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Transient behaviors of interacting electrical double layers

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Abstract The unsteady-state potential and space charge distributions between two identical, planar parallel charged surfaces immersed in an $a{:}b$ electrolyte solution are examined theoretically. The effects of the ratio of the diffusivities of counterions and coions, $D_{\mathrm{con}}/D_{\mathrm{co}}$, the mean diffusivity $(D_{\mathrm{con}}D_{\mathrm{co}})^{1/2}$, and the separation distance between two surfaces, H, on the transient distributions of electrical potential and space charges are investigated. The result of numerical simulation reveals that the extent of a system to reach its new equilibrium state depends largely on the magnitude of a scaled time $v(=Dt\kappa^2)$. For a fixed H, the greater the value of v, the closer a system to its new equilibrium state. For constant H and v, the smaller the ratio $(D_{\mathrm{con}}/D_{\mathrm{co}})$, the greater the deviation of a system from its new equilibrium state. In addition, the effect of D_{con} on this deviation is greater than that of D_{co}.

Key words Electrical double layer – non-equilibrium potential distribution – electrical interactions – Poisson equation

Introduction

For a charged surface in an electrolyte solution, an electrical double layer will be formed in the vicinity of the surface in which both the concentrations of ions and the electrical potential are functions of position. These functions are the key factors characterizing the nature of a charged surface and the associated double layer. It is assumed that the distribution of ions follows the Boltzmann distribution at equilibrium, and the electrical potential is governed by the Poisson equation [1]. Although these equilibrium distributions play an important role in the description of the electrical behavior of two interacting surfaces, cases exist in which the non-equilibrium distributions need to be considered. In Brownian encounters of dispersed entities, for example, the temporal variation in the relative position of two approaching entities causes the double layers between them to adjust their surface conditions accordingly. In this case, the significance of double-layer relaxation depends largely on the relative magnitudes of the rate of diffusion of ions and that of Brownian motion of particles. It was shown that the time necessary to establish an electrical double layer can be significant to the behavior of two interacting surfaces [2, 3]. The importance of surface charge relaxation during double-layer interaction was studied [3–5]. Another example in practice is the phenomena relevant to biocolloids, the surface of which is capable of regulating its charged status as a response to the variation in the condition of the environment [5–8]. In this case, the properties of both the charged surfaces and the associated double layers are time dependent. The time scales needed to be considered here are those for the rates of surface dissociation reactions, diffusion of ions, and the relative motion of two particles. The double-layer relaxation problem was analyzed by Lyklema [9] in which the non-equilibrium double layer was divided into two parts: the Stern layer and the diffuse layer. He concluded that the relaxation time of the later is shorter than the former which is predicted, in a semi-quantitative level, to be of the order $1/\kappa^2 D_\mathrm{i}$, where κ is the reciprocal Debye length, and D_i is the diffusivity of ions. The Overbeek–Lyklema concept of the diffuse layer quasi-equilibrium [2, 9] is investigated in some literature [5, 10–12].

The objective of the present study is to simulate, in a quantitative level, the temporal variation of two interacting non-equilibrium diffuse double layers. In particular, the effects of the essential parameters of the system under consideration on its non-equilibrium behavior are investigated. These parameters include the diffusivities of ions, the Debye length of the dispersion medium, and the separation distance between two charged surfaces.

Modeling

The analysis is begun by considering two identical, planar parallel charged surfaces separated by a distance H in an $a:b$ electrolyte solution. The surfaces remained at constant charge density. One of them is located at the origin, and the other at $r = H$, r being the distance from the former. It can be shown that the conservation of ion species and the Poisson equation lead to [13]

$$\frac{\eta}{2}\frac{\mathrm{d}\xi_\mathrm{con}}{\mathrm{d}\eta} + \frac{D_\mathrm{con}}{D}\frac{\mathrm{d}^2\xi_\mathrm{con}}{\mathrm{d}\eta^2} + \frac{aD_\mathrm{con}}{D}\left(\xi_\mathrm{con}\frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2} + \frac{\mathrm{d}\xi_\mathrm{con}}{\mathrm{d}\eta}\frac{\mathrm{d}\psi}{\mathrm{d}\eta}\right) = 0 \ , \tag{1}$$

$$\frac{\eta}{2}\frac{\mathrm{d}\xi_\mathrm{co}}{\mathrm{d}\eta} + \frac{D_\mathrm{co}}{D}\frac{\mathrm{d}^2\xi_\mathrm{co}}{\mathrm{d}\eta^2} - \frac{bD_\mathrm{co}}{D}\left(\xi_\mathrm{co}\frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2} + \frac{\mathrm{d}\xi_\mathrm{co}}{\mathrm{d}\eta}\frac{\mathrm{d}\psi}{\mathrm{d}\eta}\right) = 0 \ , \tag{2}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2} = \frac{-v}{a+b}(\xi_\mathrm{con} - \xi_\mathrm{co}) \ . \tag{3}$$

In these expressions, $\psi = F\phi/RT$, $\xi_\mathrm{con} = \rho_\mathrm{con}/\rho_0$, $\xi_\mathrm{co} = \rho_\mathrm{co}/\rho_0$, $v = Dt\kappa^2$, and $\kappa^2 = 2IF^2/\varepsilon_0\varepsilon_r RT$, where I is the ionic strength of the bulk solution, ρ_0 denotes the charge density of counterion (or coion) in the bulk liquid phase, ξ_con and ξ_co are, respectively, the scaled space charge distributions of counterion and coion, ψ is the scaled electrical potential, R and F are the gas constant and the Faraday constant, respectively, ρ_con and ρ_co are, respectively, the space charge densities of counterion and coion, $\rho_\mathrm{con} = aFC_\mathrm{con}$, $\rho_\mathrm{co} = bFC_\mathrm{co}$, C_con and C_co being the concentrations of counterion and coion, respectively, D_con and D_co are the diffusivities of counterion and coion, respectively, t is the time, T denotes the absolute temperature, ϕ is the electrical potential distribution, ε_0 and ε_r are, respectively, the permittivity of the vacuum and the relative permittivity, $\eta = r/(Dt)^{1/2}$, $D = (D_\mathrm{con}D_\mathrm{co})^{1/2}$, and

$$\rho_0 = 2IF/(a+b) \ , \tag{4a}$$

$$v = Dt\kappa^2 \ , \tag{4b}$$

where v is a scaled time. Suppose that the system is at an equilibrium state initially. We define the apparent equilibrium distribution coefficients of counterion and coion between the bulk liquid and the region between the charged surfaces, f_1 and f_2 as

$$f_1 = \int_0^H \exp(-aF\phi_\mathrm{e}/RT)\,\mathrm{d}r/H \ , \tag{5a}$$

and

$$f_2 = \int_0^H \exp(bF\phi_\mathrm{e}/RT)\,\mathrm{d}r/H \ , \tag{5b}$$

respectively, where ϕ_e is the equilibrium potential distribution. It can be shown that f_1 and f_2 are related to the surface excesses of counterion Γ_con and coion, Γ_co by

$$\Gamma_\mathrm{con} = \rho_0(f_1 - 1)H/aF \ , \tag{6a}$$

$$\Gamma_\mathrm{co} = \rho_0(f_2 - 1)H/bF \ . \tag{6b}$$

f_1 (f_2) is a measure of the deviation of $\rho_{\mathrm{con},t=0}(\rho_{\mathrm{co},t=0})$ from ρ_0 for a finite separation distance H. In the limiting case as $H \to \infty$, we have $\rho_\mathrm{con} \to \rho_\mathrm{co} \to \rho_0$ and $f_1 \to f_2 \to 1$. The initial condition assumed in the following discussions is that the charged condition on surfaces changes from the original one. This may be due to, for example, the adsorption/desorption and/or the exchange of the potential determining ions. This provides a way to illustrating the effect of each relevant parameters on the dynamic behavior of the system under consideration. It should be pointed out, however, that the present analysis is not limited to the types of initial condition assumed. Some general rules are summarized in the appendix.

For rigid surfaces, the Nernst–Planck equation leads to

$$C_i = C_{i0}\exp(-Z_iF\phi_\mathrm{B}/RT) \ , \tag{7}$$

where C_i is the concentration of species i, and C_{i0} and ϕ_B are, respectively, the concentration of ion species i at $\phi_\mathrm{B} = 0$ and the potential at boundary ($r = 0$ or $r = H$). Since both surfaces are maintained at a constant charge density, the boundary conditions associated with Eqs. (1)–(3) are

$$\xi_\mathrm{con} = \exp(-a\psi_0) \quad \text{and} \quad \xi_\mathrm{co} = \exp(b\psi_0), \quad \eta = 0 \ , \tag{8a}$$

$$\frac{\mathrm{d}\psi}{\mathrm{d}\eta} = \frac{-\sigma_0\kappa v^{1/2}}{\rho_0(a+b)} \ , \quad \eta = 0 \ , \tag{8b}$$

$$\xi_\mathrm{con} = \exp(-a\psi_H) \quad \text{and} \quad \xi_\mathrm{co} = \exp(b\psi_H), \quad \eta = H\kappa/v^{1/2} \ , \tag{8c}$$

$$\frac{d\psi}{d\eta}=\frac{\sigma_0\kappa\nu^{1/2}}{\rho_0(a+b)}\,,\quad \eta=H\kappa/\nu^{1/2}\,. \tag{8d}$$

In these expressions, σ_0 is the surface charge density, ψ_0 and ψ_H are, respectively, the scaled potentials at $r=0$ and at $r=H$. Equations (1)–(3) need to be solved simultaneously subject to Eqs. (8a)–(8d). The corresponding equilibrium distributions can be obtained from Kuo and Hsu [14].

Results and discussion

Figure 1 shows the effect of the relative magnitude of the diffusivity of counterions and that of coions on the distribution of electrical potential. The corresponding distributions of ions are shown in Fig. 2. In the numerical simulation, the system is at equilibrium initially. After a 20% reduction in the surface charge density is imposed, the dynamic behavior of the system is recorded. Figures 1 and 2 reveal that at constant H and ν, the smaller the value of $(D_{\rm con}/D_{\rm co})$, the greater the deviations of the distributions of electrical potential and space charge densities from the new equilibrium distributions. The effect of $D_{\rm con}$ on the non-equilibrium behaviors of an electrical double layer is found to be greater than that of $D_{\rm co}$. Qualitatively, this is because that the concentration of counterions near a charged surface is greater than that of coions. Therefore, the diffusion of counterions becomes the rate determining process. As shown in Fig. 1, if $(D_{\rm con}/D_{\rm co})\ll 1$, the transient potential distributions are below the new equilibrium curves. On the other hand, if $(D_{\rm con}/D_{\rm co})\gg 1$, they are very close to the new equilibrium curves.

In the limiting case as $D_{\rm con}\to 0$ and $D_{\rm co}\to\infty$, $\rho_{\rm con}=\rho^0_{\rm con}\exp(-a\psi_{\rm e})$, where $\psi_{\rm e}$ is the original scaled equilibrium potential distribution. Also, Eq. (1) vanishes, and Eqs. (2) and (3) reduce to, respectively,

$$\frac{d^2\xi_{\rm co}}{d\eta^2}-b\left(\xi_{\rm co}\frac{d^2\psi}{d\eta^2}+\frac{d\xi_{\rm co}}{d\eta}\frac{d\psi}{d\eta}\right)=0 \tag{9}$$

and

$$\frac{d^2\psi}{d\eta^2}=\frac{-\nu}{a+b}(\exp(-a\psi_{\rm e})-\xi_{\rm co})\,. \tag{10}$$

Equation (9) can be simplified further by applying the condition that surfaces are ion-impenetrable to yield

$$\frac{d\xi_{\rm co}}{dr}-b\xi_{\rm co}\frac{d\psi}{dr}=0\,. \tag{11}$$

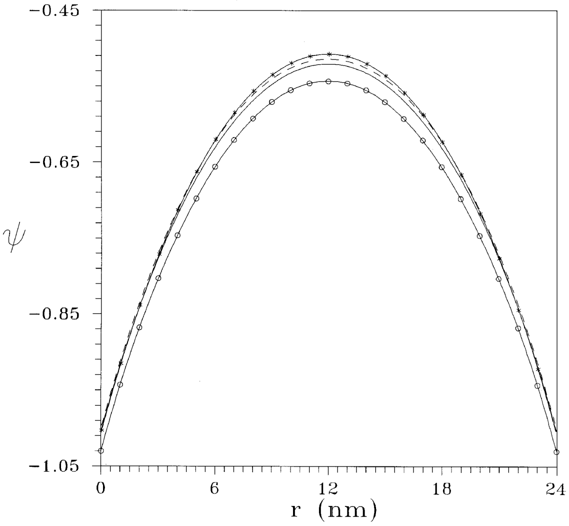


Fig. 1 Distribution of electrical potential in a double layer at various ratios of $(D_{\rm con}/D_{\rm co})$ at $t=64\times10^{-9}$ s for the case $a=b=1$, $I=10^{-3}$ M, $\varepsilon_r=78$, $T=298.15$ K, $H=24$ nm, and a 20% reduction in the surface charge density initially. Solid line: $D_{\rm con}/D_{\rm co}=1$; (∗) $D_{\rm con}/D_{\rm co}=100$; (○) $D_{\rm con}/D_{\rm co}=0.01$; dashed line: new equilibrium distribution

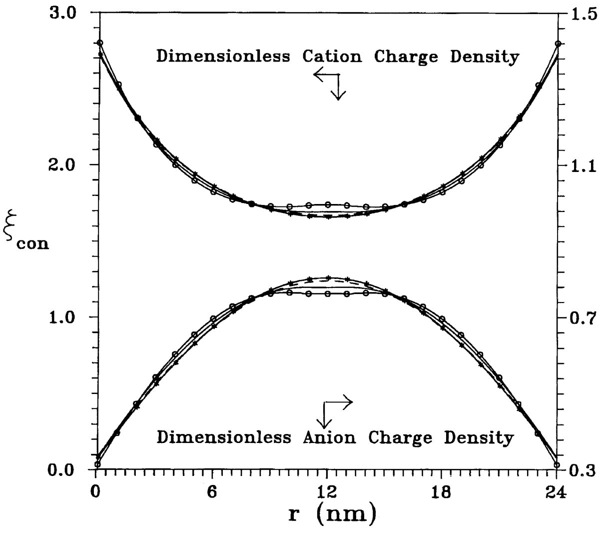


Fig. 2 Distributions of ions for the case of Fig. 1

The solution to Eqs. (10) and (11) is equivalent to that of the steady-state Poisson–Boltzmann equation with the original equilibrium counterion concentration and the Boltzmann distribution for coions. On the other hand, if $D_{\rm con}\to\infty$ and $D_{\rm co}\to 0$, the reverse is true. Note that the equilibrium distribution is a function of both a and b, but is independent of $D_{\rm con}$ and $D_{\rm co}$. Figure 2 shows that if $(D_{\rm con}/D_{\rm co})=0.01$, $\xi_{\rm con}$ is greater than the new equilibrium value near the surfaces, and the reverse is true for $\xi_{\rm co}$. This is because that both surfaces are impenetrable to ions.

Although $D_{\mathrm{con}} \ll D_{\mathrm{co}}$, the counterions and the coions reach their new equilibrium distributions at almost the same rate. This is because the movement of ions are not independent of each other; it is driven by the electric field, which is determined by the distribution of both ions. In practice, $(D_{\mathrm{con}}/D_{\mathrm{co}})$ is of the order of 0.1–10, and therefore its effect on the rate of a system to reach its equilibrium state is insignificant. However, cases may occur in which this effect needs to be considered, for example, if the medium between two surfaces is a membrane which is impermeable to counterions (coions), i.e., $D_{\mathrm{con}} \to 0$ $(D_{\mathrm{co}} \to 0)$. In this case, the Boltzmann distribution for a new equilibrium state can never be reached by counterion (coion). Also, the equilibrium potential and space charge distributions are different from those obtained by solving the corresponding equilibrium PBE.

Figure 3 illustrates the effect of the separation distance between two surfaces on the distribution of electrical potential. As in the case of Fig. 1, the system is at equilibrium initially, and a sudden drop of 20% in the surface charge density is assumed. Figure 3 reveals that the greater the separation distance, the longer is the time needed to reach equilibrium state, as expected. The maximum deviation of the non-equilibrium model from the corresponding new equilibrium model with an error less than 1% is of the order of 10% for $H = 48$ nm.

The electrical potential distributions for various D at constant H and v is shown in Fig. 4; the corresponding distributions of ions are illustrated in Fig. 5. Again, the system is at equilibrium initially, and a step change of 20% in the surface charge density is assumed. Figures 4 and 5 suggest that v can be used to judge whether a dynamic system is close to the corresponding equilibrium state. The greater the value of v, the closer a dynamic system to the corresponding equilibrium state. Note that the definition of v can be rewritten as

$$v = \frac{D/\kappa^{-1}}{\kappa^{-1}/t} = \frac{v_{\mathrm{d}}}{v_{\mathrm{e}}} \,. \tag{12}$$

This expression indicates that v is a measure for the relative magnitudes of the rate of diffusion of ions, v_{d}, and that to establish a double layer, v_{e}. Thus, the semi-quantitative result for the time scale of double-layer relaxation suggested by Lyklema [9] is justified. According to Eq. (4b), at a fixed v, t increases with both $1/\kappa^2$ and $1/D$. Therefore, double-layer relaxation can be significant if a double layer is thick (dilute solution), or the mean diffusivity of ions is small.

In the present study, the effect of ion transport through convection is neglected. This is adequate if the absolute flux of counterions, $|N_{\mathrm{con}}|$, is close to that of coions, $|N_{\mathrm{co}}|$, or the sum $N_{\mathrm{con}} + N_{\mathrm{co}}$ is small. The latter occurs if either $|N_{\mathrm{con}}| = |N_{\mathrm{co}}|$, or the concentrations of ions are low.

Fig. 3 Distributions of electrical potential in a double layer at various separation distances between surfaces at $t = 64 \times 10^{-9}$ s for the case $a = b = 1$, $I = 10^{-3}$ M, $\varepsilon_r = 78$, $T = 298.15$ K, $D_{\mathrm{con}} = D_{\mathrm{co}} = 10^{-9}$ m^2/s, and a 20% reduction in the surface charge density initially. Curve 1: $H = 24$ nm; 2: $H = 36$ nm; 3: $H = 48$ nm. Dashed lines denote the new equilibrium distribution. The maximum deviation of the non-equilibrium value from the corresponding new equilibrium value is 1.2% for $H = 24$ nm, 3.9% for $H = 36$ nm, and 11.5% for $H = 48$ nm

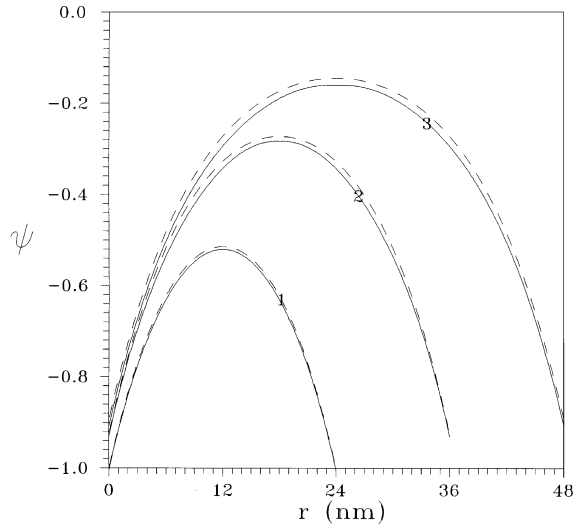
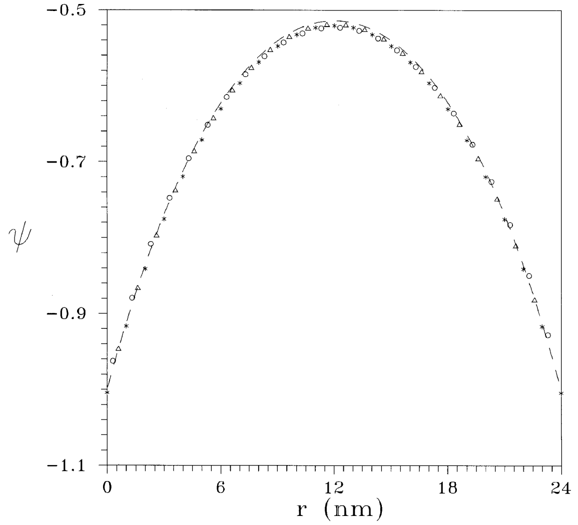


Fig. 4 Distribution of electrical potential in a double layer at constant $v(= 0.692)$ for the case $a = b = 1$, $I = 10^{-3}$ M, $\varepsilon_r = 78$, $T = 298.15$ K, $H = 24$ nm, and a 20% reduction in the surface charge density initially. (∗) $D_{\mathrm{con}} = D_{\mathrm{co}} = 10^{-9}$ m^2/s, $t = 64 \times 10^{-9}$ s; (○) $D_{\mathrm{con}} = D_{\mathrm{co}} = 10^{-8}$ m^2/s, $t = 64 \times 10^{-10}$ s; (△) $D_{\mathrm{con}} = D_{\mathrm{co}} = 10^{-10}$ m^2/s, $t = 64 \times 10^{-8}$ s. Dashed line denotes the new equilibrium distribution



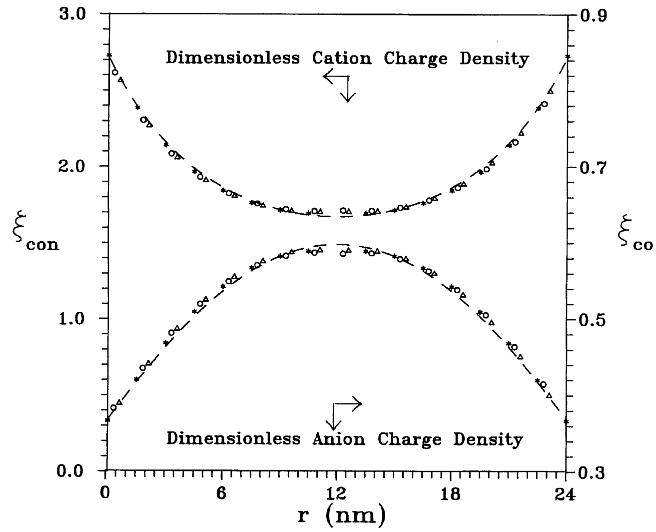


Fig. 5 Distributions of ions for the case of Fig. 4

A more rigorous analysis should take the effect of convective transport of ions into account.

It should be pointed out that the governing equations, Eqs. (1)–(3), are applicable to an arbitrary separation distance between two surfaces. However, if the two surfaces are sufficiently close to each other such that other forces (e.g., van der Waals force) become significant, the distance between them may vary with time, and an equation describing this variation is necessary. To avoid confusion the main theme of the present study, we assume that the separation distance between two surfaces is on the order of two double layers in the numerical simulation, i.e., they are not overlapped, and the changes in the surface conditions will not lead to a variation in the separation distance.

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Appendix

On the basis of the definition of the surface charge density, we have

$$\sigma_0 = \int_0^{H/2} \rho_c \, dr = -\varepsilon_0 \varepsilon_r \phi'(0) = \int_{H/2}^{H} \rho_c \, dr = \varepsilon_0 \varepsilon_r \phi'(H) , \quad (A1)$$

where ϕ' denotes the differential electrical potential. The conservation of charge, along with Eqs. (6a) and (6b), lead to

$$\sigma_0 = -F(a\Gamma_{con} - b\Gamma_{co}) = -\rho_0 H(f_1 - f_2) . \quad (A2)$$

Thus, if ϕ_e is known, f_1 and f_2 can be calculated by Eqs. (5a) and (5b), σ_0 is evaluated by Eq. (A2), and $\phi'(0)$ is determined by Eq. (A1). The value of $\psi'(0)$ needs to be satisfied by the solution of the equilibrium boundary condition at $r = 0$. Therefore, for given H, I, a, and b, $\psi(0)$, $\psi'(0)$, f_1 and f_2 are constant. The conservation of mass implies that f_1 and f_2 are constant during the course of ion migration. The values of $\psi'(0)$ at different conditions of the system are related by

$$F_2 = \frac{\psi(0)_1}{\psi(0)_2} = \frac{\rho_{0,1} H_1 (f_{1,1} - f_{2,1})}{\rho_{0,2} H_2 (f_{1,2} - f_{2,2})} , \quad (A3)$$

where subscripts 1 and 2 represent two different conditions. Here, F_2 is a measure of the relative variation between the surface charge density due to a change in the system from condition 1 to condition 2. For convenience, we define $H = 24$ nm, $I = 10^{-3}$ M, and 1 : 1 electrolyte as the base condition in the numerical simulation. The initial condition determined by f_1 and f_2 for other conditions can be evaluated by the values of f_1 and f_2 at the base condition. For example, for different $a:b$ combinations, we have, by Eq. (4a), $\rho_{0,1:1}/\rho_{0,a:b} = (a + b)/2$, and, therefore,

$$F_V = \frac{\psi(0)_{1:1}}{\psi(0)_{a:b}} = \frac{(a + b)(f_{1,1:1} - f_{2,1:1})}{2(f_{1,a:b} - f_{2,a:b})} , \quad (A4)$$

Table 1a Values of F_V, $\phi_e(0)$, f_1 and f_2 for various $a:b$. F_V is calculated by Eq. (A4) under the base condition $H = 24$ nm, $a:b = 1:1$, $I = 10^{-3}$ M, $T = 298.15$ K, and $\varepsilon_r = 78$

$a:b$	F_V	$\phi_e(0)$	f_1	f_2
1:1	1.00	−1.0000	1.9658	0.5189
1:2	1.04	−1.1291	2.2820	0.2017
1:3	1.23	−1.1398	2.4260	0.0747

Table 1b Values of F_H, $\phi_e(0)$, f_1 and f_2 for various separation distances between surfaces for the case of Table 1a. F_H is calculated by Eq. (A5)

H (nm)	F_H	$\phi_e(0)$	f_1	f_2
24	1.00	−1.0000	1.9658	0.5189
36	0.98	−0.9250	1.6195	0.6391
48	0.99	−0.8950	1.4500	0.7202

Table 1c Values of F_I, $\phi_e(0)$, f_1 and f_2 for various ionic strengths for the case of Table 1a. F_I is calculated by Eq. (A6)

I (mM)	F_I	$\phi_e(0)$	f_1	f_2
1	1.00	−1.0000	1.9658	0.5189
5	1.00	−0.4701	1.3765	0.7295
10	1.00	−0.3344	1.2545	0.7988

The values of f_1, f_2, F_V and $\phi_e(0)$ for values of $a:b$ commonly encountered in practice are summarized in Table 1a. This table reveals that at constant $a(=1)$ both $|\phi_e(0)|$ and F_V increase with $b(|\sigma_0|$ decreases with b).

As the separation distance between surfaces varies, Eq. (A3) yields

$$F_H = \frac{\psi(0)_{H_1}}{\psi(0)_{H_2}} = \frac{H_1(f_{1,H_1} - f_{2,H_1})}{H_2(f_{1,H_2} - f_{2,H_2})} \,. \tag{A5}$$

Similarly, as the ionic strength varies, it can be shown that Eq. (A3) becomes

$$F_I = \frac{\psi(0)_{I_1}}{\psi(0)_{I_2}} = \frac{\rho_{0,I_1} H_{I_1}(f_{1,I_1} - f_{2,I_1})}{\rho_{0,I_2} H_{I_2}(f_{1,I_2} - f_{2,I_2})} = \left(\frac{I_1}{I_2}\right)^{1/2} \left(\frac{f_{1,I_1} - f_{2,I_1}}{f_{1,I_2} - f_{2,I_2}}\right) \,. \tag{A6}$$

The variations in f_1, f_2, $\phi_e(0)$, and F_2 for different separation distances between surfaces, and those for different ionic strengths are summarized in Tables 1b and 1c, respectively. These tables suggest that F_2 is not sensitive to the variation in either H or I.

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