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Langmuir, 1998, 14 (24), 6793-6803 • DOI: 10.1021/la980299n

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pH Dependence of Thermodynamic Properties for a Dilute Suspension of Ion-Penetrable Spheres

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Received March 11, 1998. In Final Form: August 10, 1998

We study the pH dependence of the internal energy and osmotic pressure for a dilute suspension of ion-penetrable spheres. The charge density within the sphere is determined by the dissociation of the fixed ionizable groups, which in turn depends on the pH and the electrostatic field. When the electric potential is small compared to the thermal motion, a linear charge regulation model is always obtained with pH-dependent coefficients. The two-site dissociation models have been considered. On the basis of the linearized Poisson–Boltzmann equation, the electric potential distribution can be solved by the perturbation method. A two-particle interaction is then obtained. The effect of pH on the interaction energy is twofold. It affects the total charge carried by an isolated sphere and also the ability of charge-regulation. The charge can be regulated by the potential established by the sphere itself and that induced by other surrounding spheres. The three-body interaction has also been derived by studying the interaction free energy of a system with N particles. On the basis of the two-particle interaction energy, the second virial coefficients can then be evaluated.

1. Introduction

The interactions between colloidal particles have a profound effect on the behavior of the suspensions, such as stability, phase diagram, and rheology.^{1,2} They play an essential role in determining the structure and, therefore, the macroscopic properties of a colloidal system. Many practical applications of colloidal science revolve around the problems of controlling the forces between colloidal particles. One convenient way of regulating the electrostatic interactions is to adjust the concentration of potential-determining ions or indifferent ions.² The ions H^+ and OH^- are potential-determining ions for the oxide systems, along with a great many other colloids like the polymer latexes and various biological surfaces. In such system the surface charge and potential are determined largely by the pH value in the solution. For instance, aggregation near the isoelectric point is a well-known phenomenon due to the reduced interparticle electrostatic repulsion and is frequently used for protein separation by precipitation.

The interactions between particles can be inferred by comparing the structure factor or thermodynamic properties from experiments with that from calculations based on an assumed pair potential. For instance, the osmotic pressure measured from the osmometer or the internal energy measured by the isothermal titration calorimetry at dilute concentrations gives the information about the second virial coefficient, which is related to the two-particle interactions. As a consequence, the understanding of the

dependence of the thermodynamic properties, such as osmotic pressure and internal energy, of a colloidal suspension on the concentration of potential-determining ions (or indifferent ions) provides a simple tool to realize the interactions between particles. The main goal of our studies is to investigate the effect of pH on the electrostatic interactions between two particles and furthermore establish the pH dependence of thermodynamic properties of such colloidal system.

The basic feature of the interaction between a pair of colloidal particles can be described by the DLVO theory. This theory includes van der Waals attractions between particles, although they are generally negligible in kinetically stable suspensions. The dominant electrostatic interactions are described by the mean-field Poisson–Boltzmann equations (PB). For a system of a large number of spherical particles, numerical solution of the nonlinear PB equation is a daunting task. Part of the difficulty of calculating the interaction is due to the nonlinear nature of the PB equation which renders the problem analytically intractable except for simplest geometries.^{1,2} A common simplification is to linearize the PB equation based on Debye–Huckel approximation, which gives an exact result when the thermal energy is large compared to the electrical potential. In numerous practical applications, even when the electrostatic potential of the particles is comparable to or only slightly larger than the thermal fluctuation, the linearized PB equation still gives an acceptable qualitative and quantitative description of the system.

The theoretical framework for the exact solution of the LPB equation between two identical spherical colloidal particles have been available for some time.^{3–8} When two

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ion-impenetrable surfaces approach one another, one usually assumes either constant surface potential or constant surface charge density. Under these boundary conditions, Glendinning and Russel³ constructed a numerical solution via a multipole expansion. Recently, Ohshima⁴⁻⁶ has employed Schwartz's method to solve the LPB equation for two dissimilar spheres, and explicit analytical expressions are obtained in the form of infinite series for the potential distribution and the potential energy of the electrostatic interaction. However, the behavior of surfaces of most colloidal particles falls between the extremes of constant charge or constant potential; that is, the interaction may itself influence the degree of dissociation of surface groups so that neither surface potential or surface charge is constant during approach. Various generalized models, sometimes called charge-regulation models, were developed to describe the electrical state of the surface and bridge the two extremes.^{2,7-11} In all such models, if the potential is low compared to the thermal fluctuation, the electrostatic boundary condition at the particle surface can be linearized to give a linear surface charge-surface potential relation. Using the two-center expansion, Krozel and Saville⁷ and Carnie and Chan⁸ have obtained the force and the interaction free energy between two particles numerically. Unfortunately, the numerical results for the interaction potential between two ion-impenetrable particles are difficult to use in calculating the macroscopic properties of a suspension system. Therefore, it is usual to model the interaction as the screened Coulomb potential, and the pairwise additivity assumption is used.¹² Because of the complex, nonlocal nature of electrostatic interaction, whether the interactions can be assumed to be pairwise additive is questionable. For concentrated suspensions, a cell model is adopted to solve the PB equation.^{13,14}

Since an ion-impenetrable surface is by no means a close approximation to a real biological membrane and particles coated with an ion-penetrable polyelectrolytes, Ohshima and Kondo¹⁰ have numerically calculated the pH dependence of electrostatic interaction between two parallel planar ion-penetrable membranes with a nonlinear charge-regulation model. Recently, Ohshima and Kondo¹⁵ have shown that LPB can be exactly solved for the system of two interacting charged ion-penetrable spheres, and an explicit analytical expression for the interaction energy can be obtained. Besides providing a convenient method of mathematical treatment and possibilities for an analytical solution, an ion-penetrable sphere can be a simple model of charged gel particle, cross-linked polyelectrolytes, and linear polyelectrolytes.¹⁶⁻¹⁸ It is also a reasonable approximation for a particle covered by a layer of polyelectrolytes¹⁹ or coated with ion-

penetrable membranes^{10,20-23} or with $\kappa d \gg 1$. Here κ and d are the Debye screening length and the thickness of the charged layer, respectively. In addition, the simple form of electrostatic interactions between ion-penetrable spheres facilitates calculations of pH-dependence of thermodynamic properties, such as osmotic pressure and internal energy, of a colloidal suspension. As a consequence, we deal with charged ion-penetrable spheres (charged porous particles) in the present paper.

The paper is organized as follows. In section II two dissociation models of ionized groups within an ion-penetrable sphere are introduced by extending the surface dissociation models for an ion-impenetrable particle. When the electric potential is low enough, a linear relation between charge density and electric potential at any point within an ion-penetrable sphere is obtained. In section III the electrostatic interaction between two ion-penetrable spheres is evaluated. Section IV illustrates the study of the electric field established by N ion-penetrable spheres. The system's free energy is then derived. Section V introduces the derivations of the thermodynamic properties, such as the osmotic pressure and the internal energy of a dilute suspension. Finally, section VI contains some examples of the results and detailed discussion to further emphasize the essence of our work.

2. Dissociation Models of Ionizable Groups

Assume that ionizable groups are uniformly distributed within the charged porous spheres of radius a . Following the previous models proposed for the charge-regulation surfaces,² the degree of dissociation of the fixed ionizable group at a given point within the sphere is assumed to be determined by the law of mass action for the dissociation reactions. A single-site dissociation model has been used by Ohshima and Kondo¹⁰ to study the pH dependence of electrostatic interaction. In this paper the two-site dissociation models have been adopted, which include the zwitterionic and the amphoteric models.

The degree of dissociation of ionizable groups at a given point generally depends on the electric potential at that point. Usually, the fixed-charge density due to dissociation reactions varies nonlinearly with the electric potential. To simplify the calculation, we consider the condition that the electric potential is small compared to the thermal motion of the free ions and the electric potential associated with the exponential term can then be expanded. The general form of a linear expression relating the density of the fixed charges, ρ , to the electric potential, ϕ , that models the dissociation reaction is given by

$$\rho = \rho_0 - C\phi \quad (1)$$

where the sign of the constant ρ_0 is the same as the sign of the charge when the particle is in isolation. The constant C is always positive: its magnitude reflects the ability of the ionization reactions to maintain a constant charge density. It has the dimension of electrostatic capacitance per unit volume (farad/m³). It controls the regulation properties of the sphere in that the limit $C \rightarrow \infty$ corresponds to a sphere with a constant potential ($\phi \rightarrow \rho_0/C$) while $C \rightarrow 0$ reduces to a sphere with constant charge density.

2.1. The Zwitterion Model. The zwitterion model shows considerable promise for the treatment of biological (particular protein covered) surfaces.² In this model we

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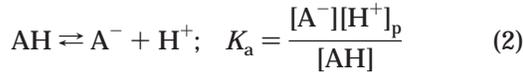
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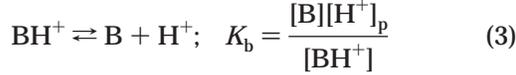
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assume a volume element which can develop positive and negative charges by the ionization of separate basic (e.g. amino) and acidic (e.g. carboxyl) groups:



and



where K_a and K_b are the acid dissociation constants. The quantities in square brackets are chemical activities and the subscript "p" refers to a point within the sphere. Here, these activities are replaced by concentrations, which implies a simple random mixing model for the chemical species or a dilute system. The concentration $[\text{H}^+]_p$ at position \mathbf{r} are estimated from the Boltzmann equation

$$[\text{H}^+]_p = [\text{H}^+] \exp\left[-\frac{e\phi(\mathbf{r})}{kT}\right] \quad (4)$$

where $[\text{H}^+]$ is the bulk concentration of the proton and ϕ is the mean electric potential which the proton experiences at position \mathbf{r} . k and T are the Boltzmann constant and temperature, respectively.

Substituting eq 4 for $[\text{H}^+]_p$ into eqs 2 and 3 and using the relations

$$N_a = [\text{AH}] + [\text{A}^-] \quad (5)$$

and

$$N_b = [\text{BH}^+] + [\text{B}] \quad (6)$$

one obtains both the negative and positive fixed-charge densities due to dissociation:

$$\rho_- = -e[\text{A}^-] = -\frac{eN_a}{1 + [\text{H}^+] \exp\left[-\frac{e\phi}{kT}\right]/K_a} \quad (7)$$

and

$$\rho_+ = e[\text{BH}^+] = \frac{eN_b}{1 + K_b \exp\left[-\frac{e\phi}{kT}\right]/[\text{H}^+]} \quad (8)$$

where N_a and N_b are the total number of acidic and basic groups per unit volume, respectively. e is the fundamental charge, $1.6 \times 10^{-19}\text{C}$. The charge density at position \mathbf{r} is therefore

$$\rho = \rho_+ + \rho_- = \frac{eN_b}{1 + K_b \exp\left[-\frac{e\phi}{kT}\right]/[\text{H}^+]} - \frac{eN_a}{1 + [\text{H}^+] \exp\left[-\frac{e\phi}{kT}\right]/K_a} \quad (9)$$

For $e\phi/kT \ll 1$, eq 9 becomes

$$\rho = \rho_0 - C\phi + O\left(\frac{e\phi}{kT}\right)^2 \quad (10)$$

with

$$\rho_0 = n_a F \left[\frac{\Theta}{1 + K_b/[\text{H}^+]} - \frac{1}{1 + [\text{H}^+]/K_a} \right] = n_a F f_2([\text{H}^+]) \quad (11)$$

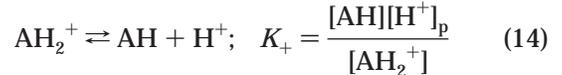
and

$$C = \frac{n_a F^2}{R_g T} \left[\frac{\Theta K_b/[\text{H}^+]}{(1 + K_b/[\text{H}^+])^2} + \frac{[\text{H}^+]/K_a}{(1 + [\text{H}^+]/K_a)^2} \right] = \frac{n_a F^2}{R_g T} f_1([\text{H}^+]) \quad (12)$$

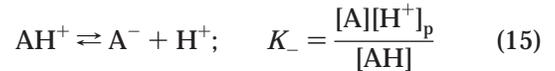
Here n_a and n_b represent the number of moles of ionizable acidic and basic groups per unit volume, respectively. Θ is the ratio of n_b to n_a . F is the Faraday constant, $96\,490\text{C/mol}$, and R_g is the gas constant. Clearly, when $\Theta = 0$ this two-site dissociation model reduces to a single-site dissociation model. Note that $\rho_0 = 0$ corresponds to the point of zero charge (pzc) for the particle. According to eq 11, the pH_{pzc} value at which $f_2 = 0$ is given by

$$[\text{H}^+]_{\text{pzc}} = K_a \left[\frac{-(\Theta - 1) + \sqrt{(1 - \Theta)^2 + 4\Theta K_b/K_a}}{2\Theta} \right] \quad (13)$$

2.2. The Amphoteric Model. The amphoteric model was introduced to describe the behavior of the oxide surface originally.² The volume element is now assumed to contain groups which can take up or release a proton



and



where K_+ and K_- are the acid dissociation constants. The total number of ionizable group N_s can be written as

$$N_s = [\text{AH}_2^+] + [\text{AH}] + [\text{A}^-] \quad (16)$$

According to eqs 14 and 15, the total fixed-charge density due to dissociation reactions is given

$$\rho = e[\text{AH}_2^+] - e[\text{A}^-] = eN_s \left[\frac{[\text{H}^+]_p}{K_+} - \frac{K_-}{[\text{H}^+]_p} \right] \left[1 + \frac{[\text{H}^+]_p}{K_+} + \frac{K_-}{[\text{H}^+]_p} \right] \quad (17)$$

The proton concentration within the sphere is assumed to obey the Boltzmann distribution in eq 4. If the potential is small, again, eq 17 can be expanded and reduced to eq 10 with

$$\rho_0 = n_s F \left[\frac{[\text{H}^+]}{K_+} - \frac{K_-}{[\text{H}^+]} \right] \left[1 + \frac{[\text{H}^+]}{K_+} + \frac{K_-}{[\text{H}^+]} \right] = n_s F f_4([\text{H}^+]) \quad (18)$$

and

$$C = \frac{n_s F^2}{RT} \left[\frac{[H^+]}{K_+} + \frac{K_-}{[H^+]} + 4 \frac{K_-}{K_+} \right] \left[1 + \frac{[H^+]}{K_+} + \frac{K_-}{[H^+]} \right]^2 = \frac{n_s F^2}{RT} f_3([H^+]) \quad (19)$$

According to eq 18, the pH_{pzc} value at which $f_4 = 0$ is then

$$[H^+]_{\text{pzc}} = \sqrt{K_+ K_-} \quad (20)$$

3. Two-Particle Interactions

The electric field is established by the fixed charge within the sphere, whose distribution in turn depends on the electric potential. Therefore, both the density of fixed charge and the potential are dependent on the separation between two particles. On the basis of the linear charge-potential relation, the electrostatic interaction between two ion-penetrable spheres can be evaluated by solving the LPB equation. In this section, we solve the LPB equation for the electric potential by the perturbation method and obtain the interaction energy by using the charge process.

3.1. Electric Potential Distribution. Consider two ion-penetrable spheres of radius a with their centers positioned at \mathbf{r}_1 and \mathbf{r}_2 in a dilute 1-1 electrolyte solution as shown in Figure 1. The electric potential at any point in the system, assuming that it is low enough, i.e. $|e\phi/kT| \ll 1$, can be described by the LPB equation

$$\nabla^2 \phi = \kappa^2 \phi - \sum_{i=1,2} \frac{\rho(\mathbf{r} - \mathbf{r}_i)}{\epsilon_r \epsilon_0} H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (21)$$

where ϵ_r and ϵ_0 are, respectively, the relative permittivity of the electrolyte solution and the permittivity of a vacuum. $\rho(\mathbf{r} - \mathbf{r}_i)$ is the fixed charge density distributed within the sphere i . $H(x)$ is the heaviside's unit function, which is 1 for $x \geq 0$ and 0 otherwise. Since the spheres are permeable to electrolyte ions, the LPB equation is also applied to the internal region of the sphere. The second term on the right-hand side of eq 21 results from the contribution of the fixed charges within the spheres. Here we assume that the relative permittivity of the internal region of the spheres is the same as that of the external bulk solution phase. It is reasonable for a highly porous particle. The fixed charges distributed within the spheres resulting from ionized groups are determined by both the bulk proton concentration and the electric potential, as shown in eqs 9 and 17. Substituting their linearized expression eq 10 for the fixed charge density, ρ , into eq 21 gives

$$\nabla^2 \phi = \kappa^2 [1 + \delta \sum_{i=1,2} H(a - |\mathbf{r} - \mathbf{r}_i|)] \phi - \frac{\rho_0}{\epsilon_r \epsilon_0} \sum_{i=1,2} H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (22)$$

Equation 22 is subject to the boundary conditions given as follows: (1) ϕ is finite at $\mathbf{r} = \mathbf{r}_i$, (2) ϕ is set to zero as $|\mathbf{r} - \mathbf{r}_i| \rightarrow \infty$, and (3) $\nabla\phi \cdot \mathbf{n}_i$ are, respectively, continuous at the surfaces of the spheres, with $|\mathbf{r} - \mathbf{r}_i| = a$ because the relative permittivity in the external solution is the same as that within the sphere. Here \mathbf{n}_i is the outward normal

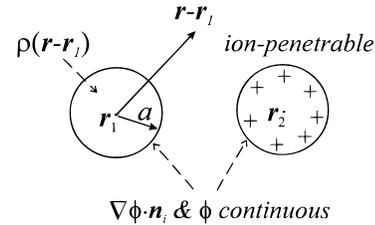


Figure 1. Two ion-penetrable spheres of radius a with their centers positioned at \mathbf{r}_1 and \mathbf{r}_2 in a dilute 1-1 electrolyte solution.

to the surface of each sphere. The parameter δ is defined as

$$\delta = \frac{C}{\kappa^2 \epsilon_r \epsilon_0} \sim O\left(\frac{n_{\text{fix}}}{n_{\text{free}}}\right) \quad (23)$$

It can be regarded as the ratio of the density of ionizable groups, n_{fix} , to that of free ions, n_{free} . Equation 22 is similar to a system of ion-penetrable spheres with a uniform charge density, $\rho_0/(1 + \delta)$ and a relative permittivity, $\epsilon_r/(1 + \delta)$, different from that of the external bulk solution phase. It should be stressed that δ is pH sensitive in the present system. If the density of the ionizable groups within the sphere is small compared the density of free ions, δ would be small compared to one according to eq 23. For a system with $\kappa^{-1} = 5$ nm at 25 °C, which corresponds to an ionic strength about 4 mM, then $\delta < 1$ if $n_{\text{fix}} \lesssim 4$ mM. In this paper, δ is assumed to be small compared to 1.

Though eq 22 is a linear partial differential equation, it is difficult to solve for a pair of spheres without resorting to complicated numerical calculations. For $\delta \ll 1$, however, a regular perturbation method can be used to solve eq 22. The electric potential can be expanded as

$$\phi = \phi_0 + \delta \phi_1 + O(\delta^2) \quad (24)$$

Inserting expression 24 into eq 22 and collecting terms of the same power of δ yields

$$\text{At } O(\delta^0): \nabla^2 \phi_0 = \kappa^2 \phi_0 - \frac{\rho_0}{\epsilon_r \epsilon_0} \sum_{i=1,2} H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (25)$$

and for $n \geq 1$

$$\text{At } O(\delta^n): \nabla^2 \phi_n = \kappa^2 \phi_n + \kappa^2 \phi_{n-1} \sum_{i=1,2} H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (26)$$

Equations 25 and 26 correspond to systems of ion-penetrable spheres with a uniform charge density ρ_0 and a nonuniform distribution $\kappa^2 \epsilon_r \epsilon_0 \phi_{n-1}(\mathbf{r})$, respectively. Both of them are subjected to the same boundary conditions as eq 22.

Equation 25 has been solved by Ohshima and Kondo¹⁵ analytically. By taking advantage of the condition that ϕ_0 and $\nabla\phi_0 \cdot \mathbf{n}_i$ are continuous at the surface of the sphere i , the solution can be expressed as a linear superposition of the unperturbed electric potential, Φ_i , due to each isolated sphere i in the system

$$\phi_0(\mathbf{r}) = \Phi_1(|\mathbf{r} - \mathbf{r}_1|) + \Phi_2(|\mathbf{r} - \mathbf{r}_2|) \quad (27)$$

where Φ_i satisfies the LPB equation

$$\nabla^2 \Phi_i = \kappa^2 \Phi_i - \frac{\rho_0}{\epsilon_r \epsilon_0} H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (28)$$

The solution for Φ_i is then given by¹⁵

$$\Phi_i^0 = A_1 \varphi_d \frac{\exp(-\kappa r_i)}{\kappa r_i}, \quad r_i \geq a \quad (29)$$

and

$$\Phi_i^i = \varphi_d \left[1 - A_2 \frac{\sinh(\kappa r_i)}{\kappa r_i} \right], \quad r_i \leq a \quad (30)$$

where $r_i = |\mathbf{r} - \mathbf{r}_i|$ and $\varphi_d = \rho_0 / (\kappa^2 \epsilon_r \epsilon_0)$. The coefficients A_1 and A_2 are, respectively,

$$A_1 = (\kappa a) \cosh(\kappa a) - \sinh(\kappa a) \quad (31)$$

and

$$A_2 = (1 + \kappa a) \exp(-\kappa a) \quad (32)$$

By substituting eq 30 for Φ_i^i into eq 26, one can solve ϕ_1 . Similar to $O(\delta^0)$, the $O(\delta^1)$ solution for ϕ_1 is obtained by a linear superposition

$$\phi_1 = \Psi_1(|\mathbf{r} - \mathbf{r}_1|) + \Psi_2(|\mathbf{r} - \mathbf{r}_2|) \quad (33)$$

where Ψ_i satisfies the LPB equation

$$\nabla^2 \Psi_i = \kappa^2 \Psi_i + \kappa^2 \Phi_i^i \quad (34)$$

The solutions for Ψ_i are given by

$$\Psi_i^0 = B_1 \varphi_d \frac{\exp(-\kappa r_i)}{\kappa r_i}, \quad r_i \geq a \quad (35)$$

and

$$\Psi_i^i = \varphi_d \left\{ B_2 \frac{\sinh(\kappa r_i)}{\kappa r_i} - \left[1 + \frac{A_2}{2} \cosh(\kappa r_i) \right] \right\}, \quad r_i \leq a \quad (36)$$

where

$$B_1 = \frac{1}{2} [(\kappa a)^2 \sinh(\kappa a) - A_1 D_1] \quad (37)$$

$$B_2 = \frac{A_2 D_1}{2} \quad (38)$$

with

$$D_1 = 2 + \kappa a + \exp(-\kappa a) \cosh(\kappa a) \quad (39)$$

From eqs 29, 30, 35, and 36, the electric potential established in the system is obtained

$$\phi(\mathbf{r}) = \psi_1(r_1) + \psi_2(r_2) \quad (40)$$

with

$$\psi_i(r_i) = \psi_i^0 + \psi_i^i = [\Phi_i^0 + \delta \Psi_i^0 + O(\delta^2)] H(r_i - a) + [\Phi_i^i + \delta \Psi_i^i + O(\delta^2)] H(a - r_i) \quad (41)$$

Here ψ_i can be considered as the electric potential established by sphere i . Note that at any order of δ , ψ_i^0 always behaves like $\exp(-\kappa r_i) / \kappa r_i$.

3.2. Interaction Energy. Once the electric field established by the two spheres is determined, the free

energy of the system containing the spheres 1 and 2 can be obtained by applying the method developed by Verwey and Overbeek.^{24,25} Taking a neutral sphere in the solution as the reference state, both the electric work done in developing the electric double layer and the chemical contribution associated with the adsorption of protons are considered. In the present case, the free energy of the system, F , depends on the distance between two centroids, R_{12} , and is given by

$$F(R_{12}) = \frac{1}{2} \int_{\Omega_1} \rho_1 \phi \, d\Omega_1 + \frac{1}{2} \int_{\Omega_2} \rho_2 \phi \, d\Omega_2 + \text{constant} \quad (42)$$

where ρ_i is the charge density distributed within the sphere i . The constant is independent of R_{12} . The integration is carried out over the volume Ω_i of the sphere i . The interaction free energy between two spheres, $V_2(R)$, is then expressed as the free energy of two spheres at center-to-center separation R minus that at infinite separation; that is, $V_2(R) = F(R) - F(\infty)$. Using eqs 10 and 27, one has

$$V_2(R) = \frac{1}{2} \int_{\Omega_1} [\rho_0 \psi_2 - C(2\psi_1 \psi_2 + \psi_2^2)] \, d\Omega_1 + \frac{1}{2} \int_{\Omega_2} [\rho_0 \psi_1 - C(2\psi_1 \psi_2 + \psi_1^2)] \, d\Omega_2 \quad (43)$$

The first term in the integral represents the interaction between the electric potential-independent fixed charge density (ρ_0) in sphere 1 and the potential (ψ_2) due to sphere 2. The second and third terms denote, respectively, the interactions of the fixed charge in sphere 1 induced by its own potential ($C\psi_1$) or by the potential associated with sphere 2 ($C\psi_2$) with the electric potential due to sphere 2.

The corresponding contributions from the integration over the volume Ω_1 are given as follows:

$$\begin{aligned} \int_{\Omega_1} \rho_0 \psi_2 \, d\Omega_1 &= \rho_0 \int_{\Omega_1} (\Phi_2^0 + \delta \Psi_2^0) \, d\Omega_1 \\ &= \frac{4\pi\epsilon_r\epsilon_0\varphi_d^2}{\kappa} A_1 [A_1 + \delta B_1 + O(\delta^2)] \frac{\exp(-\kappa R)}{\kappa R} \quad (44) \end{aligned}$$

$$\begin{aligned} \int_{\Omega_1} C\psi_1 \psi_2 \, d\Omega_1 &= C \int_{\Omega_1} \psi_1^i \psi_2^0 \, d\Omega_1 \\ &= \delta \frac{4\pi\epsilon_r\epsilon_0\varphi_d^2}{\kappa} \{ A_1 [A_1 - A_2 D_2] + O(\delta) \} \frac{\exp(-\kappa R)}{\kappa R} \quad (45) \end{aligned}$$

and

$$\begin{aligned} \int_{\Omega_1} C\psi_2^2 \, d\Omega_1 &= C \int_{\Omega_1} (\psi_2^0)^2 \, d\Omega_1 = \delta \frac{4\pi\epsilon_r\epsilon_0\varphi_d^2}{\kappa} [A_1 + \delta B_1 + O(\delta^2)]^2 \frac{1}{4\kappa R} \left\{ \left[\frac{\exp[-2\kappa(R-a)]}{2} \right] \left[\kappa(R+a) - \frac{1}{2} \right] - \kappa^2 (R^2 - a^2) E_1 [2\kappa(R-a)] \right\} \\ &\quad - \left[\frac{\exp[-2\kappa(R+a)]}{2} \right] \left[\kappa(R-a) - \frac{1}{2} \right] - \kappa^2 (R^2 - a^2) E_1 [2\kappa(R+a)] \left. \right\} \quad (46) \end{aligned}$$

Here

$$D_2 = \frac{\sinh(2\kappa a) - 2\kappa a}{4} \quad (47)$$

and $E_1(x)$ is the exponential integral and is defined as

$$E_1(x) = \int_0^x \frac{\exp(-u)}{u} du \approx \frac{\exp(-x)}{x} \left[1 - \frac{1}{x} + \frac{2}{x^2} + O\left(\frac{1}{x^3}\right) \right],$$

as $x \gg 1$ (48)

Thus, if $\kappa a \approx 5$, eq 47 can be simplified further:

$$\int_{\Omega_1} C\psi_2^2 d\Omega_1 \approx \delta \frac{4\pi\epsilon_r\epsilon_0\varphi_d^2}{\kappa} [A_1^2 + O(\delta)] \frac{\exp[-2\kappa(R-a)]}{8\kappa R} \frac{a}{R-a} \left[1 - \frac{R+a}{R-a} \frac{1}{2\kappa a} \right] \quad (49)$$

In eq 45, the fixed charge in sphere 1 caused by its own potential ($C\psi_1 \sim O(1)$) interacts with the electric potential due to sphere 2 ($\psi_2 \sim O[\exp(-\kappa R)/\kappa R]$). However, in eq 49, the interaction energy comes from the interaction between fixed charge in sphere 1 caused by sphere 2 ($C\psi_2 - O[\exp(-\kappa(R-2a))/\kappa(R-a)]$) and the electric potential due to sphere 2 (ψ_2). Accordingly, the contribution from $C\psi_2^2$ is $O[\exp(-\kappa(R-2a))/\kappa(R-a)]$, which is smaller than that from $C\psi_1\psi_2$ and can be neglected when $R \gg 2a$.

Using the result of eqs 44, 45, and 49 and adding the corresponding contributions from the integration over the volume Ω_2 of sphere 2, one finally obtains the electrostatic interaction between spheres 1 and 2

$$V_2(R) = [\alpha + O(\delta^2)] \frac{\exp(-\kappa R)}{\kappa R} + [\delta\beta + O(\delta^2)] \frac{\exp[-2\kappa(R-a)]}{2\kappa(R-a)} \frac{\kappa a}{\kappa R} \left[1 - \frac{R+a}{R-a} \frac{1}{2\kappa a} \right] \quad (50)$$

where

$$\alpha = \frac{4\pi\epsilon_r\epsilon_0\varphi_d^2}{\kappa} [A_1^2 + \delta A_1(B_1 + 2A_1 - 2A_2D_2)] \quad (51)$$

and

$$\beta = \frac{4\pi\epsilon_r\epsilon_0\varphi_d^2}{\kappa} \left(\frac{A_1^2}{4} \right) \quad (52)$$

When $\delta = 0$, eq 50 reduces to the result of the interaction between two completely dissociated ion-penetrable spheres, which is pH independent.¹⁵ When $R \gg a$, the interaction energy still acts like two completely dissociated ion-penetrable spheres but with a $O(\delta)$ pH-dependent correction. However, when $R \rightarrow 2a$, the second term on the right-hand side of eq 50 becomes important and gives an extra $O(\delta)$ contribution.

4. Interaction Energy of a System with N Particles

In this section we will study the electric field established by N ion-penetrable spheres and derive the interaction free energy of the system. Consider a monodisperse dilute system which consists of N ion-penetrable spheres with radius a . For a given configuration of N particles with their centers positioned at $\{\mathbf{r}_i\}$, where $i = 1, \dots, N$, the electric potential ϕ at any point in the system is described by the LPB equation. With eq 10 for the fixed charge density, ρ , one has

$$\nabla^2 \phi = \kappa^2 [1 + \delta \sum_{i=1}^N H(a - |\mathbf{r} - \mathbf{r}_i|)] \phi - \frac{\rho_0}{\epsilon_r \epsilon_0} \sum_{i=1}^N H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (53)$$

This linear partial-differential equation can be solved for $\delta \ll 1$ by the regular perturbation method. The electric potential is expanded as in eq 24, which is then substituted into eq 53. Collecting terms of the same power of δ gives

$$\text{At } O(\delta^0): \quad \nabla^2 \phi_0 = \kappa^2 \phi_0 - \frac{\rho_0}{\epsilon_r \epsilon_0} \sum_{i=1}^N H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (54)$$

and for $n \geq 1$

$$\text{At } O(\delta^n): \quad \nabla^2 \phi_n = \kappa^2 \phi_n + \kappa^2 \phi_{n-1} \sum_{i=1}^N H(a - |\mathbf{r} - \mathbf{r}_i|) \quad (55)$$

Subject to the boundary conditions that ϕ_n and $\nabla \phi_n \mathbf{n}_i$ are continuous at the surface of the sphere i , the solutions can be expressed as a linear superposition of the unperturbed electric potential, Φ_i for ϕ_0 and Ψ_i for ϕ_1 , due to each isolated sphere i in the system

$$\phi_0 = \sum_{i=1}^N \Phi_i(|\mathbf{r} - \mathbf{r}_i|) \quad (56)$$

and

$$\phi_1 = \sum_{i=1}^N \Psi_i(|\mathbf{r} - \mathbf{r}_i|) \quad (57)$$

where Φ_i and Ψ_i satisfy eqs 28 and 34, respectively. As a result, the solutions for Φ_i are given in eqs 29 and 30 and those for Ψ_i are given in eqs 35 and 36. The electric potential established in the system is then obtained

$$\phi(\mathbf{r}) = \sum_{i=1}^N \psi(r_i) \quad (58)$$

where $\psi(r_i)$ is defined in eq 41.

Similar to section 3.2, the electrostatic interaction energy of the system, $V_N(\{\mathbf{r}_i\})$, is defined as the free energy of the system $F(\{\mathbf{r}_i\})$ for a given configuration $\{\mathbf{r}_i\}$ minus that for $F(\mathbf{r}_i - \mathbf{r}_j \rightarrow \infty)$.

$$V_N(\{\mathbf{r}_i\}) = \frac{1}{2} \sum_{i=1}^N \left\{ \int_{\Omega_i} [(\rho_0 - C\phi)\phi - (\rho_0 - C\psi_i)\psi_i] d\Omega_i \right\} \quad (59)$$

Using eq 58 for ϕ , the interaction energy of the system is then given by

$$V_N = \frac{1}{2} \sum_{i=1}^N \left\{ \int_{\Omega_i} [\rho_0 \sum_{k \neq i} \psi_k - C(2 \sum_{k \neq j} \psi_j \psi_k + \sum_{k \neq i} \psi_k^2)] d\Omega_i \right\} \quad (60)$$

In eq 60, the leading contributions to the interaction energy V_N are from the first term in the bracket because the nonlinear terms are $O(\delta)$ smaller than the linear term in ψ_k . The nonlinear terms can be rearranged as

$$2\psi_i \sum_{k \neq i} \psi_k + \sum_{k \neq i} \psi_k^2 + 2 \sum_{\substack{k \neq i, j \neq i \\ k > j}} \psi_j \psi_k \quad (61)$$

The first two terms in eq 61 are the two-particle interactions between spheres i and k . The former denotes the interaction of the fixed charge in sphere i caused by its own potential ($C\psi_i \sim O(1)$) with the electric potential due to sphere k ($\psi_k \sim O[\exp(-\kappa R_{ik})/\kappa R_{ik}]$). The latter represents the interaction between the fixed charge in sphere i caused by sphere k ($C\psi_k \sim O[\exp(-\kappa(R_{ik} - 2a)/\kappa(R_{ik} - a))]$) and the electric potential due to sphere k (ψ_k). However, the third term is the three-particle interaction among spheres i , j , and k . That is, the fixed charge in sphere i caused by sphere j ($C\psi_j \sim O[\exp(-\kappa(R_{ij} - 2a)/\kappa(R_{ij} - a))]$) interacts with the electric potential due to sphere k (ψ_k). Here R_{ik} is the distance between spheres i and k .

In terms of two-particle interactions, the interaction energy of the system is

$$V_N = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{k=1 \\ k \neq i}}^N V_2(R_{ik}) + 2C \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \sum_{\substack{k=1 \\ k \neq i, j}}^N \int_{\Omega_i} \psi_j \psi_k d\Omega_i \quad (62)$$

The three-particle interaction is as large as $O(\delta)$ only when $R_{ij} \approx R_{ik} \approx 2a$. Since the events of three particles collision are rare compared to those of two particle collision in a dilute system, the three-particle interaction can be neglected in eq 62. This result indicates that the free energy of a system with N ion-penetrable spheres, V_N , can be evaluated by pairwise addition of interaction energy V_2 . It should be stressed that the free energy of a system with completely dissociated (or pH-independent) ion-penetrable spheres can be exactly calculated by pairwise addition of two-particle interaction energy.²⁶

5. Thermodynamic Properties

In this section, we will derive the thermodynamic properties associated with the electrostatic interactions for a dilute ion-penetrable system. The quantities related to the second virial coefficient can be evaluated by using the results of classical statistical mechanics. The effect of the bulk proton concentration on these properties can then be obtained.

5.1. Electrostatic Internal Energy and Osmotic Pressure. The osmotic pressure due to colloidal spheres can be measured by an osmometer. The electrostatic internal energy of a dilute system can also be directly measured by isothermal titration calorimetry. In other words, when the system is titrated by the same aqueous solution without the charged particles, the heat of dilution reveals the interaction energy between two charged particles. By comparing the theoretical expressions with the experimental results, one is able to find out the interaction energy between two charged particles.

In the previous section, we have shown that the electrostatic free energy of a dilute system can be calculated with pairwise additions. Consequently, the osmotic pressure Π_{el} and internal energy E_{el} associated with electrostatic interactions can be calculated by using the classical statistical mechanics under the assumption of pairwise additivity^{27,28}

$$\frac{\Pi_{\text{el}}}{ckT} = 1 - \frac{2\pi}{3} \frac{c}{kT} \int_0^\infty r^3 g(r; c, T) \frac{du(r)}{dr} dr \quad (63)$$

and

$$\frac{E_{\text{el}}}{NkT} = \frac{3}{2} + 2\pi \frac{c}{kT} \int_0^\infty r^2 g(r; c, T) u(r) dr \quad (64)$$

where c is the number concentration of the particles and $g(r; c, T)$ is the radial distribution function. $u(r)$ is the interaction potential between two particles and is assumed to be a combination of hard sphere potential, u^{hs} , and the electrostatic repulsive interaction, V_2 :

$$u(r) = u^{\text{hs}} + V_2(r; [\text{H}^+]) \quad (65)$$

To carry out the integrations in eqs 63 and 64, one has to know the radial distribution function. Since $g(r)$ depends on the number concentration and the interaction potential, a closure such as Ornstein-Zernike equation, has to be adopted. In principle, one can perform molecular simulations, such as Monte Carlo simulation, to calculate these quantities. In the dilute limit, $ca^3 \ll 1$, the radial distribution function can be approximated as $g(r) \approx \exp(-u/kT)$. Thus, the osmotic pressure and internal energy can be reduced to

$$\frac{\Pi_{\text{el}}}{ckT} = 1 + b_2 c + O(c^2) \quad (66)$$

and

$$\frac{E_{\text{el}}}{NkT} = \frac{3}{2} + E_2 c + O(c^2) \quad (67)$$

where

$$b_2([\text{H}^+]) = 2\pi \int_0^\infty [1 - \exp(-u/kT)] r^2 dr \quad (68)$$

and

$$E_2([\text{H}^+]) = 2\pi \int_0^\infty \left[\frac{u}{kT} \exp(-u/kT) \right] r^2 dr \quad (69)$$

For $V_2/kT \ll 1$, that is, $(\alpha/kT)(e^{-\kappa\sigma}/\kappa\sigma) \ll 1$, $\exp(-V_2/kT) \approx 1 - V_2/kT$. Here $\sigma = 2a$ is the diameter of the sphere. As a result, one obtains

$$b_2 = \frac{2\pi\sigma^3}{3} \left\{ 1 + 3 \frac{\alpha}{kT} \frac{1 + \kappa\sigma}{(\kappa\sigma)^3} e^{-\kappa\sigma} + \frac{3}{8} \delta \frac{\beta}{kT} \frac{1}{(\kappa\sigma)^3} [3\kappa\sigma(\kappa\sigma - 1)E_1(\kappa\sigma) - (1 + \kappa\sigma)e^{-\kappa\sigma}] + O(\delta^2) \right\} + O\left[\left(\frac{V_2}{kT}\right)^2 \sigma^3\right] \quad (70)$$

and

$$E_2 = b_2 + O\left[\left(\frac{V_2}{kT}\right)^2 \sigma^3\right] \quad (71)$$

5.2. Average Charge Density. The spheres in the system have different degrees of dissociation because of different environments around particles. In the experiment, however, the average charge density is the measurable property. An ensemble average charge density distributed within sphere 1 can be calculated by $\langle \bar{\rho} \rangle_1 = \rho_0 - C\langle \bar{\phi} \rangle_1$, where \bar{X} is the volume average of the quantity X and the bracket $\langle Y \rangle_1$ denotes the conditional ensemble

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average of Y with particle 1 fixed at origin. From eq 58 for ϕ and in terms of radial distribution function, one has

$$\langle \bar{\phi} \rangle_1 = \frac{1}{4\pi a^3} \left\{ \int_{\Omega_1} \psi_1 d\Omega_1 + \int_{2a}^{\infty} \left[\int_{\Omega_1} \psi_2 d\Omega_1 \right] c g(r) 4\pi r^2 dr \right\} \quad (72)$$

The first term at the right-hand side of eq 72 denotes the contribution associated with sphere 1 itself. The second term represents the contributions from all other spheres in the system.

At dilute limit, $ca^3 \ll 1$, the integrals can be carried out for weak interactions. Inserting eq 50 into eq 72 leads to

$$\langle \bar{\phi} \rangle_1 = \langle \bar{\phi} \rangle_s + ca^3 \langle \bar{\phi} \rangle_i \quad (73)$$

where

$$\langle \bar{\phi} \rangle_s = \varphi_d \left\{ \left[1 - \frac{A_1 A_2}{(\kappa a)^3} \right] + \delta \left[\frac{3}{(\kappa a)^3} \left(A_1 B_2 + A_1 A_2 - A_2 B_1 - \frac{A_1 A_2 D_1}{2} \right) - 1 \right] + O(\delta^2) \right\} \quad (74)$$

and

$$\langle \bar{\phi} \rangle_i = \varphi_d A_1 (A_1 + \delta B_1) \left[12\pi \frac{1 + 2\kappa a}{(\kappa a)^6} e^{-2\kappa a} \right] + O(ca^3) \quad (75)$$

$\langle \bar{\phi} \rangle_s$ represents the electric potential due to the charge within the sphere 1 itself. The first term in eq 74 corresponds to ρ_0 and the second term denotes the self-charge-regulation effect. On the other hand, $\langle \bar{\phi} \rangle_i$ means the electric potential induced by the other particles surrounding sphere 1. Using eq 73 the ensemble average charge density is then obtained.

6. Results and Discussion

In this paper, the charge-regulated interaction potential between two ion-penetrable spheres has been obtained by solving the LPB equation for $\kappa a \gg 1$ and $\delta \ll 1$. The results are based on the first-order perturbation with $O(\delta^2)$ inaccuracy. The effect of the pH and κa on the two-particle interactions will be illustrated in this section. On the basis of the interaction energy of a system with N spheres, the pH-dependence of the thermodynamic properties for the suspension, such as osmotic pressure and average charge density, has been treated at dilute limit. At the limit $V_2/kT \ll 1$, the analytical form of the second virial coefficients b_2 and E_2 are obtained in eqs 70 and 71. The average charge density can also be obtained with eq 73. However, as $V_2/kT \sim O(1)$ or larger, these thermodynamic properties have to be evaluated by integrating eqs 68, 69, and 72 numerically. These results will be discussed.

According to eq 50, the interaction energy decays with the distance R monotonically and its strength varies with the pH value. The effects of pH and R are shown in Figures 2 and 3, respectively. Figure 2 depicts the variation of the dimensionless interaction energy at $R = 2a$ with pH for various Θ at $\kappa a = 15$ and $\kappa^{-1} = 4.81$ nm. The acidic dissociation constants are assumed to be $K_a = 10^{-4}$ and $K_b = 10^{-9}$ and the apparent ionic strength is maintained to give $\kappa^{-1} = 4.81$ nm. For $\Theta = 0$, which corresponds to a single site model, $V_2(R = 2a)$ is close to zero for $\text{pH} \lesssim 3$ since most of the acid groups maintain in [AH] form and the net charge is negligible. For $\text{pH} \approx 3 \sim 5$, V_2 increases rapidly with increasing charge density because the acid

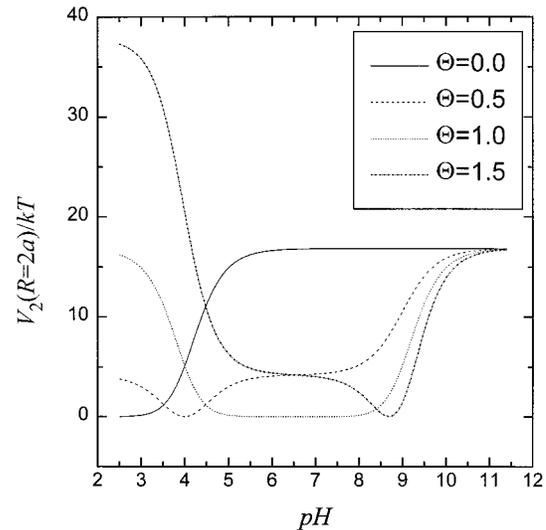


Figure 2. Variation of the dimensionless interaction energy at $R = 2a$ with pH for various Θ at $\kappa a = 15$ and $\kappa^{-1} = 4.81$ nm. $K_a = 10^{-4}$ and $K_b = 10^{-9}$.

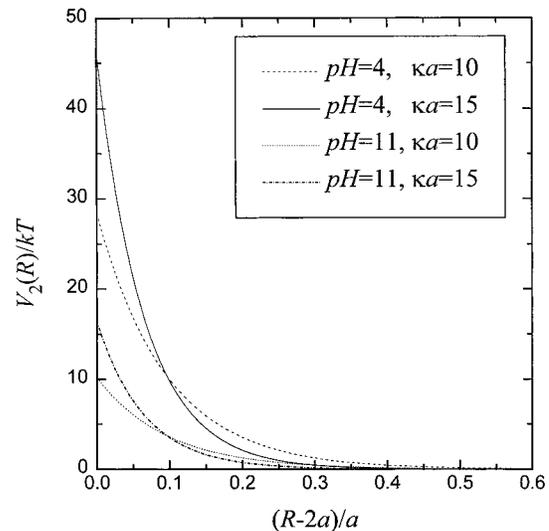


Figure 3. Variation of the interaction energy as a function of the dimensionless separation distance between particles for $\Theta = 1.5$ and $\kappa^{-1} = 4.81$ nm.

groups start to dissociate into $[A^-]$ form. For $\text{pH} \geq 5$, most of the acidic groups have dissociated into $[A^-]$ and the charge density approaches a constant.

For $\Theta > 0$, which corresponds to a two-site dissociation model, the behavior of V_2 is quite different. Note that $[H^+]_{\text{pzc}}$ for $\Theta = 0.5, 1.0, \text{ and } 1.5$ are $K_a + 2K_b, \sqrt{K_a K_b}$, and $2K_b$, respectively. It can be separated into three regions: (i) $\text{pH} \lesssim \min[\text{pH}_{\text{pzc}}, \text{p}K_a + 1, \text{p}K_b - 1]$; (ii) $\text{p}K_a + 1 \lesssim \text{pH} \lesssim \text{p}K_b - 1$; (iii) $\text{pH} \gtrsim \max[\text{pH}_{\text{pzc}}, \text{p}K_a + 1, \text{p}K_b - 1]$. In region (i), $[BH^+] \rightarrow n_b$ and $[AH] \rightarrow n_a$ as pH decreases. Thus, the interaction energy increases with decreasing pH due to the positive charge density within the sphere. In region (ii), $[A^-] \rightarrow n_a$ and $[BH^+] \rightarrow n_b$. Consequently, the sphere carries charge density $-(1 - \Theta)n_a$ and the interaction energy displays a plateau. In region (iii), $[A^-] \rightarrow n_a$ and $[B] \rightarrow n_b$ as pH increases. The interaction energy therefore increases with increasing pH due to the negative charge density inside the sphere. The largest interaction energy occurs at the maximum charge density, either n_a or n_b , which corresponds to a complete dissociation of acidic groups $[A^-]$ or basic groups $[BH^+]$. Since the largest interaction energy is about proportional to ρ_0^2 , $V_{2,\text{max}}$ at R

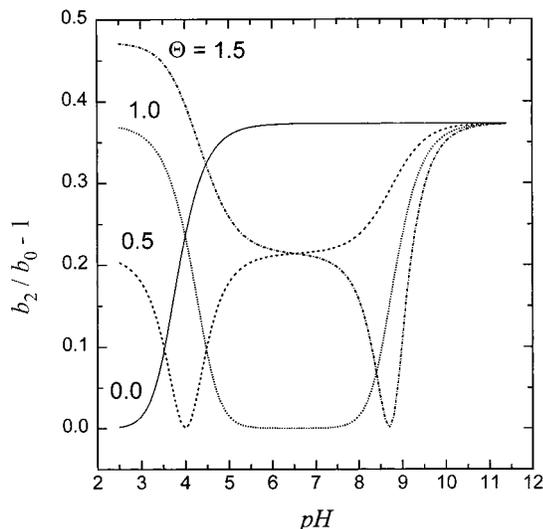


Figure 4. pH dependence of the second virial coefficient b_2 associated with the osmotic pressure for various Θ .

$= 2a$ for $\Theta = 1.5$ is about 2.25 times larger than that for $\Theta = 1.0$. Note that V_2 always has a minimum at the point of zero charge (pH_{pzc}). For $\Theta \neq 1$, this minimum is located between regions i and ii for $\Theta < 1$ or between regions ii and iii for $\Theta > 1$. When $\Theta = 1$, pH_{pzc} is located in region ii and the net charge density in this region is close to zero. As a result, there is a broad regime of negligible interaction energy. At both ends of region ii, unlike $\Theta \neq 1$, the interaction energies display a symmetric behavior. Generally speaking, the interaction potential grows with the mean charge density, which is regulated by the pH value.

The variation of the interaction energy as a function of the dimensionless separation distance between particles for $\Theta = 1.5$ and $\kappa^{-1} = 4.81$ nm is shown in Figure 3. Since the interaction energy falls very fast within $0.5a$, it can be well described by an exponential decay with respect to $(R - 2a)/a$ with a screening length κa . As a result, the interaction energy of large κa decays faster than that of small κa at a specified pH. However, $V_2(R = 2a)$ of large κa is greater than that of small κa . This result is because large particle possesses more charge than small one for a constant Debye length. On the contrary, one would expect that $V_2(R = 2a)$ is smaller for larger κa for a given particle size due to the screening effect.

The pH dependences of the second virial coefficient (b_2 and E_2) are shown in Figures 4 and 5, where $b_0 = 2^3/3\pi\sigma^3$ is the second virial coefficient associated with the hard sphere potential. Since we have only considered the repulsive forces, both b_2 and E_2 are positive. The basic features of the pH dependence are similar to that of the two-particle interaction energy. They also show three different regimes. However, b_2 varies quite significantly along the pH axis, while E_2 changes rather sharply only around the point of zero charge. At $\text{pH} = (\text{pH})_{\text{pzc}}$, the system exhibit the behavior of a hard sphere system with $b_2 = b_0$. For $\text{pH} \neq (\text{pH})_{\text{pzc}}$, $b_2 > b_0$ indicates that the repulsive interaction force leads to an Δa increase in the effective radius of the hard spheres. Δa can be as large as $0.14a$ when $\text{pH} = 3$. When the system is diluted, however, the repulsive interaction force results in an exothermic behavior which cannot be explained by a pure hard-sphere potential.

The charge density distribution within an ion-penetrable sphere gives us an idea about the effect of the charge-regulation on the two-particle interaction and thermodynamic behavior of the system. As we can see

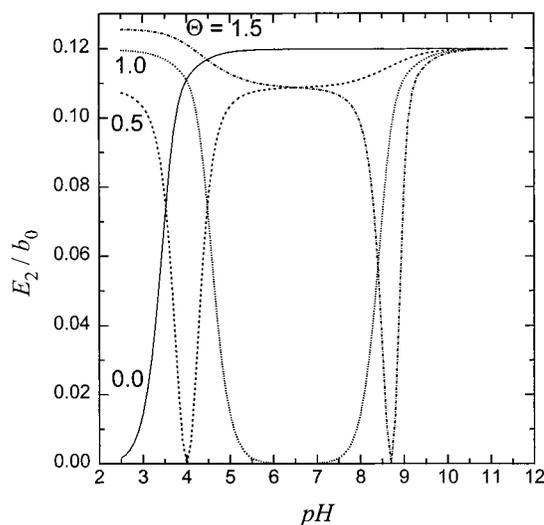


Figure 5. pH dependence of the second virial coefficient E_2 associated with the internal energy for various Θ .

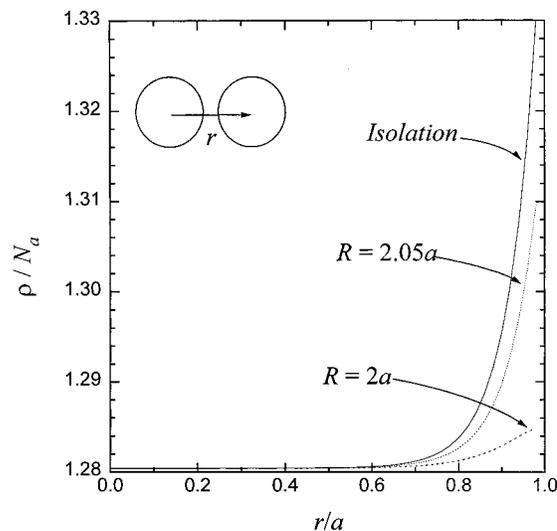


Figure 6. Charge density distribution within an ion-penetrable sphere for $\kappa a = 15$, $\text{pH} = 3$, and $\Theta = 1.5$.

from Figure 6, the charge density increases as, we move away from the center of the sphere. Since the potential is nearly constant, i.e. a Donnan potential, from the center to $r \approx 0.6a$, the charge density stays almost the same in this regime. However, the potential decreases rapidly from $r \approx 0.8a$ to the surface, and thus the charge density increases accordingly. The relatively small change of ρ/N_a (1.28–1.33) in this regime is because of small value of C in eq 1. In the case of isolation ($R = \infty$), i.e., without the interference of other objects, the result is the outcome of the self-charge-regulation. The charge density distribution does not change much as R decreases. Only when particles are close enough can the distribution be greatly affected by each other. When two particles are in contact, i.e. $R = 2a$, the effect of induced charge-regulation near the surface is as important as that due to self-charge-regulation. Consequently, both effects cancel out each other and the charge density approaches uniform within the sphere. This indicates that the self-charge-regulation is the leading factor that has to be considered when the system is in the dilute condition. Note that in this example $\kappa a = 15$, which suggests a fairly thin double layer. One would expect that, as κa decreases, the charge-regulation

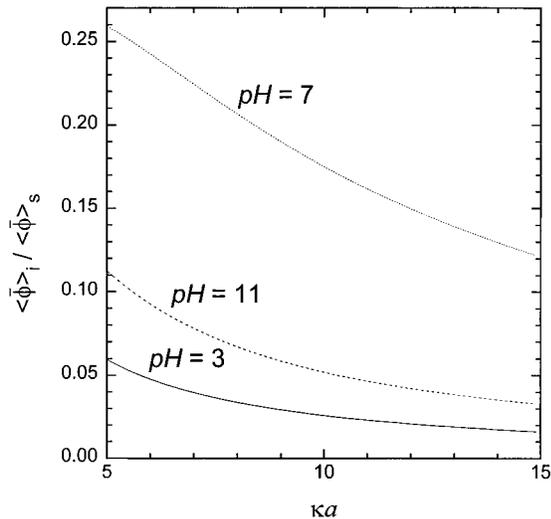


Figure 7. Effects of κa and pH on the ratio of the potential associated with an isolated sphere $\langle \bar{\phi} \rangle_i$ to that induced by surrounding particles $\langle \bar{\phi} \rangle_s$.

phenomena induced by other particles would become more and more significant.

For a linear expression between the charge density and the electric potential, the ensemble average mean charge density $\langle \bar{\rho} \rangle_1$ of a sphere is also a linear function of the ensemble average mean electric potential $\langle \bar{\phi} \rangle_1$. The potential $\langle \bar{\phi} \rangle_1$ consists of the potential associated with an isolated sphere $\langle \bar{\phi} \rangle_s$ and that induced by surrounding particles $\langle \bar{\phi} \rangle_i$. The former includes both ρ_0 and self-charge-regulation contributions. Therefore, the contribution associated with the induced charge-regulation effect to the thermodynamic properties can be revealed from the ratio of $\langle \bar{\phi} \rangle_i$ to $\langle \bar{\phi} \rangle_s$. Figure 7 depicts the effects of κa and pH on the ratio of $\langle \bar{\phi} \rangle_i$ to $\langle \bar{\phi} \rangle_s$. As shown in eq 77, the induced potential $\langle \bar{\phi} \rangle_i$ depends on the radial distribution function of particles around a centered particle $g(r)$. In a dilute suspension, $g(r)$ can be approximated as $\exp(-V_2/kT)$. Thus for large V_2 , it is more difficult for the particles to stay within the short enough range to affect the electric potential and also the charge density of the centered particle. In other words, the particle tends to expel surrounding particles further away as V_2 increases. According to the results in Figures 2 and 3, when pH is away from $(\text{pH})_{\text{pzc}}$, a large value of κa gives rise to a high interaction energy at a constant Debye length. Therefore, the effect of the pH value is reflected on the interaction potential between two spheres, which in turn affects the induced electric potential $\langle \bar{\phi} \rangle_i$. As one can see in Figure 2, $V_2(\text{pH} = 3) > V_2(\text{pH} = 11) > V_2(\text{pH} = 7)$. This immediately leads to $\langle \bar{\phi} \rangle_i / \langle \bar{\phi} \rangle_s (\text{pH} = 7) > \langle \bar{\phi} \rangle_i / \langle \bar{\phi} \rangle_s (\text{pH} = 11) > \langle \bar{\phi} \rangle_i / \langle \bar{\phi} \rangle_s (\text{pH} = 3)$ for a constant value of κa . This result implies that $\langle \bar{\phi} \rangle_i$ is obviously more noticeable for smaller V_2 and thus the importance of $\langle \bar{\phi} \rangle_i$ relative to $\langle \bar{\phi} \rangle_s$ grows as the mean charge density of the sphere gets smaller. Actually, the effect of κa on $\langle \bar{\phi} \rangle_i / \langle \bar{\phi} \rangle_s$ is 2-fold. In addition to affecting the $g(r)$, κa also affects the strength of the electric potential directly. The outcome of $\langle \bar{\phi} \rangle_i / \langle \bar{\phi} \rangle_s$ is determined by the competition between the two effects. Figure 7 shows that the induced electric potential $\langle \bar{\phi} \rangle_i$ becomes less comparable to $\langle \bar{\phi} \rangle_s$ as κa increases. This means that the effect of κa on $g(r)$ prevails and the surrounding particles are expelled far enough so that the electric potential due to the sphere itself dominates. However, if the particles are forced to be in close contact by setting $g(r \geq 2a) = 1$, the ratio of $\langle \bar{\phi} \rangle_i$ to $\langle \bar{\phi} \rangle_s$ is found to increase with κa and reach about 0.5 for $\kappa a \gg 1$. This

result is in accordance with our discussion in Figure 6 that the self- and induced charge-regulation becomes equally important when two particles are close enough to affect each other's electric potential.

Note that the contribution associated with the induced charge-regulation by surrounding particles also depends on the volume fraction of the particles, ca^3 . For low volume fraction, we can conclude that it is not as important as the contribution associated with the self charge-regulation. However, when $ca^3 \sim O(1)$, we expect that this effect has to be taken into account since $g(r = 2a)$ increases significantly. In addition, the three-particle interaction also becomes important as we have shown in section IV. In other words, a pairwise additivity assumption is no longer valid at high concentration. To circumvent these problems, previous studies^{29–32} often adopt the Wigner–Seitz cell approximation to describe the multibody interactions. A more rigorous approach to study the electrostatic interactions for concentrated suspensions is to solve the LPB equation for a given configuration of N particles subject to a periodic boundary condition. An ensemble average of every possible configuration, which can be obtained by Monte Carlo simulations, gives us the interaction free energy and the thermodynamic properties of the system at any concentration. This is a formidable task for a system of ion-impenetrable spheres. However, a system containing ion-penetrable spheres can provide mathematically tractable results, at least for $\delta \ll 1$. Thus, it may be a good model system to investigate the many-body problems associated with electrostatic interactions and test the accuracy of the cell model.

The osmotic pressure of protein solutions, such as bovine serum albumin, varies significantly with pH and salt concentration, and a large increase in osmotic pressure is observed when proteins are denatured.^{33,34} It is believed that the change in pH alters the charge density on the surface of the protein, thereby causes changes in protein conformation and osmotic pressure. In the system of ion-penetrable spheres, the conformation of the particle does not vary with pH; however, the change in the charge density due to different pH is enough to modify the osmotic pressure of the system significantly. Our result can explain experimental observation of Kanal et al. qualitatively.³³ The asymmetry in their results can be partly attributed to $\Theta \neq 1$. In this work, we have considered only one kind of acidic and basic group. For many systems, such as proteins, it is very possible that several different kinds of ionizable groups are involved. It may explain why the variation of the osmotic pressure as a function of pH as shown in the work of Kanal et al. is slightly more complicated than what we have presented here. Nonetheless, it is fairly easy to generalize our work to include more acidic and basic groups.

In our analysis, the attraction forces have not been taken into account. It is a reasonable assumption for a kinetically stable, dilute suspension. When the system is at high concentration, however, a more realistic interaction potential, which includes the van der Waals forces in

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addition to the hard sphere and electrostatic interactions, should be considered. The attraction force will reduce the energy barrier and often gives rise to a primary and a secondary minima in the two-particle interaction as illustrated in DLVO theory. For thermodynamically stable suspensions, the osmotic pressure of the system will be reduced by the attraction forces. To investigate the phenomena of flocculation or coagulation of the particles, which often occurs around the point of zero charge, the attractions have to be included, too.

Since ions are assumed penetrable inside the particle, one would expect that there exists a volume distribution of charges within the particle. This limits the application of this model. When $\kappa a \gg 1$, however, the electric potential inside the sphere is nearly a constant except close to the

surface of the sphere. In this limit, it is a reasonable model for a particle covered with thick ion-penetrable membranes. For mathematical simplicity, we also made the assumption that the relative permittivity of the internal region of the particle is the same as that of the external bulk solution phase. It seems to imply that there is no solid phase in the particle. Nonetheless, as a first approximation, this model can be used for a system containing highly porous particles, such as charged gel particles.

Acknowledgment. This research is supported by the National Council of Science of Taiwan under Grant No. NSC 87-2214-E-008-009.

LA980299N