JOURNAL OF COLLOID AND INTERFACE SCIENCE 174, 250–257 (1995)

Critical Coagulation Concentration of Cations for Negatively Charged Particles with an Ion-Penetrable Surface Layer

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Received November 23, 1994; accepted February 10, 1995

The critical coagulation concentration (CCC) of cations in a suspension of negatively charged colloidal particles and arbitrary *a:b* electrolyte is derived. Here, a particle comprises a rigid core and an ion-penetrable surface layer. The latter contains fixed charges due to either the dissociation of the functional groups it bears or the adsorption of ions in the liquid phase. We show that, if the potential in the surface layer is high, the CCC ratio of cations follows that predicted by the Schulze–Hardy rule. On the other hand, if the potential in the surface layer is low, the CCC ratio deviates appreciably from this rule, in general. On possible exception is that the fixed charges arise from the exchange of cations in the liquid phase with the protons of the functional groups in the surface layer to form a metal complex, and the subsequent dissociation of this complex. The binding of the cations with dissociated functional groups needs to be strong enough, and there are sufficiently many functional groups. © 1995 Academic Press, Inc.

Key Words: **critical coagulation concentration; asymmetric electrolytes; surface layer, charged, ion-penetrable; fixed charge distribution, nonuniform; Schulze–Hardy rule; ion-exchange membrane.**

1. INTRODUCTION

The critical coagulation concentration (the minimum concentration of ions to induce coagulation of a colloidal dispersion) ratio of cations required to destabilize a suspension of charged colloidal dispersion can be estimated by the classic Schulze–Hardy rule. For negatively charged particles, this rule predicts that the CCC ratio of cations is proportional to the inverse sixth power of their valences (1). For instance, the CCC ratio of cations of valences 3, 2, and 1 is $3^{-6}:2^{-6}:1^{-6}$. Rigorously, the Schulze–Hardy rule is applicable for planar particles having a high surface potential, and it requires that the electrolyte in the liquid phase be symmetric. Despite the fact that some of these assumptions are obviously violated, the CCC ratio predicted by the Schulze–Hardy rule is found to match the experimental observations for a wide class of colloidal dispersions.

The derivation of the Schulze–Hardy rule is based on a rigid surface of constant potential. Although the rigid surface model is adequate for most of inorganic colloids, it is inappropriate to some of the dispersed entities in practice, e.g., biological cells and particles covered with an artificial membrane (2–7). In these cases, a particle comprises a rigid, uncharged core and an ion-penetrable surface layer. The latter contains fixed charges due to either the dissociation of the functional groups or the adsorption of ions from the liquid phase. For instance, the peripheral zone of human erythrocytes contains a glycoprotein layer about 15 nm thick which possesses some ionogenic groups and forms the outer boundary of the lipid layer (8, 9).

In an analysis of the interaction between an ion-penetrable particle and a solid particle, Terui *et al.* (10) derived expressions for the interaction potential and the electrostatic interaction force between particles. The analysis was extended to various combinations of two types of particle, and expressions for CCC were derived (11). These analyses (10, 11) were based on the following conditions: (a) The potential at the surface of a particle is sufficiently low such that a linearized version of the governing Poisson–Boltzmann equation can be employed. (b) The electrolyte is symmetric. (c) The fixed charges in the surface layer are uniformly distributed.

In this report, the applicability of the Schulze–Hardy rule to colloidal particles covered with an ion-penetrable surface layer is investigated. In particular, the effects of the level of potential and the type of the fixed charge distribution in the surface layer on the CCC ratio of cations are examined. Since asymmetric electrolytes are not uncommon in practice, the relevant result for a general *a:b* electrolyte solution is highly desirable. This is also taken into account in the present analysis.

2. ANALYSIS

The analysis is begun by considering a planar surface immersed in an *a:b* electrolyte solution. As illustrated in Fig. 1, the surface comprises a rigid core and a charged, ion-penetrable surface layer of dimensionless thickness d. The latter contains fixed charges, and without loss of generality, we assume that these charges are negative.

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0021-9797/95 $12.00

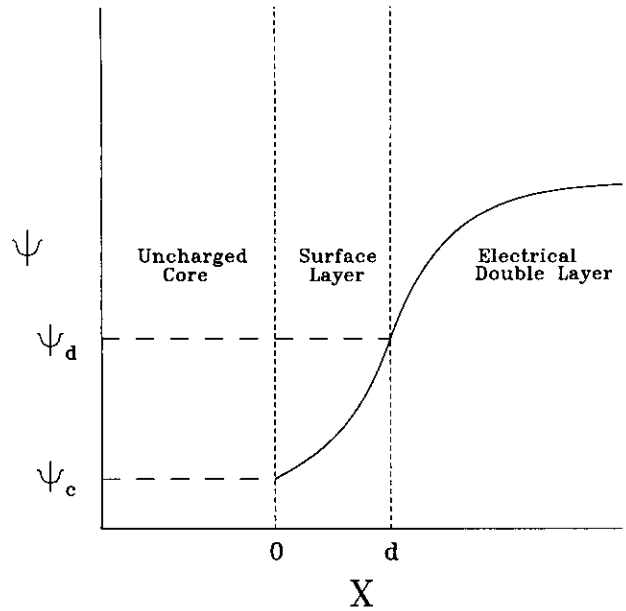

FIG. 1. A schematic representation of the system under consideration: d is the dimensionless thickness of surface layer, ψ_c and ψ_d are, respectively, the dimensionless potential at core–surface layer interface and that at surface layer–liquid interface.

2.1. Uniformly Distributed Fixed Charges

Suppose that the distribution of the fixed charges in the surface layer is uniform with density N_0. The electrostatic potential distribution is governed by

$$d^2\psi/dX^2 = (g + iN)/(a + b), \quad i = 0, 1, \qquad [1]$$

where $g = [\exp(b\psi) - \exp(-a\psi)]$, $\kappa^2 = a(a + b) n_a^0 e^2/\epsilon_0\epsilon_r k_B T$, $\psi = e\phi/k_B T$, $X = \kappa r$, and $N = ZN_0N_A/an_a^0$. In these expressions e, ϕ, k_B, and T are, respectively, the elementary charge, the electrostatic potential, the Boltzmann constant, and the absolute temperature, r is the distance, ϵ_0 and ϵ_r are, respectively, the permittivity of the vacuum and the relative permittivity, κ denotes the reciprocal Debye length, Z and N_A are, respectively, the valence of fixed charges and the Avogadro number, n_a^0 is the number concentration of cations in the bulk liquid phase, and i is a region index ($i = 1$ for surface layer, $i = 0$ for double layer region). The boundary conditions associated with [1] for an isolated surface are

$$\psi \to 0 \text{ and } (d\psi/dX) \to 0 \quad \text{as } X \to \infty \qquad [1a]$$

$$\psi(X \to d^+) = \psi(X \to d^-) = \psi_d \quad \text{and}$$
$$(d\psi/dX)|_{X\to d^-} = (d\psi/dX)|_{X\to d^+} \qquad [1b]$$

$$\psi \to \psi_c \text{ and } (d\psi/dX) \to 0 \quad \text{as } X \to 0, \qquad [1c]$$

where ψ_c and ψ_d are, respectively, the dimensionless potential at the core–surface layer interface ($X = 0$) and that at the surface layer–liquid interface ($X = d$). It can be shown that an approximate solution to [1] for the double-layer region is (12)

$$\tanh(a\psi/4) = [\tanh(a\psi_d/4)]\exp[-k_3(X - d)]. \qquad [2]$$

In this expression the parameter k_3 is defined by

$$k_3 = \begin{cases} [(k - 2)k_1 + 2k_2]/k, & k \leq 4, \\ [2k_1 + (k - 2)k_2]/k, & k > 4, \end{cases} \qquad [2a]$$

where $k_1 = 2/\{k^{1/2}[(k/2)^{2/(k-2)} - 1]\}$, $k_2 = 2/k^{1/2}$, and $k = 2 + 2b/a$. If X is large enough, [2] reduces to

$$\psi = (4/a)[\tanh(a\psi_d/4)]\exp[-k_3(X - d)]. \qquad [3]$$

For two identical, parallel surfaces separated by a dimensionless distance $L + 2d$, a differential force balance yields

$$dF_R = -\rho d\phi, \qquad [4]$$

where dF_R is the differential electrostatic repulsion force per unit area between surfaces and ρ denotes the space charge density. Integrating [4] from ∞ to $d + L/2$, $X = d + L/2$ being the position of the middle plane between surfaces, gives the electrostatic repulsion force F_R as

$$F_R = an_a^0 k_B T\{(1/b)[\exp(b\psi_m) - 1] + (1/a)[\exp(-a\psi_m) - 1]\}, \qquad [5]$$

where ψ_m denotes the dimensionless potential at $X = d + L/2$. If L is large enough, ψ_m is low, and its value for two parallel surfaces is twice that for a single surface. Expanding F_R in its Taylor series around $\psi_m = 0$ and employing [3] and [5], we have

$$F_R = a(a + b)n_a^0 k_B T\psi_m^2/2 = 32(1 + b/a)n_a^0 k_B T[\tanh^2(a\psi_d/4)]\exp(-k_3L). \qquad [6]$$

The electrostatic potential energy, V_R, is calculated by

$$V_R = \kappa^{-1}\int_L^\infty F_R dL = \frac{32(a + b)n_a^0 k_B T}{ak_3\kappa}[\tanh^2(a\psi_d/4)]\exp(-k_3L). \qquad [7]$$

The van der Waals attraction energy, V_A, is

$$V_A = -A_{132}\kappa^2/12\pi L^2, \quad [8]$$

where A_{132} is the Hamaker constant. The total interaction energy between surfaces, V_T, is the sum of V_A and V_R, i.e.,

$$V_T = V_A + V_R \quad [9]$$

At the CCC of cations, $n^0_{a,c}$,

$$V_T = 0 \quad \text{at } L = 2 \quad [10]$$

Equations [7] through [10] lead to

$$n^0_{a,c} = \frac{\tanh^4(a\psi_d/4)}{a^5(a+b)k_3^2\exp(4k_3)} \times \frac{(4\pi\epsilon_0\epsilon_r)^3(k_BT)^5(192)^2}{e^6A_{132}^2\pi}. \quad [11]$$

2.1.1. Evaluation of ψ_d. We assume that the surface layer is sufficiently thick. In this case, ψ_c approaches the dimensionless Donnan potential ψ_{Don}. We have

$$\psi_c \to \psi_{Don} \text{ and } d^2\psi/dX^2 \to 0 \quad \text{as } X \to 0. \quad [12]$$

The value of ψ_{Don} can be evaluated by applying [12] to [1] with $i = 1$ to give

$$\exp(b\psi_{Don}) - \exp(-a\psi_{Don}) + N = 0. \quad [13]$$

Solving [1] with $i = 0$ subject to [1a] yields

$$\frac{d\psi}{dX} = -\mathrm{Sgn}(\psi)\left(\frac{2}{a+b}\right)^{1/2}\left\{\frac{1}{b}[\exp(b\psi) - 1] + \frac{1}{a}[\exp(-a\psi) - 1]\right\}^{1/2}. \quad [14]$$

Similarly, solving [1] with $i = 1$ subject to [1b] and applying [14], we obtain

$$\frac{d\psi}{dX} = -\mathrm{Sgn}(\psi)\left(\frac{2}{a+b}\right)^{1/2}\left\{\frac{1}{b}[\exp(b\psi) - 1] + \frac{1}{a}[\exp(-a\psi) - 1] + N(\psi - \psi_d)\right\}^{1/2}. \quad [14a]$$

The relation between ψ_d and ψ_{Don} can be determined by [14a], [1c], and [12] as

$$\psi_d = \psi_{Don} + \frac{1}{N}\left\{\frac{1}{b}[\exp(b\psi_{Don}) - 1] + \frac{1}{a}[\exp(-a\psi_{Don}) - 1]\right\}. \quad [15]$$

If the potential in surface layer is sufficiently high, $\tanh(a\psi_d/4) \to -1$, and [11] reduces to

$$n^0_{a,c} \propto 1/[a^5(a+b)k_3^2\exp(4k_3)]. \quad [16]$$

Furthermore, if the electrolyte is symmetric ($a = b = v$), then $k_3 = 1$, and [16] becomes

$$n^0_{a,c} \propto 1/v^6. \quad [16a]$$

This is the same as the result for rigid surfaces, i.e., the Schulze–Hardy rule. On the other hand, if the surface potential is low, $\tanh(a\psi_d/4) \to (a\psi_d/4)$. In this case, [13] suggests that $\psi_{Don} \simeq [-N/(a+b)]$, and [15] leads to

$$\psi_d \simeq \psi_{Don} + (a+b)\psi_{Don}^2/2N \simeq [-N/2(a+b)]. \quad [17]$$

Here, N is a function of both n^0_a and a. On the basis of [11], we conclude that

$$n^0_{a,c} \propto 1/[a(a+b)k_3^{2/5}\exp(4k_3/5)]. \quad [18]$$

For symmetric electrolytes, this expression reduces to

$$n^0_{a,c} \propto 1/v^2. \quad [18a]$$

2.2. Nonuniformly Distributed Fixed Charges

Suppose that the fixed charges in the surface layer arise from the dissociation of the functional groups it bears according to the reaction

$$AH \to A^- + H^+, \quad [19]$$

where AH and A^- are the acidic functional groups and the conjugated basic groups, respectively. The functional groups are assumed to distribute uniformly with density N_0. We have, at equilibrium,

$$K_a = (n_{A^-})(n_{H^+})/(n_{AH}), \quad [20]$$

where K_a represents the equilibrium constant, n_{A^-}, n_{AH}, and n_{H^+}, are, respectively, the number concentrations of A^-, AH, and H^+. A number balance for the functional groups yields

$$N_0 N_A = n_{AH} + n_{A^-}. \quad [21]$$

The distribution of H^+ follows the Boltzmann distribution

$$n_{H^+} = n^0_{H^+}\exp(-\psi), \quad [22]$$

where $n^0_{H^+}$ represents the number concentration of H^+ in the bulk liquid phase. Suppose that the bulk concentrations of H^+ and OH^- are negligible compared to that of the electrolyte. Then the potential distribution for an isolated surface is governed by

$$d^2\psi/dX^2 = (g + iN_a)/(a + b), \quad i = 0, 1. \quad [23]$$

The symbols used here are the same as those used in Section 2.1, except that the dimensionless fixed charge distribution is denoted by N_a. The value of N_a can be determined by [20] through [22], we have

$$N_a = (N_0 N_A/an^0_a)/[1 + (n^0_{H^+}/K_a)\exp(-\psi)]. \quad [23a]$$

Integrating [23] with $i = 1$ subject to [1b] and applying [14], we have

$$\frac{d\psi}{dX} = -\mathrm{Sgn}(\psi)\left(\frac{2}{a+b}\right)^{1/2}\left\{\frac{1}{b}[\exp(b\psi) - 1] + \frac{1}{a}[\exp(-a\psi) - 1] + N_b - N_b(\psi_d)\right\}^{1/2}, \quad [24]$$

where

$$N_b = (N_0 N_A/an^0_a)\ln[\exp(\psi) + (n^0_{H^+}/K_a)]. \quad [24a]$$

Employing [1c] and [12] to [24] yields

$$\ln\left[\frac{\exp(\psi_d) + n^0_{H^+}/K_a}{\exp(\psi_{Don}) + n^0_{H^+}/K_a}\right] = \frac{1}{N(Z=1)}\left\{\frac{1}{b}[\exp(b\psi_{Don}) - 1] + \left(\frac{1}{a}\right)[\exp(-a\psi_{Don}) - 1]\right\}. \quad [25]$$

Similarly, applying [12] to [23] with $i = 1$ gives

$$\exp(b\psi_{Don}) - \exp(-a\psi_{Don}) + \frac{N(Z=1)}{1 + n^0_{H^+}[\exp(-\psi_{Don})]/K_a} = 0. \quad [25a]$$

If $n^0_{H^+}/K_a \to 0$, i.e., the dissociation of the functional groups is complete, then [25] and [25a] reduce to [15] and [13], respectively, with $N = N(Z = 1)$. In this case, the CCC ratio of cations is described by [16] if the potential is high and by [18] if the potential is low. On the other hand, if $(n^0_{H^+}/K_a) \gg 1$ and the potential in the surface layer is low, [25a] yields

$$\psi^2_{Don} + (g_1 + g_2)\psi_{Don} + g_2 \simeq 0, \quad [26]$$

where

$$g_1 = 1 + n^0_{H^+}/K_a \quad [26a]$$

$$g_2 = N(Z = 1)/(a + b). \quad [26b]$$

Solving [26] for ψ_{Don} and noting that $g_1 \gg g_2$ for a typical N_0, we obtain

$$\psi_{Don} \simeq -(g_2/g_1 + 2g_2^2/g_1^3). \quad [27]$$

In this case, [25] leads to

$$(\psi_d - \psi_{Don})/g_1 \simeq \psi^2_{Don}/2g_2. \quad [28]$$

Substituting [27] into [28] gives

$$\psi_d \simeq -g_2/2g_1, \quad [29]$$

and therefore

$$\tanh(a\psi_d/4) \to -N_0 N_A/8g_1(a + b)n^0_a. \quad [30]$$

Substituting this expression into [11] yields [18]. It can be shown that if $n^0_{H^+}/K_a \gg 1$ and the potential in the surface layer is high, the variation of $n^0_{a,c}$ is described by [16].

2.3. *Binding of Cations to Functional Groups*

Suppose that the fixed charges in the surface layer arise from the interaction between the cations in the liquid phase with the functional groups in the surface layer through two steps in series: exchange of cations with the protons of functional groups to form a metal complex, followed by the dissociation of this complex to yield fixed charges. The first step can be expressed by

$$CH_a + M^{a+} = CM + aH^+, \quad [31]$$

where CH_a, M^{a+}, and CM represent, respectively, the functional group, the cation, and the metal complex. If we define the equilibrium constant of [31] as K'_a, then

$$K'_a = (n_{CM})(n_{H^+})^a/(n_{CH_a})(n_{M^{a+}}), \quad [32]$$

where n_{CH_a}, n_{CM}, and $n_{M^{a+}}$ denote, respectively, the number concentration of CH_a, CM, and M^{a+}. The distribution of M^{a+} follows the Boltzmann distribution, i.e.,

$$n_{M^{a+}} = n_a^0 \exp(-a\psi). \quad [33]$$

The dissociation of metal complex CM can be expressed by

$$CM = C^{a-} + M^{a+}, \quad [34]$$

where C^{a-} is the dissociated functional groups which yield negative fixed charges in the surface layer. Suppose that the equilibrium constant of [34] is K_e. Then

$$K_e = (n_{C^{a-}})(n_{M^{a+}})/(n_{CM}), \quad [35]$$

where $n_{C^{a-}}$ is the number concentration of C^{a-}. The overall reaction of [31] and [34] is

$$CH_a = C^{a-} + aH^+. \quad [36]$$

The associated equilibrium constant K_c is

$$K_c = K_a' K_e = (n_{C^{a-}})(n_{H^+})^a/(n_{CH_a}). \quad [37]$$

The distribution of H^+ is described by [22], and a number balance for the functional groups gives

$$N_0 N_A = n_{C^{a-}} + n_{CH_a} + n_{CM}. \quad [38]$$

The potential distribution for the present case is

$$d^2\psi/dX^2 = (g + iN_c)/(a + b), \quad i = 0, 1. \quad [39]$$

The symbols used here are the same as those used in Section 2.1, except that the dimensionless fixed charge distribution is denoted by N_c. The value of N_c can be determined by [22], [33], [35], [37], and [38] as

$$N_c = \frac{(N_0 N_A/n_a^0)}{\{1 + [[(n_{H^+}^0)^a/K_c] + (n_a^0/K_e)]\exp(-a\psi)\}}. \quad [39a]$$

Integrating [39] with $i = 1$ subject to [1b] and applying [14], we obtain

$$\frac{d\psi}{dX} = -\mathrm{Sgn}(\psi)\left(\frac{2}{a+b}\right)^{1/2}\left\{\frac{1}{b}[\exp(b\psi) - 1] + \frac{1}{a}[\exp(-a\psi) - 1] + N_d - N_d(\psi_d)\right\}^{1/2}, \quad [40]$$

where

$$N_d = (N_0 N_A/a n_a^0)\ln[\exp(a\psi) + [(n_{H^+}^0)^a/K_c] + (n_a^0/K_e)]. \quad [40a]$$

Employing [1c] and [12] to [40] yields

$$\ln\left\{\frac{\exp(a\psi_d) + [(n_{H^+}^0)^a/K_c] + (n_a^0/K_e)}{\exp(a\psi_{Don}) + [(n_{H^+}^0)^a/K_c] + (n_a^0/K_e)}\right\} = \frac{1}{N(Z=1)}\left\{\frac{1}{b}[\exp(b\psi_{Don}) - 1] + \frac{1}{a}[\exp(-a\psi_{Don}) - 1]\right\}. \quad [41]$$

The value of ψ_{Don} is determined by employing [12] to [39] with $i = 1$ to give

$$\exp(b\psi_{Don}) - \exp(-a\psi_{Don}) + \frac{N(Z=a)}{1 + \{[(n_{H^+}^0)^a/K_c] + (n_a^0/K_e)\}\exp(-a\psi_{Don})} = 0. \quad [41a]$$

If the potential in the surface layer is high, $n_{a,c}^0$ is described by [16]. In the following discussion, we assume that the potential is low. On the basis of [41b], we have

$$\psi_{Don}^2 + (1/a)(g_3 + a^2 g_2)\psi_{Don} + g_2 \simeq 0, \quad [42]$$

where

$$g_3 = 1 + (n_{H^+}^0)^a/K_c + n_a^0/K_e. \quad [42a]$$

Solving [42] yields

$$\psi_{Don} \simeq -\left\{\frac{g_2}{(g_3 + a^2 g_2)/a} + \frac{2g_2^2}{[(g_3 + a^2 g_2)/a]^3}\right\}. \quad [43]$$

From [41] we have

$$a(\psi_d - \psi_{Don})/g_3 \simeq \psi_{Don}^2/2g_2. \quad [44]$$

2.3.1. Small N_0. If the number of functional groups is small, the potential in the surface layer is low, and $g_3 \gg g_2$. Following the procedure presented in 2.2 we obtain

$$\psi_{\mathrm{Don}} \simeq -[(ag_2/g_3) + (2a^3g_2^2/g_3^3)]. \quad [45]$$

Substituting [45] into [44] yields

$$\psi_{\mathrm{d}} \simeq -ag_2/2g_3. \quad [46]$$

Suppose that $(n_{\mathrm{a}}^0/K_{\mathrm{e}}) \ll [(n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}}]$. Then

$$g_3 \simeq 1 + (n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}} \simeq (n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}}. \quad [47]$$

In this case, it can be shown that

$$\tanh(a\psi_{\mathrm{d}}/4) \rightarrow -aK_{\mathrm{c}}N_0N_{\mathrm{A}}/[8(n_{\mathrm{H}^+}^0)^a(a+b)n_{\mathrm{a}}^0]. \quad [48]$$

Substituting [48] into [11] yields

$$n_{\mathrm{a,c}}^0 \propto 1/[(n_{\mathrm{H}^+}^0)^{4a/5}a^{1/5}(a+b)k_3^{2/5}\exp(4k_3/5)]. \quad [49]$$

For symmetric electrolytes, this expression becomes

$$n_{\mathrm{a,c}}^0 \propto 1/[(n_{\mathrm{H}^+}^0)^{4v/5}v^{6/5}]. \quad [49a]$$

Similarly, if $(n_{\mathrm{a}}^0/K_{\mathrm{e}}) \gg [(n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}}]$, then

$$g_3 \simeq 1 + n_{\mathrm{a}}^0/K_{\mathrm{e}} \simeq n_{\mathrm{a}}^0/K_{\mathrm{e}}. \quad [50]$$

We have

$$\tanh(a\psi_{\mathrm{d}}/4) \simeq -aK_{\mathrm{e}}N_0N_{\mathrm{A}}/[8(a+b)(n_{\mathrm{a}}^0)^2]. \quad [51]$$

Substituting [51] into [11] gives

$$n_{\mathrm{a,c}}^0 \propto 1/[a^{1/9}(a+b)^{5/9}k_3^{2/9}\exp(4k_3/9)]. \quad [52]$$

For symmetric electrolytes, this expression becomes

$$n_{\mathrm{a,c}}^0 \propto 1/v^{2/3}. \quad [52a]$$

If the magnitude of $(n_{\mathrm{a}}^0/K_{\mathrm{e}})$ and that of $[(n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}}]$ are of the same order, the expression for $n_{\mathrm{a,c}}^0$ is complicated. However, the value of $n_{\mathrm{a,c}}^0$ is bounded by [49] and [52]. If both $(n_{\mathrm{a}}^0/K_{\mathrm{e}})$ and $[(n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}}]$ are small, $g_3 \simeq 1$. According to [46]

$$\tanh(a\psi_{\mathrm{d}}/4) \simeq -aN_0N_{\mathrm{A}}/[8(a+b)n_{\mathrm{a}}^0]. \quad [53]$$

Substituting this expression into [11] yields

$$n_{\mathrm{a,c}}^0 \propto 1/[a^{1/5}(a+b)k_3^{2/5}\exp(4k_3/5)]. \quad [54]$$

For symmetric electrolytes, [54] leads to

$$n_{\mathrm{a,c}}^0 \propto 1/v^{6/5} \quad [54a]$$

TABLE 1
Summary of the Discussions in Section 2.4.1[a]

K_{c}	K_{e}	Dissociation of CM	Relative concentration	CCC
Small	Small	Difficult	$n_{\mathrm{CH_a}} \gg n_{\mathrm{C^{a-}}}$	
			$n_{\mathrm{CM}} \gg n_{\mathrm{C^{a-}}}$	—
Small	Large	Easy	$n_{\mathrm{CH_a}} \gg n_{\mathrm{CM}}$	[49]
Large	Small	Difficult	$n_{\mathrm{CM}} \gg n_{\mathrm{CH_a}}$	[52]
Large	Large	Easy	$n_{\mathrm{C^{a-}}} \gg n_{\mathrm{CH_a}}$	
			$n_{\mathrm{C^{a-}}} \gg n_{\mathrm{CM}}$	[54]

Note. The value of N_0 is small.

2.3.2. Small K_e. A small K_{e} implies that the binding between $C^{\mathrm{a}-}$ and $M^{\mathrm{a}+}$ is strong. In this case, $g_3 \simeq n_{\mathrm{a}}^0/K_{\mathrm{e}}$. Since the dissociation of CM is negligible, $C^{\mathrm{a}-}$ is small, and the potential in the surface layer is low. Furthermore, if N_0 is small, $g_3 \gg g_2$, and $n_{\mathrm{a,c}}^0$ is described by [52]. If N_0 is large enough that $g_2 \gg g_3$, then [44] gives

$$\psi_{\mathrm{Don}} \simeq -(1/a + 2/a^3g_2). \quad [55]$$

Substituting [55] into [45] yields

$$\psi_{\mathrm{d}} \simeq -1/a. \quad [56]$$

We have

$$\tanh(a\psi_{\mathrm{d}}/4) \simeq a\psi_{\mathrm{d}}/4 \simeq -1/4. \quad [57]$$

In this case, $n_{\mathrm{a,c}}^0$ is described by [16]. In other words, the Schulze–Hardy rule is applicable, even if the potential in the surface layer is low.

DISCUSSION

According to [35], $K_{\mathrm{e}} \rightarrow \infty$ implies $n_{\mathrm{CM}} \rightarrow 0$. This suggests that the binding of the dissociated functional groups with cations is weak. Furthermore, if $a = 1$, then $g_3 = g_1$, and [46] reduces to [29]. Thus, 2.3.1 is a special case of 2.2. Note that if K_{c} is small, both $(n_{\mathrm{H}^+}^0)^a/K_{\mathrm{c}}$ and $n_{\mathrm{CH_a}}\exp(a\psi)/n_{\mathrm{C^{a-}}}$ are large, which implies $n_{\mathrm{CH_a}} \gg n_{\mathrm{C^{a-}}}$. Similarly, various relative magnitudes of K_{c} and K_{e} lead to different results. These are summarized in Table 1.

Section 2.3 is a generalization of Section 2.2. This is because the functional groups in the surface layer may exist in three possible forms in the former, namely, $\mathrm{CH_a}$, $\mathrm{C^{a-}}$, and CM. Here, $\mathrm{M^{a+}}$ and $\mathrm{H^+}$ are competing with each other for the association with $\mathrm{C^{a-}}$. In the case of large K_{c}, the association of $\mathrm{M^{a+}}$ with functional groups is negligible, and the amount of fixed charges increases. This is consistent with [40]. The results discussed in Section 2.3 can be regarded as a neutralization effect in which the charged groups in the

TABLE 2
Variation in the Ratio $(n^0_{a,c})_{a:b}/(n^0_{a,c})_{3:3}$ as a Function of the Type of Electrolyte Used

a:b	Uniform or nonuniform fixed charges [18]	Cation binding, N_0 small: K_e large, K_c small [49][a]	Cation binding, N_0 small: K_e small, K_c large [52]	Cation binding, N_0 small: K_e large, K_c large [54]	Cation binding, N_0 large, K_e small [16][b]
3:3	1.000	1.000	1.000	1.000	1.000
3:2	1.147	1.147	1.079	1.147	0.958
3:1	1.270	1.270	1.142	1.270	0.652
2:3	1.886	3.616×10^{13}	1.188	1.363	11.494
2:2	2.250	4.315×10^{13}	1.310	1.627	11.391
2:1	2.736	5.247×10^{13}	1.461	1.978	9.582
1:3	5.545	1.620×10^{27}	1.589	2.303	1035.876
1:2	6.645	1.942×10^{27}	1.758	2.759	809.947
1:1	9.000	2.630×10^{27}	2.080	3.737	729.000

Note. The numerator and the denominator are, respectively, the value of $n^0_{a,c}$ for an a:b electrolyte and that for a 3:3 electrolyte.
[a] pH is 7 in the bulk liquid phase.
[b] The result for a high potential in the surface layer is the same as this column.

surface layer are neutralized by the adsorption of free cations.

Table 2 shows the variation in the ratio ($n^0_{a,c}$ of a:b electrolyte/$n^0_{a,c}$ of 3:3 electrolyte) for the case where the potential in the surface layer is low. As can be seen from this table, if the potential is low, the Schulze–Hardy rule is inappropriate. One possible exception is that the binding of cations with dissociated functional groups is strong, and N_0 is large enough. As shown in the third column of Table 2, if the functional groups in the surface layer are inactive (small K_c), the CCC ratio can be extraordinarily large.

According to [20], a small K_a implies that the functional group AH is inactive. In this case, if N_0 is large, following the same procedure as that employed in the derivation of [27]–[30] for $g_2 \gg g_1$ leads to

$$n^0_{a,c} \propto 1/[a(a+b)k_3^2\exp(4k_3)]. \qquad [58]$$

Similarly, a small K'_a (or K_c) implies that the functional group CH_a is inactive. If N_0 is large, following the same procedure as that employed in the derivation of [55]–[57] for $g_2 \gg g_3$ yields [16].

For rigid particles in an a:b electrolyte solution if the rate of surface dissociation reaction is fast, the surface potential is approximately constant. In this case, the CCC ratio of cations can be obtained from [11] by replacing ψ_d with ψ_0, the dimensionless surface potential; i.e.,

$$n^0_{a,c} = \frac{\tanh^4(a\psi_0/4)}{a^5(a+b)k_3^2\exp(4k_3)} \times \frac{(4\pi\epsilon_0\epsilon_r)^3(k_BT)^5(192)^2}{e^6A_{132}^2\pi}. \qquad [59]$$

CONCLUSION

We conclude that if the surface potential of the dispersed entities is high, the CCC ratio of cations for particles covered by an ion-penetrable membrane bearing negative charges follows the Schulze–Hardy rule. On the other hand, for low surface potentials, this ratio deviates appreciably from the Schulze–Hardy rule, except that the cations in the liquid phase are capable of binding strongly to the functional groups in the surface layer, and there are sufficiently many functional groups.

ACKNOWLEDGMENT

This work was supported by the National Science Council of the Republic of China.

APPENDIX: NOTATIONS

a	valence of cation
b	valence of anion
A_{132}	Hamaker constant
d	dimensionless thickness of surface layer
e	elementary charge
F_R	electrostatic repulsion force per unit area
g	function of electrostatic potential
g_1	quantity defined by [26a]
g_2	quantity defined by [26b]
g_3	quantity defined by [42a]
i	index representing the region
k	$2 + (2b/a)$, a measure of the degree of asymmetry of electrolyte
k_1,k_2	functions of k defined after [2a]
k_3	linear combination of k_1 and k_2 defined by [2a]
k_B	Boltzmann constant
K_a	equilibrium constant defined by [20]
K'_a	equilibrium constant defined by [32]
K_c	equilibrium constant defined by [37]
K_e	equilibrium constant defined by [35]

L dimensionless distance between two surfaces
n_a^0 number concentration of cations in bulk liquid phase
$n_{a,c}^0$ critical number concentration of cations
n_i number concentration of species i
N dimensionless fixed charge distribution
N_0 distribution of fixed charges or density of functional groups
N_A Avogadro number
N_a, N_b dimensionless fixed charge distribution
N_c, N_d dimensionless fixed charge distribution
r position variable
T absolute temperature
υ valence of a symmetric electrolyte
V_A van der Waals attraction energy
V_R electrostatic potential energy
V_T total interaction energy
X dimensionless position variable
Z valence of fixed charges
ϵ_0 permittivity of the vacuum
ϵ_r relative permittivity
κ reciprocal Debye length
ρ space charge density
ϕ electrostatic potential
ψ dimensionless electrostatic potential
ψ_0 dimensionless surface potential of a rigid surface
ψ_c dimensionless potential at the core–surface layer interface ($X = 0$)
ψ_d dimensionless potential at the surface layer–liquid interface ($X = d$).
ψ_{Don} dimensionless Donnan potential
ψ_m dimensionless potential at the midpoint between two surfaces

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