

Effects of multivalent salt addition on effective charge of dilute colloidal solutions

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The effective charge Z^* is often invoked to account for the accumulation of counterions near the colloid with intrinsic charge Z . Although the ion concentrations c_i are not uniform in the solution due to the presence of the charged particle, their chemical potentials are uniform everywhere. Thus, on the basis of ion chemical potential, effective ion concentrations c_i^* , which can be experimentally measured by potentiometry, are defined with the pure salt solution as the reference state. The effective charge associated with the charged particle can then be determined by the global electroneutrality condition. Monte Carlo simulations are performed in a spherical Wigner-Seitz cell to obtain the effective charge of the colloid. In terms of the charge ratio $\alpha = Z^*/Z$, the effects of added salt concentration, counterion valency, and particle charge are examined. The effective charge declines with increasing salt concentration and the multivalent salt is much more efficient in reducing the effective charge of the colloidal solution. Moreover, the extent of effective charge reduction is decreased with increasing intrinsic charge for a given concentration of added salt. Those results are qualitatively consistent with experimental observations by electrophoresis. © 2006 American Institute of Physics. [DOI: 10.1063/1.2390707]

I. INTRODUCTION

A colloidal dispersion, consisting of many charged particles and small ions, is a very complicated system. To describe the equilibrium and dynamic properties of colloidal solutions, the concept of effective charge is commonly adopted in the literature.¹⁻⁴ The essential idea associated with charge renormalization is that counterions accumulate in the vicinity of the surface of the colloid carrying intrinsic charge Z because of strong electrostatic coupling. That is, the electrostatic attraction is large compared to the thermal energy $k_B T$. Consequently, the decorated object (charged particle plus counterions) may be regarded as a single entity which possesses an effective charge, Z^* . The effective charge (in absolute value) can be much less than the intrinsic charge, $Z^* \ll Z$. The determination of Z^* is dependent on which physical property is considered. It is frequently regarded as an adjustable parameter in a fit of experimental data with approximated models. For instance, the effective charge can be inferred from voltammetry, electrophoresis, or small-angle neutron scattering.⁵⁻⁸

The concept of effective charge basically characterizes a battle fought between energy and entropy in minimizing the free energy of a solution of mobile charges in the neighbor-

hood of charged particles. For a charged sphere of size a , the electric potential energy of a counterion on the surface is finite, $\psi_s \sim -Z/a$. The entropy associated with the counterion is proportional to $k_B T \ln V$ with the available volume V . At infinite dilution ($V \rightarrow \infty$), the isolated, charged sphere is unable to bind a counterion at finite temperature and the effective charge is the intrinsic charge, $Z^* = Z$. However, in all practical colloidal systems, the counterion entropy is finite, $\sim k_B T \ln c$, owing to finite counterion concentration c . As a result, it is expected that charge renormalization takes place eventually when the electrostatic energy gain overcomes the counterion entropy loss.

Theoretically, the effective charge can be determined according to various definitions. The simple and intuitive definition is the two-state scenario, i.e., condensed and free counterions. The boundary between the two states is arbitrarily defined. For example, one can choose the position r^* at which the local concentration of counterions $c(r^*)$ equals the mean value $\langle c \rangle$, i.e., $c(r^*) = \langle c \rangle$. Since the counterions between the particle surface and the chosen boundary neutralize an equivalent number of charges on the particle, the effective charge is thus the rest charge of the charge carried by the particle.⁵ Similarly, one can also define the boundary as the location where the interaction energy of the counterion with the parent particle is equal to the thermal energy.⁹ Nonetheless, such definitions of effective charge do not relate to thermodynamic quantities of colloidal solutions.

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Another approach in determining the effective charge is the electric field felt by a counterion far from the parent particle.¹ The electric potential profile is often calculated by the Poisson-Boltzmann (PB) mean-field theory. Because of the mathematical difficulty caused by its nonlinear nature, a linearized approximation is typically employed to obtain analytical expressions. This well-known Debye-Hückel (DH) approximation is justified as the thermal fluctuation dominates over the electrostatic interaction. Therefore it is inadequate in describing highly charged particles because the electrostatic energy of counterions near the particle's surface exceeds the thermal energy. Far from the charged surface, however, the electrostatic potential still follows the DH expression since the thermal energy becomes dominant. By matching the analytical DH solution with Z^* to the "exact" numerical solution with Z at a distance away from the particle, the effective charge is obtained. Similarly, the long distance behavior of the exact electrostatic repulsion between two identical colloids with Z can be matched by the effective pair potential with Z^* based on the DH approximation. The latter accounts for screening of the intrinsic charge by counterions. Since the effective pair potential is closely related to physical properties such as the bulk modulus of the colloidal crystals,¹ the effective charge based on this definition may be extracted from experiments.

The DH approach can be generalized to all physical properties associated with a salt-free dispersion. For a thermodynamic property ω such as osmotic pressure, its relation to the intrinsic charge Z^* may be available under the condition of weak coupling, i.e., $\omega_{\text{DH}}(Z^*)$. If we obtain the property ω of a colloidal solution with intrinsic charge Z , then the effective charge of this dispersion is defined as Z^* if $\omega_{\text{DH}}(Z^*) = \omega(Z)$. The advantage of the DH approach is that analytical expressions are generally available for various properties and further uses. Nonetheless, this method may be inadequate to display the microscopic picture near the charged particle, particularly for the existence of multivalent counterions. Monte Carlo simulations^{3,10} have shown that for a salt-free dispersion with multivalent counterions, some physical properties, such as chemical potential and surface potential, do not reach a plateau value for large intrinsic charges, but instead they pass through a maximum, and decrease again as Z increases. This consequence indicates that for two salt-free colloidal dispersions containing charged particles of the same size and volume fraction, their thermodynamic property, in particular, ω , may be the same even though they possess different particle charges Z^* and Z , i.e., $\omega(Z^*) = \omega(Z)$. As a result, one may define Z^* as the effective charge for the dispersion with Z if $Z > Z^*$. There exists a maximally attainable value of ω at which $Z = Z^*$.

In a salty dispersion, the effective charge associated with a colloid may be altered due to the screening effect. The charge renormalization based on the far-field behavior reveals that for low intrinsic charge, Z^* is only slightly changed as a substantial amount of monovalent electrolyte is added.¹ For ionic strength up to five times that of counterions, Z^* changes by approximately 10%. In general, on the basis of the DH approach, the effective charge is increased with the added salt concentration for a fixed Z . On the other

hand, as the intuitive two-state model is used, the effective charge declines with increasing salt concentration.¹¹ Since the added salt itself can have direct contributions to some thermodynamic properties, the definitions of Z^* based on such thermodynamic properties are unable to provide insight on the effect of salt addition on the effective charge. Besides the existing contradiction and difficulty, the added salt in most studies is monovalent. The addition of multivalent salt, however, can lead to significant ion-ion correlation and strong coupling between colloid and multivalent counterion.

In this paper, we explore the effects of multivalent salt addition on the effective charge of a dilute colloidal dispersion on the basis of ion chemical potential. In Sec. II we propose an effective charge, which is thermodynamically well defined and can be determined by potentiometry experiments. This definition is essentially equivalent to the ionic activity coefficient in a pure salt solution. In Sec. III the details of Monte Carlo simulations in a spherical Wigner-Seitz cell are briefly described. The residual chemical potentials of ions (activity coefficients) are calculated and thereby the effective concentrations of coions and counterions can be obtained. In Sec. IV the effective charge of a colloid is determined based on the global charge neutrality condition. First, we examine the effective charge of a salt-free dispersion. The charge ratio Z^*/Z decays monotonically with increasing intrinsic charge. When simple $z_+ : z_-$ salt is added, the strong Coulomb interaction between multivalent counterion and colloid leads to rapid decay of the effective charge. Some conclusions are summarized in Sec. V.

II. EFFECTIVE CHARGE BASED ON CHEMICAL POTENTIAL

Consider a dilute solution of charged colloid with intrinsic charge $Z < 0$ and counterions with valency z_c . When a given amount (N) of $z_+ : z_-$ salt is added into the dilute colloidal solution with volume V , one knows the concentration of the added salt ($c_s = N/V$) and thus the intrinsic ion concentrations, $\nu_{\pm} c_s$, where $\nu_+ z_+ = \nu_- z_-$. For example, addition of 2:1 salt gives counterion concentration $c_s (\nu_+ = 1)$ and coion concentration $2c_s (\nu_- = 2)$. Owing to strong electrostatic interaction between ion and charged colloid, however, the solution is not ideal at all. The chemical potential of the ion is then given by

$$\mu_i = \mu_i^0 + \mu_i^r + k_B T \ln c_i, \quad (1)$$

where μ_i^r denotes the residual chemical potential due to electrostatic interactions. The deviation from the ideal part, $k_B T \ln c_i$, comes from both ion-ion and colloid-ion interactions. Note that in the absence of charged colloids, $\mu_i^r(c_s)$ may exist for a dilute multivalent salt solution with concentration c_s due to the ion-ion interaction. Since the intrinsic ion concentration c_i is unable to represent the ion chemical potential in the presence of a charged colloid, its effective ion concentration c_i^* (or activity) can be unambiguously defined as

$$\mu_i = \mu_i^0 + \mu_i^s(c_i^*) + k_B T \ln c_i^*, \quad (2)$$

where $\mu_i^s(c_i^*)$ represents the residual chemical potential in an electrolyte solution with concentration c_i^* . That is, the effective ion concentration in the colloidal solution corresponds to the ion concentration in a salt reservoir with the same ion chemical potential. It may be determined by potentiometric experiments.

As in the thermodynamics for electrolyte solutions, one can adopt the activity coefficient to represent the residual chemical potential. In accord with Eqs. (1) and (2), the activity coefficient is related to the effective ion concentration by

$$\gamma_i = c_i^*/c_i = \exp[\mu_i^r - \mu_i^s(c_i^*)]. \quad (3)$$

Note that the activity coefficient defined here is different from the conventional definition for simple electrolyte solutions. The reference state for the latter is based on the infinite-dilution behavior, i.e., $\gamma_i = \exp(\beta\mu_i^r)$. For pure multivalent salt solutions, one generally has $\gamma_i < 1$ due to electrostatic attraction. In our case, however, the reference state is the added salt solution. For any pure salt solution, one has $\mu_i^r = \mu_i^s(c_i^*)$ and therefore $\gamma_i = 1$ and $c_i^* = c_i$. Equation (3) clearly shows that our definition of activity coefficient reflects the influence of the charged colloid only. As will be shown later, $\mu_i^s(c_i^*) \approx 0$ for dilute 1:1 salt solutions and the nonideality comes primarily from the charged colloid.

The electrostatic interactions between colloids and counterions lead to nonideal behavior of the colloidal solution. For electrolyte solutions, activity coefficients are employed to describe the nonideality quantitatively. For colloidal solutions, however, the concept of effective charge is often used to depict its nonideal behavior. Unfortunately, the thermodynamic meaning of the effective charge is quite ambiguous. If the system can be described by simple two-state scenario (adsorbed ions and free ions), then the effective charge Z^* and the effective ion concentration c_i^* can be clearly defined. The latter is simply the free ion concentration, while the former is the intrinsic charge minus the total adsorbed charge. Since the two-state model is only justified for short-range interactions, it cannot be directly applied to the colloidal solution with long-range Coulombic interactions. There exist ion distributions in the vicinity of the charged colloids and thereby the value of the effective charge varies with the boundary that one chooses to represent the colloid. Obviously, this definition does not possess any thermodynamic meaning. An alternative approach is to determine the free (effective) ion concentrations based on chemical potential. When a colloidal solution is at thermodynamic equilibrium, the chemical potential of the ion is uniform everywhere. In principle, the effective ion concentration can be determined by measuring its chemical potential, as demonstrated in Eq. (2). The effective charge of the colloid can then be obtained from the electroneutrality condition for the system. In order to illustrate the thermodynamic meaning of the effective charge based on ion chemical potential, we shall consider the cases with/without salt addition.

First, we consider a salt-free colloidal solution. The concentration of the particle with intrinsic charge $-Z > 0$ is c_p

and the effective concentration of counterion with valency z_c is c_c^* . Similar to ions, the chemical potential of the charged colloid is expressed as

$$\mu_p = \mu_p^0 + \mu_p^r + k_B T \ln c_p = \mu_p^0 + k_B T \ln c_p \gamma_p, \quad (4)$$

where γ_p depicts the activity coefficient associated with the colloid. Evidently, one can also define an effective colloidal concentration (activity) $c_p^* = c_p \gamma_p$. Then the electroneutrality condition demands $Zc_p^* - z_c c_c^* = 0$. However, the conventional approach based on the concept of counterion condensation is to adopt the true colloidal concentration c_p with effective charge Z^* . The global electroneutrality condition requires that

$$Z^* c_p - z_c c_c^* = 0. \quad (5)$$

The relation between intrinsic charge and effective charge is then

$$Z\gamma_p = Z^*. \quad (6)$$

Equation (5) indicates that the effective charge of the colloidal particle can be determined by $Z^* = z_c c_c^*/c_p$ if the effective counterion concentration c_c^* is measured. The “degree of ionization” (α) of a salt-free colloidal solution is defined as

$$\alpha = \frac{c_c^*}{c_c}, \quad (7)$$

where c_c represents the intrinsic counterion concentration (uniform distribution). We have to emphasize that since only the Coulomb interaction is involved in this study, counterions are always dissociated completely. Nevertheless, its strong, long-ranged nature leads to nonuniform ion distribution and thus alters the effective counterion concentration (activity). Therefore, the degree of ionization is not related to any chemical reaction. Because of $c_c = Zc_p/z_c$, the effective charge can also be obtained by measuring the degree of ionization in a salt-free solution,¹² $Z^*/Z = \alpha$. This consequence indicates that the activity coefficient of the charged colloid is equivalent to its degree of ionization in a dilute salt-free dispersion,

$$\gamma_p = \alpha = \gamma_c, \quad (8)$$

where the counterion activity coefficient is $\gamma_c = c_c^*/c_c$.

A salt-free colloidal solution is similar to an unsymmetrical electrolyte solution. According to the thermodynamic theory for a solution of a strong electrolyte, individual activity coefficients cannot be simply measured experimentally. For a binary salt, one measures the mean ionic activity coefficient defined as¹³

$$\ln \gamma_{\pm} = \frac{\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-}{\nu_+ + \nu_-}, \quad (9)$$

where $C_{\nu_+} A_{\nu_-} \rightarrow \nu_+ C^{z_+} + \nu_- A^{z_-}$ with $\nu_+ z_+ = \nu_- z_-$. For a salt-free colloidal dispersion, the chemical equation describing the dissociation of the macroion [Particle (P) + Counterions (C)] is $PC_{Z/z_c} \rightarrow P^Z + (Z/z_c)C^{z_c}$, where $\nu_- = 1$ and $\nu_+ = Z/z_c$. Substituting Eq. (8) into Eq. (9) yields the mean ionic activity coefficient of the colloidal solution γ_{\pm}

$=\alpha=\gamma_+=\gamma_-$. The above analysis indicates that the effective charge associated with the charged colloid (Z^*) is thermodynamically well defined and is consistent with the thermodynamic framework for strong electrolyte solutions. Instead of using γ_p and γ_c , we adopt Z^* and c_c^* to characterize the salt-free system. Since the apparent counterion concentration c_c^* can be conveniently measured by potentiometry such as ion selective electrode, the effective charge Z^* of a charged colloid can be unambiguously decided.

Next let us consider addition of simple $z_+:z_-$ salt with concentration c_s in the colloidal solution. If the effective ion concentrations are represented by c_+^* and c_-^* , then the condition of global charge neutrality necessitates

$$Z^*c_p - z_c c_c^* + z_- c_-^* - z_+ c_+^* = 0. \quad (10)$$

Again, the effective concentration c_i^* is related to the activity coefficient γ_i by $\gamma_i = c_i^*/\nu_i c_s$ with $\nu_+ z_+ = \nu_- z_-$. Thus, Eq. (9) gives a relationship among the ion activity coefficients as follows:

$$(\gamma_p - \gamma_c) + \frac{\nu_- z_- c_s}{Z c_p} (\gamma_- - \gamma_+) = 0, \quad (11)$$

where $\gamma_p = \alpha = Z^*/Z$. For small amount of salt addition, $Z c_p \gg \nu_- z_- c_s$, the colloidal solution behaves similar to the salt-free case, $\alpha \cong \gamma_c$. On the other hand, as $Z c_p \ll \nu_- z_- c_s$, the colloid causes a small perturbation to the solution of strong electrolyte, $\gamma_+ \cong \gamma_-$. If one can measure all effective ion concentrations in the system, then the effective charge of the charged particle can be determined by Eq. (10). Apparently, for $c_s = 0$, the above definition reduces to that associated with the salt-free solution.

III. CELL MODEL AND SIMULATION

It is very common to adopt a spherical Wigner-Seitz (WS) cell to investigate the physical properties associated with colloidal solutions.^{1-5,9,10,12,14-16} The cell model approximation reduces a colloidal solution, containing many charged particles and small ions, to just a single colloid problem. While the interactions among charged particles are ignored, the interaction between small ions with "their" charged particle and with small ions are explicitly considered in the same cell. Thereby the cell model approach can be regarded as an approximate attempt to factorize the partition function in the particle coordinates, and hence, the many-colloid problem is substituted by a single-colloid problem.¹⁶ The symmetry of the cell may reduce the problem further to a one-dimensional one and allow analytical treatment for mean-field theories. The spherical cell model is justified for dilute dispersions. Previous studies^{3,4} also concluded that the results based on WS cell simulations agree quite well with those obtained by periodic boundary condition (cubic cell) because the particle charge is strongly screened.

On the basis of the WS cell model, we consider a charged sphere with radius a and valency $-Z > 0$ located at the center of a spherical cell of radius R . We employ the primitive model in which the solvent, water in this case, is represented by a continuum medium of uniform dielectric constant ϵ_r (≈ 80). The charge of the ion is positioned at the

center of the hard sphere and each of the ions is made up of a material with the same dielectric constant as the solvent. The cell radius R is inversely proportional to the number concentration of the charge particle $c_p^{1/3}$ and is related to the volume fraction of charged colloids, ϕ , by $R = a\phi^{-1/3}$. Since the number of ions in the system is finite, one is able to write down the partition function and the integration is possibly performed analytically for weak Coulomb coupling limit.¹⁰

A. Partition function

Within a cell there are N_c counterions with valency z_c , N_+ positive ions with valency z_+ , and N_- negative ions with valency z_- . The electroneutrality condition is satisfied because of $Z = N_c z_c$ and $z_+ N_+ = z_- N_-$. Since Coulomb interactions dominate, van der Waals interactions are ignored. The partition function of the system is expressed as

$$\mathcal{Z}(a, R, Z, z_c, z_+, z_-, N, \ell_B) = \frac{1}{N!} \int \cdots \int e^{-\beta \mathcal{H}} d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (12)$$

where $\ell_B = e^2/4\pi\epsilon_r\epsilon_0 k_B T$ (≈ 0.71 nm in aqueous solution at 298 K) denotes the Bjerrum length and $N = N_c + N_+ + N_-$. The Hamiltonian \mathcal{H} is given by

$$\beta \mathcal{H} = \ell_B \left[\sum_{i=1}^N \frac{Z z_i}{r_i} + \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \frac{z_i z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right], \quad (13)$$

where \mathbf{r}_i denotes the position of the ion i with valency z_i . On the right-hand side of Eq. (13), the first term comes from the electrostatic attraction between ions and the charged particle, while the second term denotes the electrostatic interactions among ions. For simplicity, the dielectric mismatch between the charged particle and the solvent is ignored.

In accordance with the partition function, all thermodynamic properties can be obtained. The Helmholtz free energy is related to the partition function by $\beta \mathcal{F} = -\ln \mathcal{Z}$ and the chemical potential is given by $\beta \mu_i = (\partial \mathcal{F} / \partial N_i)_{V, T, Z, N_{j \neq i}}$. In the weak coupling limit, $\beta \mathcal{H} \ll 1$, the integrand in the partition function can be expanded in series, $\exp(-\beta \mathcal{H}) \approx 1 - \beta \mathcal{H}$, and the N -dimensional integration becomes analytically tractable. The result should be consistent with the Poisson-Boltzmann theory under the Debye-Hückel approximation.¹⁰ The condition of weak coupling corresponds to low charged particle of large radius, low valency ions, and high dielectric constant. However, this stringent condition is often violated in most interesting situations. For strong electrostatic coupling, the partition function can only be evaluated numerically. In order to account for the effect of ion fluctuation and correlation, we perform Monte Carlo simulations to calculate ion chemical potentials and thus effective ion concentrations based on the WS cell model.

B. Monte Carlo simulation

A short description of Monte Carlo (MC) simulation is given below. The simulation details can be seen elsewhere.¹⁷ The system simulated in the present work comprises a charged sphere of radius a fixed at the center of a spherical

cell with radius R and a collection of hard spheres with valency $\pm z_i=1, 2,$ or 3 . The diameter of the counterion d is assumed 0.4 nm and is taken as the unit for the spatial length, i.e., $\tilde{\mathbf{r}}_i=\mathbf{r}_i/d$. At 298 K, the dimensionless energy parameter in Coulombic interaction $(\ell_B/d)z_i z_j/|\tilde{\mathbf{r}}_i-\tilde{\mathbf{r}}_j|$ is thereby $E^*=\ell_B/d=1.785$. The simulations were conducted under conditions of constant volume V , temperature T , and total number of ions N . The initial configuration for a given number of ions was obtained by randomly putting the ion within the cell without overlapping each other. The system was equilibrated for about 10^6 MC steps per ion and the production period for each simulation was 10^6 steps per ion. The moves adopted in our simulations were bead displacement motions. Bead displacement moves involve randomly picking an ion and displacing it to a new position in the vicinity of the old position. The new configurations resulting from the moves were accepted according to the standard Metropolis acceptance criterion, $P_{\text{acc}}=\min[1, \exp(-\Delta U_{ei}/k_B T)]$, where ΔU_{ei} is the change in the total electrostatic energy of the system due to the move.

C. Chemical potential and effective concentration

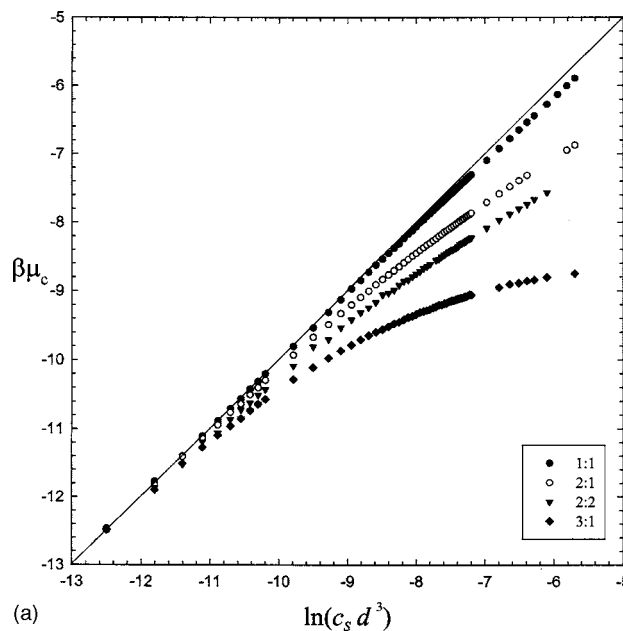
The effective (free) ion concentration c^* is determined by its mean chemical potential. As defined in Eq. (2), $\mu(c^*)$ in a salt solution with ion concentration c^* equal to $\mu(c)$ in a colloidal solution with intrinsic ion concentration c . For convenience, the reference chemical potential in Eq. (1) is set to zero, $\mu_i^0=0$. The ideal (ion concentration) and residual chemical potentials vary with the radial position and can be evaluated from MC. We divide the spherical volume into 20 spherical shells and record the number of ions in each cell. The residual chemical potential is obtained by Widom's method,¹⁸ which is the reversible work required to add an ion with the valency z_i to the system,

$$\mu_i^r = -k_B T \ln \langle \exp(-\Delta U_i/k_B T) \rangle. \quad (14)$$

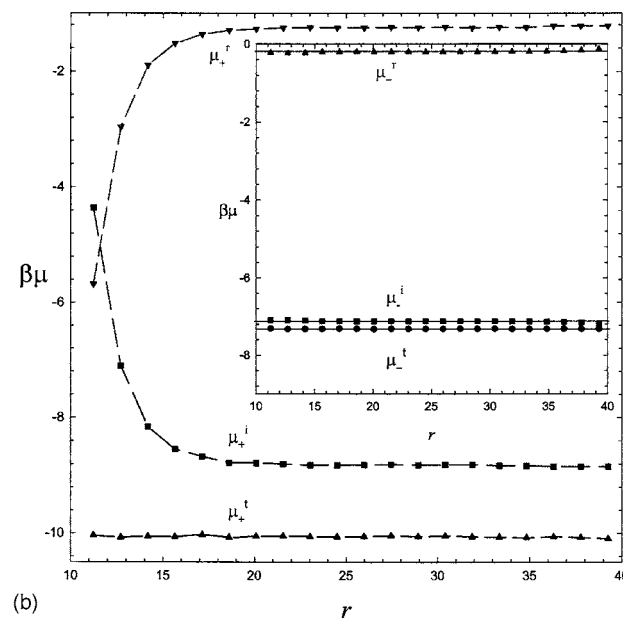
Note that at thermodynamic equilibrium the total chemical potential is a constant everywhere.

In order to determine the effective ion concentration, we have to know the reference relation between chemical potential and salt concentration, $\mu(c_s)$, for various salt solutions. They can be obtained by MC simulations in a WS cell in the absence of the charged colloid, i.e., corresponding to pure salt solutions. Figure 1(a) shows the variation of $\beta\mu$ with $\ln c_s d^3$ for simple $z_+:z_-$ salt. Since $\mu^r < 0$ due to electrostatic attraction, the counterion chemical potential is $\beta\mu < \ln c_s d^3$ for high enough concentrations. The deviation from the ideal behavior is significant for multivalent salts and is most serious for 3:1 salt. For a dilute solution of monovalent salt, since $\beta\mu^r(r=R) \cong 0$, one has $\beta\mu \cong \ln c(r=R)d^3$. Therefore, the effective ion concentration can also be estimated from the ion concentration at the cell boundary, $c_i^* \cong c_i(r=R)$. For multivalent salt, however, μ has to be calculated and Fig. 1(a) is used to estimate c_i^* .

Figure 1(b) demonstrates typical distributions of ion concentration $c_i d^3$, its residual chemical potential μ_i^r , and total chemical potential μ_i for the addition of 3:1 salt in a dilute colloidal solution with $Z=100$. Owing to electrostatic



(a)



(b)

FIG. 1. (a) The variation of the counterion chemical potential $\beta\mu_c$ with the salt concentration $c_s d^3$ for various simple salts. (b) The typical variation of the ideal (μ^i), residual (μ^r), and total (μ^t) chemical potentials with the radial position r for 3:1 salt with $a=10$, $R=40$, and $Z=80$. The results for coion $z_-=1$ are shown in the inset. The dotted lines are drawn to guide the eyes.

attraction of the charged colloid, the trivalent counterion concentration $c_+(r)$ decays rapidly from the particle surface to the boundary of the WS cell. It corresponds to the fast decay of the ideal chemical potential. On the contrary, the residual chemical potential is quickly increased with r . Nonetheless, the total chemical potential is essentially constant for all radial position r , as illustrated in Fig. 1(b). Note that Widom's method may be inaccurate for the μ_i^r calculation at the concentrated region (in the vicinity of the charged particle) or at small N_+ (near the cell boundary). Evidently, in the present case, the salt concentration is high enough and thereby the ion concentrations at the cell boundary cannot represent their effective concentrations. That is, c^* has to be

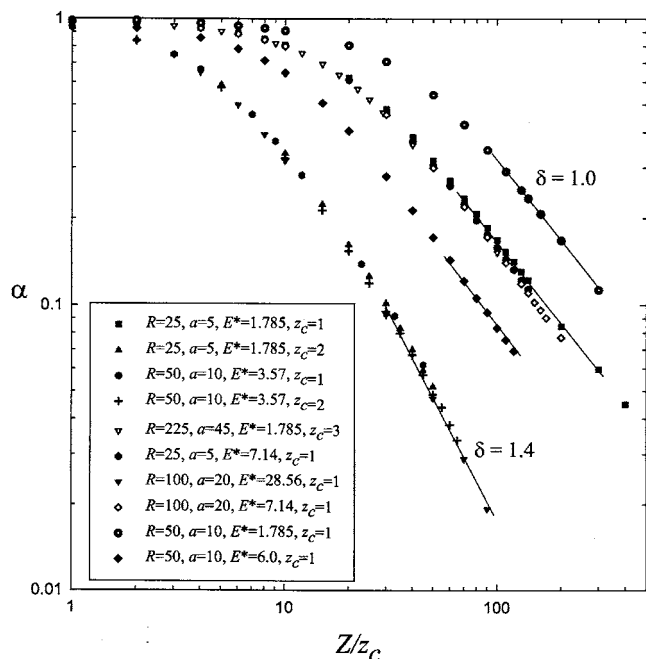


FIG. 2. The variation of the charge ratio Z^*/Z with Z/z_c for a salt-free dispersion with various combinations of $\{R, a, E^*, z_c\}$. The exponent δ is for the approximate scaling relation $\alpha \sim (Z/z_c)^{-\delta}$.

determined from the relationship between the ion concentration and its chemical potential in a pure salt solution, $\mu(c_s)$, as provided in Fig. 1(a).

IV. RESULTS AND DISCUSSION

The effective charge of colloids in a dilute solution is thermodynamically defined based on ion chemical potential. It is closely related to the activity coefficient of macroion and can be reduced to the typical definition for binary electrolyte solutions. Similarly, the effective ion concentration in the colloidal solution is equivalent to the ionic activity and can be experimentally determined by potentiometry. As a result, for a salty dispersion, the effective charge of colloids can be obtained by using the electroneutrality condition if all effective ion concentrations are known. On the basis of spherical WS cell model, we perform MC simulations to evaluate the effective ion concentrations and thereby the effective charge for colloidal dispersions with/without salt addition. Besides monovalent salt, particular interests will be focused on the effect of multivalent counterion.

A. Salt-free colloidal solution

In a salt-free dispersion, the effective charge is proportional to the degree of ionization α , as shown in Eqs. (6)–(8). According to the partition function, α is a function of Z/z_c , a/λ , and R/λ , where $\lambda = z_c^2 \ell_B$.¹⁰ Figure 2 depicts the variation of the charge ratio $\alpha = Z^*/Z$ with the number of counterions Z/z_c for various combinations $\{a, R, E^*, z_c\}$. As anticipated, α descends gradually from unity at small value of Z/z_c but drops fast at large value of Z/z_c . Under the same condition of $\{a/\lambda, R/\lambda\}$, data points of different combinations of $\{a, R, \ell_B, z_c\}$ fall into a single curve. For example, the condition $(R=50, a=10, \ell_B=3.57, z_c=2)$ is equivalent to

$(R=100, a=20, \ell_B=28.56, z_c=1)$. For a given R/a and Z/z_c , Fig. 2 discloses that Z^* declines with increasing λ , which depicts the characteristic length associated with Coulomb interaction. For instance, stronger Coulomb coupling due to lower dielectric constant leads to a smaller effective charge of colloid.

When Z/z_c is large enough, it seems that the scaling relation is followed, $\alpha \sim (Z/z_c)^{-\delta}$ with $\delta \geq 1$. When the Coulomb coupling is weak, one has $\delta=1$ and thus Z^* reaching a constant for large enough Z . In other words, as the charge density of the colloid exceeds approximately a certain value, the counterions seem to condense on the sphere. This consequence is very similar to the so-called Manning condensation taking place along an infinitely long charged rod.¹⁹ On the other hand, as the Coulomb coupling is strong, the exponent δ is greater than unity and therefore $Z^* \sim 1/(Z^{\delta-1})$. For example, one has $\delta \approx 1.4$ for the condition $R/\lambda=14.0$ and $a/\lambda=2.8$. This consequence discloses the fact that the effective charge is essentially decreased with increasing intrinsic charge. Although the intrinsic charge is very large, the Coulomb attraction strongly favors “counterion condensation” and effectively leads to a weakly charged particle. As shown in Fig. 2, the charged sphere possesses an effective charge of about $Z^* \approx 2$ for $Z/z_c=100$. Note that for $\delta > 1$, there exists a maximum Z^* as Z is increased owing to the competition between counterion entropy and electrostatic attraction.¹⁰

B. Effective ion concentrations (activity coefficient)

The effective ion concentration is determined by the ion chemical potential or activity coefficient according to Fig. 1(a). For monovalent salt, it can be evaluated from the ion concentration at the WS cell boundary as well. Since the coion is repelled from the charged sphere, one expects that its effective concentration is greater than its intrinsic concentration, i.e., $c_-^* > c_-$. However, due to the small volume fraction associated with the double layer region and the electrostatic contribution to the residual chemical potential, the effective coion concentration is essentially equal to its intrinsic concentration, i.e., $c_-^*/c_- = \gamma_+ \approx 1$. Figure 3(a) demonstrates the variation of the effective coion concentration with its intrinsic concentration for various $z_+ : z_-$ added salts at $R=40, a=10$, and $Z=100$. All data points fall at the straight line with the slope unity. That is, the effective coion concentration in a salty colloidal dispersion can be simply estimated from the added salt concentration.

Since $c_-^* \approx c_-$, the effective counterion concentrations play an important role in determining the effective charge. Figure 3(b) shows the variation of the effective concentration of added counterion (c_+^*/c_+) with the added salt concentration $c_s = c_+$, while Fig. 3(c) illustrates the variation of the effective concentration of original counterion (c_c^*/c_c) with the added salt concentration. Note that for $R=40, c_i d^3 = 10^{-4}$ corresponds to 2.6 mM and $c_c d^3 = 3.73 \times 10^{-4}$ for $Z=100$. As indicated in Figs. 3(b) and 3(c), the effective concentrations of both added counterion (c_+^*) and original counterion (c_c^*) rise with increasing c_s . Although the increment of

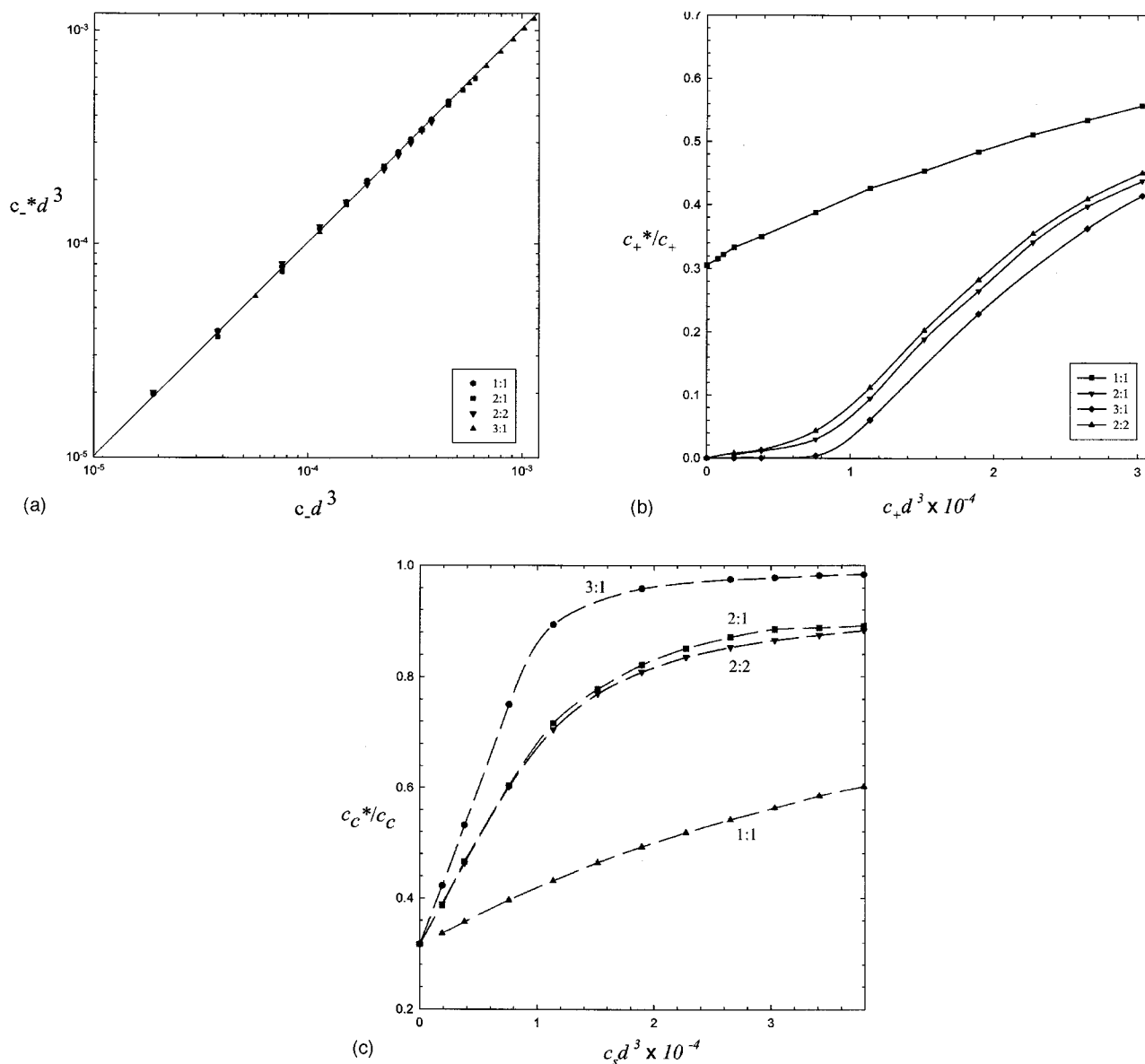


FIG. 3. (a) The effective coion concentration c_-^* is plotted against the intrinsic coion concentration c_- for various multivalent salts. (b) The effective concentration of added counterion, c_+^*/c_+ (activity coefficient), is plotted against the intrinsic counterion concentration c_+ for various multivalent salts. The solid curves are drawn to guide the eyes. (c) The effective concentration of original counterion, c_c^*/c_c (activity coefficient), is plotted against the salt concentration c_s for various multivalent salts. The dotted curves are drawn to guide the eyes.

c_+^* with increasing c_s is anticipated, the fact that $c_+^* < c_+$ reveals that some of the added counterions are “condensed” on the colloid.

For monovalent salt, there is actually no difference between original and added counterions in terms of Coulomb interaction. As a result, the activity coefficients for original and added counterions should be the same,

$$\gamma_+ = \frac{c_+^*}{c_+} = \frac{c_c^*}{c_c} = \gamma_c. \quad (15)$$

Comparison between Figs. 3(b) and 3(c) for 1:1 salt confirms the validity of Eq. (15). For example, as $c_+d^3 \rightarrow 0$, $c_+^*/c_+ \cong c_c^*/c_c \approx 0.31$. The monovalent counterion may play two roles: replacement and “condensation.” First, some original condensed counterions are replaced by added counterions. Secondly, some added counterions are attracted to the colloid

because it still possesses significant effective charge. If the first mechanism dominates, then monovalent salt addition has an insignificant influence on the effective charge. If Z^* is independent of c_s , then one must have $\gamma_+ = 1$ according to Eqs. (10) and (15). Obviously, this result disagrees with Eq. (15) because of $\gamma_c < 1$. The above analysis reveals that the second mechanism plays an important role. Since some of the added counterions are attracted to the colloid, one expects that the effective charge may decline due to monovalent salt addition.

For multivalent salt, the added counterions (multivalent) have stronger Coulomb attraction than the original counterions (monovalent) and it can be roughly classified into two regimes. For $c_s d^3 \lesssim 10^{-4}$, c_+^*/c_+ is close to zero as shown in Fig. 3(b) and c_c^*/c_c grows rapidly as illustrated in Fig. 3(c). When the added salt concentration is low, most of the mul-

tivalent counterions are accumulated in the vicinity of the colloid. This leads to the release of the monovalent counterions. On the other hand, for $c_s d^3 \geq 10^{-4}$, c_+^*/c_+ is increased with increasing c_s , but c_+^*/c_+ seems to approach an asymptote close to unity. This result reveals that a small amount of monovalent counterions is always in the neighborhood of the colloid. For high salt concentration, most of monovalent counterions are already released and multivalent counterions left in the bulk solution rises with added salt concentration. Nonetheless, just like addition of monovalent salt, a part of the newly added multivalent counterions continues to be attracted to the colloid. Therefore, salt addition leads to reduction of the effective charge.

C. Effective charge

Once the effective ion concentrations are obtained, the effective charge associated with a colloid can be determined by Eq. (10) based on the electroneutrality condition. For a given R and a , the effective charge is a function of intrinsic charge and added salt concentration, i.e., $Z^*(Z, c_s)$. Figure 4(a) shows the variation of the charge ratio Z^*/Z with the added 1:1 salt concentration for a specified Z with $R=40$ and $a=10$. Evidently, the effective charge declines with increasing c_s . The effective charge of a colloid represents a consequence of the competition between Coulomb attraction and counterion entropy. Our simulation results indicate that when monovalent salt is added, the loss of counterion entropy is responsible for the decrease of the effective charge. Moreover, the counterion fluctuation-correlation effect may provide additional attraction between counterions and colloids. Figure 4(a) also shows that for a given amount of salt addition, the effect of salt addition on Z^* is more significant for a colloid with smaller Z than for one with larger Z . Since a colloid with larger intrinsic charge has higher free counterion concentration, one expects that more amount of salt is required to provide added counterions, which can neutralize the particle charge. Thus the extent of the change of the charge ratio, $\Delta\alpha$, can be assumed as a function of the ratio of added salt concentration to the intrinsic counterion concentration, c_s/c_c (or c_s/Z). As shown in the inset of Fig. 4(a), the data points for three different values of Z fall into a single curve, confirming this relationship. Note that $\Delta\alpha = \alpha(c_s=0) - \alpha(c_s)$ with $\alpha = Z^*/Z$ and the concentration range of added salt in Fig. 4(a) corresponds to $c_s \leq c_c$. The fact that the change in α grows with c_s/Z instead of c_s indicates that at high enough salt concentration, one may have $\alpha(Z_1) < \alpha(Z_2)$ for $Z_1 < Z_2$ even though $\alpha_0(Z_1) > \alpha_0(Z_2)$, where $\alpha_0 = \alpha(c_s=0)$. Moreover, the approximately linear relation between $\Delta\alpha$ and c_s/c_c at higher values of c_s/c_c reveals that the effective charge may approach zero essentially at high enough salt concentration.

Figure 4(b) illustrates the variation of Z^*/Z with the intrinsic charge for a given c_s with $R=40$ and $a=10$. In a salt-free colloidal solution ($c_s=0$), the charge ratio Z^*/Z is monotonically decreased from unity toward zero. This is simply because of the increase in Coulomb attraction and the decrease in counterion entropy as Z grows. Unlike the salt-free case, there exists a maximum value of the charge ratio α

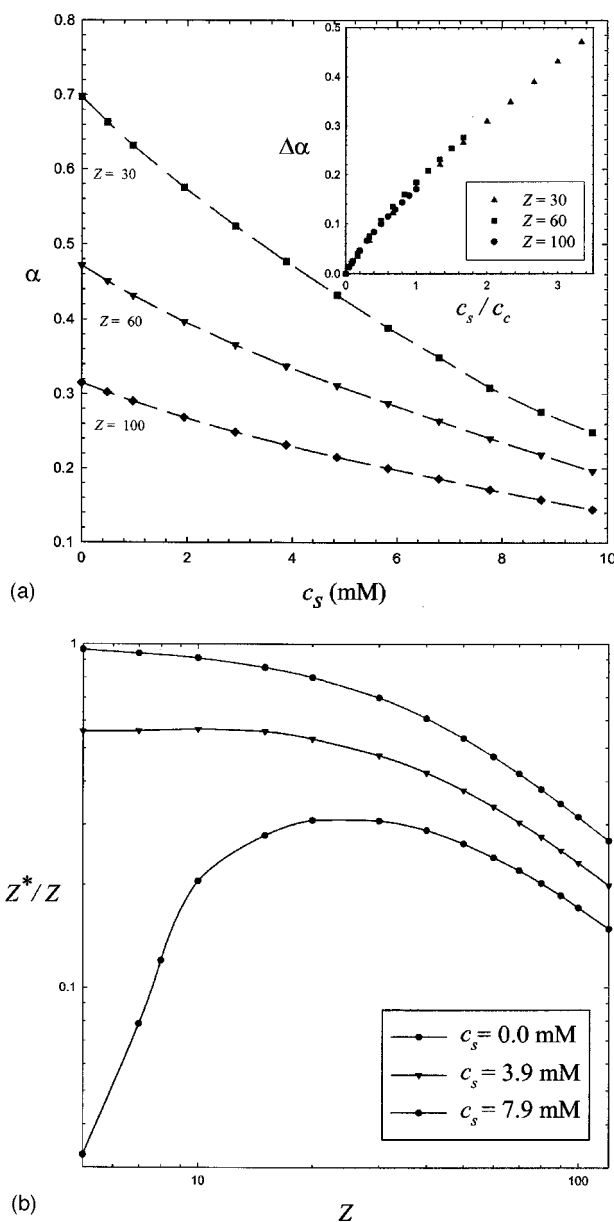


FIG. 4. (a) The variation of the charge ratio α with the monovalent salt concentration c_s for colloid with different values of intrinsic charge Z . The dotted curves are drawn to guide the eyes. The data points are replotted in the inset for $\Delta\alpha = \alpha_0 - \alpha$ vs c_s/c_c . (b) The variation of the charge ratio Z^*/Z with the intrinsic charge Z for different monovalent salt concentrations. The solid curves are drawn to guide the eyes.

under a constant salt concentration. It can also be attributed to the competition between Coulomb attraction (increasing Z) and counterion entropy (decreasing Z). There are two limits. (i) For $c_c \gg c_s$, the colloidal dispersion behave just like the salt-free case. As a result, α declines with increasing Z . (ii) For $c_c \ll c_s$, decreasing Z is equivalent to increasing c_s/Z , which magnifies the effect of salt addition. Consequently, α declines with decreasing Z . The compromise between these two effects results in α_{\max} for a specified c_s .

Addition of multivalent salt can reduce the effective charge much more efficiently than addition of monovalent salt. As shown in Fig. 5, the effective charge is plotted against the salt concentration for various multivalent salts with $Z=100$ ($c_c \approx 10$ mM). The effective charge drops very

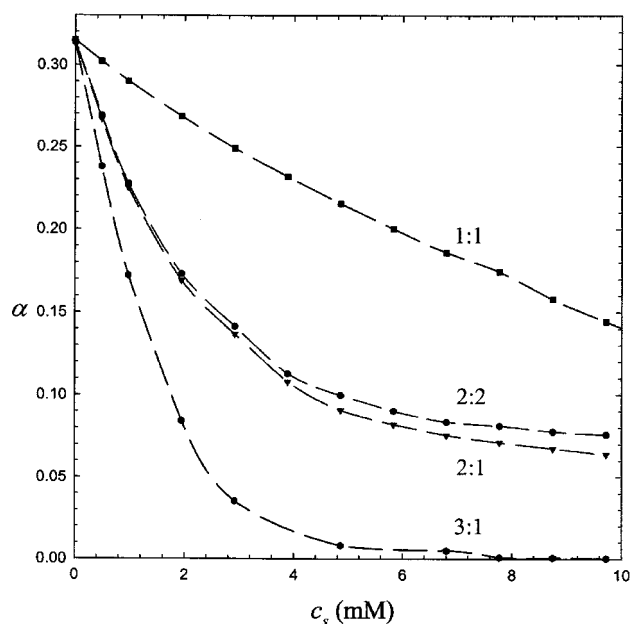


FIG. 5. The variation of the charge ratio α with the salt concentration c_s for $a=10$, $R=40$, and $Z=100$. The simple added salts include 2: 1, 2: 2, and 3: 1 multivalent counterions. The dotted curves are drawn to guide the eyes.

quickly upon addition of 3:1 salt. For example, the effective charge becomes $Z^*/Z \approx 0.02$ for 3 mM 3:1 salt, but is still $Z^*/Z \approx 0.14$ for 10 mM 1:1 salt. According to the PB theory, the effect of salt addition is usually understood in terms of the ionic strength, $I=(c_+z_+^2+c_-z_-^2)/2$. If the effectiveness of reducing Z^* is proportional to the ionic strength, then the equivalent concentrations are 6:4:3:1 for 3:1, 2:2, 2:1, and 1:1 salts, respectively, for the same salt concentration. That is,

$$\alpha(z_c) \approx \alpha_0 - \Delta\alpha(z_c=1) \left[\frac{I(z_c)}{I(z_c=1)} \right]$$

for a specified c_s . This simple model would predict that $Z^*/Z \approx 0$ for 3 mM 3:1 salt based on the result of monovalent salt. It agrees approximately with the simulation result. This model also predicts that 2:2 salt is more effective than 2:1 salt. This result is inconsistent with our simulation result, as illustrated in Fig. 5. Nonetheless, the differences between these two salts are quite small.

The results of monovalent salt reveal that the reduction of Z^* by salt addition is more significant for colloids with lower Z . In order to have the same extent of α reduction ($\Delta\alpha$), the added salt concentration for $Z=60$ must be twice that for $Z=30$. It is anticipated that α for $Z=30$ will be lower than α for $Z=60$ eventually as the salt concentration continues increasing. In the dilute limit, however, it is difficult to observe this phenomenon simply by addition of a monovalent salt. With the addition of 3:1 salt, this effect is clearly confirmed in Fig. 6 for $Z=30, 60, 100$. Despite the fact that the charge ratio for $Z=30$ is the highest, $\alpha_0 \approx 0.7$, it decays rapidly with c_s and becomes lowest at about $c_s \approx 1$ mM. In other words, for a given amount of salt, the influence on the effective charge decreases with increasing intrinsic charge. The relation $Z^*(Z, c_s)$ can be reexpressed as $\Delta\alpha(c_s/c_c)$, as

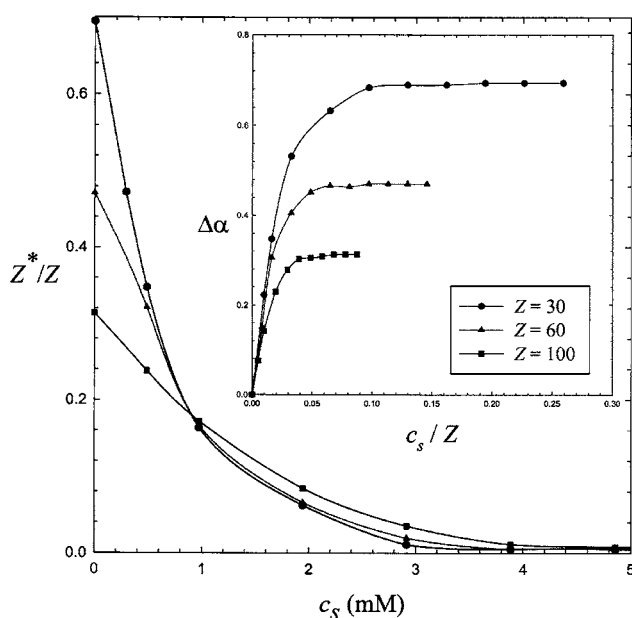


FIG. 6. The variation of the charge ratio α with the concentration of 3: 1 salt, c_s , for colloid with different values of intrinsic charge Z . The solid lines are drawn to guide the eyes. The data points are redrawn in the inset for $\Delta\alpha = \alpha_0 - \alpha$ vs c_s/Z .

demonstrated in the inset of Fig. 4(a) for monovalent salt. For weak Coulomb coupling, an approximately linear relation is observed. However, as shown in the inset of Fig. 6, addition of multivalent salt results in significant deviation from the weak-coupling behavior. Because of the strong attraction between multivalent counterion and colloid, $\Delta\alpha$ is increased rapidly from the weak-coupling to strong-coupling regimes. While an approximately linear increase is displayed in the former regime, $\Delta\alpha$ approaches a constant, $\Delta\alpha \approx \alpha_0$, in the latter regime.

A colloidal dispersion can be kinetically stabilized by electrostatic repulsions. The accumulation of counterions around the charged particle forms the diffuse layer of the electric double layer.²⁰ The overlap of the electric double layers associated with two colloids leads to repulsion. It is generally accepted that for a colloid with constant surface charge, salt addition leads to the decrease of the thickness of the diffuse layer (Debye screening length κ^{-1}) and therefore weakens the electrostatic repulsion between two colloids. According to the present study, the reduction of the electrostatic repulsion due to salt addition can also be explained by the decrease of the effective charge associated with the colloid. Moreover, the addition of multivalent salt is able to lessen the effective charge very efficiently. Consequently, the van der Waals attraction between two colloids can overcome the electrostatic repulsion easily and results in colloidal aggregation. Precipitation of colloids due to addition of multivalent salt is frequently observed experimentally.

The effective charge is often determined experimentally by electrophoresis. The generic approximate expression relating the electrophoretic mobility of a protein to its effective charge is $\mu_E \sim Z^*$ for the same particle size.²¹ In accordance with electrokinetic phenomena, the electrophoretic mobility μ_E associated with a charged particle is proportional to its ζ

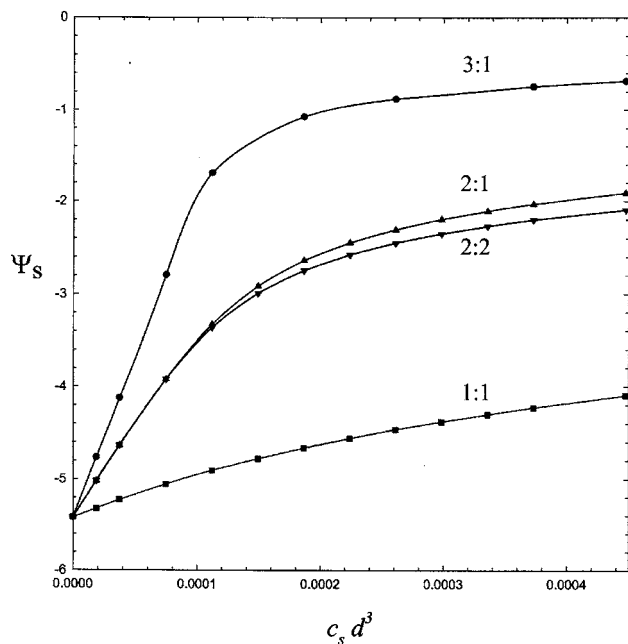


FIG. 7. The dimensionless surface potential $\Psi_s = \beta e \psi_s$ is plotted against the salt concentration c_s for various multivalent salts with $Z=100$. The solid lines are drawn to guide the eyes.

potential,²² which is approximately equivalent to the surface potential Ψ_s . As a result, $\mu_E \sim \Psi_s$. The aforementioned analysis indicates that $Z^* \sim \Psi_s$. Note that such a definition of effective charge is based on transport properties, instead of thermodynamics. Figure 7 shows that the influence of salt addition on the surface potential for $Z=100$. The qualitative behavior of Ψ_s is quite similar to Z^* based on ion chemical potential. The absolute value of the surface potential declines with increasing c_s . The effect of multivalent salt is much more significant than monovalent salt. Nevertheless, the fact that $Z_1^*/Z_2^* \neq \Psi_{s,1}/\Psi_{s,2}$ indicates that different definitions of effective charge may give different values of Z^* . According to the linearized PB theory, the surface potential is related to the ionic strength by $\Psi_s \sim Z/(1+\kappa a)$. Therefore, $\alpha \sim (1+\kappa a)^{-1}$ due to $Z^* = Z\alpha(c_s)$. Since $\kappa = (8\pi\ell_B I)^{1/2}$, the effective charge based on electrophoretic mobility also declines with increasing c_s , and is reduced very efficiently by addition of multivalent salt.

It is important to compare the effective charge based on ion chemical potential with that based on far-field behavior. Within the PB theory, the latter has been obtained by using the analytic solutions for a sphere.^{23,24} It is shown that at high enough intrinsic charge, nonlinear effects come into play and the effective charge is dramatically affected by salt addition.²³ Moreover, the effective charge depends on electrolyte asymmetry besides the Debye length. For a given value of the ionic strength, the effective charge may differ by a factor exceeding 2 between 2:1 and 1:2 cases.²⁴ Those phenomena agree qualitatively with our findings. However, Z^* based on far-field behavior grows with increasing salt concentration. For example, in the limit of diverging intrinsic charge with monovalent salt, the effective charge can be simply expressed by²³

$$\frac{\ell_B}{a} Z^* = 4\kappa a + 6 + O\left(\frac{1}{\kappa a}\right).$$

Note that it is the exact expansion of the correct result in the limit of large κa . This consequence is opposite to that based on chemical potential, which declines with increasing c_s . Evidently, the definition based on far-field behavior is unable to explain the determination of Z^* by electrophoresis, which decays with c_s .²¹

V. CONCLUSION

In a solution containing charged particles, counterions are always accumulated in the vicinity of the surface of the charged particle with intrinsic charge Z . The effective charge Z^* is therefore invoked to represent the physical behavior of such a highly charged colloidal dispersion. The value of the effective charge changes with its definition. In other words, it is model dependent. Unfortunately, a thermodynamic definition of Z^* , which can also be experimentally measurable, is generally lacking. In this study, we propose an operational definition of the effective charge, which is thermodynamically well defined and can be determined by potentiometry.⁷ On the basis of this definition, we are able to investigate the effect of multivalent salt addition on the effective charge of a dilute colloidal dispersion.

Although the ion concentrations c_i are not uniform in the solution due to the presence of the charged particles, their chemical potentials are uniform everywhere. Therefore, on the basis of ion chemical potential, one can define an effective ion concentration c_i^* , which can be experimentally measured by ion-selective electrode. Note that c_i^* reduces to c_i in the absence of charged colloids. This definition is essentially equivalent to the ionic activity coefficient ($\gamma_i = c_i^*/c_i$) with the pure salt solution as the reference state. Once all the effective ion concentrations are obtained, the effective charge associated with the charged particle can then be determined by the global electroneutrality condition. In fact, the effective charge denotes the activity coefficient associated with the colloid, $\gamma_p = Z^*/Z$. Our approach is consistent with the conventional thermodynamic theory for a solution of a strong electrolyte. Applying such a definition to a salt-free colloidal solution yields a result similar to that of an unsymmetrical electrolyte solution. For example, consider small charged particles with valency $Z=-4$ and counterions with $z=+1$. If one regards them as a colloid solution and applies current definition, then the result is consistent with that regarding them as a strong electrolyte solution (activity coefficient).

In order to explore the influence of adding multivalent salt, Monte Carlo simulations are performed in a spherical Wigner-Seitz cell to obtain the effective charge of the colloid. In terms of the charge ratio $\alpha = Z^*/Z$, the effects of added salt concentration, counterion valency, and particle charge are examined. The effective charge declines with increasing salt concentration and the multivalent salt is much more efficient in reducing the effective charge of the colloidal solution. Moreover, the extent of effective charge reduction is decreased with increasing intrinsic charge for a given concentration of added salt. Those results are qualitative con-

sistent with experimental observations by electrophoresis. We have investigated dilute systems containing particle size of about 4 nm ($a=10$) with surface charge density of about 0.1 C/m^2 ($Z \sim 100$). They correspond to the micellar or protein solution. Nonetheless, our results can be generally applied to typical colloidal dispersions with much larger a and Z .

ACKNOWLEDGMENTS

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¹S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, and P. Pincus, *J. Chem. Phys.* **80**, 5776 (1984).

²E. Trizac, L. Bocquet, and M. Aubouy, *Phys. Rev. Lett.* **89**, 248301 (2002).

³R. D. Groot, *J. Chem. Phys.* **95**, 9191 (1991).

⁴M. J. Stevens, M. L. Falk, and M. O. Robbins, *J. Chem. Phys.* **104**, 5209 (1996).

⁵J. M. Roberts, J. J. O'Dea, and J. G. Osteryoung, *Anal. Chem.* **70**, 3667 (1998).

⁶V. K. Aswal and P. S. Goyal, *Phys. Rev. E* **67**, 051401 (2003).

⁷C. C. Hsiao, T.-Y. Wang, and H.-K. Tsao, *J. Chem. Phys.* **122**, 144702 (2005).

⁸R. D. Void and M. J. Void, *Colloid and Interface Chemistry* (Addison-Wesley, Reading, MA, 1983).

⁹V. Sanghiran and K. S. Schmitz, *Langmuir* **16**, 7566 (2000).

¹⁰W. L. Hsin, T.-Y. Wang, Y.-J. Sheng, and H.-K. Tsao, *J. Chem. Phys.* **121**, 5494 (2004).

¹¹M. Muthukumar, *J. Chem. Phys.* **120**, 9343 (2004).

¹²T.-Y. Wang, T.-R. Lee, Y.-J. Sheng, and H.-K. Tsao, *J. Phys. Chem. B* **109**, 22560 (2005).

¹³D. A. McQuarrie, *Statistical Mechanics* (Happer & Row, New York, 1976).

¹⁴G. V. Ramanathan, *J. Chem. Phys.* **88**, 3887 (1988).

¹⁵L. Belloni, *Colloids Surf., A* **140**, 227 (1998).

¹⁶M. Deserno and C. Holm, *Electrostatic Effects in Soft Matter and Biophysics* (Kluwer Academic, Netherlands, 2001), p. 27; H. Wennerström, B. Jönsson, and P. Linse, *J. Chem. Phys.* **76**, 4665 (1982).

¹⁷Y.-J. Sheng and H.-K. Tsao, *Phys. Rev. Lett.* **87**, 185501 (2001); *Phys. Rev. E* **66**, 040201(R) (2002); C.-H. Ho, H.-K. Tsao, and Y.-J. Sheng, *J. Chem. Phys.* **119**, 2369 (2003).

¹⁸D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, New York, 1996).

¹⁹G. S. Manning, *J. Chem. Phys.* **51**, 924 (1969).

²⁰E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

²¹J. Gao, F. A. Gomez, R. Härter, and G. W. Whitesides, *Proc. Natl. Acad. Sci. U.S.A.* **91**, 12027 (1994).

²²R. F. Probstein, *Physicochemical Hydrodynamics: An Introduction* (Wiley, New York, 1994).

²³M. Aubouy, E. Trizac, and L. Bocquet, *J. Phys. A* **36**, 5835 (2003).

²⁴G. Téllez and E. Trizac, *Phys. Rev. E* **70**, 011404 (2004).