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Adsorption Profiles and Solvation of Ions at Liquid-Liquid Interfaces and Membranes

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1. Introduction

1.1 Motivations

Electro-chemical and physical processes at liquid-liquid interfaces and across membranes are broadly important in many systems. These processes are relevant for cellular and physiological systems (34; 18), biotechnology (12), everyday applications such as portable batteries, and even in speculative scenarios for the origin of life (31). Biologically, ion transport is essential for the creation of transmembranous and transcellular electric potential, fluid transport, and maintaining cellular volume (1); the failure in the regulation of the above would lead to such conditions as septicemia induced pulmonary edema, electrolyte abnormalities in pyelonephritis of early infancy, hypovolemia and hyponatremia (8). In the chemistry community, there has been a long interest in the rich electrochemistry associated with interfacial charge transfer that is important in, for example, hydrometallurgy and two-phase electrolysis (36).

The interaction of ionic species, particularly proteins and nucleic acids, with interfaces and membranes has become exceedingly important in our understanding of biological systems (34) and in processes such as genetic transformation, since the latter specifically involves DNA crossing cellular membranes. Moreover, important biomolecular processes take place more efficiently at heterogeneous media than in homogeneous systems, as demonstrated in the example of DNA renaturation at water-phenol interfaces (12). Therefore, the study of ionic profiles at interfaces also leads to a better understanding of these various biomolecular processes. In general, *in situ* experimental techniques are required to evaluate interface phenomena. For example, x-ray-standing waves measurements provide the profile of ions (2; 3) and also more recently of nucleic acids (4; 21), both along hard surfaces in aqueous solutions (29; 38; 33; 20). Recent experimental techniques have detected ion density profiles at liquid-liquid interfaces with the use of x-ray reflectivity measurements (23; 24). These experiments provide direct knowledge of electrostatic interactions among ionic species

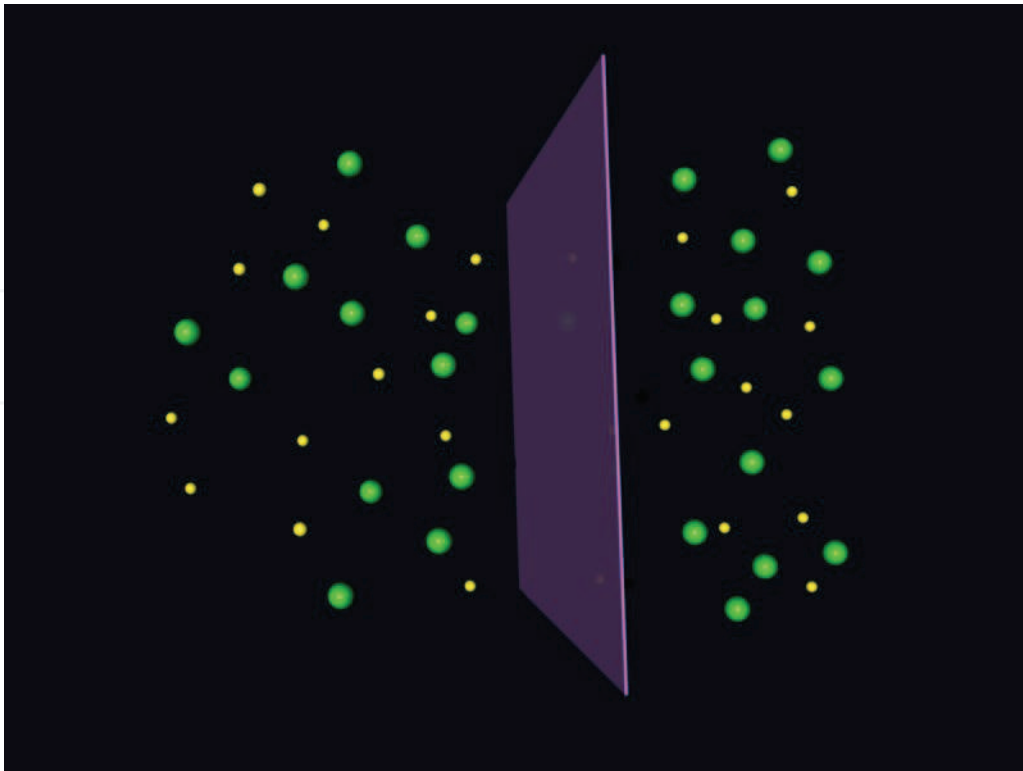


Fig. 1. A single charged plate in salt solution. The system is symmetric with respect to $z = 0$. Without loss of generality, the charged plate is assumed to have a positive surface-charge density σ , with counterions (yellow) and coions (green) present on both sides of the plate.

at interfaces and can be easily extended to analyze the adsorption of proteins and nucleic acids at liquid-liquid interfaces.

In their experimental study (23; 24), Luo *et al.* demonstrated that the predictions from Gouy-Chapman theory did not match well with x-ray reflectivity measurements, presumably due to its neglect of molecular-scale structure in the liquid solution. To better fit their experimental data and the free-energy profile of the ions, the authors instead formally introduce an *ad hoc* term in the electrostatic energy, which presumably includes effects from short-range correlations and which can be theoretically approximated by the potential of mean force, experienced by single ions near the interface, obtainable from molecular dynamics (MD) simulations. Notwithstanding the absence of a fundamental theoretical framework for the aforementioned system of a planar liquid-liquid interface, progress has been made with phenomenological approaches, including the example of a Ginzburg-Landau theory of ions solvation and their distribution around an interface (32).

1.2 Statement of problem

In this work, we will present a top-down thermodynamic formulation for the system of dissolved ions in immiscible polar-binary mixtures. In our formulation, we can naturally incorporate details such as the interaction between ions and background solvents, at the mean-field level, via the Born approximation (25; 26). We will then relate the various hitherto phenomenological parameters, namely, the bulk ion densities in each phase as well as the distribution potential across the interface, to the fundamental parameters of our system that include the dielectric constant of each phase and the size and charge of dissolved ions. In addition, the full nonlinear Poisson-Boltzmann equation follows from a variational principle

and can be analytically solved for the electrostatic potential and for the ion density profiles without further approximations. Electro-neutrality, in our formulation, simply manifests from consistency requirement with thermodynamics.

We emphasize that to ensure full analytical tractability, we have not included the full effects of such features as finite ion-size interaction or correlation effects beyond mean-field. While research works that investigate the aforementioned effects as well as other specific types of component interactions are present elsewhere (43; 28; 11), the exact results contained in this work enable a concise quantitative assessment of the importance of finite-ion size interaction and correlation effects in these systems predicted by more complex models.

1.3 Phenomenology

As an important consequence of thermodynamics and electrostatics, we will demonstrate the physics of *differential adsorption* of ions near an interface, which is a general phenomenon occurring between two phases of different dielectric medium wherein ions are selectively driven into confinement near, or expulsion from, the interface based on their charge polarity. In particular, we will consider examples involving both neutral and charged membranes partitioning two chemically different environments. Given the long-standing interest in this topic across diverse disciplines and the many still unresolved issues, it is inevitable that there exists many prior works on the subject with very different emphases and approaches. For example, chemists have traditionally focussed on detailing the microscopic molecular interactions between ions, solvents, and the different types of membranes (36; 19; 7). For the same reason, there exists considerable varied usage of terminology (27) regarding similar concepts. For clarity, we will henceforth explicitly consider in this work only permeable membranes. In addition, to establish notations and conventions, we will refer to the potential gradient across the interface, due to the different existing bulk ions densities in the two phases, as the distribution potential Φ_D . The cases of neutral and charged membranes (regardless of polarity) would correspond to the terminology of nonpolarizable and polarizable liquid-liquid interfaces, respectively, as discussed in chemistry literature. While partial results regarding these systems have been derived in various contexts and guises, our present work represents a unifying framework in a complete, mean-field thermodynamic formulation for the system of dissolved ions in immiscible polar binary mixtures, within which we can derive rigorous relations between the different phenomenological parameters of the system that would otherwise be unrelated when treated in the context of electrostatics alone.

1.4 Chapter organization

In what follows, we will present, in section II, our thermodynamic formalism in terms of a mean-field Ω -potential and derive, via variational principle, the relevant electrostatics and thermodynamic constraints in our system. We will then proceed in section III to consider full solutions to the nonlinear Poisson-Boltzmann equation in this new context and demonstrate the general mechanism of differential adsorption of ions across a liquid-liquid interface. Section IV concludes our paper.

2. Thermodynamics of ion solvation

2.1 Variational approach

In this section, we construct a thermodynamic potential to describe the equilibrium properties of salt ions dissolved in a pair of immiscible fluids. These fluids can be homogeneous or of two respective phases of a segregated mixture. For each phase $\alpha = \{A, B\}$, we indicate

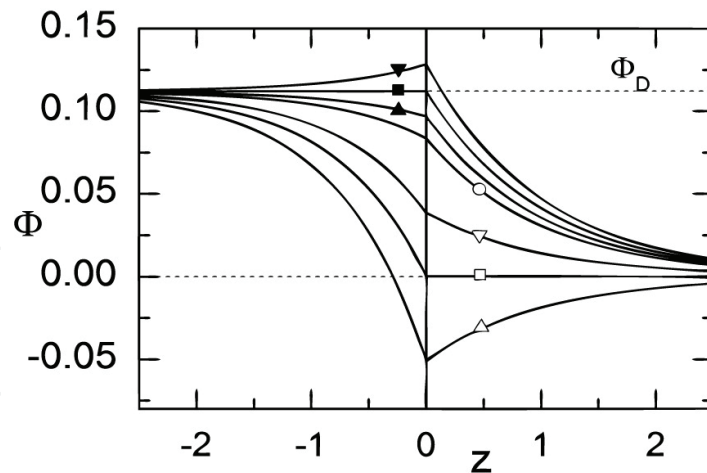


Fig. 2. Comparison of the electrostatic potential across a positively and negatively charged membrane in nitrobenzene/water solution at 68F. The surface charge densities are quoted in units of $\epsilon_A \kappa_A$ and $\Phi'_D \approx 0.112$. The potential is plotted for $\sigma = -1.5(\triangle)$, $\sigma = -0.93(\square)$, $\sigma = -0.5(\nabla)$, $\sigma = 0(\circ)$, $\sigma = 0.15(\blacktriangle)$, $\sigma = 0.32(\blacksquare)$, $\sigma = 0.5(\blacktriangledown)$.

the dielectric constant as ϵ_α and denote the ion number bulk densities by $\rho_{0,i}^\alpha$ for each of the ion species i . Far away from the interface, there is a relative potential difference between the phases, known as the distribution potential Φ_D . As we demonstrate below, a number of relations between these bulk quantities arise from the condition of equal chemical potential for each of the species: $\mu_i^A = \mu_i^B$.

2.2 Ω -potential

The thermodynamics with this equilibrium condition are formulated by constructing the Ω -potential (equals to $-PV$ where P is the pressure and V is the volume) for each phase α as follows:

$$\Omega^\alpha = \Omega_{el}^\alpha + \Omega_{th}^\alpha + \Omega_{sol}^\alpha, \quad (1)$$

where we have divided the potential into a contribution due to electrostatics Ω_{el} , to thermodynamics Ω_{th} , and to solvation interactions Ω_{sol} . In what follows, all energy quantities will be measured in units of $k_B T$, all length scales in units of the Bjerrum length $\ell_B = e^2/k_B T$, and all ionic charges quoted as multiples of the fundamental electron charge e . The electrostatic part delineates the free-energy dependence on the dielectric constant ϵ^α and imposes Gauss' law via a Lagrange-multiplier constraint using the electrostatic potential Φ :

$$\Omega_{el}^\alpha = \int \frac{\epsilon_\alpha}{8\pi} |\mathbf{E}^\alpha(\mathbf{x})|^2 - \int \Phi^\alpha \left[\nabla \cdot \frac{\epsilon_\alpha \mathbf{E}^\alpha(\mathbf{x})}{4\pi} - \sum_i Z_i \rho_i^\alpha - \rho_F \right]. \quad (2)$$

The total charge density is obtained from the charges of free ions and a contribution ρ_F from fixed charges. We will only consider the case where these charges are present at the interface between media. As these charges are not present in the bulk, they will only contribute to terms determining the boundary conditions for the fields and concentrations.

On the other hand, the thermodynamic contribution consists of the entropy associated with the ions, treated as point particles, in solution as well as their corresponding chemical

potentials

$$\Omega_{th}^{\alpha} = \int \left(\sum_i \rho_i^{\alpha}(\mathbf{x}) \log \left[\frac{\rho_i^{\alpha}(\mathbf{x})}{e} \right] - \sum_i \mu_i^{\alpha} \rho_i^{\alpha}(\mathbf{x}) \right) \quad (3)$$

where μ_i^{α} are the chemical potentials of the species within each phase, and they will be specified by the equilibrium constraint that they should be equal across the interface.

Lastly, the solvation interaction between the ions and the respective polar solvent in each phase is modeled by the mean-field Born approximation of polarization;

$$\Omega_{sol}^{\alpha} = \int \sum_i g_i^{\alpha} \rho_i^{\alpha}, \quad (4)$$

where the Born polarization energy g_i^{α} is given by

$$g_i^{\alpha} = \frac{Z_i^2 e^2}{8\pi \epsilon^{\alpha} R_i}, \quad (5)$$

for ions with valency Z_i and radius R_i . As expected, we note that an increase in dielectric constant ϵ^{α} or in the ionic radius R_i for a given valence Z_i facilitates solvation of ions in polar mixtures and leads to an overall lower Born energy. Consequently, Born's model predicts a larger solubility for anions (which are generally larger in size due to reduction in redox chemistry) than for the corresponding cations. As we will see in subsequent sections, both charge properties and the size factor play an important role in the physics of ion solvation near a boundary interface.

2.3 Dimensional analysis and charge neutrality

To examine the consequence of our thermodynamic formulation of ion solvation in immiscible polar binary mixtures, we first perform dimensional analysis on the electrostatic term. We note that the Ω -potential is an extensive quantity by construction: $\Omega_{el}^{\alpha} \propto V$, where V is the volume of the overall system. For the immiscible binary mixtures consisting of one positive and one negative ionic species, respectively, we define the total charge density $\rho_c^{\alpha}(\mathbf{x}) = |Z_+| \rho_+^{\alpha}(\mathbf{x}) - |Z_-| \rho_-^{\alpha}(\mathbf{x})$ and assume that it has a nonvanishing zero mode and observe that its contribution to the energy density is $(\rho_{0c}^{\alpha})^2 \int d\mathbf{x} \int d\mathbf{y} \frac{1}{|\mathbf{x}-\mathbf{y}|}$. Based on the dimensionality of the various factors within the integral, it is straightforward to see that $\Omega_{el}^{\alpha}|_{\mathbf{k}=0} \propto V^{5/3}$, for $\rho_{0c}^{\alpha} \neq 0$, which is inconsistent with the thermodynamic construction of the extensive Ω -potential. Therefore, the requirement of consistency with equilibrium thermodynamics automatically imposes charge neutrality in the overall system; namely, $\rho_0^{\alpha} = 0$ (we note that this electroneutrality condition in linearized approaches appears as a restriction to avoid the divergence in the potential (9)).

2.4 Variational principle to system equations and constraints

From Eq. (1), variation with respect to the electric field \mathbf{E}^{α} , the Lagrange multiplier (electrostatic potential) Φ^{α} , and the number density ρ_{\pm}^{α} readily yields the relations

$$\delta \mathbf{E}^{\alpha} : \quad \mathbf{E}^{\alpha}(\mathbf{x}) = -\nabla \Phi^{\alpha}(\mathbf{x}), \quad (6)$$

$$\delta \Phi : \quad \nabla \cdot \left[\frac{\epsilon^{\alpha} \mathbf{E}^{\alpha}(\mathbf{x})}{4\pi} \right] = \sum_i Z_i \rho_i^{\alpha}, \quad (7)$$

$$\delta \rho_i^{\alpha} : \quad \mu_i^{\alpha} = \log \rho_i^{\alpha}(\mathbf{x}) + Z_i \Phi^{\alpha}(\mathbf{x}) + g_i^{\alpha}. \quad (8)$$

We note that Eqs. (6) and (7) simply reproduce, respectively, the expressibility of the electric field \mathbf{E} in terms of a scalar potential Φ^α and the Gauss' law in electrostatics. The last relation in Eq. (8) provides an explicit expression of the chemical potential for each phase in terms of its respective *input* parameters such as the dielectric constants and ion sizes. It is now obvious that the thermodynamic condition of equal chemical potentials across the different phases α would provide further constraints on the respective bulk ionic densities.

To use these relations, we first introduce notation for the limiting values of our quantities away from the interface, i.e. in the bulk. For the potential, we define $\Phi_\infty^A = \Phi_D$ and $\Phi_\infty^B = 0$. The difference $\Phi_\infty^A - \Phi_\infty^B = \Phi_D$ is the Donnan or distribution potential. The particle densities achieve a uniform value away from the interface, that is their bulk concentration, denoted by $\rho_{0,i}^\alpha$. The minimum of the potential occurs when the electric field away from the interface approaches zero, and this in turn is equivalent to the condition of overall electroneutrality:

$$\sum_i Z_i \rho_i^\alpha = 0. \quad (9)$$

When we consider the equilibrium of the joint system, minimization of the total Ω potential requires the equality of the chemical potential of each species:

$$\mu_i^A = \mu_i^B. \quad (10)$$

The equations (6-8) are equivalent to the Poisson-Boltzmann equation. In addition, a useful form of the Boltzmann distribution for the equilibrium ionic profiles follows from Eq.(8):

$$\rho_i^\alpha(\mathbf{x}) = \rho_0^\alpha \exp[-Z_i(\Phi^\alpha(\mathbf{x}) - \Phi_\infty^\alpha)]. \quad (11)$$

The Poisson-Boltzmann equation and the Boltzmann distribution are often taken as the starting points for most analysis presented in literature on these systems. We note that they follow naturally from our fundamental Ω -potential [Eq. (1)]. Many other properties of electrolyte systems can furthermore be derived by suitable analysis of this functional. The properties of osmotic pressure, for example, have been extensively discussed in this framework (6).

We now obtain explicit solutions for a single symmetric salt dispersed in two media. In this case, the ions have equal charge magnitudes which we take as $Z_\pm = \pm 1$. We use the indices $i = +, -$ for these species and note that, due to the electroneutrality condition, their bulk densities are equal. This bulk density will be denoted as $\rho_0^\alpha = \rho_{0,+}^\alpha = \rho_{0,-}^\alpha$. Taking the logarithm of Eq. (11) readily yields

$$\log \rho_\pm^A(\mathbf{x}) \pm \Phi^A(\mathbf{x}) = \log \rho_0^A \pm \Phi_D \quad (12)$$

Again, a similar expression to Eq. (12), modulus the term containing the distribution potential, applies to the less polar phase B. Now upon substituting Eq. (12) and the corresponding expression for phase B into Eq. (8), as well as imposing equal chemical potentials across boundary, we obtain the following relations

$$\log \rho_0^A + \Phi_D - g_+^A = \log \rho_0^B - g_+^B, \quad (13)$$

$$\log \rho_0^A - \Phi_D - g_-^A = \log \rho_0^B - g_-^B. \quad (14)$$

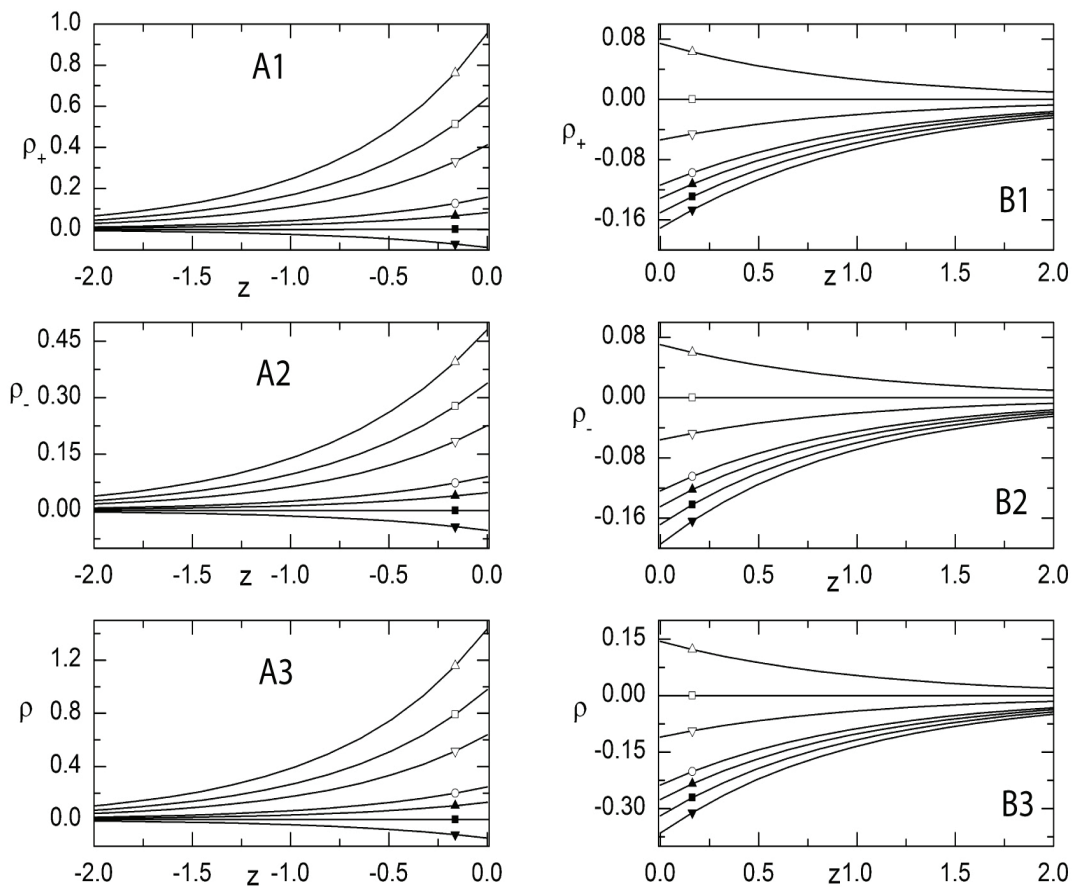


Fig. 3. Comparison of the ion distributions of ions in the two polar phases, $A (z < 0)$ and $B (z > 0)$ characterized by ϵ_A and ϵ_B , respectively, when the surface density of the interface is $\sigma = -1.5(\triangle)$, $\sigma = -0.93(\square)$, $\sigma = -0.5(\nabla)$, $\sigma = 0(\circ)$, $\sigma = 0.15(\blacktriangle)$, $\sigma = 0.32(\blacksquare)$, $\sigma = 0.5(\blacktriangledown)$. (1) Cations. (2) Anions. (3) Total charge density $\rho = \rho_+ + \rho_-$. The curves are presented in separate plots because of difference in concentrations. For this particular plot, we use a range of surface charge densities σ in units of $\epsilon_A \kappa_A$ and $\Phi'_d = 0.112$ for the nitrobenzene/water solution at 68F.

We can now take the sum and difference of the two equations to obtain the relations

$$\log \rho_0^A + \bar{g}_A = \log \rho_0^B + \bar{g}_B, \tag{15}$$

$$2\Phi_D + \Delta g_A = \Delta g_B, \tag{16}$$

where we have defined the average Born polarization energy over ions of both charge polarity, $\bar{g}_\alpha = g_{\alpha+} + g_{\alpha-}$, and the corresponding differential Born energy, $\Delta g_\alpha = g_{\alpha+} - g_{\alpha-}$ between the cations and anions. In terms of these two quantities, we can relate the bulk ion densities and the distribution potential to the dielectric constants ϵ_α in each phase via

$$\frac{\rho_0^A}{\rho_0^B} = e^{\bar{g}_B - \bar{g}_A} = e^{-\Delta g_\alpha} \tag{17}$$

$$\Phi_D = -\frac{1}{2} \Delta_\alpha \Delta g \tag{18}$$

where $\Delta_\alpha \Delta g = \Delta g_A - \Delta g_B$.

2.5 Summary

In summary, we have thus shown in Eq. (17) that the ratio between the bulk densities $\rho_{0,\pm}^\alpha$ is related to the difference of the average Born solvation energy between the two phases, while in Eq. (18) the distribution potential Φ_D is related to the difference in the differential Born energy between ion types in the two phases. We note that even though the above formulation has been done for a neutral liquid-liquid interface wherein the charge distribution of the system resides completely amongst the dissolved ions in the bulk, it is straightforward to generalize to the case where a surface charge exists on the interface itself.

To determine the equilibrium ion density profiles $\rho_\pm^\alpha(\mathbf{x})$ as well as the electrostatic potential $\Phi(\mathbf{x})$, it remains for us to solve the Poisson equation [Eq. (7)] after applying the integrability condition [Eq. (6)] as well as the thermodynamic ansatz of the Boltzmann distribution for the ion density [Eq. (11)]. We will illustrate with two classes of examples in the subsequent section involving non-polarizable (neutral) but permeable membranes as well as polarizable (charged) membranes.

3. Electrostatic phenomenology of differential adsorption

3.1 Case study defined

As mentioned in the Introduction, it is now feasible to make precise experimental detection of the ion distributions near liquid-liquid interfaces (23; 24). It has been found that while the mean-field Poisson-Boltzmann framework provides a generally good description for the ion profiles that matches well with experimental results obtained by x-ray structural measurements, the linearized Guoy-Chapman approximation is insufficient for most general cases (24). For completeness, we will now illustrate the solution to the Poisson-Boltzmann equation for the case when the membrane across the two dielectric media is charged (polarizable), including the particular interesting case of the neutral (non-polarizable) interface. Furthermore, our liquid-liquid interface is treated as an infinite two-dimensional plane so that we do not need to consider surface terms. We thus essentially reduce our system to a one-dimensional problem. Denoting the lateral distance from the membrane by z , we will now formulate the full non-linear Poisson-Boltzmann equation with the proper boundary conditions and obtain the corresponding electrostatic potential $\Phi^\alpha(z)$ and ion density profiles $\rho_\pm^\alpha(z)$ in each phase α .

3.2 Analytic mean-field formulation

To begin, we analytically formulate our system in which the two phases A and B are in equilibrium, where each phase is characterized by its respective constant dielectric permittivity ϵ_A and ϵ_B , as follows:

$$\epsilon_A \nabla \cdot \mathbf{E}^A = \rho_c^A, \quad z > 0, \quad (19)$$

$$\epsilon_B \nabla \cdot \mathbf{E}^B = \rho_c^B, \quad z < 0, \quad (20)$$

subject to the following boundary conditions at $z = 0$:

$$\epsilon_B E_z^B \Big|_{z \rightarrow 0^-} - \epsilon_A E_z^A \Big|_{z \rightarrow 0^+} = 4\pi\sigma, \quad (21)$$

$$E_x^A \Big|_{z \rightarrow 0^+} = E_x^B \Big|_{z \rightarrow 0^-}, \quad (22)$$

$$E_y^A \Big|_{z \rightarrow 0^+} = E_y^B \Big|_{z \rightarrow 0^-}. \quad (23)$$

Making use of Eq. (6) and substituting the Boltzmann distribution for ion density profile [Eq. (11)], we now take advantage of the one-dimensional nature of our system and collapse the above formulation into a single equation, written in terms of the electrostatic potential $\Phi^\alpha(z)$, to obtain the Poisson Boltzmann-equation representation of the Gauss' law:

$$\frac{d^2\Phi^A}{dz^2} = (\kappa^A)^2 \sinh(\Phi^A - \Phi_D), \quad z < 0, \quad (24)$$

$$\frac{d^2\Phi^B}{dz^2} = (\kappa^B)^2 \sinh \Phi^B, \quad z > 0, \quad (25)$$

where, respectively, $\kappa^\alpha = \sqrt{4\pi e^2 \rho_0^\alpha / \epsilon^\alpha kT}$ is the inverse Debye screening length, and $\rho_0^\alpha = Z_+^2 \rho_{0,+}^\alpha + Z_-^2 \rho_{0,-}^\alpha$ is the weighted sum of the bulk densities of the ions in the two phases, $\alpha = A, B$. The inverse Debye screening length has been so defined as to scale the electrostatic potential Φ^α dimensionless. The corresponding boundary conditions for the potential are as follows:

$$\Phi^A \Big|_{z \rightarrow 0^-} = \Phi^B \Big|_{z \rightarrow 0^+}, \quad (26)$$

$$\epsilon^A \frac{d\Phi^A}{dz} \Big|_{z \rightarrow 0^-} - \epsilon^B \frac{d\Phi^B}{dz} \Big|_{z \rightarrow 0^+} = 4\pi\sigma, \quad (27)$$

$$\frac{d\Phi^A}{dz} \Big|_{z \rightarrow -\infty} = 0, \quad (28)$$

$$\frac{d\Phi^B}{dz} \Big|_{z \rightarrow +\infty} = 0. \quad (29)$$

3.3 Full nonlinear solution

The general solution to the full nonlinear Poisson-Boltzmann equation can be readily found (41). At present, we simply furnish the particular solution for our system of nonpolarizable liquid-liquid interface specified by the above boundary conditions:

$$\Phi^A(z) = \Phi_D - 4 \tanh^{-1}(C_A e^{\kappa_A z}), \quad z < 0, \quad (30)$$

$$\Phi^B(z) = 4 \tanh^{-1}(C_B e^{-\kappa_B z}), \quad z > 0. \quad (31)$$

As shown, Eqs. (30) and (31) are expressed in terms of the two integration constants, C_A and C_B , and as such, physically meaningful solutions would correspond to the range of $|C_\alpha| \leq 1$. Alternatively, we can rewrite $C_\alpha = \exp(-\kappa_\alpha z_\alpha)$, and the solutions now take the form of $\Phi^A(z) = \Phi_D - 4 \operatorname{sgn}(C_A) \tanh^{-1} e^{\kappa_A(z-z_A)}$, and $\Phi^B(z) = 4 \operatorname{sgn}(C_B) \tanh^{-1} e^{-\kappa_B(z-z_B)}$, where $\operatorname{sgn}[\cdot]$ is the sign function. The choice of signs in the above solutions is such that the integration constants are positive when we have a neutral interface, $\sigma = 0$.

In terms of the integration constants C_A and C_B , the continuity equation in Eq. (26) reads:

$$\frac{(1+C_A)(1+C_B)}{(1-C_A)(1-C_B)} = e^{\frac{\Phi_D}{2}}. \quad (32)$$

while the Gauss' law in Eq. (27) takes the form of

$$\frac{4\epsilon_A \kappa_A C_A}{C_A^2 - 1} - \frac{4\epsilon_B \kappa_B C_B}{C_B^2 - 1} = 4\pi\sigma. \quad (33)$$

This system of equations admits the following simple algebraic solutions for C_A and C_B :

$$C_A = \frac{\epsilon_A \kappa_A + \epsilon_B \kappa_B \cosh \Phi_D/2 - R}{2\pi\sigma + \epsilon_B \kappa_B \sinh \Phi_D/2}. \quad (34)$$

$$C_B = \frac{\epsilon_B \kappa_B + \epsilon_A \kappa_A \cosh \Phi_D/2 - R}{-2\pi\sigma + \epsilon_A \kappa_A \sinh \Phi_D/2}, \quad (35)$$

where

$$R^2 = (2\pi\sigma)^2 + (\epsilon_A \kappa_A)^2 + (\epsilon_B \kappa_B)^2 + 2\epsilon_A \kappa_A \epsilon_B \kappa_B \cosh \Phi_D/2. \quad (36)$$

Thus, we have now determined the constants of integration explicitly in terms of the input parameters ϵ_A , ϵ_B , and Φ_D .

3.4 Equilibrium ion profiles

We can now write down the positive and negative ion densities in a straightforward manner:

$$\rho_{\pm}^A(z) = \rho_0^A \left(\frac{1 \pm C_A e^{\kappa_A z}}{1 \mp C_A e^{\kappa_A z}} \right)^2, \quad (37)$$

$$\rho_{\pm}^B(z) = \rho_0^B \left(\frac{1 \mp C_B e^{-\kappa_B z}}{1 \pm C_B e^{-\kappa_B z}} \right)^2. \quad (38)$$

To illustrate the profiles of the electrostatic potential $\Phi(z)$ and of the ion distributions $\rho_{\pm}^{\alpha}(z)$ across an interface, we will now consider, in particular, the system of a polarizable membrane between a nitrobenzene solution [$\epsilon^B = 35.7\epsilon_0$ at 68F] of sodium chloride and a water solution [$\epsilon^A = 80.4\epsilon_0$ at 68F] of the same salt. Given the size ratio between the ions of $R_+/R_- \approx 0.695$, we obtain the following normalized relations between the various Born solvation energies: $g_+^A \approx 0.662$, $g_-^A \approx 0.446$, $g_+^B \approx 1.44$, and $g_-^B \equiv 1$. Thus, it follows readily that $\rho_0^A/\rho_0^B = e^{1.33} \approx 3.79$ and $\Phi_D \approx 0.112$, which implies that $\kappa^A/\kappa^B \approx 1.30$. We display the resulting plots in Figs. 2 and 3.

3.5 Excess interfacial charge

The excess interfacial charge, Q_{\pm}^{α} , defined as

$$Q_{\pm}^{\alpha} = \int_0^{\infty} dz [\rho_{\pm}^{\alpha}(z) - \rho_0^{\alpha}], \quad (39)$$

and due physically to the accumulation or depletion of charges near the interface as the ions migrate across the boundary, can also be obtained in analytical closed-form for the present case of planar interface. We note that the excess charge Q_{\pm}^{α} has the dimensions of charge density per unit of transverse area. Upon direct evaluation, we obtain

$$Q_{\pm}^A = \frac{1}{2\pi} \frac{\epsilon_A \kappa_A C_A}{1 \mp C_A}, \quad (40)$$

$$Q_{\pm}^B = -\frac{1}{2\pi} \frac{\epsilon_B \kappa_B C_B}{1 \pm C_B}. \quad (41)$$

The total excess charge in each phase α can be simply evaluated by $Q^{\alpha} = Q_+^{\alpha} + Q_-^{\alpha}$. In addition, the net charge flux across the interface can be defined as $\Delta Q = \frac{1}{2}(Q^B - Q^A)$. The

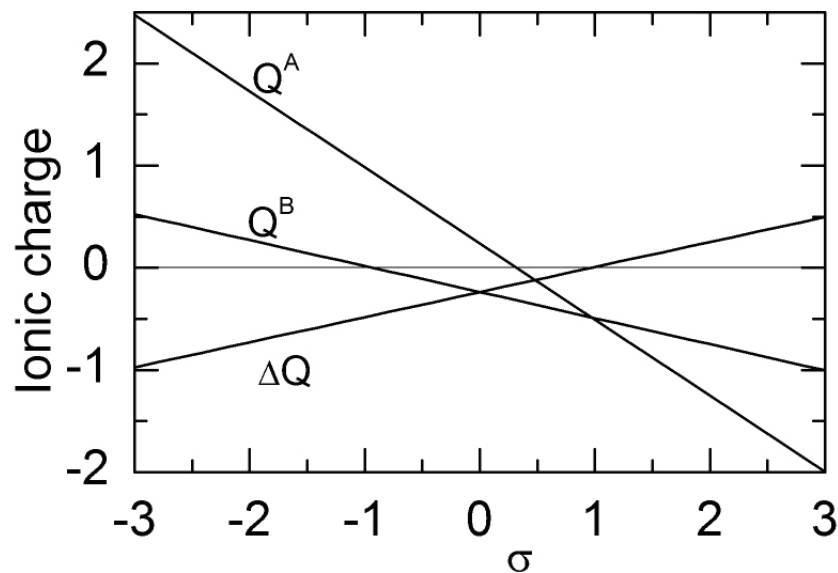


Fig. 4. Plots of the total excess charge Q^A , Q^B and the net charge flux across the interface ΔQ . For this particular plot, we use a range of surface charge densities σ in units of $\epsilon_A \kappa_A$ and $\Phi'_d = 0.112$ for the nitrobenzene/water solution at 68F.

total net charge accumulated in each phase compensates for the charge introduced by the polarizable membrane to the overall system such that the relation $\sigma + Q^A + Q^B = 0$ holds at all times. The plot of Q^A , Q^B and ΔQ for various values of the surface charge density σ is shown in Fig. 4.

3.6 Extension to polarizable membranes

In the case of polarizable membranes, we see that the additional surface charge density can have dramatic effects on the electrostatic potential and charge distributions of the two phases. As shown in Fig. 2, there exists a sufficiently large surface charge density on the interface, $\sigma^{*\alpha}$, at each phase α such that the electric field vanishes as manifested by the corresponding constant electrostatic potential. The further addition of surface charges, either positive or negative, reverses the sign of the potential gradient and of the excess charge in the corresponding phase. The critical surface charge densities are found to be

$$\sigma^{*A} = \frac{1}{2\pi} \epsilon_B \kappa_B \sinh \frac{\Phi_D}{2}, \quad (42)$$

$$\sigma^{*B} = -\frac{1}{2\pi} \epsilon_A \kappa_A \sinh \frac{\Phi_D}{2}. \quad (43)$$

It can be also checked that at these critical surface charge densities, our expressions for the excess charge Q^α and the net charge flux across the interface ΔQ also vanish in the respective phase (Fig. 4). Notwithstanding the seeming linearity that both Q^α and ΔQ follow with respect to the surface density σ , we do observe a slight jump across $\sigma = 0$ thereby establishing a small deviation to perfect linearity.

3.7 Properties of the solutions

We now consider a few general properties of our solutions. Firstly, we note that the distribution potential Φ_D across the interface, itself generated by the different dielectric constants of each phase, is only dependent upon ion types and not of their concentration. Thus, in the absence of any ions in the system, we must then recover a uniform potential. Indeed, we observe exactly that in approaching the limit of zero ionic concentration where the gradient of the potential across the interface gradually decreases; the required net jump Φ_D is being pushed outwardly towards infinity.

Another noteworthy feature is the asymptotic behavior of the potential at large distances from the interface. In the limit of $z \rightarrow \infty$, we have $\Phi^A \approx \Phi_D - 4C_A \exp(\kappa_A z)$, and $\Phi^B \approx 4C_B \exp(-\kappa_B z)$. Thus, we see that the integration constants now act as potential sources in the solution form for the linearized version of the Poisson-Boltzmann equation. Given that each integration constant satisfies the constraint of $|C_\alpha| \leq 1$, the asymptotics always arises from a linear source of maximum potential $\Phi_{max} \leq 4$.

Lastly, we remark that our results are consistent with the Born description of solvation energy: since cations are in general smaller in size due to their oxidized state, the solvation free energy is always more negative when compared with their anionic counterpart, provided that they are both subjected to the same solvent of the same constant dielectric permittivity. Therefore, it is always thermodynamically more favorable to dissolve more of the cations in the more polar phase and redistribute the density profiles of the remaining ions accordingly in both phases. The validity of our argument remains even when the membrane becomes charged in the same polarity as the cations. In general, we do not expect that the multivalency of the dissolved ions would qualitatively change the behavior of the differential adsorption phenomenon described herein, at the mean-field level, other than to intensify its effect as evident in the prefactor of our Born expression of solvation energy.

4. Conclusions

4.1 Summary of results

In this work, we have constructed a self-contained thermodynamic formulation of ion solvation in binary immiscible polar mixtures and described the general phenomenon of differential ion adsorption at liquid-liquid interfaces via the full nonlinear Poisson-Boltzmann framework. Assuming the Born model of solvation and using the mechanics of the Ω -potential, our formulation presents a fundamental, mean-field description that relates the experimentally detectable bulk-ion densities in each phase, as well as the distribution potential across the membrane, to the respective dielectric constants and sizes of each ion species present in the two phases. We note that electrostatics alone is insufficient in capturing the physics of ion solvation and interfacial adsorption.

4.2 Future research

Our work can be generalized in several ways. Our formulation models the dissolved ions specifically as point particles and the liquid-liquid interface as sharp. Immiscible multicomponent liquids in some cases can lead to the broadening of interfaces (16; 17). In such instances, adsorption of ionic component in slabs of immiscible liquids has been recently considered using liquid-liquid weak segregation approximations (32). Thus, it is of interest to consider other morphologies and systems than those presented in this work. As a refinement to our model, it is also possible to incorporate further molecular details in the construction of our thermodynamic potential. This can be done, for example, with the explicit inclusion of

short-range interactions between the ions by replacing our expression of Ω_{sol}^{α} by

$$\Omega_{sol}^{\alpha} = \int \int d\mathbf{r}d\mathbf{r}' G_{sr}(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') \rho(\mathbf{r}) \quad (44)$$

One could then consider components with more complicated structures than point ions, such as polyelectrolytes, and consider the additional effects introduced by these new degrees of freedom (10; 28). Though protein adsorption on hard surfaces have been analyzed (11), a general description of macroion adsorption to liquid interfaces is lacking. Such a general description would be highly useful, as, for example, the phenomenon of DNA adsorption to the interface among liquid surfaces is crucial in cell biology (34; 18). The inclusion of proteins and/or DNA molecules in the system and the study of their corresponding adsorption phenomenon along liquid-liquid interfaces will be presented elsewhere. We point out in passing that the long-range interaction of electrostatics would not contribute at the mean-field level due to overall electro-neutrality.

4.3 Outlook

It is our hope to have demonstrated in this work that the differential adsorption of ions is a general phenomenon in electrostatics that occurs along interfaces between different dielectric media. Such chemical environments are ubiquitous in many biological systems at the cellular and physiological levels (1). In particular, it was pointed out by Onsager (31) regarding the potential importance of such a "primordial oil slick" in the early development of life. The phenomenon of thermodynamically driven, selective confinement of ions and the consequent breaking of charge-conjugation symmetry near a liquid-liquid interface would provide just the physical mechanisms necessary for the essential organic molecules to aggregate in close, two-dimensional proximity to each other, where the process of diffusion would have worked much more efficiently in bringing together these molecules and starting the chain reaction of life than in the otherwise three-dimensional scenario in the bulk. It is our further hope to generalize our results in this work to other interfacial geometries such as the cylindrical and spherical cases.

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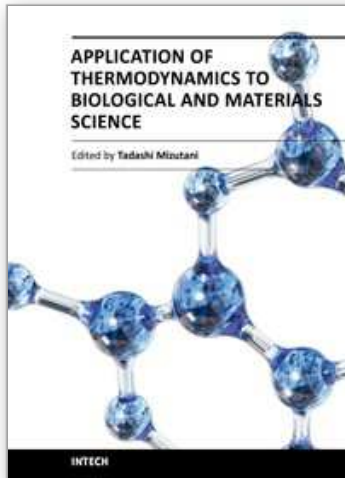
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