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In this Brief Report, we calculate the electric-double-layer (EDL) electrostatic potential in a system of several layers of immiscible electrolytes. Verwey-Niessen theory predicts that at the interface between two immiscible electrolytes back-to-back EDLs are formed. The present analysis extends this idea to the case where the immiscible liquids are contained inside a domain with given electrostatic potentials at its boundaries, where the thickness of the individual liquid layer can be comparable to the EDL thickness. Such a system gives rise to a situation where the overall EDL electrostatic potential in the system is dictated by the competitive influences of the boundary-induced effects and the effects induced by the jump in the ion-solvent interaction potential at the liquid-liquid interfaces.

We shall start from the free-energy description of the system, expressing the free energy $F$ as

$$ F = \int f(\psi, n_{\pm}) d^3 r, $$

where $f$ is the free-energy density expressed as (assuming monovalent ions and based on a mean-field approach)

$$ f = f_b - \frac{1}{2} \epsilon(r)(\nabla \psi)^2 + (n_+ - n_-) e \psi + k_B T \left( n_+ \ln \left( \frac{n_+}{n_{\infty}} \right) - 1 \right) \\
+ n_- \left( \ln \left( \frac{n_-}{n_{\infty}} \right) - 1 \right) \\
+ \beta_+(r)n_+ + \beta_-(r)n_- + \text{const.} \tag{2} $$

Here $f_b$ is the free-energy density of the solvent, $k_B T$ is the thermal energy, $\psi$ is the electrostatic potential, $e$ is the electric charge, $\epsilon$ is the permittivity, $n_{\infty}$ is the bulk ionic number density, $n_\pm$ are ionic number densities, and $\beta_\pm$ are the ion-solvent interaction energies with the solvent.

As the system consists of immiscible liquids of a known spatial arrangement, $f_b$ is known beforehand. Thus the equilibrium conditions can be obtained by employing $\delta F / \delta \psi = 0$ and $\delta F / \delta n_\pm = 0$, i.e.,

$$ \frac{\delta F}{\delta \psi} = \frac{d}{dy} \left[ \epsilon(y) \frac{d \psi}{dy} \right] + e(n_+ - n_-) = 0 \tag{3} $$

and

$$ \frac{\delta F}{\delta n_\pm} = \pm e \psi + k_B T \ln \left( \frac{n_\pm}{n_{\infty}} \right) + \beta_\pm(y) = 0. \tag{4} $$
In the Debye-Hückel approximation, the above two equations can be analytically solved as

\[ \bar{\psi}_1 = K_1 \exp\left(\frac{h_1}{\lambda'_1} \bar{\psi}\right) + K_2 \exp\left(-\frac{h_1}{\lambda'_1} \bar{\psi}\right) \]

\[ - \exp(-\bar{\beta}_{1,-}) - \exp(-\bar{\beta}_{1,+}) \]

\[ \exp(-\bar{\beta}_{1,-}) + \exp(-\bar{\beta}_{1,+}) \]

for \( 0 \leq \bar{\psi} \leq 1 \)

(12)

and

\[ \bar{\psi}_2 = K_3 \exp\left(\frac{h_1}{\lambda'_2} \bar{\psi}\right) + K_4 \exp\left(-\frac{h_1}{\lambda'_2} \bar{\psi}\right) \]

\[ - \exp(-\bar{\beta}_{2,-}) - \exp(-\bar{\beta}_{2,+}) \]

\[ \exp(-\bar{\beta}_{2,-}) + \exp(-\bar{\beta}_{2,+}) \]

for \( 1 \leq \bar{\psi} \leq 1 + \frac{h_2}{h_1} \)

(13)

where \( \lambda'_1 = \sqrt{\frac{2e_1}{\epsilon(\exp(\bar{\beta}_{1,-})+\exp(\bar{\beta}_{1,+})})} \)

\( \lambda'_2 = \sqrt{\frac{2e_2}{\epsilon(\exp(\bar{\beta}_{2,-})+\exp(\bar{\beta}_{2,+})})} \)

and \( K_1, K_2, K_3, \) and \( K_4 \) are constants.

These constants can be evaluated in the presence of the following boundary conditions:

\[ (\bar{\psi}_1)_{\bar{\psi}=0} = \bar{\zeta}_1, \quad (\bar{\psi}_1)_{\bar{\psi}=1} = \bar{\psi}_c, \quad (\bar{\psi}_2)_{\bar{\psi}=1} = \bar{\psi}_c, \quad (\bar{\psi}_2)_{\bar{\psi}=1 + \frac{h_2}{h_1}} = \bar{\psi}_c, \]

\[ (\bar{\psi}_1)_{\bar{\psi}=0} = \bar{\zeta}_2, \quad \left( \frac{d\bar{\psi}_1}{d\bar{\psi}} \right)_{\bar{\psi}=1} = \left( \frac{d\bar{\psi}_2}{d\bar{\psi}} \right)_{\bar{\psi}=1} \]

(here \( \bar{\psi}_c \) will be determined \( a \) posteriori), so as to obtain

\[ \bar{\psi}_1 = (B_1 + \bar{\psi}_c) \frac{\sinh\left(\frac{h_1}{\lambda'_1} \bar{\psi}\right)}{\sinh\left(\frac{h_1}{\lambda'_1} \bar{\psi}_c\right)} + (B_1 + \bar{\xi}_1) \frac{\sinh\left(\frac{h_1}{\lambda'_2} (1 - \bar{\psi})\right)}{\sinh\left(\frac{h_1}{\lambda'_2} \bar{\psi}_c\right)} - B_1 \]

(15)

and

\[ \bar{\psi}_2 = (B_2 + \bar{\psi}_c) \frac{\sinh\left(\frac{h_1}{\lambda'_1} \bar{\psi}\right)}{\sinh\left(\frac{h_1}{\lambda'_1} \bar{\psi}_c\right)} + (B_2 + \bar{\xi}_2) \frac{\sinh\left(\frac{h_1}{\lambda'_2} (\bar{\psi} - 1)\right)}{\sinh\left(\frac{h_1}{\lambda'_2} \bar{\psi}_c\right)} - B_2, \]

(16)

where \( B_1 = \frac{\exp(-\bar{\beta}_{1,-}) - \exp(-\bar{\beta}_{1,+})}{\exp(-\bar{\beta}_{1,-}) + \exp(-\bar{\beta}_{1,+})} \approx \frac{\bar{\beta}_{1,-} - \bar{\beta}_{1,+}}{2}, B_2 = \frac{\exp(-\bar{\beta}_{2,-}) - \exp(-\bar{\beta}_{2,+})}{\exp(-\bar{\beta}_{2,-}) + \exp(-\bar{\beta}_{2,+})} \approx \frac{\bar{\beta}_{2,-} - \bar{\beta}_{2,+}}{2} \) (here we use the condition, to be demonstrated later, that our analytical results are mostly valid for \( |\beta_{1/2,-}| < 1 \)), and

\[ \bar{\psi}_c = \frac{\bar{\epsilon}_1}{\bar{\epsilon}_1 \coth\left(\frac{h_1}{\lambda'_1}\right)} - \frac{B_1 \coth\left(\frac{h_1}{\lambda'_1}\right)}{\bar{\epsilon}_1 \coth\left(\frac{h_1}{\lambda'_1}\right)} + \frac{\bar{\epsilon}_2}{\bar{\epsilon}_1 \coth\left(\frac{h_1}{\lambda'_2}\right)} - \frac{B_2 \coth\left(\frac{h_1}{\lambda'_2}\right)}{\bar{\epsilon}_2 \coth\left(\frac{h_1}{\lambda'_2}\right)} \]

(17)
βplot for different values of permittivity ratios of the two fluids. In this plot, $\bar{\psi}_c,i/i_k$ for different values of permittivity ratios as well as different values of the layer thickness of the two fluids. In this plot, $h_1/\lambda = 4$ and $\xi_1 = \xi_2 = 0.1$. In both of these plots $\beta_{1,+} = \beta_{2,+} = 0$. The above results can be generalized for a system of $N$ immiscible electrolyte layers as

$$\tilde{\psi}_i = (B_i + \tilde{\psi}_{c,i,i-1}) \sinh \left[ \frac{1}{\xi_i} \sum_{k=1}^{i} h_k - \bar{y} \right]$$

$$+ (B_i + \tilde{\psi}_{c,j,j+1}) \sinh \left[ \bar{y} - \frac{1}{\xi_j} \sum_{k=1}^{j} h_k \right] - B_i$$

(for $1 \leq i \leq N$),

where $\tilde{\psi}_{c,i,j}$ is the potential at the interface between the adjacent layers $i$ and $j$. Note that the known potentials at the bottom and the top boundaries are denoted as $\tilde{\psi}_{c,0,1}$ and $\tilde{\psi}_{c,N/N+1}$, respectively, while the unknown interface potential is

$$\tilde{\psi}_{c,i,i+1} = \frac{\tilde{\psi}_{c,i,i+1}}{\tilde{\psi}_{c,i,i+1}} \sinh \left( \frac{h_{i+1}}{\lambda_i^*} \right) - B_i \coth \left( \frac{h_i}{\lambda_i^*} \right)$$

$$+ \frac{\tilde{\psi}_{c,i+1,i+2}}{\tilde{\psi}_{c,i+1,i+2}} \sinh \left( \frac{h_{i+1}}{\lambda_i^*} \right) - B_{i+1} \coth \left( \frac{h_{i+1}}{\lambda_{i+1}^*} \right)$$

$$\left( \text{for } 1 \leq i \leq N-1 \right),$$

where $\lambda_i^* = \lambda \sqrt{\exp(-\beta_{i,-}) \exp(-\beta_{i,+})}$ and $B_i = \exp(-\beta_{i,-}) \exp(-\beta_{i,+}) \approx \beta_{i,-} B_{i,-}$ (here we use the condition, to be demonstrated later, that our analytical results are mostly valid for $|\beta_{i,\pm}| < 1$).
From the known values of $\psi_{c,0/1}$ and $\psi_{c,N/N+1}$, one can employ Eqs. (18) and (19) successively to obtain the potential distribution within any layer $i$ and the potential at the interface between any two adjacent layers $i$ and $i + 1$. Henceforth, we shall provide results only corresponding to $N = 2$; however, Eqs. (18) and (19) can always be invoked to provide results for any $N$.

We first study the electrostatic potential variations for the case of no ion-solvent interaction potentials [see Figs. 2(a) and 2(b)]. A smaller permittivity for a given liquid implies that the corresponding potential gradient must be steeper, as is evident from Figs. 2(a) and 2(b). For $h_1/h_2 > 1$, the relative EDL thickness (with respect to the entire channel height) is enhanced, whereas for $h_1/h_2 < 1$, it is diminished [see Fig. 2(b)].

Figures 3(a)–3(c) represent the central results of this Brief Report, demonstrating the effect of finite ion-solvent interaction energies. As a consequence, the overall electrostatic potential in the system will result from the mutually augmenting and nullifying effects of the EDLs at the boundaries and those induced by the jumps in ion-solvent interaction potential at the interfaces between the layers. We first consider the case of layers with identical permittivities and thicknesses [Fig. 3(a)]. A jump for the anions (i.e., a finite positive $\beta_{1,-}$ or $\beta_{2,-}$) lowers the overall anion concentration in the system [see Eq. (5)]. For example, in the case of a finite positive $\beta_{1,-}$, the lower electrolyte layer acquires a net positive charge. For large enough values of $\beta_{1,-}$, instead of screening the wall charge, this charge has the opposite effect of letting the electrostatic potential increase over the value prescribed at the wall. By contrast, a finite positive $\beta_{1,+}$ lowers the overall cation concentration in the system and brings additional negative charges into the lower layer, leading to a fast screening of the wall potential and large negative potential values.

Figures 3(b) and 3(c) show the coupled effects of finite interfacial ion-solvent interaction energy jumps as well as differences in the permittivity and the layer thickness of the two liquids. As has been discussed before, $h_1/h_2 > 1$ implies a more dominant influence of the wall EDL (since the EDL thickness has been fixed relative to $h_1$), whereas $h_1/h_2 < 1$ signifies the reverse. Also, such a variation in the thicknesses of the individual layers will imply unequal effects of the jumps in ionic energies $\beta_{1,\pm}$ or $\beta_{2,\pm}$. For $h_1/h_2 > 1$ [see Fig. 3(b)], a jump in $\beta_{2,\pm}$ has a much less pronounced effect. The effect is further decreased in case $\epsilon_1/\epsilon_2 < 1$. On the contrary, jumps in $\beta_{1,\pm}$ have a remarkable influence on the overall potential. Depending on whether the jump amplifies (caused by a jump in $\beta_{1,-}$) or reverses (caused by a jump in $\beta_{1,+}$) the boundary effect, one gets either an almost uniformly enhanced (as compared to the boundary potential) potential across the entire domain or a substantially large (compared to the magnitude of the wall potential) negative potential across the major portions of the domain. For $h_2/h_1 > 1$, interfacial effects show a greater influence on the overall electrostatic potential in the system for the case where there is a jump in the ionic interaction potential $\beta_{2,\pm}$ [see Fig. 3(c)].

The present model can also be used to study an interesting limiting case, where an unbounded liquid medium is separated by a very thin layer of immiscible electrolyte (i.e., we consider $h_1/h_2 < 1$) (see Fig. 4). Most of the interesting effects occur within the thin electrolyte layer and, accordingly, we show results for a distance from the lower boundary up to $y/(h_1 + h_2) \approx 0.2$. These results can be easily interpreted from the results corresponding to Fig. 3(c).

FIG. 4. (Color online) Variation of the electrostatic potential for the case when the top fluid layer is much thicker than the bottom one ($h_2 \gg h_1$; we take $h_2/h_1 = 30$). We provide results for different $\beta_1$’s (only the $\beta_1$ that has a finite nonzero value is mentioned). Other parameters are $h_1/\lambda = 4$ and $\zeta_1 = 0.1$.