# 帶電薄膜系統之靜電交互作用：非點電荷模型(3/3)

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## 一、中文摘要

本文由理論角度探討離子尺寸對膠體懸浮液的臨界凝聚濃度之影響；液相中可以是(*a*:*b*)+(*c*:*b*)型的混合電解質。文中延伸了傳統基於點電荷假設的分析至較廣泛的情況。我們証明若粒子帶負電，則傳統模型將高估臨界凝聚濃度與粒子間之電斥力。在高 pH，低反離子價數，與反離子較大時，臨界凝聚濃度將較高。

**關鍵詞**: 臨界凝聚濃度, 離子尺寸, 生物膠體, 帶電薄膜

## Abstract

The critical coagulation concentration (CCC) for the case planar particles covered by a charge-regulated membrane layer immersed in a mixed (*a*:*b*)+(*c*:*b*) electrolyte solution is evaluated theoretically. We extend previous analyses in that a general charged condition in the membrane layer, which mimics biological cells, is considered, and the sizes of the charged species are taken into account. For particles carry net negative fixed charge the classic point charge model overestimates both CCC and the electrical repulsive force between two particles. CCC is high if pH is high, the valence of counterions is low, and the size of counter-ions is large; these results are consistent with experimental observations in the literature.

**Keywords**: CCC, ionic size, biocolloid, charged membrane

## 二、緣由與目的

Critical coagulation concentration (CCC) is one of the most important characteristics of a colloidal dispersion. Experimental observations reveal that the variation of CCC as a function of the valence of counterions follows roughly the inverse sixth power law, the so-called Schulze-Hardy rule. This rule was interpreted theoretically by the DLVO model[1], which considered the electrical repulsive force and the van der Waals attractive force between two particles. For non-rigid particles such as biocolloids and particles covered by an artificial membrane, the classic DLVO model needs to be modified accordingly. Terui et al.,[2] for example, derived expressions for the electrical interaction potential and the interaction force between an ion-penetrable particle and a rigid particle for the case of low electrical potential, symmetric electrolyte, and uniformly distributed fixed charge in the former. The analysis was extended to various types of particles, and expressions for CCC were obtained.[3] Hsu and Kuo[4] derived an analytical expression for the CCC of counterions in an arbitrary *a*:*b* electrolyte. The electrical interaction between two dissimilar spherical particles covered by an ion-penetrable charged membrane in an *a*:*b* electrolyte solution was estimated by Hsu and Kuo.[5] A perturbation method was applied to solve the governing nonlinear Poisson-Boltzmann equation, and approximate analytical expressions for potential distribution, stability ratio, and CCC of counterions were derived.

The results discussed above are all based on the classic Gouy-Chapman model[1] in which charged species are treated as point charges. Valleau and Torrie[6] and Bhuiyan et al.[7] adopted a modified Gouy-Chapman model to examine the property of electrical double layer, and they concluded that the effective radii of mobile ions plays a significant role. Both Monte Carlo simulation and statistical mechanics approaches were adopted by researchers[8-10] to study the effect of ionic sizes on the behavior of electrical double layer, and they all concluded that it is significant. Hsu and Kuo[11] and Kuo and Hsu[12] investigated the effect of the sizes of charged species on the electrical properties of a particle covered by an ion-penetrable charged membrane. The electrical interaction between two particles, each is covered by an ion-penetrable charged membrane in an asymmetric electrolyte solution was estimated by Kuo and Hsu[13] by taking the effect of the sizes of charged species into account. Kuo et al.[14] studied the electrical interaction force and the potential-energy barrier between a particle covered by an ion-penetrable charged membrane and a planar charged surface by taking the sizes of all the charged species into account.

In the present study, the classic DLVO model is extended to the case when particles are coated by a charge-regulated membrane layer, in a general electrolyte solution. In particular, the effect of the sizes of charged species on CCC is analyzed. The presence of multivalent counterions on the behavior of the system under consideration is also examined by allowing the liquid phase to contain two types of counterions.

## 三、理論

We consider two identical planar particles; each comprises a rigid, uncharged core and an ion-penetrable membrane layer of scaled thickness $d$. These particles are immersed in a mixed $(a{:}b)$ + $(c{:}b)$ electrolyte solution, where $a$ and $c$ are the valences of cations and $b$ is the valence of anions. The membrane layer contains uniformly distributed functional groups, the dissociation of which yields negative fixed charges. The symmetric nature of the present problem implies that only the interval $(-\infty, X_L]$ needs to be considered, $X_L$ being the location of the middle plane between two particles. Let $\sigma_{ca}$, $\sigma_{an}$, and $\sigma_f$ be the effective radii of cations, anions, and fixed charged groups, respectively. Without loss of generality, we assume that $\sigma_{ca} < \sigma_{an} < \sigma_f$. The fixed charged groups are arranged so that the margin of the leftmost one coincides with the core-membrane interface, and the margin of the rightmost one coincides with the membrane-liquid interface. For convenience, the system is divided into five regions. Region I, $X<X_{ca}$, which comprises the charge-free region $(-\infty<X<0)$ and the inner uncharged membrane $(0<X<X_{ca})$, $X$ being the scaled distance. Region II, $X_{ca}<X<X_{an}$, which contains cations only. Region III, $X_{an}<X<X_i$, which contains both cations and anions. Region IV, $X_i<X<X_o$, which contains all charged species. Region V, $X_o<X$, which includes the outer uncharged membrane $(X_o<X<d)$ and the liquid phase $(d<X<\infty)$. Here, $X_i$ and $X_o$ are respectively the locations of the inner and outer planes of fixed charge, and $X_{ca}$ and $X_{an}$ represent respectively the most interior locations of positive and negative charges. $X_i$ is the effective scaled radius of fixed charged group. The scaled symbols are defined by $X = \kappa x$, $X_{ca} = \kappa\sigma_{ca}$, $X_{an} = \kappa\sigma_{an}$, $X_i = \kappa\sigma_f$, and $X_o = d - \kappa\sigma_f$, $\kappa$ and $x$ being respectively the reciprocal Debye length and the distance from the rigid core.

### 3.1. Dissociation of functional groups

We assume that the membrane layer contains both acidic and basic functional groups. The dissociation of these functional groups can be described by

$$AH \leftrightarrow A^- + H^+, K_a \tag{1}$$

$$BH \leftrightarrow B^- + H^+, \ K_b \tag{2}$$

In these expressions, $K_a$ and $K_b$ are equilibrium constants. It can be shown that the concentration of negative fixed charges, $N_-$, and that of positive fixed charges, $N_+$, are

$$N_- = (N_a K_a / C_{H^+})/(1 + K_a / C_{H^+}) \tag{3}$$

$$N_{+} = N_b/(1 + K_b/C_{H^+}) \qquad (4)$$

Here, $N_a$ and $N_b$ are respectively the concentrations of acidic and basic functional groups in the membrane layer. Assuming Boltzmann distribution, the concentration of $H^+$, $C_{H+}$, can be expressed by

$$C_{H^+} = C_{H^+}^0 \exp(-\psi) \qquad (5)$$

where $C_{H^+}^0$ is the bulk concentration of $H^+$.

### 3.2. Interaction energy

According to the DLVO theory, the total interaction energy between two particles, $V_T$, is the sum of $V_R$ and $V_A$, that is,

$$V_T = V_R + V_A \qquad (6)$$

where $V_R$ and $V_A$ are, respectively, the electrical repulsive energy and van der Waals attractive energy. $V_R$ can be calculated by

$$V_R = \frac{2}{\kappa}\int_{X_L}^{\infty} F_R \cdot dX_L \qquad (7)$$

where $F_R$ is the electrical interaction force between two particles. $F_R$ can be evaluated by

$$\frac{F_R}{b n_b^0 k_B T} = \frac{1}{b}\left(e^{b\psi_m} - 1\right) + \frac{1-\xi}{a}\left(e^{-a\psi_m} - 1\right) + \frac{\xi}{c}\left(e^{-c\psi_m} - 1\right) \qquad (8)$$

where $\psi_m$ is the scaled electrical potential on the middle plane between two particles which can be calculated by the Poisson-Boltzmann equation, which takes the sizes of all the charged species into account, and the associated boundary conditions. $V_A$ can be evaluated by

$$V_A = -\frac{A_{132}\kappa^2}{48\pi(X_L - d)} \qquad (9)$$

where $A_{132}$ is the Hamaker constant. At CCC, both the total interaction energy and its derivative with respect to the distance between two particles vanish. We have

$$V_T = 0 \ \text{ and } \ \frac{dV_T}{dX_L} = 0 \qquad (10)$$

These expressions can be used to determine CCC.

## 四、結果與討論

The effect of ionic sizes on the electrical interaction force and the total interaction energy between two particles are examined through numerical simulation. For illustration, we assume that the net fixed charge in membrane layer is negative. The scaled membrane thickness in the numerical simulations is assumed to be on the order of 1.5. We assume that the Hamaker constant, $A_{132}$, is constant, and the van der Waals interaction energy is a function of the separation distance between two particles.

The simulated results shows the scaled electrical potential $|\psi|$ has a local maximum as $X_L$ varies, which does not present, however, in the corresponding PCM where $|\psi|$ decreases monotonically with $X_L$. In general, PCM will overestimate $|\psi|$. This is because fixed charge only exists in region IV in the present model, but it is present in the whole membrane layer in the corresponding PCM.

For a fixed pH, the scaled electrical repulsive force decreases with the increase in $X_L$, as expected. Both the scaled electrical repulsive force and the total interaction energy increase with the increase in pH for pH<7, and becomes almost constant for pH>7. This is because if pH is low, the degree of dissociation of acidic functional groups is small, and at the same time, it is easy for $H^+$ to bind to basic functional groups. These lead to a low concentration of negative fixed charge in membrane layer, and, therefore, a small electrical repulsive force and small total interaction energy. On the other hand, if pH is sufficiently high, the dissociation of acidic functional groups is essentially complete, and the concentration of negative fixed charge remains constant, so are the electrical repulsive force and total interaction energy. The results also reveal that assuming PCM will overestimate the electrical repulsive force, and the deviation increases with pH.

Another result reveals that both the scaled repulsive force and the total interaction energy decrease with the increase in $d$. Here, the total number of functional groups in the membrane layer is held constant. This is because if the total number of functional groups is fixed, the thinner the membrane, the more concentrated the fixed charge, and the greater the electrical interaction and the total interaction energy.

For simplicity, we assume that cations (counterions) with various valences have the same size. From the simulation, we know that the higher the valence of cations, the smaller the scaled repulsive force and the total interaction energy. This is because the membrane is negatively charged, and, therefore, the higher the valence of cations, the greater its shielding effect, which leads to a lower absolute potential and smaller repulsive force and total interaction energy. Moreover, the result suggests that the larger the $\xi$, the lower the scaled repulsive force and the total interaction energy.

For a fixed separation distance between two particles, the higher the ionic strength, the smaller the electrical repulsive force and the total interaction energy. This is because the increase in the concentration of electrolyte has the effects of increasing the degree of screening of the surface charge by counterions and decreasing the thickness of double layer.

The effect of ionic sizes suggests that the electrical repulsive force increases with $X_{ca}$, that is, the larger the cations the larger the electrical repulsive force. This is because the smaller the cations the easier for them to bond to the negative fixed charge in membrane layer, which has the effect of lowering the absolute electrical potential. The same order was also observed in the literatures.[15-17] Moreover, the electrical repulsive force decreases with the increase in $X_{an}$. The change in the repulsive force as $X_{an}$ varies, however, is inappreciable.

For fixed sizes of anions (coions) and fixed charge, the larger the size of cations (counterions), the higher the CCC. This is because that the electrical repulsive force increases with $X_{ca}$, the potential barrier of the total interaction energy increases with $\mathrm{X_{ca}}$ also, and this leads to a higher CCC. This is consistent with the result presented in literatures.[18,19]

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