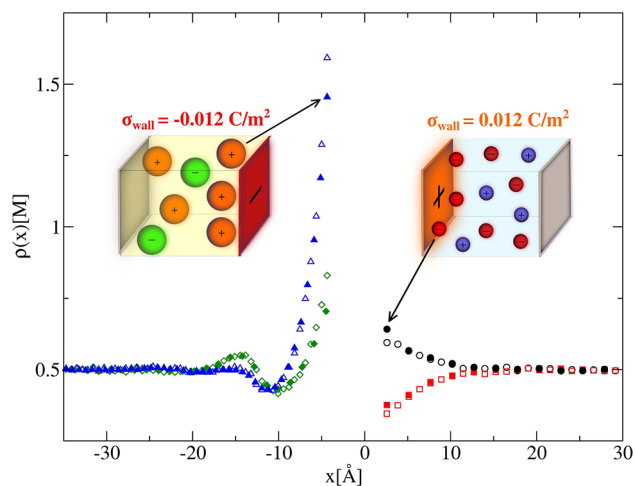


Figure 6. Ion density profiles as a function of the distance to the dielectric discontinuity for TBATPB 0.5 M in nitrobenzene ($x < 0$) and LiCl 0.5 M in water ($x > 0$). Empty symbols correspond to the MC simulation data already shown in Figure 5, in which excluded-volume effects, between-layer ion correlations, and polarization effects are taken into account consistently. Filled symbols correspond to two independent MC simulations in which polarization effects and between-layer ion correlations are neglected, as depicted in the insets (see main text for further details).

consistently in these additional MC simulations in the primitive model. Nevertheless, this approach completely neglects polarization effects and electrostatic between-layer ion correlations. In Figure 6, the resulting electrolyte density profiles for these two independent simulations are collated with the MC results already displayed in Figure 5, where ion correlations and polarization effects are included consistently. From this comparison, it is observed that the electrolyte profiles are very similar in both instances, except near the dielectric discontinuity. Moreover, the contact value of organic ions in nitrobenzene is higher if polarization effects and electrostatic between-layer ion correlations are included. Inorganic ions in water display the opposite behavior, as is observed in Figure 6. This trend is consistent with the attraction (repulsion) that charged particles in nitrobenzene (water) experience toward the dielectric interface due to the presence of image charges in the water (nitrobenzene) phase. In addition, as Figure 7 shows, the charge inversion and the inversion of the electric field already displayed in Figure 5 disappear if the diameter of organic ions in oil is equated with the diameter of inorganic ions in water, 4.25 Å. This occurs even in the presence of polarization effects and electrostatic between-layer ion correlations. Thus, we conclude that the charge overcompensation and inversion of the electric field displayed by our MC simulations in the oil phase is mainly driven by the excluded-volume effects associated with the large organic ions.

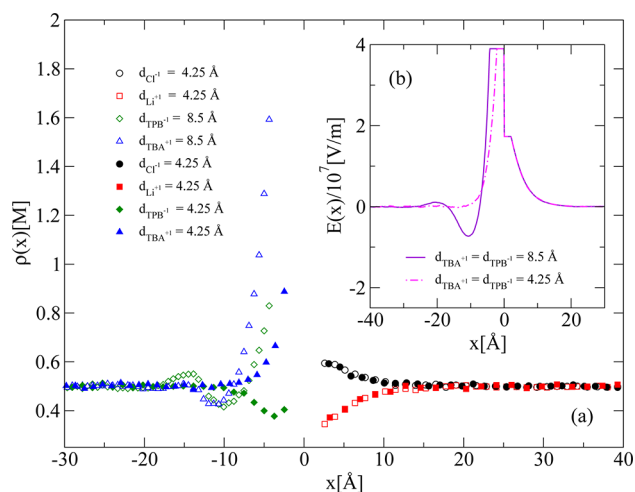


Figure 7. Ion density profiles (a) and electric field (b) as a function of the distance to the dielectric discontinuity for 0.5 M TBATPB in nitrobenzene ($x < 0$) and 0.5 M LiCl in water ($x > 0$). The empty symbols in (a) and the solid line in (b) correspond to the MC simulation data already shown in Figure 5. The filled symbols in (a) and the dotted-dashed line in (b) correspond to setting the size of organic ions in nitrobenzene equal to the size of inorganic ions in water. Excluded-volume effects, between-layer ion correlations, and polarization effects are included consistently in both instances.

Polarization effects and electrostatic between-layer ion correlations produce an additional short-ranged effective interaction, which is particularly relevant to the interfacial behavior of charged particles close to the ITIES.

Finally, in order to observe the impact of the inversion of the electric field on some experimentally measurable thermodynamic properties, we plot the excess surface charge density and differential capacity in Figure 8 as a function of the Galvani potential, under the same conditions as those used in Figure 3, except that the total concentration has been augmented 5-fold. As can be observed, the deviation of the NLPB and MNLPB

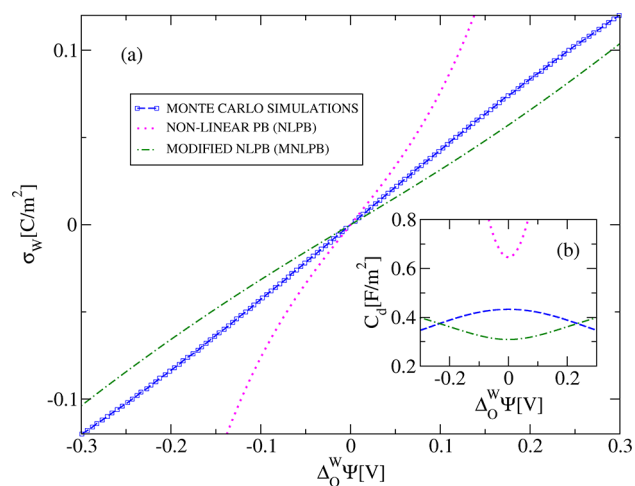


Figure 8. Excess surface charge density, σ_w (a), and differential capacity, C_d (b), as a function of the difference of the bulk electrostatic potential, $\Delta_0^w\Psi$. In nitrobenzene, the concentration of TBATPB is 0.5 M. In water, the concentration of LiCl is 0.5 M. Empty squares and dashed lines correspond to MC results. Dotted and dotted-dashed lines denote results from the nonlinear Poisson–Boltzmann and the modified nonlinear Poisson–Boltzmann theories, respectively.

theories from MC data is more significant in this instance. In fact, the differential capacity obtained from MC simulations displays a maximum at the point of zero charge. This result, which contrasts with the typical minimum predicted by the classical NLPB and MNLPB theories, should be detectable macroscopically in differential capacity experiments.^{40–42} Additionally, our MC simulations suggest that this phenomenon is associated with the occurrence of the inversion of the electric field, like-charge attraction, and charge inversion at the ITIES.

In summary, we demonstrate in this work that excluded-volume effects associated with large organic ions in oil can induce charge inversion, like-charge attraction, and an inversion of the electric field in the vicinity of the interface separating two immiscible electrolytes, even in the presence of only monovalent ions. These effects are significantly enhanced near the dielectric discontinuity by polarization effects and electrostatic between-layer ion correlations. It should be possible to detect them at the ITIES using X-ray reflectivity measurements.^{49–52} In fact, these effects could be further enhanced by either lowering the solvent dielectric constant or by increasing the valence of the ionic species. Charge inversion at the ITIES in the absence of ion transfer is analogous to that observed in both aqueous colloidal suspensions and strongly charged polyelectrolytes in the presence of high concentrations of multivalent ions,^{33–37} as well as on charged surfaces in the presence of divalent salts including the hard core of the ions in the analysis.^{17,29} Nevertheless, to the best of our knowledge, this is the first time charge inversion has been predicted at the interface between two liquid media. On the other hand, it is worth mentioning that our coarse-grained approach is easily generalizable to more complex scenarios and goes beyond the classical Poisson–Boltzmann picture from first principles (i.e., nonadjustable parameters are required). Furthermore, our treatment is economical and simple enough that it allows us to study systems that we could not simulate using explicit solvent particles.

One interesting consequence of the concentration dependence of the inversion of the electric field near the ITIES is the possibility of reversibly trapping and releasing small charged nanoparticles or biomolecules, not only by varying the electric field applied at the ITIES but also by controlling the electrolyte concentration. This possibility stresses the relevance of ion correlations and polarization effects at electrified liquid–liquid interfaces, which are completely neglected in the widely used Poisson–Boltzmann theory. Notice that these effects are also relevant when the electrical double layer is formed in the absence of an electric field, that is, when an excess charge appears at both sides of a liquid–liquid interface due to the ionic transfer between both immiscible liquids. In this instance, the difference in the ionic solubility in both solvents is the driving mechanism for the formation of the electrical double layer at the liquid interface.^{2,3} Macroscopically, this phenomenon is observed as an ionic partitioning, which could be seen as a difference in the ionic concentration of an electrolyte inside and outside a cell under typical physiological conditions.

Within the NLPB theory, macro-ion adsorption at the ITIES has been studied analytically in the absence of an electric field.³ When we include the effects studied here, it would be interesting to analyze a more realistic scenario in which ions and small charged nanoparticles can cross the dielectric interface.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of the Monte Carlo implementation and mean field calculations of the ion partitioning in water/nitrobenzene systems are provided. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: m-olvera@northwestern.edu.

Notes

The authors declare no competing financial interest.

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