Thermodynamics of Ion Solvation and Differential Adsorption at Liquid-Liquid Interfaces and Membranes

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We construct a mean-field formulation of the thermodynamics of ion solvation in immiscible polar binary mixtures. Assuming an equilibrium planar interface separating two semi-infinite regions of different constant dielectric medium, we study the electrostatic phenomenon of differential adsorption of ions at the interface. Using general thermodynamic considerations, we construct the mean-field $\Omega$-potential and demonstrate the spontaneous formation of an electric double-layer around the interface necessarily follow. In our framework, we can also relate both the bulk ion densities in the two phases and the distribution potential across the interface to the fundamental Born free energy of ion polarization. We further illustrate this selective ion adsorption phenomenon in respective examples of fully permeable membranes that are neutral, negative, or positive in charge polarity.

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I. INTRODUCTION

Electro-chemical and physical processes at liquid-liquid interfaces and across membranes are broadly important in many systems. Examples range from cellular and physiological systems to everyday applications, such as portable batteries, as well as scenarios for the origin of life and also biotechnology. Biologically, ion transport is essential for transmembranous and transcellular electric potential, fluid transport, and maintaining cellular volume; 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. 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, hydometallurgy and two-phase electrolysis.

The interaction of ionic species, particularly proteins and nucleic acids, with interfaces and membranes has become exceedingly important in our understanding of biological systems 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. 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 and also more recently of nucleic acids, both along hard surfaces in aqueous solutions. On the other hand, recent experimental techniques have detected ion density profiles at liquid-liquid interfaces with the use of x-ray reflectivity measurements. These experiments provide direct knowledge of electrostatic interactions among ionic species at interfaces and can be easily extended to analyze the adsorption of proteins and nucleic acids at liquid-liquid interfaces.

In their experimental study, 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 in-
terface, progress has been made with phenomenological approaches, including the example of a Ginzburg-Landau theory of ions solvation and their distribution around an interface [13].

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 [14, 15]. 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 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.

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 a neutral membrane, a negatively charged membrane, as well as a positively charged one 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 [16, 17, 18]. For the same reason, there exists considerable varied usage of terminology [18] 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 $\Phi_D$. 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.

In what follows, we will present, in section II, our thermodynamic formalism in terms of a mean-field $\Omega$-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.

II. THERMODYNAMICS OF ION SOLVATION

For the system of dissolved salt ions in polar binary mixtures, there are several parameters that have been, as previously mentioned, traditionally considered as independent inputs to the formulation of such systems. These input parameters include, for each phase $\alpha$, the dielectric constants $\varepsilon_\alpha$, the bulk ion densities $\rho_0^{\alpha, \pm}$, and the distribution potential across the interface $\Phi_D$. To further characterize these parameters, we now turn to thermodynamic considerations. We will henceforth denote the two polar phases by $\alpha = A, B$ with $A$ labeling the more polar phase. In principle, the condition of equilibrium implies equal chemical potential across the interface, $\mu^A_{\pm} = \mu^B_{\pm}$, which should in turn determine the bulk densities of the salt ions existing in each of the two phases. The thermodynamics with this equilibrium condition are formulated by constructing the $\Omega$-potential (equals to $-PV$ where $P$ is the pressure and $V$ is the volume) for each phase $\alpha$ as follows:

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

where we have divided the potential into a contribution due to electrostatics $\Omega_{el}$, to thermodynamics $\Omega_{th}$, and to solvation interactions $\Omega_{sol}$. 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 $\varepsilon$ and imposes Gauss’ law via a Lagrange-multiplier constraint using the electrostatic potential $\Phi$:

\[
\Omega_{el}^\alpha = \int \frac{e^2 |E^\alpha(x)|^2}{8\pi} - \int \Phi^\alpha(\nabla \cdot \frac{e^2 E^\alpha(x)}{4\pi} - \rho^\alpha_+(x) - \rho^\alpha_-(x)).
\]

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 $\mu^\alpha_{th}$,

\[
\Omega_{th}^\alpha = \rho^\alpha_+(x) \log \left[ \frac{\rho^\alpha_+(x)}{e} \right] + \rho^\alpha_-(x) \log \left[ \frac{\rho^\alpha_-(x)}{e} \right] - \mu^\alpha_+ \rho^\alpha_+(x) - \mu^\alpha_- \rho^\alpha_-(x),
\]

where the chemical potentials 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:

\[
\Omega_{sol}^\alpha = -g^\alpha_+ \rho^\alpha_+(x) - g^\alpha_- \rho^\alpha_-(x),
\]

where the Born polarization energy $g^\alpha_{\pm}$ is given by

\[
g^\alpha_{\pm} = \frac{Z_{\pm}^2 e^2}{8\pi \varepsilon^\alpha R_{\pm}},
\]

for ions with valency $Z_{\pm}$ and radius $R_{\pm}$. As expected, we note that an increase in dielectric constant $\varepsilon^\alpha$ or in the ionic radius $R_{\pm}$ for a given valence $Z_{\pm}$ 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.

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 $\Omega$-potential is an extensive quantity by construction: $\Omega_{el}^\alpha \propto V$, where $V$ is the volume of the overall system. Defining the total charge density $\rho^\alpha_0(x) = |Z_+|\rho^\alpha_+(x) + |Z_-|\rho^\alpha_-(x)$, we assume that it has a nonvanishing zero mode and observe that its contribution to the energy density is $(\rho^\alpha_0)^2 \int d\mathbf{x} \int d\mathbf{y} |\mathbf{y}|^{-1}$. Based on the dimensionality of the various factors within the integral, it is straightforward to see that $\Omega_{el}^\alpha |_{k=0} \propto V^{5/3}$, for $\rho^\alpha_0 \neq 0$, which is inconsistent with the thermodynamic construction of the extensive $\Omega$-potential. Therefore, the requirement of consistency with equilibrium thermodynamics automatically imposes charge neutrality in the overall system; namely, $\rho^\alpha_0 = 0$ (we note that this electroneutrality condition in linearized approaches appears as a restriction to avoid the divergence in the potential $V$).

From Eq. (4), variation with respect to the electric field $E^\alpha$, the Lagrange multiplier (electrostatic potential) $\Phi^\alpha$, and the number density $\rho^\alpha_\pm$ readily yields the relations

\[
\delta E^\alpha : E^\alpha = -\nabla \Phi^\alpha(x),
\]

\[
\delta \Phi : \nabla \cdot \left[ \frac{e^2 E^\alpha(x)}{4\pi} \right] = \rho^\alpha_+(x) + \rho^\alpha_-(x),
\]

\[
\delta \rho^\alpha_\pm : \log \rho^\alpha_\pm(x) \pm \Phi^\alpha(x) - g^\alpha_\pm = \mu^\alpha_\pm.
\]

We note that Eqs. (6) and (7) simply reproduce, respectively, the expressibility of the electric field $E^\alpha$ in terms of a scalar potential $\Phi^\alpha$ 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 $\alpha$ would provide further constraints on the respective bulk ionic densities. To make connection with the distribution potential $\Phi_D$, we also need to introduce explicitly now the further assumption of Boltzmann distribution for the ion densities. In particular, we have, for the more polar phase $A$,

\[
\rho^A_\pm(x) = \rho^A_0 e^{\mp \Phi^A(x)} e^{\pm \Phi_D},
\]

while a similar expression (modulus the exponential factor of the distribution potential $\Phi_D$) applies to the less polar phase $B$. Taking the logarithm of Eq. (9) readily yields

\[
\log \rho^A_\pm(x) \pm \Phi^A(x) = \log \rho^A_0 \pm \Phi_D
\]

Again, a similar expression to Eq. (10), modulus the term containing the distribution potential, applies to the less polar phase $B$. Now upon substituting Eq. (10) and the corresponding expression for phase $B$ into Eq. (8), as well as imposing equal chemical potentials across boundary, we obtain the following relations

\[
\log \rho^A_0 + \Phi_D - g^A_+ = \log \rho^B_0 - g^B_+,
\]

\[
\log \rho^A_0 - \Phi_D - g^A_- = \log \rho^B_0 - g^B_-.
\]

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

\[
\log \rho^A_0 + g_A = \log \rho^B_0 + g_B,
\]

\[
2\Phi_D + \Delta g = \Delta g_B.
\]
As mentioned in the Introduction, it is now feasible to make precise experimental detection of the ion distributions near liquid-liquid interfaces [11, 12]. 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 [12]. 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 $\rho^{\alpha}_{i}(z)$ in each phase $\alpha$.$\n$$\n$FIG. 2: Comparison of the electrostatic potential across a positively and negatively charged membrane in nitrobenzene/water solution at 68°F. The surface charge densities are plotted for $\sigma = -1.5(\triangle)$, $\sigma = -0.93(\square)$, $\sigma = -0.5(\nabla)$, $\sigma = 0(\bullet)$, $\sigma = 0.15(\blacktriangle)$, $\sigma = 0.32(■)$, $\sigma = 0.5(\nabla)$.

III. ELECTROSTATICS OF DIFFERENTIAL ADSORPTION

where we have defined the average Born polarization energy over ions of both charge polarity, $\tilde{g}_\alpha = g_{\alpha+} + g_{\alpha-}$, 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 $\varepsilon_\alpha$ in each phase via

$$\frac{\rho_0^A}{\rho_0^B} = e^{\tilde{g}_B - \tilde{g}_A} = e^{-\Delta g}$$  \hspace{1cm} (15)$$

$$\Phi_D = -\frac{1}{2} \Delta g$$  \hspace{1cm} (16)$$

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

In summary, we have thus shown in Eq. (15) that the bulk densities $\rho_{0,\pm}^\alpha$ are related to the difference of the average Born solvation energy between the two phases, while in Eq. (16) the distribution potential $\Phi_D$ 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 $\rho^\alpha_i(x)$ as well as the electrostatic potential $\Phi(x)$, it remains for us to solve the Poisson equation [Eq. (2)] after applying the integrability condition [Eq. (11)] as well as the thermodynamic ansatz of the Boltzmann distribution for the ion density [Eq. (10)]. 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.

Making use of Eq. (4) and substituting the Boltzmann distribution for ion density profile [Eq. (3)], 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:

$$\frac{d^2 \Phi^A}{dz^2} = (\kappa^A)^2 \sinh(\Phi^A - \Phi_D) , \hspace{1cm} z < 0 , \hspace{1cm} (22)$$

$$\frac{d^2 \Phi^B}{dz^2} = (\kappa^B)^2 \sinh\Phi^B , \hspace{1cm} z > 0 , \hspace{1cm} (23)$$

where, respectively, $\kappa^\alpha = \sqrt{4\pi e^2 \rho_{0,\pm}^\alpha / e^0kT}$ is the inverse Debye screening length, and $\rho_{0,\pm}^\alpha = Z_\alpha \rho_{0,\pm}^\alpha + Z^2 \rho_{0,-}^\alpha$ is the combined bulk densities of the ions in the two phases,
The general solution to the full nonlinear Poisson-Boltzmann equation can be readily found. At present, we simply furnish the particular solution for our system of nonpolarizable liquid-liquid interface specified by the above boundary conditions:

\[ \Phi^A(z) = \Phi_D - 4 \tanh^{-1} (C_A e^{\kappa_A z}), \quad z < 0, \]  
\[ \Phi^B(z) = 4 \tanh^{-1} (C_B e^{-\kappa_B z}), \quad z > 0. \]

As shown, Eqs. (28) and (29) 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 \( |C_A| \leq 1 \). Alternatively, we can rewrite \( C_A = \exp (-\kappa_A z) \), and the solutions now take the form of \( \Phi^A(z) = \Phi_D - 4 \text{sgn}(C_A) \tanh^{-1} e^{\kappa_A(z-z_A)} \), and \( \Phi^B(z) = 4 \text{sgn}(C_B) \tanh^{-1} e^{-\kappa_B(z-z_B)} \), where \( \text{sgn} [ \cdot ] \) 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. (24) reads:

\[ \frac{(1+C_A)(1+C_B)}{(1-C_A)(1-C_B)} = e^{\Phi_D}. \]

while the Gauss’ law in Eq. (25) takes the form of

\[ 4\epsilon_A \kappa_A C_A = 4\epsilon_B \kappa_B C_B . \]

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

\[ C_A = \frac{\epsilon_A \kappa_A + \epsilon_B \kappa_B \cosh \Phi_D/2 - R}{2\pi \sigma + \epsilon_B \kappa_B \sinh \Phi_D/2}, \]

\[ C_B = \frac{\epsilon_B \kappa_B + \epsilon_A \kappa_A \cosh \Phi_D/2 - R}{-2\pi \sigma + \epsilon_A \kappa_A \sinh \Phi_D/2}. \]

\( \alpha = A, B \). The inverse Debye screening length has been so defined as to scale the electrostatic potential \( \Phi^\alpha \) dimensionless. The corresponding boundary conditions for the potential are as follows:

\[ \varepsilon^A \frac{d\Phi^A}{dz} \bigg|_{z=0}^- = \Phi^B \bigg|_{z=0}^+, \quad (24) \]

\[ \varepsilon^B \frac{d\Phi^B}{dz} \bigg|_{z=0}^- = 4\pi \sigma, \quad (25) \]

\[ \frac{d\Phi^A}{dz} \bigg|_{z=-\infty} = 0, \quad (26) \]

\[ \frac{d\Phi^B}{dz} \bigg|_{z=+\infty} = 0. \quad (27) \]

The curves are presented in separate plots because of difference in concentrations. For this particular plot, we use a range of surface charge densities \( \sigma = 0.15(\square), \sigma = 0.93(\square), \sigma = 0.5(\triangledown), \sigma = 0.32(■), \sigma = 0.5(\blacktriangledown) \). (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 \( \sigma = 0.15(\square), \sigma = 0.93(\square), \sigma = 0.5(\triangledown), \sigma = 0.32(■), \sigma = 0.5(\blacktriangledown) \). (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 \( \sigma = 0.15(\square), \sigma = 0.93(\square), \sigma = 0.5(\triangledown), \sigma = 0.32(■), \sigma = 0.5(\blacktriangledown) \). (1) Cations. (2) Anions. (3) Total charge density \( \rho = \rho_+ + \rho_- \).
where

$$R^2 = (2\pi\sigma)^2 + (\epsilon_{AKA})^2 + (\epsilon_{BBB})^2 + 2\epsilon_{AKA}\epsilon_{BBB}\cosh \Phi_D/2.$$  \hspace{1cm} (34)

Thus, we have now determined the constants of integration explicitly in terms of the input parameters $\epsilon_A$, $\epsilon_B$, and $\Phi_D$. As such, we can write down the positive and negative ion densities in a straightforward manner:

$$\rho^A_\pm(z) = \rho^A_0 \left( \frac{1 \pm C_A e^{\kappa_A z}}{1 \pm C_A e^{-\kappa_A z}} \right)^2,$$  \hspace{1cm} (35)

$$\rho^B_\pm(z) = \rho^B_0 \left( \frac{1 \pm C_B e^{\kappa_B z}}{1 \pm C_B e^{-\kappa_B z}} \right)^2.$$  \hspace{1cm} (36)

To illustrate the profiles of the electrostatic potential $\Phi(z)$ and of the ion distributions $\rho^\alpha_\pm(z)$ across an interface, we will now consider, in particular, the system of a polarizable membrane between a nitrobenzene solution [$\epsilon^B = 35.7\varepsilon_0$ at 68F] of sodium chloride and a water solution [$\epsilon^A = 80.4\varepsilon_0$ 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 $g^B \approx 1$. Thus, it follows readily that $\rho^A_0/\rho^B_0 = \varepsilon^{3.33} \approx 3.79$ 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.

The excess charge, $Q^\alpha_\pm$, defined as

$$Q^\alpha_\pm = \int_0^\infty dz \left[ \rho^\alpha_+(z) - \rho^\alpha_0 \right],$$  \hspace{1cm} (37)

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 $Q^\alpha_\pm$ has the dimensions of charge density per unit of transverse area. Upon direct evaluation, we obtain

$$Q^A_\pm = \frac{1}{2\pi} \frac{\epsilon_{AKA} C_A}{1 + C_A},$$  \hspace{1cm} (38)

$$Q^B_\pm = -\frac{1}{2\pi} \frac{\epsilon_{BBB} C_B}{1 + C_B}. $$  \hspace{1cm} (39)

The total excess charge in each phase $\alpha$ can be simply evaluated by $Q^\alpha = Q^A_\pm + Q^B_\pm$. In addition, the net charge flux across the interface can be defined as $\Delta Q = \frac{1}{2}(Q^B - Q^A)$. The 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 $\Delta Q$ for various values of the surface charge density $\sigma$ is shown in Fig. 4.

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 $\alpha$ 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

$$\sigma^A = \frac{1}{2\pi} \epsilon_{BBB} C_B \sinh \Phi_D,$$  \hspace{1cm} (40)

$$\sigma^B = -\frac{1}{2\pi} \epsilon_{AKA} C_A \sinh \Phi_D.$$  \hspace{1cm} (41)

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

We now consider a few general properties of our solutions. Firstly, we note that the distribution potential $\Phi_D$ 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 $\Phi_D$ 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 $z \to \infty$, 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 $\Phi_{\text{max}} \leq 4$.

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.

IV. CONCLUSIONS

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 $\Omega$-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.

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 [21]. In such instances, adsorption of ionic component in slabs of immiscible liquids has been recently considered using liquid-liquid weak segregation approximations [12]. 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 $\Omega_{\text{sol}}^\alpha$ by

$$\Omega_{\text{sol}}^\alpha = \int \int dr dr' G_{\text{sr}}(r-r') \rho(r') \rho(r)$$

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 [22, 23]. Though protein adsorption on hard surfaces have been analyzed [24], 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 [1, 2]. 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.

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 [5]. In particular, it was pointed out by Onsager [3] regarding the potential importance of such a “primodial 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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