A theoretical exploration of the influencing factors for surface potential*

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Although it has been widely used to probe the interfacial property, dynamics, and reactivity, the surface potential remains intractable for directly being measured, especially for charged particles in aqueous solutions. This paper presents that the surface potential is strongly dependent on the Hofmeister effect, and the theory including ion polarization and ionic correlation shows significant improvement compared with the classical theory. Ion polarization causes a strong Hofmeister effect and further dramatic decrease to surface potential, especially at low concentration; in contrast, ionic correlation that is closely associated with potential decay distance overestimates surface potential and plays an increasing role at higher ionic concentrations. Contributions of ion polarization and ionic correlation are respectively assessed, and a critical point is detected where their contributions can be exactly counteracted. Ionic correlation can be almost neglected at low ionic concentrations, while ion polarization, albeit less important at high concentrations, should be considered across the entire concentration range. The results thus obtained are applicable to other interfacial processes.

Keywords: Hofmeister effect, ionic activity, interfacial process, potential distribution

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1. Introduction

Surface potential is at the Stern plane of charged particles (Fig. 1) and has been used to probe the interfacial properties, dynamics, and reactivity. A number of methods based on zeta (ξ) potential,[1,2] negative adsorption,[3] positive adsorption,[4,5] and pH indicator[6] have been used to obtain surface potential. It has important implications for a variety of nano/colloidal systems such as clay minerals, proteins, and membranes. Notwithstanding, for these charged particles in aqueous solutions, the direct measurement of surface potential remains a difficult task, and hence zeta (ξ) potential that obviously has a small value is often used to represent surface potential[7–9] (see Fig. 1). On the other hand, not a few theories have been developed to predict surface potential, such as Poisson–Boltzmann theory,[4,5,10] self-consistent field theory,[11] classical density functional theory,[12–14] and integral-equation theory.[15]

Generally, the theories currently used to predict surface potential overlook Hofmeister (or specific ion) effects. Specific ion effects, which were first observed about 120 years ago, have been found to be ubiquitous and play a central role in physical, chemical, biological, and colloidal sciences.[16–18] A variety of experimental phenomena can be explained by use of ion specificities, such as DNA conformation and stability,[16,19–21] activity coefficient,[22] interfacial tension of electrolyte solutions,[23,24] colloidal forces,[25,26] and buffer.[27,28] Through the effects of interactions between ions and charged surfaces, ions and ions as well as ions and solvent molecules, the specific ion effect exhibits pronounced influences on the distributions of ions at the interface and in bulk solutions,[29] which further alters the results of surface potential. Therefore, it is no wonder that classical theories that neglect Hofmeister effects are unlikely to make a sound prediction.[28–30] The surface potential expression with the inclusion of specific ion effects due to the enhanced ion polarization in the diffuse layer has recently been derived in our laboratory;[31,32] however, the physical meanings of the ion polarization and ionic correlation in this expression remain ambiguous, and such investigations are of necessity in order to promote our understanding of surface potential; meanwhile, insightful clues can be provided towards its direct measurement.

In the present work, the respective contributions of ion polarization and ionic correlation to surface potential are also evaluated for the various colloidal systems and a wide range of ionic concentrations. Strong ionic correlation between condensed counterions can lead to attractive interaction among colloidal particles[33] as well as charge reversal.[34] On the

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other hand, ionic correlation at high salt concentrations can reduce the counterion concentration in the diffuse layer.[35] This adds the difficulty in measuring the surface potential because ionic correlation usually works in a collaborative manner with ion polarization. We are not aware which is more important for the surface potential determination, ion polarization or ionic correlation. How these two factors behave at different ionic concentrations also remains unclear to us. In the meantime, surface potential decays gradually in the electric double layer (Fig. 1), and the relationship between the potential distribution and decay distance is explored, which helps to understand the difference from zeta (ξ) potential. To address the above issues, the rest of this paper is organized as follows. In Section 2, we show the theoretical surface potential expressions with only Coulomb force as well as correction by ionic correlation, ion polarization, and both factors. In Section 3, the presence of strong ion polarization is evidenced, and then the respective contributions of ionic polarization and ionic correlations are evaluated. In Section 4 the main conclusions are drawn from the present study.

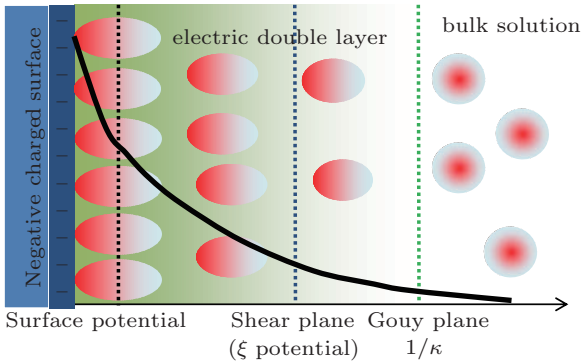


Fig. 1. (color online) Counterion distribution, relative positions of surface, and zeta (ξ) potentials as well as schematic representation of these potentials, each as a function of the potential decay distance that starts from the charged surface and extends towards the bulk solutions (thick solid curve).

2. Surface potential theories

In this section, the various surface potential theories that are developed on the basis of the Poisson–Boltzmann (PB) equation are elaborated. For a given system, ion polarization and ionic correlation usually function collaboratively, and are intractable to distinguish for the experimental researchers.

2.1. Ion–surface Coulomb interaction

For a binary electrolyte system, ions in the diffuse layer should abide by the Boltzmann distribution,

$$f_i(x) = f_i^0 \exp\left[-\frac{Z_i F \varphi(x)}{RT}\right], \tag{1}$$

where f_i^0 (in units: mol·L^{-1}) is the ionic concentration in bulk solution, $\varphi(x)$ (in unit V) is the potential in the electric double layer, and Z_i is the ionic valence, F (in units: C·mol^{-1}) is the Faraday constant, R (in unit: J·mol^{-1}·K^{-1}) is the gas constant, and T (in unit: K) is the absolute temperature.

The mean ion concentration in the diffuse layer equals

$$\tilde{f}_i = \frac{N_i \kappa}{S} = \kappa \int_0^{1/\kappa} f_i(x)\mathrm{d}x, \tag{2}$$

where N_i (mol·g^{-1}) is the amount of the i ion that interacts with the charged particle surface, S (dm^2·g^{-1}) is the surface area of the charged particle, and κ (dm^{-1}) is the Debye–Hückel parameter.

In our previous work,[36] the potential distribution $\varphi(x)$ of the binary electrolyte system containing monovalent and divalent counterions (e.g., NaCl + $CaCl_2$) was derived on the basis of the nonlinear Poisson–Boltzmann (PB) equation,

$$\varphi(x) = \frac{RT}{F} \ln\left[\left(\frac{f_+^0 + 3f_{2+}^0}{f_+^0 + 2f_{2+}^0}\right)\left(\frac{1-\lambda\,\mathrm{e}^{-\kappa x}}{1+\lambda\,\mathrm{e}^{-\kappa x}}\right)^2 - \frac{f_{2+}^0}{f_+^0 + 2f_{2+}^0}\right], \tag{3}$$

where

$$\lambda = \frac{\sqrt{f_+^0 + 3f_{2+}^0} - \sqrt{(f_+^0 + 2f_{2+}^0)\exp(F\varphi_0/RT) + f_{2+}^0}}{\sqrt{f_+^0 + 3f_{2+}^0} + \sqrt{(f_+^0 + 2f_{2+}^0)\exp(F\varphi_0/RT) + f_{2+}^0}}. \tag{4}$$

In Eq. (4), φ_0 represents the potential at the original plane of the diffuse layer (or Stern plane), and here is regarded as surface potential (see Fig. 1).

Introducing the potential distribution function into Eq. (1) and then combining Eq. (2), we arrived at

$$\tilde{f}_i = \kappa \int_0^{1/\kappa} f_i^0 \exp\left[-\frac{ZF\varphi(x)}{RT}\right]\mathrm{d}x \approx f_i^0 \cdot m \exp\left[-\frac{Z_i F \varphi_0}{2RT}\right], \tag{5}$$

with

$$\kappa = \sqrt{\frac{8\pi F^2 (\frac{1}{2}\sum f_k^0 Z_k^2)}{\varepsilon RT}}. \tag{6}$$

In Eq. (5), ε is the dielectric constant of water (8.9×10^{-10} C^2·J^{-1}·dm^{-1}), F (C·mol^{-1}) is the Faraday constant, m, also referred to as A_{ij}^{-1} in some papers,[37] is written as $m = 0.526\ln(f_+^0/f_{2+}^0) + 1.992$, where f_+^0 and f_{2+}^0 refer to the concentrations of univalent and bivalent ions, respectively.[31]

Then the following expressions can be derived for the binary system (i and j)

$$\begin{cases} \dfrac{N_i \kappa}{mS} \exp\left[\dfrac{Z_i F \varphi_0}{2RT}\right] = f_i^0, \\ \dfrac{N_j \kappa}{mS} \exp\left[\dfrac{Z_j F \varphi_0}{2RT}\right] = f_j^0. \end{cases} \tag{7}$$

As a result, the surface potential of the classical theory (φ_0^{C}) can be given as,

$$\varphi_0^{\mathrm{C}} = \frac{2RT}{(Z_i - Z_j)F} \ln \frac{f_i^0 N_j}{f_j^0 N_i}. \tag{8}$$

Equation (8) is the derivative of the original PB equation where only Coulomb interaction occurs between ions and surface.

2.2. Ionic correlation

It is apparent that ionic correlation affects the ion-exchange process and hence this factor should be taken into account:[38,39]

$$\mu_i^{\mathrm{Bulk}} = \mu_{i0} + RT \ln f_i^0 + RT \ln \gamma_i^0 = \mu_{i0} + RT \ln a_i^0, \tag{9}$$

where μ_{i0} is the standard chemical potential, while f_i^0, a_i^0, and γ_i^0 are respectively the ionic concentration, ionic activity, and ionic activity coefficient in the bulk solution. That is, the $RT \ln \gamma_i^0$ term results from ionic correlation in a non-ideal system.[38] The ionic activity is the effective ionic concentration in solution and there are several empirical formulae of calculating the ionic activity and ionic activity coefficient.[40]

The chemical potential in the diffuse layer can be written as

$$\tilde{\mu}_i^{\mathrm{DL}} = \mu_{i0} + RT \ln \tilde{f}_i + RT \ln \tilde{\gamma}_i = \mu_{i0} + RT \ln \tilde{a}_i, \tag{10}$$

where $\tilde{f}_i$, $\tilde{a}_i$, and $\tilde{\gamma}_i$ are respectively the concentration, activity, and activity coefficient in the diffuse layer.

According to the previous studies,[31,37,41] ionic activity represents a function of the Coulomb energy ($\tilde{w}$), and the activity coefficient in the diffuse layer equals[37]

$$\begin{aligned} \tilde{\gamma}_i^{-1} &= \kappa \int_0^{1/\kappa} \exp(-\tilde{w}_i/RT)\mathrm{d}x \\ &= \kappa \int_0^{1/\kappa} \exp(-Z_i F \varphi(x)/RT)\mathrm{d}x \\ &= m \exp\left(-Z_i F \varphi_0/2RT\right). \end{aligned} \tag{11}$$

When the ion exchange process reaches equilibrium, we have $\mu_i^{\mathrm{Bulk}} = \mu_i^{\mathrm{DL}}$, and so the combination of Eqs. (9)–(11) leads to

$$\tilde{f}_i m^{-1} \exp(Z_i F \varphi_0/2RT) = a_i^0. \tag{12}$$

In consideration of ionic correlation, the PB expression is modified into

$$\begin{aligned} \nabla^2 \varphi(x) &= -\frac{4\pi F}{\varepsilon} \sum Z_i f_i(x) \\ &= -\frac{4\pi F}{\varepsilon} \sum Z_i a_i^0 \exp\left[-Z_i F \varphi(x)/RT\right]. \end{aligned} \tag{13}$$

Expressions similar to Eq. (7) can be derived as

$$\begin{cases} \dfrac{N_i \kappa}{mS} \exp\left[\dfrac{Z_i F \varphi_0}{2RT}\right] = a_i^0, \\ \dfrac{N_j \kappa}{mS} \exp\left[\dfrac{Z_j F \varphi_0}{2RT}\right] = a_j^0, \end{cases} \tag{14}$$

where

$$\kappa = \sqrt{\frac{8\pi F^2 (\frac{1}{2} \sum a_k^0 Z_k^2)}{\varepsilon RT}}. \tag{15}$$

As a result, surface potential with the inclusion of ionic correlation is

$$\varphi_0^{\mathrm{I}} = \frac{2RT}{(Z_i - Z_j)F} \ln \frac{a_i^0 N_j}{a_j^0 N_i}. \tag{16}$$

It can be seen from the above descriptions that the ionic activity in solution has been taken into account by considering ion size and ionic dispersion potentials of ion–ion and ion–interface interactions.[28]

2.3. Ion polarization

As is well known, strong electric fields (10^8 V·m^{-1} ~ 10^9 V·m^{-1}) often exist at the surfaces of colloidal particles.[31,32,42–50] As reported previously, the strongly polarizable ions can be adsorbed on the air–water and oil–water interfaces thus affecting the interfacial tensions.[23] For the negatively charged colloidal particles, the ions at their interfaces should be polarized more significantly,[51,52] and the addition of polarization energy ($\tilde{w}_i^{\mathrm{p}}$) is absolutely needed. Therefore equation (14) is converted into the following equations:[29]

$$\begin{cases} \dfrac{N_i \kappa}{mS} \exp\left[\dfrac{Z_i F \varphi_0 + \tilde{w}_i^{\mathrm{p}}}{2RT}\right] = a_i^0, \\ \dfrac{N_j \kappa}{mS} \exp\left[\dfrac{Z_j F \varphi_0 + \tilde{w}_j^{\mathrm{p}}}{2RT}\right] = a_j^0. \end{cases} \tag{17}$$

The above equation can be further transformed into[53]

$$N_i a_j^0 \exp\left[\frac{Z_i F \varphi_0 - Z_j F \varphi_0 + \Delta \tilde{w}^{\mathrm{p}}}{2RT}\right] = N_j a_i^0, \tag{18}$$

with

$$\begin{aligned} \Delta \tilde{w}^{\mathrm{p}} &= \tilde{w}_i^{\mathrm{p}} - \tilde{w}_j^{\mathrm{p}} \\ &= -\tilde{p}_i \tilde{E} - (-\tilde{p}_j \tilde{E}) \\ &= -\tilde{p}_i \kappa \int_0^{1/\kappa} E(x)\mathrm{d}x + \tilde{p}_j \kappa \int_0^{1/\kappa} E(x)\mathrm{d}x \\ &= \tilde{p}_i \kappa (\varphi_0 - \varphi_{1/\kappa}) + \tilde{p}_j \kappa (\varphi_0 - \varphi_{1/\kappa}) \\ &\approx \tilde{p}_i \kappa \varphi_0 - \tilde{p}_{\mathrm{j}} \kappa \varphi_0 = \Delta \tilde{p} \kappa \varphi_0, \end{aligned} \tag{19}$$

where $\tilde{p}$ and $\tilde{E}$ refer to the mean dipole moment in the diffuse layer and electric field strength, respectively; $\varphi_{1/\kappa}$ is the potential at $x = 1/\kappa$ (the upper limit of the electric double layer) and converged to the null point, as verified by the potential distributions in Section 3.

The exponential term in Eq. (18) equals

$$\begin{aligned} & Z_iF\varphi_0 - Z_jF\varphi_0 + \Delta\tilde{p}\kappa\varphi_0 \\ = & \left[1 + \frac{\Delta\tilde{p}\kappa}{(Z_i+Z_j)F}\right] Z_iF\varphi_0 - \left[1 - \frac{\Delta\tilde{p}\kappa}{(Z_i+Z_j)F}\right] Z_jF\varphi_0 \\ = & \beta_i Z_iF\varphi_0 - \beta_j Z_jF\varphi_0. \end{aligned} \tag{20}$$

Then the coefficients β_i and β_j are

$$\begin{cases} \beta_i = 1 + \dfrac{\Delta\tilde{p}\kappa}{(Z_i+Z_j)F}, \\ \beta_j = 1 - \dfrac{\Delta\tilde{p}\kappa}{(Z_i+Z_j)F}. \end{cases} \tag{21}$$

The coefficients β_i and β_j represent functions of the dipole moment difference ($\Delta\tilde{p}$) of the i and j ions. Based on Eqs. (18) and (20), further correction to the surface potential by considering ion polarization turns Eq. (16) into

$$\varphi_0^{\mathrm{HI}} = \frac{2RT}{(\beta_i Z_i - \beta_j Z_j)F} \ln \frac{a_i^0 N_j}{a_j^0 N_i}. \tag{22}$$

At low ionic concentrations, the effect of ionic activity can be neglected, that is, φ_0^{HI} should be approximately equal to φ_0^{H} given below

$$\varphi_0^{\mathrm{H}} = \frac{2RT}{(\beta_i Z_i - \beta_j Z_j)F} \ln \frac{f_i^0 N_j}{f_j^0 N_i}. \tag{23}$$

The specific ion effects due to ion polarization are embodied with coefficients β_i and β_j, which are sensitive to the choice of ion pairs because ion polarizabilities in the diffuse layer are probably different.[29] Note that φ_0^{H} refers to the surface potential corrected with ion polarization but not with ionic correlation. The PB equation cannot be resolved analytically for the mixed electrolyte solutions (e.g., NaCl + $CaCl_2$) in the presence of the polarization effect.[54] As an alternative, we consider the polarization effect on the basis of the mean energy that is obtained directly from the PB equation.

3. Results and discussion

3.1. Ion polarization in experimental observations

The coefficients β_{Na} and β_{Ca} can be derived from Na^+–Ca^{2+} exchange equilibrium experiment,[43] and their empirical expressions are $\beta_{\mathrm{Na}} = 0.0213\ln\sqrt{I} + 0.7669$ and $\beta_{\mathrm{Ca}} = -0.0213\ln\sqrt{I} + 1.2331$, where I is the ionic strength.[31] The difference between β_{Na} and β_{Ca} reflects the polarization difference between Ca^{2+} and Na^+. From the empirical expressions and Eq. (21), the experimental polarization difference between Ca^{2+} and Na^+ in the electric double layer can be

$$\Delta\tilde{p}^{\mathrm{DL}} = 3(\beta_{\mathrm{Ca}} - 1)F/\kappa = (-0.0639\ln\sqrt{I} + 0.6993)F/\kappa. \tag{24}$$

On the other hand, according to the classical theory, the polarization effect for a given ion and the polarization difference between Ca^{2+} and Na^+ are estimated by

$$\tilde{p}^{\mathrm{C}} = \varepsilon_0\varepsilon_{\mathrm{w}}\alpha^*\tilde{E} = 4\pi\varepsilon_0\varepsilon_{\mathrm{w}}\alpha^*\kappa(\varphi_0 - \varphi_{1/\kappa}), \tag{25}$$

$$\Delta\tilde{p}^{\mathrm{C}} = 4\pi\varepsilon_0\varepsilon_{\mathrm{w}}(\alpha^*_{\mathrm{Ca}} - \alpha^*_{\mathrm{Na}})\kappa(\varphi_0 - \varphi_{1/\kappa}), \tag{26}$$

where

$$\alpha_i^* = \frac{3V_{\mathrm{i}}(\varepsilon_i - \varepsilon_{\mathrm{w}})}{4\pi(\varepsilon_i + 2\varepsilon_{\mathrm{w}})},$$

ε_0 is the dielectric constant in a vacuum and $\varepsilon_i = 1 + 4\pi\alpha_i/V_{\mathrm{i}}$,[55] α_i^* is the effective ion polarizability in the solution, and ε_i and ε_{w} are the relative dielectric functions of the i ion and water, respectively, V_{i} is the ionic volume, and α_i is the static polarizability of the i ion, with $\alpha_{\mathrm{Ca}} = 0.4692$ Å^3 and $\alpha_{\mathrm{Na}} = 0.139$ Å^3, respectively.[55,56] According to the Ca^{2+}/Na^+ exchange equilibrium results with different ionic strengths,[43] φ_0 can be calculated by use of Eq. (22). The potential at the distance $1/\kappa$ ($\varphi_{1/\kappa}$) is determined through the potential distribution of Eq. (3).[36]

Figure 2 shows the polarization differences between Ca^{2+} and Na^+ ions, obtained by the experimental electric double layer ($\Delta\tilde{p}^{\mathrm{DL}}$) and classical ($\Delta\tilde{p}^{\mathrm{C}}$) theory. Owing to the neglect of ion polarization, the classical theory assumes that the dipole moments of Ca^{2+} and Na^+ ions are close to each other and in addition, their difference does not show an observable change with the increase of ionic strength. These are apparently in discrepancy with the experimental observations. On the contrary, the electron configuration analysis is perfectly in line with the experimental observations in that there exists a remarkable difference between Ca^{2+} and Na^+ dipole moments and the polarization effect of the former should be considerably larger (Fig. 2). As mentioned above, the strong electric fields (10^8 V·m^{-1} ~ 10^9 V·m^{-1}) often exist at the interfaces of colloidal particles and in many other systems. Under such strong electric fields, the dipole moments of interacting counterions should be significantly affected and exhibit a considerable increase, and the increment differences between two different counterions can be substantial: e.g., Ca^{2+} and Na^+ investigated in this work. As compared with Na^+, the electron clouds of Ca^{2+} are obviously softer and accordingly Ca^{2+} corresponds to a much stronger polarization effect when interacted with the negatively charged surface, which should be responsible for arousing the Hofmeister effects among the various ions. In addition, the polarization difference between Ca^{2+} and Na^+ ($\Delta\tilde{p}^{\mathrm{DL}}$) shows an increase with the decrease of ionic strength, and this trend becomes more conspicuous at relatively small ionic strengths ($I \leq 0.04$ mol·L^{-1}, see Fig. 2). Neither these experimental results nor electron-configuration results can be properly explained by the classical theory. The classical theory seriously underestimates the effective polarization of counterions. As a matter of fact, the various counterions near the charged surfaces should be polarized to a different degree, depending on their electron configurations.

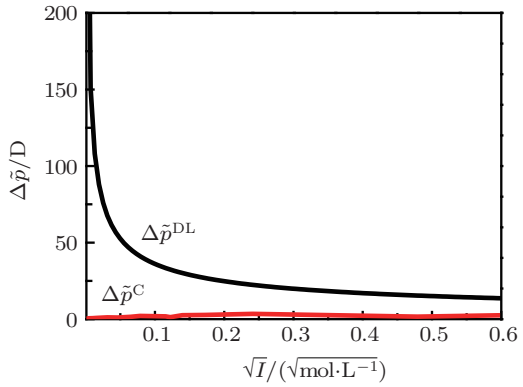


Fig. 2. (color online) Polarization differences between the Ca^{2+} and Na^{+} ions ($\Delta\tilde{p}$, in Debye), each as a function of the root square of ionic strength ($\sqrt{I}$), in $mol^{1/2}\cdot L^{-1/2}$) in solution.

It is worth noting that the water should be also polarized by a strong electric field,[57] but which is obviously less than the charge dipole such as Ca^{2+} and Na^{+} ions;[58–60] that is, the water solvent has a limited influence on the interactions between ions and surface charges that are mainly responsible for specific ion effects. Moreover, the influence of the ionic solution has already been included in the surface potential expression by ionic correlation (for the details, see Subsection 2.2.).

3.2. Influence of ion polarization on surface potential

Si^{4+} and Al^{3+} are the principal constituents for most clay minerals, and isomorphous substitutions with metal ions of almost the same radii create permanent negative charges, e.g., usually the substitutions of Mg^{2+}/Al^{3+} for montmorillonite. It seems very difficult for lattice cations to be replaced by ions from the surfaces and bulk solutions, especially Ca^{2+} and Na^{+} that have substantially larger radii than Si^{4+} and Al^{3+}. Table 1 lists the surface potentials of montmorillonite (mean size: 1480 nm) and rutile titania (TiO_2, mean size: 25 nm),[32] that have been calculated by the various schemes in Section 2, i.e., the classical theory (φ_0^{C} with only Coulomb interaction) as well as those with the addition of ion polarization (φ_0^{H}), ionic correlation (φ_0^{I}), and both effects (φ_0^{HI}). It shows that inclusion of only ion polarization (φ_0^{H}) can achieve comparable results to those with considering both ion polarization and ionic correlation (φ_0^{HI}); instead, the ionic correlation in bulk solutions seems to play a minor role, because the φ_0^{I} values show severe deviations from those of φ_0^{HI} whereas they are close to the data of the classical theory (φ_0^{C}). A good example is montmorillonite with I (ionic strength) = 2.5 $mmol\cdot L^{-1}$, where φ_0^{C}, φ_0^{I}, φ_0^{H}, and φ_0^{HI} are equal to −201.1, −207.5, −106.3, and −109.7 mV, respectively. It can be found that the inclusion of ion polarization in φ_0^{H} and φ_0^{HI} causes a dramatic decrease to surface potential and results in only approximately half the value from the classical theory (φ_0^{C}). That is, the ion polarization should be of vital importance in all the presented cases (Table 1). A careful analysis of ionic correlation will be performed later.

Polarization and gathering of counterions in proximity to the negatively charged surfaces cause an enhancement of the shielding effect on the surface charges, which further leads to a substantial decrease to surface potential. It is in good agreement with the predicted result of ion polarization. Instead, few researchers[55,56,61–63] insist that Hofmeister effects should result from the dispersion energy and ionic steric effect that are known to be significant only in the case of relatively high ion concentration. This seems to be a discrepancy with the fact that Hofmeister effects are more evident at low ionic concentrations due to the more pronounced enhancement of ion polarization in the electric double layer. With inclusion of ion polarization, the surface potentials (φ_0^{H} and φ_0^{HI}) show an obvious decrease as compared with those from the classical theory (φ_0^{C}) (see Table 1).

Table 1. Values of ionic strength (I) of solution containing Na^{+} and Ca^{2+} ions and surface potentials (φ_0) for montmorillonite and rutile titania (TiO_2) suspended in these solutions that are obtained by the various schemes in Section 2. Units of ionic strength and surface potential are $mmol\cdot L^{-1}$ and mV, respectively.

	I[a]	φ_0^{C}	φ_0^{I}	φ_0^{H}	φ_0^{HI}
Montmorillonite	2.52	−201.1	−207.5	−106.3	−109.7
	2.72	−183.2	−193.1	−97.0	−102.3
	5.35	−140.7	−154.4	−75.3	−82.7
Rutile titania	14.30	−96.2	−114.7	−52.5	−62.6
	14.98	−89.4	−108.0	−48.7	−58.9
	15.03	−80.2	−99.0	−43.7	−54.0
	16.69	−58.9	−78.7	−32.2	−43.0
	18.52	−31.5	−52.0	−17.2	−28.4

[a] Data of ionic strengths are cited from Ref. [32].

Figure 3 shows the variations of surface potentials for illite, i.e., φ_0^{C}, φ_0^{H}, φ_0^{I}, and φ_0^{HI} with the root square of ionic strength ($\sqrt{I}$),[43] corresponding to a much wider range of ionic concentrations than those shown in Table 1. Being in accordance with the results of montmorillonite and rutile titania (TiO_2), the surface potentials of illite decrease with the increase of ionic strengths, and especially, a more pronounced change rate on the surface potentials has been detected at relatively low ionic strengths. The logarithm functions can be established between the calculated surface potentials and root square of ionic strengths as follows:

$$\varphi_0^{C} = 0.04\ln(\sqrt{I}+0.044) - 0.05 (R^2 = 0.96), \quad (27)$$

$$\varphi_0^{I} = 0.023\ln(\sqrt{I}+0.017) - 0.088 (R^2 = 0.88), \quad (28)$$

$$\varphi_0^{H} = 0.026\ln(\sqrt{I}+0.019) - 0.044 (R^2 = 0.97), \quad (29)$$

$$\varphi_0^{HI} = 0.012\ln(\sqrt{I}-0.013) - 0.076 (R^2 = 0.89). \quad (30)$$

The correlation coefficients (R^2) given in Eqs. (27)–(30) indicate that these fitted functions describe reasonably the relationships between surface potentials (φ_0^{C}, φ_0^{H}, φ_0^{I}, and φ_0^{HI})

and ionic strengths (I). The correlation coefficients from the classical theory with ion polarization correction are close to 1.0, which demonstrates the fine prediction results for the two surface potentials ($\varphi_0^{\rm C}$ and $\varphi_0^{\rm H}$), while those relating to the ion correlation correction ($\varphi_0^{\rm I}$ and $\varphi_0^{\rm HI}$) are somewhat less satisfactory, which may be caused by the charge oscillation at high ion concentration. Nonetheless, the changed trends of these two surface potentials (Eqs. (28) and (30)) are correctly described and also in agreement with the other two cases (Eqs. (27) and (29)). According to the $\varphi_0^{\rm H}$ versus $\varphi_0^{\rm C}$ results in Table 1 and Fig. 3, the surface potentials will be altered by 20.0% ~ 50.0% when ion polarization is included. For surfaces with variable charges, charge and surface potential may be reversed at high ionic strengths;[56,64] however, the montmorillonite and illite systems under study possess permanent charges resulting from isomorphous substitutions, and the surface charge densities will not be easily altered by ion strength, polarization, and other factors. Accordingly, charge oscillation may take place occasionally, while charge reversion is unlikely to occur.

The contribution of ion polarization ($\Delta\varphi_0^{\rm H}$) can be evaluated by the difference between Eqs. (30) and (28) and expressed as

$$\Delta\varphi_0^{\rm H} = 0.012\ln(\sqrt{I}-0.013) - 0.023\ln(\sqrt{I}+0.017)+0.012. \quad (31)$$

Therefore, ion polarization in the electric double layer strongly affects the surface potential and its contribution is quantitatively evaluated. The surface potential decays gradually within ionic solution, and then the potential distribution $\varphi(x)$ can be described by the nonlinear PB equation.[36]

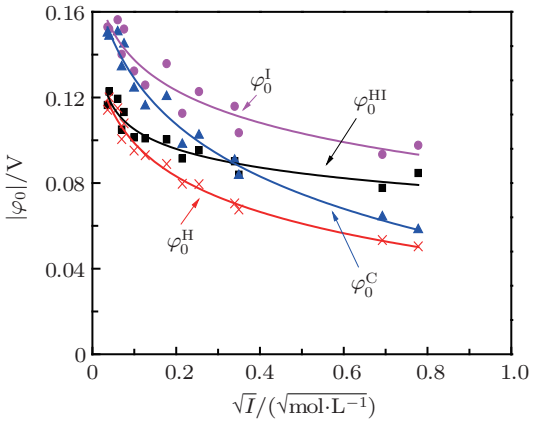


Fig. 3. (color online) Variations of surface potentials (φ_0, in unit V) of illite in ionic solutions with root square of ionic strength ($\sqrt{I}$, in $\rm mol^{1/2}\cdot L^{-1/2}$).

The surface potential decays gradually within ionic solution, and the potential distribution $\varphi(x)$ does not need to additionally consider the ion polarization because this factor has already been accounted for during the calculation of surface potential. In order to investigate the relationship between potential distribution and ionic concentration, two ionic strengths (0.01 $\rm mol\cdot L^{-1}$ and 0.6 $\rm mol\cdot L^{-1}$) are selected for the NaCl + $CaCl_2$ mixed solution ($f_{\rm Na}^0 = 3f_{\rm Ca}^0$). The various surface potentials are calculated by use of Eqs. (27)–(30), and the corresponding variations of potential distribution $\varphi(x)$ with decay distance x which are derived from Eq. (3) are plotted in Fig. 4. The $\phi(x)^{\rm H}$ and $\varphi(x)^{\rm HI}$ potentials descend quickly with the increase of decay distance x, because the counterions with a larger distance away from the charged surface are dramatically less polarized. As a result, Hofmeister effects due to ion polarization show a pronounced decrease with the increase of decay distance (x).

The $\varphi(x)^{\rm H}$ and $\varphi(x)^{\rm HI}$ potentials approach to the null point at $x = 2.40$ nm for $I = 0.6$ $\rm mol\cdot L^{-1}$ whereas at $x = 13.3$ nm for $I = 0.01$ $\rm mol\cdot L^{-1}$, indicating an apparently faster decay rate at higher ion concentrations. In addition, at a given ionic strength, the $\varphi(x)^{\rm H}$ and $\varphi(x)^{\rm HI}$ potentials that include ion polarization vanish at the identical distances as the $\varphi(x)^{\rm I}$ potential. This demonstrates that the forces generated by the surface charges are independent of ion polarization. At low concentrations (e.g., $I = 0.01$ $\rm mol\cdot L^{-1}$ in Fig. 4(a)), ion polarization makes an important contribution to the surface potential and potential distribution, and the inclusion of only ion polarization in the electric double layer is already sufficient to obtain reasonable results as indicated by the comparable $\varphi(x)^{\rm H}$ and $\varphi(x)^{\rm HI}$ data (Fig. 4), which accord with the surface potential data shown in Table 1 and Fig. 3. However, at relatively high concentrations (e.g., $I = 0.6$ $\rm mol\cdot L^{-1}$ in Fig. 4(b)), the $\varphi(x)^{\rm H}$ results seem to deviate significantly from those of $\varphi(x)^{\rm HI}$, and it suggests that only the ion polarization effect cannot correctly account for the surface potential nor potential distribution, which will be discussed in the following.

3.3. Influence of ionic correlation on surface potential

As indicated in Fig. 3, surface potentials including ionic correlation in bulk solution ($\varphi_0^{\rm I}$) change inversely with the increase of ionic strength. Ionic correlation affects the distribution of counterions near the charged surface and further the surface potentials. At low ionic concentrations, surface potentials that include only ionic correlation ($\varphi_0^{\rm I}$) have obvious deviations from those of $\varphi_0^{\rm HI}$ but are rather close to the classical surface potentials ($\varphi_0^{\rm C}$). This indicates that at low ion concentrations, ionic correlation plays a minor role in determining the surface potential. However, when ion concentrations gradually increase, the $\varphi_0^{\rm I}$ values begin to diverge from those of $\varphi_0^{\rm C}$, and instead the $\varphi_0^{\rm I}$ and $\varphi_0^{\rm HI}$ results become gradually closer to each other, implying a strengthening role played by ionic correlation.[35] In a manner similar to Eq. (31), the contribution of ionic correlation to surface potential ($\Delta\varphi_0^{\rm I}$) can be assessed by the difference between Eqs. (30) and (29), and expressed mathematically as

$$\Delta\varphi_0^{\rm I} = 0.012\ln(\sqrt{I}-0.013) - 0.026\ln(\sqrt{I}+0.019)-0.032. \quad (32)$$

It can be found that at high ion concentrations, ionic correlation affects surface potentials even more apparently than ion polarization (Fig. 3). For example, at $I = 0.6$ mol·L^{-1}, $|\Delta\varphi_0^{\mathrm{I}}| = 29.3$ mV and $|\Delta\varphi_0^{\mathrm{H}}| = 14.1$ mV. The former ($|\Delta\varphi_0^{\mathrm{I}}|$) neglects ionic correlation and results in an obviously larger deviation from φ_0^{HI}. Accordingly, ionic correlation is a factor that greatly affects surface potential, especially at high ion concentrations. At the same time, it is found that even at such high ion concentrations, ion polarization cannot be ignored ($|\Delta\varphi_0^{\mathrm{H}}| = 14.1$ mV for $I = 0.6$ mol·L^{-1}), which is quite different from the effect of ionic correlation at low ion concentrations. In addition, this gives a good explanation to the very slight influence of ionic correlation on the data shown in Table 1, for all the investigated cases therein are of rather low ion concentration.

Figure 4 shows that the potential distribution with considering the ionic correlation [$\varphi(x)^{\mathrm{I}}$] becomes obviously less with the increase of decay distance (x), and the decay rates of $\varphi(x)^{\mathrm{I}}$ are more dramatic at higher ion concentrations. As discussed in Subsection 3.2, at a given ionic strength, the $\varphi(x)^{\mathrm{I}}$, $\varphi(x)^{\mathrm{H}}$, and $\varphi(x)^{\mathrm{HI}}$ potentials vanish at the same distances that are strongly concentration-dependent, that is, these potentials are equal to zero at $x = 2.40$ nm for $I = 0.6$ mol·L^{-1} while $x =$ 13.3 nm for $I = 0.01$ mol·L^{-1}, respectively. This is assertive evidence for the association of concentration-associated ionic correlation for surface potential with the potential distribution. Accordingly, ionic correlation in bulk solution should be included when determining the surface potential and potential distribution.

At rather low ionic strengths ($I \leq 0.01$ mol·L^{-1}), the polarization effect predominates during the determination of surface potential and potential distribution, whereas the effect of ionic correlation can be almost neglected (Figs. 3 and 4). With the increase of ionic strength, each of these two effects plays a definite role and it is their synergy that results in the accurate surface potential and potential distribution. Compared with the referenced φ_0^{HI} data, the polarization effect is underestimated whereas ionic correlation overestimates surface potential. Therefore, there should exist a critical point on the φ_0^{HI} curve where these two factors can be exactly counteracted, and for the illite system, the critical ionic strength (I_{c}) equals 0.16 mol·L^{-1} (see Fig. 5), that is, at $I < 0.16$ mol·L^{-1}, $|\Delta\varphi_0^{\mathrm{H}}| > |\Delta\varphi_0^{\mathrm{I}}|$; at $I = 0.16$ mol·L^{-1}, $|\Delta\varphi_0^{\mathrm{H}}| = |\Delta\varphi_0^{\mathrm{I}}|$, and at $I > 0.16$ mol·L^{-1}, $|\Delta\varphi_0^{\mathrm{H}}| < |\Delta\varphi_0^{\mathrm{I}}|$. The presence of critical ionic strengths (I_{c}) can be safely extended to other systems albeit the exact values may change accordingly. The ion polarization and ionic correlation make a larger contribution to the surface potential (φ_0^{HI}) at very low and high concentrations, respectively (Fig. 5). What should be noteworthy is that the effect of ionic correlation can be almost neglected at rather low ion concentrations, while ion polarization, although it makes less of a contribution to the ionic correlation at high concentrations, is still indispensable for the surface potential (φ_0^{HI}) and potential distribution [$\varphi(x)^{\mathrm{HI}}$] and hence should be considered across the entire concentration range (see Fig. 5).

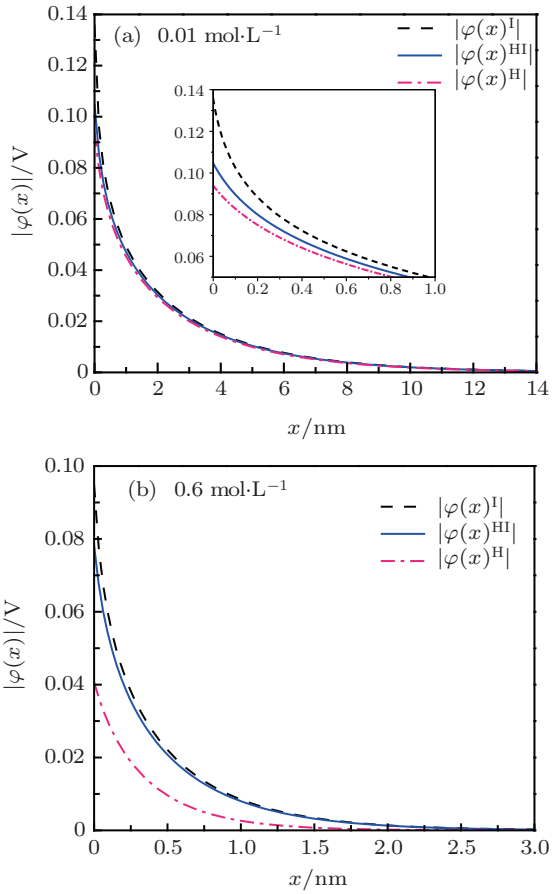


Fig. 4. (color online) Variations of the potential distribution ($|\varphi(x)|$, in V) with decay distance (x, in nm) at two different values of ionic strength (I): (a) 0.01 mol·L^{-1} and (b) 0.6 mol·L^{-1}.

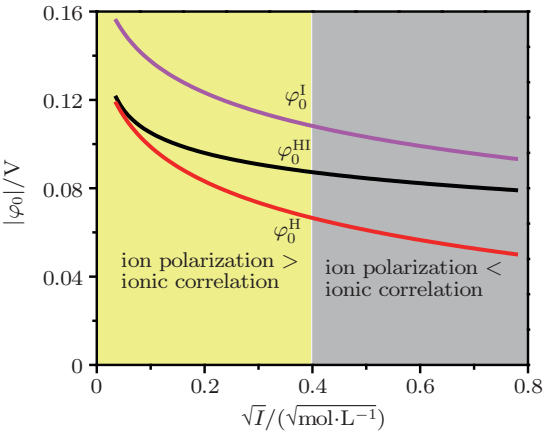


Fig. 5. (color online) Illustration of region divisions of surface potentials (φ_0^{HI}, in V) of illite according to the relative contributions of ion polarization and ionic correlation.

4. Conclusions

The surface potential has been widely used to characterize the interfacial property, dynamics, and reactivity, while it is currently still a difficult task for the direct measurement. In this work, a number of significant pending problems appearing in the recently proposed surface potential expression are

addressed, thus providing insightful clues for the direct measurement and striding towards the understanding of surface potential and further interfacial behaviors.

The various theories of surface potentials are elaborated, including the classical theory and recently developed one covering both ion polarization and ionic correlation. The ion polarization that is responsible for Hofmeister effects may be distinct for the various ions, and the polarization difference between two selected ions shows an obvious increase with the decrease of ion concentration. These cannot be explained properly by the classical theory and so the predicted surface potentials deviate substantially from those from the recently developed theory. The polarization effect decreases with the increase of ion concentration and causes the surface potential and potential distribution to decrease dramatically, especially at low ionic concentrations. Unlike the ion polarization that underestimates the surface potential, ionic correlation overestimates the surface potential and plays an increasing role with the increase of ion concentration. Surface potential decays quickly in ionic solution, and the null points of decay distances are identical for the various theories but different from the various ionic concentrations, thus providing good support of the fact that ionic correlation should be associated closely with surface potential.

The respective contributions of ion polarization and ionic correlation to the surface potential are evaluated for different systems, and the results indicate that these two factors are more significant at low and high ionic concentrations. There exists a critical point on each of the surface potential curves where the contributions of these two factors can be counteracted exactly. For an illite system, the critical ionic strength (I_c) equals 0.16 mol·L^{-1}. The ionic correlation can be almost neglected at low ionic concentrations, while ion polarization also plays a definite role at high ionic concentrations albeit less than ionic correlation should be considered in calculating the surface potential and potential distribution across the entire concentration range. In addition, the apparent difference between surface and zeta (ξ) potentials can be viewed through the analysis of potential distributions, which clearly shows that zeta (ξ) potential is obviously less than surface potential and the confusion of these two conceptions can lead to ridiculous results. These conclusions should be applicable to other interfacial processes.

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