

Derivation of Analytical Expressions for the Electrical Potential Distribution in Lipid Structures

Shiojenn Tseng

Department of Mathematics, Tamkang University, Tamsui, Taipei 25137, Taiwan

Ji-Ming Jiang and Jyh-Ping Hsu*

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Received: December 18, 2004; In Final Form: February 23, 2005

The electrical potential inside a lipid structure, which is described by a modified Poisson–Boltzmann equation in the literature (Borukhov et al. *Electrochim. Acta* **2000**, 46, 221), is solved, taking into account the effects of ionic sizes. Here, a micelle comprises an ionic surfactant layer and an aqueous core; the dissociation of the former yields a charged surface. The governing equation, which was solved numerically in a previous study for spherical geometry (Hsu et al. *J. Phys. Chem. B* **2003**, 107, 14429), is solved analytically in this study for planar, cylindrical, and spherical geometries. The analytical results obtained are readily applicable for the evaluation of the spatial distributions of counterions inside a lipid structure. We show that if the linear size of a reverse micelle is fixed, the degree of dissociation of the surfactant layer follows the order planar > cylindrical > spherical.

1. Introduction

Lipid-stabilized water-in-oil microemulsions, which are capable of exhibiting many specific behaviors of interest such as clustering and electrical percolation, have various potential usages in practice.^{1–5} Although experimental studies^{6,7} reveal that these behaviors relate closely to the electrical interactions between dispersed liquid entities, relevant theoretical descriptions are still very limited. Depending upon the temperature and types of amphiphiles, reverse micelles can assume various structures.^{8,9} Micelle systems are usually stabilized by the addition of ionic surfactants, the dissociation of which yields a fixed charge on the surface of a reverse micelle. Apparently, both the structure and the thermodynamic properties of a reverse micelle^{10–12} depend largely on the electrical contribution associated with this fixed charge.

Most of the theoretical studies on the electrical interactions in microemulsion systems are based on the classic Poisson–Boltzmann equation, where ionic species are treated as point charges.^{13–16} Tsao et al.,¹³ for instance, solved the spatial distribution of counterions enclosed in cylindrical and spherical micelles by deriving a series solution to the associated Poisson–Boltzmann equation. Approximate analytical expressions for the electrical potential were derived, and the upper limit for the concentration of counterions, which occurs at the center of the aqueous core of a micelle, was discussed for the case of complete dissociation of ionic surfactants. In follow-up studies, Tsao et al. investigated the effects of salt addition¹⁴ and partial dissociation of surfactant molecules¹⁵ on the distribution of counterions in a micelle. They concluded that if the density of surface charge is high, the effects of the curvature of the micelle and that of the addition of a salt on the distribution of counterions are insignificant. Also, the degree of dissociation

of surfactant molecules depends not only on the geometry of a micelle but also on the dissolution of a particle inside the micelle. The electrical potential distribution based on the classic Poisson–Boltzmann equation in the diffuse double layer near a flat plate, outside a cylinder, and outside a sphere are available in the literature.¹⁷ Theoretical results for the distribution of ionic species for both cylindrical and spherical microemulsions, reverse micelles, and vesicles are also available.^{11,12,18–20}

As mentioned above, a Poisson–Boltzmann equation has the drawback of being unable to take into account the steric effects arising from the finite sizes of ionic species. While this effect may be unimportant to other applications, it can be significant for the present case when the size of a micelle is small. Tsao et al.¹⁵ proposed that the effect of ionic size can be neglected if the radius of a micelle is larger than about 40 times the radius of the ionic species. If this is not the case, then a more rigorous approach such as a molecular simulation needs to be employed. Alternatively, the Poisson–Boltzmann equation can be modified to take the effects of finite ionic size into account.^{21,22} On the basis of a locally ideal mixing assumption²³ and a modified Poisson–Boltzmann equation, we examined the effect of ionic size on both the degree of dissociation of the surfactant shell of a spherical reverse micelle and the spatial distribution of the ionic species.²⁴

In this study, analytical expressions for the electrical potential in planar, cylindrical, and spherical reverse micelles are derived by solving a modified Poisson–Boltzmann equation, which takes the effect of ionic size into account. The results obtained are readily applicable to the evaluation of the spatial distribution of counterions and the degree of dissociation of surfactant molecules. Analytical expressions where the ionic size is negligible can be recovered as the limiting cases of the present study. The modified Poisson–Boltzmann equation was employed in our previous study for spherical reverse micelles and was solved numerically.²⁴ Here, attempts are made to derive

* Author to whom correspondence should be addressed. Fax: 886-2-23623040. E-mail: jphsu@ntu.edu.tw.

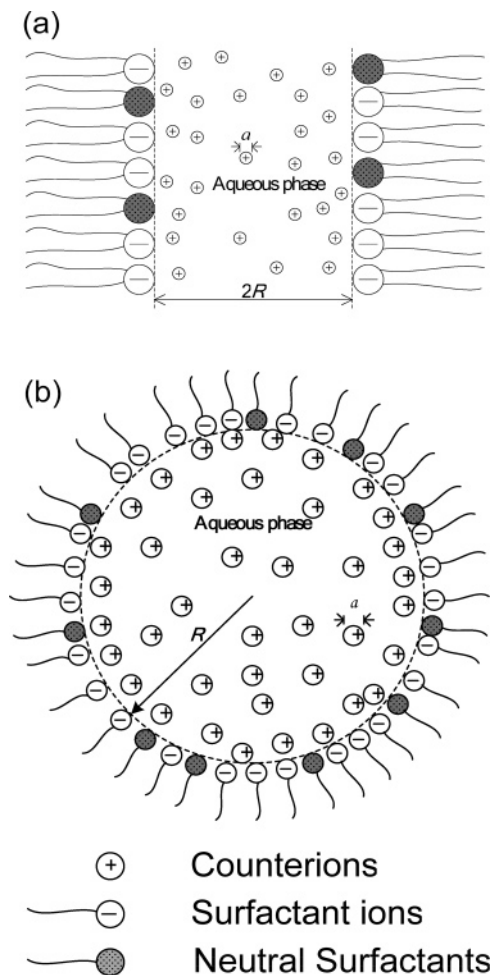


Figure 1. Schematic representation of the system under consideration, where the lipid structure comprises an aqueous core and a surfactant layer. a is the diameter of counterions, and $2R$ is the distance between two bilayers of a planar micelle or the diameter of a cylindrical or a spherical micelle.

analytical solutions, which are more readily applicable for further applications.

2. Analysis

Referring to Figure 1, we consider three types of reverse micelle systems: planar, cylindrical, and spherical reverse micelle. Here, a micelle is composed of an ionic surfactant layer and an aqueous core. For simplicity, we assume that the counterions arising from the dissociation of the functional groups of the former are the only ionic species in the latter. Let $2R$ be the characteristic size of the system under consideration. For a planar micelle, it is the separation distance between two bilayers and the diameter for both the cylindrical and spherical micelle. According to Borukhov et al.,²² the variations of the electrical potential $\psi(r)$ and the concentration of counterions $c(r)$ in the aqueous core of a micelle can be described, respectively, by

$$\frac{1}{r^m} \frac{d}{dr} \left(r^m \frac{d\psi}{dr} \right) = - \left(\frac{c_0 z e}{\epsilon} \right) \frac{\exp(-ze\psi/kT)}{1 - \phi + \phi \exp(-ze\psi/kT)} \quad 0 \leq r \leq R \quad (1)$$

$$c(r) = \frac{c_0 \exp(-ze\psi/kT)}{1 - \phi + \phi \exp(-ze\psi/kT)} \quad 0 \leq r \leq R \quad (2)$$

In these expressions, r is the distance from the center of a

micelle, c_0 and z are, respectively, the concentration at $r = 0$ and the valence of the counterions. ϵ is the relative permittivity of the aqueous phase, and e , k , and T are the elementary charge, the Boltzmann constant, and the absolute temperature, respectively. $\phi = c_0 a^3$ is the volume fraction of counterions at $r = 0$, a being the diameter of the counterions, and m is a shape index, respectively. For a simpler presentation, the scaled distance $x = r/R$ and the scaled electrical potential $y = ze\psi/kT$ are used in subsequent discussions. In terms of these variables, eqs 1 and 2 become, respectively

$$\frac{1}{x^m} \frac{d}{dx} \left(x^m \frac{dy}{dx} \right) = -(\kappa R)^2 \frac{\exp(-y)}{1 - \phi + \phi \exp(-y)} \quad 0 \leq x \leq 1 \quad (3)$$

and

$$\frac{c(x)}{c_0} = \frac{\exp(-y)}{1 - \phi + \phi \exp(-y)} \quad 0 \leq x \leq 1 \quad (4)$$

where $\kappa = (c_0 z^2 e^2 / \epsilon kT)^{1/2}$ is the reciprocal Debye length. The symmetric nature of the present problem suggests that

$$\frac{dy}{dx} = 0 \quad \text{at } x = 0 \quad (5)$$

Applying Gauss' law to the boundary (i.e., surfactant layer) of a micelle yields

$$\frac{dy}{dx} = \sigma \quad \text{at } x = 1 \quad (6)$$

where $\sigma = zeR\sigma'/\epsilon kT$ is the scaled surface charge density, σ' being the surface charge density. Because the charge on the boundary of a micelle arises from the dissociation of the functional groups on the surfactant layer, σ' can be expressed as

$$\sigma' = -ze\rho X_S \quad (7)$$

where ρ is the surface density of dissociable functional groups and X_S is the mole fraction of dissociated functional groups or the degree of dissociation of the surfactant layer. Suppose that the surfactant ions and the associated neutral species form a regular solution thermodynamically, i.e., the entropy of mixing can be evaluated based on a locally ideal mixing assumption.²³ Then, applying the equilibrium condition to the surfactant layer yields^{15,24}

$$\frac{c_S X_S}{1 - X_S} \exp\left(\frac{\gamma}{k_B T} (1 - 2X_S)\right) = K_d \quad (8)$$

where c_S is the concentration of counterions on the surfactant layer, K_d is the equilibrium constant associated with the dissociation of ionic surfactants, and γ is the effective interaction energy per molecule arising from headgroup repulsion. If the headgroup repulsion energy is much less than the thermal energy, i.e., $\gamma/kT \ll 1$, then eq 8 can be rewritten as

$$X_S = \frac{1}{1 + \lambda} \left[1 + \frac{\lambda(1 - \lambda)}{(1 + \lambda)^3} \frac{\gamma}{k_B T} + O\left(\frac{\gamma}{k_B T}\right)^2 \right] \quad (9)$$

where $\lambda = c_S/K_d$. For illustration, we assume that $\gamma = 0$ and $z=1$.

If we let^{14,15}

$$y(x) = 2 \ln S(x) \quad 0 < S(x) \leq 1 \quad (10)$$

then eq 3 becomes

$$[(1 - \phi)S^2 + \phi] \left\{ 2x \left[S \frac{d^2 S}{dx^2} - \left(\frac{dS}{dx} \right)^2 \right] + 2mS \frac{dS}{dx} \right\} + (\kappa R)^2 x S^2 = 0 \quad (11)$$

The symmetry nature of the present problem requires that

$$\frac{dS}{dx} = 0 \quad x = 0 \quad (11a)$$

Expanding $S(x)$ in its Maclaurin series, we obtain

$$S(x) = \sum_{n=0}^{\infty} \alpha_n x^n \quad (12)$$

If we choose $y(x=0) = 0$, then eq 11a implies that $(\alpha_0, \alpha_1) = (1, 0)$. The other values of α_n , $n = 2, 3, \dots$, can be evaluated by substituting eq 12 into eq 11 and letting the coefficients of x^n vanish. The results thus obtained are summarized in Table 1. Note that the corresponding electrical potential for the point charge case can be recovered by letting $\phi = 0$ in eq 11 and Table 1. Note that α_n is a function of κR and ϕ , and because both of them are related to c_0 , the value of α_n can be calculated if c_0 is known. Here, the boundary condition expressed in eq 6 can be used to solve c_0 . In terms of scaled symbols, we have

$$\frac{dy}{dx} \Big|_{x=1} = \sigma = \frac{2 \sum_{n=1}^{\infty} (2n\alpha_{2n})}{\Xi_\alpha} \quad (13)$$

where $\Xi_\alpha = \sum_{n=0}^{\infty} \alpha_{2n}$. Substituting eqs 4 and 13 into eq 9 yields

$$\rho \frac{z^2 e^2 R}{\epsilon k T} \Xi_\alpha + 4 \left[1 + \frac{c_0/K_d}{(1 - \phi)\Xi_\alpha^2 + \phi} \right] \sum_{n=1}^{\infty} n\alpha_{2n} = 0 \quad (14)$$

For a given set of parameters $\{\rho, z, a, R, K_d\}$, c_0 can be determined by solving the algebraic equation, eq 14, and the degree of dissociation X_S can be evaluated by

$$\sigma = \frac{2 \sum_{n=1}^{\infty} (2n\alpha_{2n})}{\Xi_\alpha} = -\rho \frac{z^2 e^2 R}{\epsilon k T} X_S \quad (15)$$

2.1. Limiting Cases. If the sizes of ionic species are negligible, then $\phi = 0$. In this case, it can be shown that for planar micelles ($m = 0$)^{8,9,13}

$$y = 2 \ln \cos \left(\frac{\kappa R}{\sqrt{2}} x \right) \quad (16a)$$

Substituting this expression into eq 13 yields

$$\frac{\kappa R}{\sqrt{2}} \tan \left(\frac{\kappa R}{\sqrt{2}} \right) = \frac{-\sigma}{2} \quad (16b)$$

This expression implies that $(\kappa R)^2 < \pi^2/2$ for planar micelles. Similarly, for cylindrical micelles ($m = 1$), we have^{9,13}

$$y = 2 \ln \left[1 - \frac{(\kappa R)^2}{8} x^2 \right] \quad (17a)$$

Substituting this expression into eq 13, we obtain

$$\frac{(\kappa R)^2}{8 - (\kappa R)^2} = \frac{-\sigma}{4} \quad (17b)$$

This expression indicates that $(\kappa R)^2 < 8$ for cylindrical micelles. Derivation of an analytical relation between κR and σ for the case of spherical micelles ($m = 2$) and $\phi = 0$ is nontrivial. However, the coefficients of the series solution for electrical potential coincide with those of Tsao et al.¹⁴

Under the Debye–Huckel condition, the electrical potential is low, $y \leq 1$, and eq 3 can be approximated by

$$\frac{1}{x^m} \frac{d}{dx} \left(x^m \frac{dy}{dx} \right) = (\kappa R)^2 \frac{y - 1}{1 - \phi y} \quad 0 \leq x \leq 1 \quad (18)$$

This equation can be solved by expanding $y(x)$ as

$$y(x) = \sum_{n=0}^{\infty} \beta_n x^n \quad (19)$$

The symmetry condition $(dy/dx)_{x=0} = 0$ and $y(x=0) = 0$ leads to $(\beta_0, \beta_1) = (0, 0)$. The first four nonzero values of β_n are listed in Table 2. It can be shown that the results of the point charges can be recovered by letting $\phi = 0$.

3. Results and Discussion

The simulated variations in the degree of dissociation of the surfactant layer of a micelle, X_S , as a function of its scaled size, R , for various sizes of counterions, a , are illustrated in Figure 2. This figure suggests that, for a fixed value of R , the magnitude of X_S follows the order planar micelle > cylindrical micelle > spherical micelle. This is consistent with the results obtained by Tsao et al.¹⁵ Figure 2 also reveals that the increase in the value of R has the effect of increasing the value of X_S . This is because the larger the linear size of a micelle, the more space is available for the distribution of the dissociated counterions. According to Figure 2, X_S reaches an equilibrium value when R exceeds about 4 nm. That is to say that the influence of the size of counterions on the degree of dissociation of the surfactant layer becomes insignificant when the linear size of a micelle exceeds about 10 times that of the counterions. Figure 2 indicates that the larger the counterions, the larger the value of X_S , i.e., the finite size of counterions has the effect of increasing the degree of dissociation of the surfactant layer of a micelle. This is because for a fixed value of K_d , the larger the counterions, the lower the value of c_s , and therefore, the higher the degree of dissociation, as predicted by the mass action model.⁹

In this work, a constant charge condition is specified at the surfactant layer, and we focus mainly on the effects of the size of the counterions. It should be pointed out that the dissociation of surfactant molecules might in turn affect the nature of the lipid structure, including the size of a micelle. If this is the case, then the present analysis needs to be coupled with the theory for the formation of a micelle. In general, the thermodynamic consideration of micelle formation can be divided into several contributions. Besides the translational entropy and the intermicelle interactions, the interfacial energy and the bending

TABLE 1: First Six Nonzero Coefficients α_n ($n \geq 2$) of the Series Solution for the Electrical Potential for Various Geometries

Parallel Plates ($m = 0$)	
α_2	$\frac{-(\kappa R)^2}{4}$
α_4	$\frac{(\kappa R)^4(1 + 2\phi)}{96}$
α_6	$\frac{-(\kappa R)^6(1 - 14\phi + 28\phi^2)}{5760}$
α_8	$\frac{(\kappa R)^8(1 + 348\phi - 1260\phi^2 + 1016\phi^3)}{645120}$
α_{10}	$\frac{-(\kappa R)^{10}(1 - 12628\phi + 77052\phi^2 - 133384\phi^3 + 69904\phi^4)}{116121600}$
α_{12}	$\frac{-(\kappa R)^{12}(1 + 675694\phi - 6161204\phi^2 + 17544080\phi^3 - 19844944\phi^4 + 7796768\phi^5)}{30656102400}$
Cylinder ($m = 1$)	
α_2	$\frac{-(\kappa R)^2}{8}$
α_4	$\frac{(\kappa R)^4\phi}{128}$
α_6	$\frac{-(\kappa R)^6(-7\phi + 10\phi^2)}{9216}$
α_8	$\frac{(\kappa R)^8(25\phi - 81\phi^2 + 59\phi^3)}{294912}$
α_{10}	$\frac{-(\kappa R)^{10}(-585\phi + 3193\phi^2 - 5119\phi^3 + 2526\phi^4)}{58982400}$
α_{12}	$\frac{(\kappa R)^{12}(10080\phi - 81429\phi^2 + 213895\phi^3 - 227927\phi^4 + 85426\phi^5)}{8493465600}$
Sphere ($m = 2$)	
α_2	$\frac{-(\kappa R)^2}{12}$
α_4	$\frac{-(\kappa R)^4(1 - 6\phi)}{1440}$
α_6	$\frac{-(\kappa R)^6(5 - 126\phi + 156\phi^2)}{362880}$
α_8	$\frac{-(\kappa R)^8(107 - 7874\phi + 21852\phi^2 - 15000\phi^3)}{261273600}$
α_{10}	$\frac{-(\kappa R)^{10}(2671 - 420220\phi + 2097444\phi^2 - 3192312\phi^3 + 1518192\phi^4)}{172440576000}$
α_{12}	$\frac{-(\kappa R)^{12}(258803 - 79988062\phi + 593623396\phi^2 - 1481633776\phi^3 + 1522225872\phi^4 - 554661408\phi^5)}{376610217984000}$

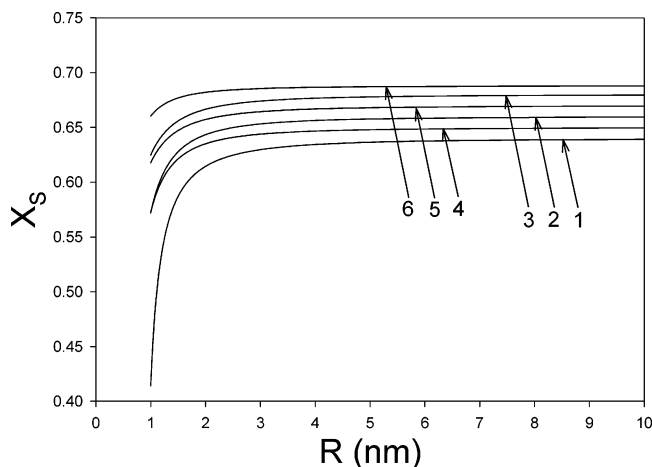
energy associated with the lipid structure can eventually play an essential role in determining the equilibrium structure. Usually, the electrostatic contribution can be incorporated into the interfacial tension^{8–10} and the curvature elasticity.^{9,11,19}

It should be pointed out that the goal of this study is to derive an analytical solution for the electrical potential inside reverse micelles of various shapes taking into account the effects of ionic sizes. Knowledge about this electrical potential is essential to subsequent analyses such as the estimation of the spatial distribution of ionic species. The electrical potential described

by the modified Poisson–Boltzmann equation,²² eq 1, was solved numerically for spherical reverse micelles in our previous study.²⁴ Since analytical results are more readily applicable to further applications, it is solved analytically in the present study, and in addition to spherical geometry, planar and cylindrical geometries are also considered; these include essentially all types of reverse micelles. The mathematical treatments, i.e., the solution procedure and the results obtained, are exact, as can be justified by comparing the present solutions with the corresponding numerical results. Verifying the accuracy of eq

TABLE 2: First Four Nonzero Coefficients β_n ($n \geq 2$) of the Series Solution for the Electrical Potential under the Debye–Hückel Condition

β_2	$-\frac{(\kappa R)^2}{2(m+1)}$
β_4	$-\frac{(\kappa R)^4(1-\phi)}{8(m+1)(m+3)}$
β_6	$-\frac{(\kappa R)^6(1-\phi)(m+1-3m\phi-7\phi)}{48(m+1)^2(m+3)(m+5)}$
β_8	$-\frac{(\kappa R)^8(1-\phi)(15m^2\phi^2+94m\phi^2+127\phi^2-10m^2\phi-48m\phi-38\phi+m^2+2m+1)}{384(m+1)^3(m+3)(m+5)(m+7)}$

**Figure 2.** Variation of X_S as a function of R for the case when $K_d = 4 \text{ nm}^{-3}$ and $\rho = 1 \text{ nm}^{-2}$. $m = 2$ for curves 1 and 4, $m = 1$ for curves 2 and 5, $m = 0$ for curves 3 and 6. $a = 0.5 \text{ nm}$ for curves 1–3, and $a = 0.7 \text{ nm}$ for curves 4–6.

1 by comparing its performance with that of other approaches, for example, Monte Carlo simulation, hypernetted chain, anisotropic hypernetted chain,²⁵ and others, is not our purpose.

In summary, the effects of the size of ionic species on the electrical potential in a micelle are investigated. A modified Poisson–Boltzmann equation, which takes the steric effects of ion size into account, is solved by a power series method, and exact analytical expressions can be obtained under limiting conditions. The results of numerical simulation reveal that for a fixed linear size of micelle, the degree of dissociation of its surfactant layer follows the order planar micelle > cylindrical micelle > spherical micelle. The finite size of the counterions is found to have the effect of increasing the degree of dissociation of the surfactant layer. If the linear size of a micelle exceeds about 10 times that of counterions, then the influence of counterions size on the degree of dissociation of the surfactant layer is insignificant.

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

References and Notes

- (1) Bisceglia, M.; Acosta, E.; Kurlat, D.; Ginzberg, B. *Colloids Surf., A* **1996**, *108*, 137.
- (2) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J. R.; Woolfrey, J. L. *Langmuir* **1995**, *11*, 738.
- (3) Nitsch, W.; Plucinski, P. *J. Colloid Interface Sci.* **1990**, *136*, 338.
- (4) Hun, C. *J. Colloid Interface Sci.* **1979**, *71*, 408.
- (5) Ekwall, P.; Mandell, L.; Fontell, K. *J. Colloid Interface Sci.* **1970**, *33*, 215.
- (6) Lemaire, B.; Bothorel, P.; Roux, D. *J. Phys. Chem.* **1983**, *87*, 1023.
- (7) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *J. Phys. Chem.* **1995**, *99*, 8222.
- (8) Hunter, R. J. *Foundations of Colloid Science*; Oxford: New York, 1992.
- (9) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic: San Diego, 1992.
- (10) Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1983**, *87*, 2996.
- (11) Overbeek, J. Th. G.; Verhoeckx, J.; de Bruyn, P. L.; Lekkerkerker, H. N. W. *J. Colloid Interface Sci.* **1987**, *119*, 422.
- (12) Rahaman, R. S.; Hatton, T. A. *J. Phys. Chem.* **1991**, *95*, 1799.
- (13) Tsao, H. K. *J. Phys. Chem. B* **1998**, *102*, 10243.
- (14) Tsao, H. K. *Langmuir* **1999**, *15*, 4981.
- (15) Tsao, H. K.; Sheng, Y. J.; Lu, C. Y. D. *J. Chem. Phys.* **2000**, *113*, 10304.
- (16) Chen, P. L.; Tsao, H. K.; Lu, C. Y. D. *J. Chem. Phys.* **2000**, *113*, 4808.
- (17) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersion*; Cambridge University Press: Cambridge, 1989.
- (18) Bratko, D.; Luzar, A.; Chen, S. H. *J. Chem. Phys.* **1988**, *89*, 545.
- (19) Lekkerkerker, H. N. W. *Physica A* **1989**, *159*, 319.
- (20) Winterhalter, M.; Helfrich, W. *J. Phys. Chem.* **1988**, *92*, 6865.
- (21) Borukhov, I.; Andelman, D.; Orland, H. *Phys. Rev. Lett.* **1997**, *79*, 435.
- (22) Borukhov, I.; Andelman, D.; Orland, H. *Electrochim. Acta* **2000**, *46*, 221.
- (23) Evans, D. F.; Wennerstrom, H. *The Colloidal Domain*; VCH: New York, 1994.
- (24) Hsu, J. P.; Jiang, J. M.; Tseng, S. J. *J. Phys. Chem. B* **2003**, *107*, 14429.
- (25) Bratko, D. *Chem. Phys. Lett.* **1990**, *169*, 555.