The effect of surface dipoles and of the field generated by a polarization gradient on the repulsive force

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Abstract

Double-layer and hydration interactions have been coupled into a single set of equations because both are dependent on the polarization of the water molecules. The coupled equations involve the electric fields generated by the surface charge and surface dipoles, as well as the field due to the neighboring dipoles in water. The dipoles on the surface are generated through the counterions' binding to sites of opposite charge. The equations obtained were employed to explain the restabilization observed experimentally at large ionic strengths for colloidal particles on which protein molecules were adsorbed. Polar molecules adsorbed on a charged surface of colloidal particle can generate a field either in the same direction as that generated by the charge or in the opposite direction. The effect of the sign of the dipole of the adsorbed polar molecules on the interaction between surfaces was also examined.

Keywords: Hydration force; Double-layer interaction; Surface dipoles; Restabilization

1. Introduction

The traditional double-layer theory combines the Poisson equation with the assumption that the polarization is proportional to the macroscopic electric field, and uses Boltzmann distributions for the concentrations of the ions. The potential of mean force, which should be used in the Boltzmann distribution, is approximated by the mean value of the electrical potential. The macroscopic field \( E \) and the polarization \( P \) are related via the Poisson equation

\[
\varepsilon_0 \frac{dE}{dz} = \rho - \frac{dP}{dz},
\]

where \( \rho \) is the charge density due to the ions, \( \varepsilon_0 \) is the vacuum permittivity, and \( z \) is the distance from the middle between two surfaces, which are considered planar and parallel. In the traditional treatment, \( E \) and \( P \) are assumed to be proportional:

\[
P = \chi E,
\]

\( \chi \) being the electrical susceptibility. Equation (2), however, can be used only when the electric field is sufficiently uniform, hence when the polarization gradient is sufficiently small. When this condition is not satisfied, the polarization gradient generates an additional electric field, because the fields acting on a water molecule due to the neighboring water dipoles do not compensate each other any longer. Only the fields induced by the neighboring dipoles are important because those caused by the more remote ones are screened by the intervening water molecules. Indeed, the dielectric constant is unity between two neighboring dipoles, but very large for the remote ones [1].

A large polarization gradient is generated in an aqueous electrolyte solution, either when the surface charge density is large or/and when there are dipoles on the surfaces. A general theory accounting for the above effects was developed in a previous article [2]. Two applications of this theory are examined in the present article. First we consider a colloidal dispersion or an emulsion stabilized by the adsorption of an ionic surfactant or a protein. In this case, the dissociation of the surfactant or protein molecules generates a charge that in the traditional theory is responsible for the stability of the system. The classic theory also predicts that, as a result of screening, the repulsive double-layer force decreases as the ionic strength increases. There are, however, experimental results [3] that show that, as the concentration of electrolyte increases, the stability ratio decreases and passes through a

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minimum, after which it increases. In other words, the colloidal system is restabilized at sufficiently high electrolyte concentrations. To explain the restabilization, we examine a colloidal system stabilized with adsorbed protein molecules in the presence of NaCl as electrolyte. The increase in electrolyte concentration displaces the dissociation equilibria to smaller degrees of dissociation. While the positive and negative surface charges are thus decreased, each of the neutralized charges is replaced by an ion pair (dipole). In addition, when the polarization gradient is sufficiently large, the neighboring dipoles in water generate a strong electric field. At high electrolyte concentrations the repulsion is dominated by the field generated by the surface dipoles, which propagates through water because of the local interactions between its molecular dipoles; this field is responsible for the restabilization.

Second we examine the case in which polar molecules present in water are adsorbed on the surface. They can polarize the water molecules nearby in the same direction or provide a repulsion. This means that the adsorption of the polar molecules is expected to affect the repulsion.

The basic equations derived in previous papers [1,2] are first summarized; this is followed by examination of the above-described two cases. In contrast to the previous article in which the calculations were carried out in the linear approximation, nonlinear equations are employed in the present article.

2. Theoretical framework

Let us consider that near a surface the water is composed of a succession of ice-like layers, parallel to the surface, which are assumed to be planar. The electric field \( E_P \) that acts on a water molecule of layer \( i \) and is generated by the neighboring water molecules through their dipoles can be expressed as [2,4]

\[
E_P(z_i) = C_i m_{i-1} + C_0 m_i + C_1 m_{i+1},
\]

where \( m_i \) is the average dipole moment in layer \( i \), \( C_0 \) and \( C_1 \) are interaction coefficients given by

\[
C_0 = -\frac{3.766}{4\pi \varepsilon_0 \varepsilon'' l^3}, \quad C_1 = \frac{1.827}{4\pi \varepsilon_0 \varepsilon'' l^3},
\]

where \( l \) is the distance between the centers of two adjacent water molecules, and \( \varepsilon'' \) is the dielectric constant for the medium, \( \varepsilon'' \) being the exact dielectric constant of the material. \( m_i \) is the dipole moment as a function of \( z \).

Expanding in series and neglecting higher-order terms, one obtains

\[
E_P \approx (C_0 + 2C_1) m_i + C_1 \Delta^2 \frac{\partial^2 m}{\partial z^2} \approx C_1 \Delta^2 \frac{\partial^2 m}{\partial z^2},
\]

where \( \Delta \) is the distance between the centers of two adjacent water layers, and \( m(z) \) is the dipole moment as a function of \( z \).

In traditional Lorentz–Debye theory, the local field that acts on a water dipole is given by \( E + P/3\varepsilon_0 \), where \( E \) is the macroscopic field and \( P \) is the polarization [5]. In the present case, the local field \( E_{\text{local}} \) should also include the field \( E_P \) generated by the neighboring dipoles of a water molecule.

Consequently,

\[
E_{\text{local}} = E + E_P + P/3\varepsilon_0 \\
= E + C_1 \Delta^2 (\partial^2 m/\partial z^2) + P/3\varepsilon_0.
\]

The average dipole moment of a water molecule is given by \( m = \gamma E_{\text{local}} \), where \( \gamma \) is the polarizability. Using for \( \gamma \) the Clausius–Mossotti equation,

\[
\gamma = 3\varepsilon_0 \varepsilon_0 (\varepsilon - 1)/(\varepsilon + 2),
\]

where \( \varepsilon_0 \) is the volume of a molecule and \( \varepsilon \) is the dielectric constant of water, and because \( P = m/\varepsilon_0 \), one finally obtains

\[
m(z) = \varepsilon_0 \varepsilon_0 (\varepsilon - 1) E(z) + \varepsilon_0 \varepsilon_0 (\varepsilon - 1) C_1 \Delta^2 \frac{\partial^2 m}{\partial z^2}.
\]

Assuming Boltzmann distributions for the ions, one can write

\[
\rho = -2\varepsilon e \sinh(e\Psi/kT),
\]

where \( \varepsilon e \) is the bulk electrolyte concentration. By combination of Eqs. (1) and (8), the Poisson equation becomes [2]

\[
\frac{\partial^2 \Psi(z)}{\partial z^2} = \frac{2\varepsilon e}{\varepsilon_0} \sinh\left(\frac{e\Psi}{kT}\right) + \frac{1}{\varepsilon_0 \varepsilon_0} \frac{\partial m(z)}{\partial z}.
\]

Equations (7) and (9) constitute a system of equations for \( \Psi \) and \( m \). To obtain particular solutions of Eqs. (7) and (9), boundary conditions must be provided.

When there are dipoles on the surface, the average field that they generate and that is acting on the first water layer is given by [4]

\[
E_s = (p/\varepsilon')\left[2\pi \varepsilon_0 (A/\pi + \Delta')^{3/2}\right],
\]

where \( p \) is the normal component of the dipole moment of the surface dipoles, \( \varepsilon' \) is the local dielectric constant of the medium, \( A \) is the surface area per dipole of the surface (1/\( A \) is the surface dipole density), and \( \Delta' \) is the distance between a surface dipole and the center of the first layer of water molecules.

The electric field that is acting on the first water layer and is induced by the nearby water molecules can be obtained from Eq. (3) in which the term containing \( m_{i-1} \) is absent:

\[
E_{P1} = C_0 m_1 + C_1 m_2.
\]
Consequently, the dipole moment in the layer of water closest to the surface is given by

\[
m_{|z=-d} = \gamma E_{\text{local}} = \gamma (E + E_s + E_p + P/3\varepsilon_0)
\]

\[
= \varepsilon_0 \varepsilon_0 (\varepsilon - 1)(E + E_s + E_p)_{|z=-d}
= -m_{|z=d},
\]

where 2d is the distance between the two plates.

The electroneutrality condition provides a second boundary condition:

\[
\sigma = \frac{1}{2} \int_{-d}^{d} \rho d z = \frac{1}{2} \int_{-d}^{d} \left( \varepsilon_0 \frac{\partial^2 \Psi}{\partial z^2} - \frac{1}{\varepsilon_0} \frac{\partial m}{\partial z} \right) d z
\]

\[
= \frac{1}{2} \left[ \varepsilon_0 \left( \frac{\partial \Psi}{\partial z} \right)_{|z=d} - \frac{\partial \Psi}{\partial z} \right]_{|z=-d} - \frac{1}{\varepsilon_0} \left( m_{|z=d} - m_{|z=-d} \right)
\]

\[
= \varepsilon_0 \frac{\partial \Psi}{\partial z} \bigg|_{z=d} - \frac{1}{\varepsilon_0} m_{|z=d}.
\]

Expressions for the surface charge \( \sigma \) and dipole densities are derived in the next section, where the dissociations of the surface groups are taken into account.

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\]

\[
= \varepsilon_0 \frac{\partial \Psi}{\partial z} \bigg|_{z=d} - \frac{1}{\varepsilon_0} m_{|z=d}.
\]

Equation (15) can be established by decomposing the pathway of \( \Psi_s \) versus \( \sigma \) in a succession of infinitesimal changes at constant charge followed by changes at constant \( \Psi_s \).

The electrostatic free energy due to the electric field, which includes the interactions with the neighboring dipoles, is given by

\[
F_{\text{ele}} = \frac{1}{2} \int_{-d}^{d} \left( \varepsilon_0 E(z) + m(z) \right) E(z) - m(z) \frac{E_p(z)}{\varepsilon_0} d z.
\]

The excess entropy contribution to the free energy is [7]

\[
F_{\text{entropy}} = kT \sum_{i=-d}^{d} \left( c_i \ln \left( \frac{c_i}{c_{i,0}} \right) - c_i + c_{i,0} \right) d z
\]

\[
= -c_E kT \sum_{i=1,2} \int_{-d}^{d} \left[ (-1)^i e^{\Psi} \exp \left( \frac{(-1)^{i+1} e^{\Psi}}{kT} \right) \right]
\]

\[
+ \exp \left( \frac{(-1)^{i+1} e^{\Psi}}{kT} \right) - 1 \right] d z.
\]

The free energy of the surface layer formed by the surface dipoles and the water molecules between them is assumed independent of 2d.

3. Colloidal restabilization in protein–latex systems

Molina-Bolivar and Ortega-Vinuesa have studied the stability of polystyrene colloidal particles stabilized with an adsorbed layer of protein (IgG), and observed that the stability ratio decreased with increasing ionic strength of NaCl and passed through a minimum at sufficiently large electrolyte concentrations, after which the system was restabilized [3]. This anomalous restabilization of the colloidal system at high electrolyte concentrations cannot be explained in the framework of classic DLVO theory. As the concentration of electrolyte increases, DLVO theory predicts that the colloidal system becomes increasingly unstable. In what follows it is shown that the present theory, which takes into account the effect of the fields generated by the surface dipoles and the neighboring water molecules in the liquid, can explain the restabilization.

The surface charge is generated through the dissociation of the acidic and basic sites of the protein molecules. However, as the concentration of electrolyte increases, the dissociation equilibria are displaced in the direction of lower dissociations and the charges are replaced by ion pairs (dipoles).

Neglecting the adsorption of Cl\(^-\) anions onto the basic sites, the surface charge can be calculated by considering the equilibrium

\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-,\]

\[
S_A \leftrightarrow S_A^- + \text{H}^+,\]

\[
S_B \leftrightarrow S_B^+ + \text{OH}^-,\]

\[
S_A^- + \text{Na}^+ \leftrightarrow S_A^- + \text{Na},\]

where \( S_A \) is an acidic site, \( S_A^- \) a dissociated acidic site, \( S_B \) a basic site, \( S_B^+ \) a dissociated basic site, and \( S_A^- + \text{Na} \) an ion pair formed on an acidic site.

The following equilibrium equations can therefore be written:

\[
K_H = \frac{(1 - w - x)[\text{H}^+][\text{S}]}{x}, \quad (18)
\]

\[
K_{\text{OH}} = \frac{(1 - y)[\text{OH}^-][\text{S}]}{y}, \quad (19)
\]

\[
K_\text{Na} = \frac{(1 - w - x)[\text{Na}^+][\text{S}]}{w}. \quad (20)
\]

Here \( x \) is the fraction of acidic sites occupied by hydrogen ions, \( w \) is the fraction of acidic sites occupied by sodium ions, \( y \) is the fraction of basic sites occupied by OH\(^-\) ions,
and \([H^+]_S, [Na^+]_S,\) and \([OH^-]_S\) are the concentrations of the corresponding ions at the surface.

The ionic concentrations at the surface can be related to their bulk concentrations via the Boltzmann expressions

\[
[H^+]_S = [H^+] \exp \left( \frac{-e\Psi_S}{kT} \right),
\]
\[
[Na^+]_S = [Na^+] \exp \left( \frac{-e\Psi_S}{kT} \right),
\]
\[
[OH^-]_S = [OH^-] \exp \left( \frac{e\Psi_S}{kT} \right),
\]
where \(e\) is the protonic charge, and \(\Psi_S\) is the surface potential.

Consequently, the surface charge density is given by

\[
\sigma = e[N_B(1 - y) - N_A(1 - x - w)],
\]
where \(N_B\) is the surface density of the basic sites and \(N_A\) is the surface density of the acidic sites. Because we assume that surface dipoles are formed through the adsorption of \(Na^+\) only, the dipole density on the surface \((1/A)\) is given by \(wN_A\).

The isoelectric point of IgG is between 6.0 and 8.0 [3]. By selecting its value as 7.0, the surface charge becomes zero at pH 7 and Eq. (24) leads to

\[
N_B(1 - y) = N_A(1 - x - w).
\]

Combining Eqs. (25), (18)–(20), one obtains

\[
K_{OH} = \frac{10^{-7}}{\frac{10^{-7}N_B}{k_B N_A} - \frac{N_A}{N_A} N_B},
\]
which allows calculation of \(K_{OH}\) in terms of \(K_H\) and the ratio \(N_B/N_A\).

By use of the Derjaguin approximation, the repulsive interaction energy between two identical spherical particles of radius \(a\) is given by

\[
V_R = \pi a \int_{H_0}^{\infty} (F - F_\infty) \, dH,
\]
where \(H_0\) is the minimum distance between the surfaces of the two spheres, and \(F_\infty\) is the repulsive free energy per unit area between two infinitely separated plates. The van der Waals attractive interaction between two particles has the form [10]

\[
V_A = -\frac{A_H}{6} \left[ \frac{2a^2}{H_0(4a + H_0)} \right] + \frac{2a^2}{(2a + H_0)^2},
\]
where \(A_H\) is the Hamaker constant. When \(H_0 \ll a\), \(V_A\) can be approximated by \(V_A = -A_H a/12H_0\). The total interacting free energy \(V_T\) between the two spheres is therefore given by

\[
V_T = V_A + V_R.
\]

The stability ratio \(W\), which constitutes a measure of the stability of the colloidal system, is defined as

\[
W = \frac{k_r}{k_s},
\]

\[
k_r\text{ being the rate constant for rapid coagulation and } k_s\text{ the rate constant for slow coagulation.}
\]

where \(\beta\) is a hydrodynamic correction factor, \(u = H_0/a\), \(V_T\) is the total interaction free energy between two colloidal particles, and \(V_A\) is the interaction free energy due to van der Waals attractive forces. The hydrodynamic correction factor \(\beta\) is taken as unity.

The calculations were carried out for the conditions under which the experiments were carried out: pH 8.0 and \(D = 2a = 204\) nm. The values of the parameters are not known. Assuming for the distance between two acidic sites or two basic sites a value of 7 Å, one obtains \(N_A = N_B = 2 \times 10^{18} \text{ m}^{-2}\). Typical values for the \(pK_H\) of amino acid residues of globular proteins are in the range 1.95–9.5 [11], and the value of 8 \(\times 10^{-10}\) M was selected for \(K_H\) (p\(K_H = 9.1\)). For the \(K_{Na}\) of human erythrocytes, values of the order of 1 M or larger fitted the experimental data reasonably well [12]. The value of 1 M was therefore selected as the \(K_{Na}\) of IgG. The value \(A_H = 3.2 \times 10^{-20}\) J, which has the right order of magnitude, was selected for the Hamaker constant.

By use of the above equations and values of the parameters, the nonlinear equations were solved numerically. The boundary value problem (Eqs. (7) and (9)), with the appropriate boundary conditions (Eqs. (12), (13) and the symmetry condition for \(\Psi\)) was solved using the standard shooting method and the bvp4c Matlab routine. Initial guesses were provided by the exact solutions in the linear approximation. The free energy \(F\) was obtained by adding the van der Waals interaction to the double-layer interaction calculated using Eqs. (14)–(17) and (27). The stability ratio was calculated by taking 300 Å as the largest value of \(H_0\). The results are compared with the experimental data in Fig. 1 for three values of \(p/\varepsilon\). There are three regions in the figure: the DLVO stabilization region, the rapid aggregation region, and the restabilization region. DLVO theory can explain the behavior in the first two regions, in which the stability of a colloidal system decreases with increasing salt concentration until the concentration reaches the so-called critical coagulation concentration (ccc). Then the colloidal system aggregates rapidly, because the repulsive electric field is suppressed by the high salt concentration.

DLVO theory fails to explain the restabilization. However, by coupling the electric fields induced by the surface charge and surface dipoles and by the neighboring dipoles in water, one can obtain agreement with the experimental
Fig. 1. Stability ratio \( W \) versus salt concentration. The experimental data are from Fig. 6 of Ref. [3]. pH 8.0, \( D = 2a = 204 \text{ nm} \), \( N_A = N_B = 2 \times 10^{18} \text{ m}^{-2} \), \( K_H = 8 \times 10^{-10} \text{ M} \), \( K_{Na} = 1 \text{ M} \), \( A_H = 3.2 \times 10^{-20} \text{ J} \). (a) \( \rho/\varepsilon' = 1 \text{ Debye} \); (b) \( \rho/\varepsilon' = 1.8 \text{ Debye} \); (c) \( \rho/\varepsilon' = 3 \text{ Debye} \).

results and provide a possible explanation for this phenomenon. The adsorption of \( \text{Na}^+ \) ion on the surface, which is stimulated by higher salt concentrations, increases the density of surface dipoles. The surface dipoles polarize the nearby water molecules, which in turn polarize the next layer and so on. The force generated by the overlap of the polarization layers of the two plates, often called hydration force, is responsible for the restabilization of the colloidal system as soon as the concentration of the electrolyte becomes higher than a critical stabilization concentration (csc).

4. Effect of the dipoles adsorbed on the surface

Some polar molecules present in water can be adsorbed onto the surface of colloidal particles. They can polarize nearby water molecules and this polarization propagates from layer to layer. It is assumed that the surface has a fixed charge and that the only surface dipoles are those of the adsorbed polar molecules. Figure 2 illustrates two different kinds of adsorption. In the first one (A), the adsorbed polar molecules expose to the liquid the same charge as that of the surface. The polarization generated by the dipoles of the adsorbed molecules is in this case, in the same direction as that generated by the charge. Consequently, the polarization induced in water is larger than that generated by the surface charge alone. As a result, the repulsion between the two plates is expected to be stronger than that generated by the surface charge alone.

In the second kind of adsorption (Fig. 2B), the dipole exposes to the solution a charge opposite of that of the surface. Correspondingly, the dipole generates a field opposite of that generated by the surface charge, and the adsorption is expected to decrease the repulsive force between the two plates. However, if the surface charge is small, then the dipoles of the adsorbed molecules alone generate repulsion.

Figure 3 presents the results of the calculations. They show that at large distances the repulsive force is always stronger than that predicted by DLVO theory, regardless the sign of the surface dipoles. This occurs because the gradient of the polarization generated by the charge induces a field in the same direction as that of the charge, and this makes the interactions to be of longer range than those predicted by the traditional Poisson–Boltzmann equation. At short distances which, however, should not be smaller than two layers of water molecules (\( \sim 8 \text{ Å} \)) for the calculation to be physically meaningful, the repulsion is stronger than that predicted by DLVO theory when the surface dipoles act in the same direction as the charge and weaker in the opposite case.

5. Conclusions

The kind of adsorption of polar molecules onto the surface of particles can affect interaction between particles. If the electric field generated by the adsorbed dipoles has the same direction as the electric field generated by the charge, the adsorbed dipoles increase the repulsion. If the electric field generated by those dipoles is in a direction opposite that generated by the charge, the adsorbed dipoles weaken the repulsion.
The theory could successfully explain the restabilization of protein-stabilized polymer latexes; the increase in surface dipole density with increasing electrolyte concentration, generated by the binding of the counterions to sites of opposite charge, is in this case responsible for this effect. This occurs because the repulsive force generated by the surface dipoles more than compensates for the decrease in repulsion caused by screening.

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