The Influence of Ionic Dispersion Potentials on Counterion Condensation on Polyelectrolytes

Mathias Boström,* David R. M. Williams, and Barry W. Ninham[†]

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, Australian National University, Canberra, Australia 0200

Received: February 7, 2002; In Final Form: May 21, 2002

The prevalent theories for polyelectrolytes have not been able to describe the experimentally observed ion specificity found at high ion concentrations for counterion condensation and conformational transitions. One important source of ion specificity missed in these theories is the dispersion force that acts between an ion and the cylindrical polyion surface. Here, we solve the cylindrical Poisson−Boltzmann equation numerically in the presence of ionic dispersion potentials. We demonstrate that ionic dispersion forces have important influences on ionic distributions and potentials. This influence increases with increasing concentration reflecting that specific ion effects are observed only at high concentrations.

I. Introduction

Manning's[1] counterion condensation theory has in the past provided a both simple and effective approach to interpretation and analysis of the effects of salt on the stability and conformational transitions of DNA duplexes, and other polyelectrolytes. The cylindrical Poisson−Boltzmann model has recently been used extensively to investigate, e.g., thermodynamic transitions of various nucleic acid complexes.[2−4] The relationship between the condensation model and the Poisson−Boltzmann model has been established.[5−7] The only property of an ion that is significant according to these models is the charge. In other words, all 1:1 salts should according to theory give the same result. Hayter performed small-angle neutron scattering experiments on micellar systems and quite successfully compared with theory.[8] However, spherical micelles, polyelectrolytes, and threadlike (cylindrical) micelles all show marked ion specificity whether consisting of charged or uncharged surfactant. It is for instance experimentally well-known that at high concentrations the midpoint transition temperature (T_m) of order−disorder transitions become ion specific. Different results were for instance found using CH_3COONa, $NaCl$, and $NaClO_4$ salt solutions, following a Hofmeister series.[4]

Clearly to explain these results an ion-specific potential needs to be included in the theory. There is strong evidence that the dispersion potential is this missing potential. It is ion specific, acts on all ions, and we will show dispersion potentials have an important influence on ionic distributions near cylindrical polyion surfaces. In this paper we treat water as a continuum, in order that the main idea is not obscured by considerations of water structure. Of course, in the end a macroscopic continuum model may not be accurate enough to describe all specific ion−polyelectrolyte interactions. A microscopic theory such as the one introduced by Lyubartsev et al.[9,10] may have to be used. However, we believe that the much simpler macroscopic model can contribute to our understanding of the physics of specific ion−polyelectrolyte interactions.

Ion specific, or Hofmeister, effects in biological and biochemical systems have been known since 1888, when Hofmeister[11] defined series of cations and anions according to the concentration of salt required to precipitate proteins from whole egg white. Hofmeister series have, e.g., been found in studies of protein stability,[12] ion transport,[13] and cutting efficiency of DNA.[14] Another example is the experimental surface tension of salt solutions,[15] which not only depends on ion charge and concentration but also on ionic species. We recently showed how this could be accounted for by invoking a dispersion potential between an ion and the air−water interface.[16] Dubois et al.[17] used osmotic measurements varying concentration as well as nature of counterion. The headgroup area was measured as a function of surfactant volume fraction. The area per headgroup is an in-built measure of the lateral electrostatic repulsion, and they found that the only explanation for the experimentally observed ion specificity was the ionic strength dependent dispersion mechanism. They also measured ion-specific double-layer forces between charged surfaces across electrolyte solutions. At 0.1 M salt concentration there is a decrease of a factor 5 of the pressure when chloride counterions are replaced with bromide for a spacing of 40 Å. At lower concentration, i.e., high dilution, the two equations of state merge for both counterions. In fact, forces can vary in magnitude by a factor of 50, or more, by simply changing the counterion from, e.g., bromide to acetate.[18] The problem lies in the separation of forces between particles into double layer and van der Waals forces, which is fundamentally incorrect.[19,20] We have recently shown that when ionic dispersion potentials are included in the formalism on the same level as electrostatic forces, a new theory emerges which can accommodate specific ion effects.[21] How important the effect of dispersion potentials is depends on several factors, e.g., on salt concentration and on magnitude and sign of dispersion potentials and surface charge. The threading process that occurs when aqueous solution of polymers and cyclodextrins are mixed basically depends on the solvent properties and temperature. Lo Nostro et al.[22] determined experimentally the relationship between threading time, which is ion specific, and the frequency dependent polarizability of the ions.

---
　* Corresponding author. E-mail: mtb110@rsphysse.anu.edu.au.
　[†] Present address: Department of Chemistry and CSGI, University of Florence, 50019 Sesto Fiorentino, Italy.

Counterion Condensation on Polyelectrolytes

J. Phys. Chem. B, Vol. 106, No. 32, 2002 **7909**

The purpose here is to demonstrate qualitative effects of including previously ignored ionic dispersion potentials between the ions and the interface (in general there will also be contributions from image potentials, and to a smaller degree from ionic dispersion interactions between ions). In the present work we demonstrate how ionic dispersion potentials acting between ions and a polyion–solution interface can be incorporated in the Poisson–Boltzmann formalism. We also demonstrate that they have important influence on ion distributions. In Section II we discuss the theory and models used in our numerical calculations. We consider a macroscopic model for the polyion as a charged cylinder in a 1:1 salt solution. When ionic dispersion potentials are accounted for the charge distribution outside a polyion surface become highly counterion specific, and hence so should the interaction between DNA and proteins.[23–25] We note that the interaction between DNA double helical polyelectrolytes are experimentally known to depend strongly on the choice of univalent counterion, while being insensitive to the choice of co-ion.[26] The co-ion distribution near the interface is shown to be particularly sensitive to the dispersion potentials that act on the co-ions (anions). A very important quantity is the surface adsorption excess, which is directly related to the Donnan salt exclusion coefficient, and according to conventional theories to the thermal stability of nucleic acid helices.[2,3] The surface adsorption excess of ions is

$$\Gamma_\pm (c_0) \propto \int_{r_{min}}^{R} [c_0 - c_\pm(r)] r \, dr \qquad (1)$$

Here c_0 is the constant salt concentration in the midpoint between two polyions a distance $2R$ apart, $c_\pm(r)$ is the actual concentration for cations (+) and anions (−) which varies with radius (r). We take the closest radius of approach (r_{min}) to be equal to the sum of cylinder radius and ion radius. Since it does not add anything here to use a finite R we take it to go to infinity. We will show that ionic distributions and surface excess become highly ion specific when we take dispersion potentials into account. The results of numerical calculations, which show that the influence of dispersion potential increases with concentration, are presented in Section III. This suggests that there is a possible way to accommodate many specific ion effects when the macroscopic models are extended to include dispersion potentials. Finally, in Section IV we end with a brief summary.

II. Theory

The self-consistent electric potential ϕ at a distance r from the center of a charged cylinder is found by solving numerically the nonlinear cylindrical Poisson–Boltzmann equation,

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\phi}{dr} \right) = -e(c_+ - c_-)/\epsilon_w \epsilon_0 \qquad (2)$$

where the ion concentrations are given by

$$c_\pm(r) = c_0 \exp(-\beta[\pm e\phi(r) + U_\pm(r)]) \qquad (3)$$

Here e is the proton charge, $\beta = 1/(k_B T)$, k_B is Boltzmann constant, T is temperature, c_0 is the bulk concentration of either ion (we assume 1:1 salts), and ϵ_w is the dielectric constant of water. The crucial difference between our calculation and the standard approach is that we include an extra potential $U(r)$, which in our case is the dispersion potential acting between the cylinder and the ion. The boundary conditions follow from global charge neutrality. The first boundary condition is that r $d\phi/dr$ vanishes at infinity. The second is that

$$(r_{DNA} + r_{ion}) \frac{d\phi}{dr}^{r=r_{DNA} + r_{ion}} = -\zeta/(2\pi\epsilon_0\epsilon_w) \qquad (4)$$

where the average charge per unit length on the cylindrical polyelectrolyte surface is $\xi = -e/b$. The average axial charge spacing ($b \approx 1.7$ Å) and the cylindrical radius ($r_{DNA} \approx 9.4$ Å), were chosen having a B form DNA duplex in mind.[4,27] The theory is, of course, quite general and can be used on any cylindrical system. To make clear the influence of dispersion potentials we take the ion radius ($r_{ion} = 2$ Å) to be the same for anions and cations. We assume that the ions cannot get closer than this to the cylindrical interface.

In previous calculations the interaction potential $U_\pm$ between each ion and the interface was neglected. Here it is taken to receive contributions from the effective ionic dispersion potential between an ion and the effective cylindrical surface. In a corresponding microscopic model this corresponds to including dispersion interactions between the ion and all of the molecules that make up the cylindrical polyion. The polarizability of an ion is different from an equivalent volume of water and the ion will therefore experience a dispersion potential toward or away from an interface. To calculate the dispersion potential between an ion and a charged cylinder in water we need to know the excess polarizability of the ion in water and the effective dielectric response functions of polyion and water. While the polarizability of ions in air has been calculated,[28] the polarizability of ions in water remains unknown. However, the static excess polarizability of ions can be estimated from partial molar volumes of the bulk solutions and the index of refraction increment of different salt solutions, which is different for different salt solutions.[29] The dispersion potential also depends on a characteristic frequency (ω_0), which is unknown, but must be between an infrared and an UV frequency. In Gaussian units the excess polarizability of an ion, α^*, has dimensions of volume, and a lower bound would be say $\alpha^* = 1$ Å^3. It can in fact much larger, e.g., for an unhydrated anion of radius 2 Å, $\alpha^* \approx 30$ Å^3. α^* can be negative due to electrostriction. For CH_3COO^-, having approximately the same electron density as water, we expect very little excess polarizability, for Br^- we expect large excess polarizability. All these parameters can be lumped together into an interaction constant B. For the interaction between an ion with an air–water interface it can be estimated as $B \approx (n_w^2 - n_{air}^2)\alpha^*(0)\hbar\omega_0/8$. With the parameters taken to be $\omega_0 = 10^{15}$ rad/s, $\alpha^* = 2$ Å^3, and $n_w = 1.33$ one finds that a typical value is $B = 2 \times 10^{-50}$ J m^3. We recently showed that one can accommodate surface tension changes at an air–water interface for a large group of salts, i.e., combinations of cations and anions, if dispersion coefficients of this order of magnitude were used.[16] For our examples they ranged from −5 to 31 × 10^{-50} J m^3 but the magnitude can in fact be substantially larger than this. The calculated dispersion coefficients near hydrocarbon–water interfaces are typically only slightly smaller in magnitude than near air–water interfaces reflecting the corresponding changes in surface tension with added salt (i.e., in the surface excess). Sometimes the dispersion potential even changes sign when we replace an air–water with an oil–water interface, this explains why the surface excess for certain salt solutions has the opposite sign at oil–water interfaces than it has at air–water interfaces. The hydrated ion size and other effects not directly included in the Poisson–Boltzmann equation will also influence the surface tension change; however, this sign change in surface excess cannot readily be explained by simply fitting different hydrated ion radii for different ions. The same is true for the physical properties of polyelectrolytes and micelles.

The nonretarded dispersion interaction between a particle and a cylinder in the Hamaker approximation is[30]

$$U_\pm(r) \approx \frac{NB_\pm}{x^3}$$
$$\left\{ \int_0^\pi d\phi \int_0^1 \frac{y\, dy(x/r_{DNA})^3}{[y^2 \sin^2[\phi] + (y \cos[\phi] + 1 + x/r_{DNA})^2]^{5/2}} \right\} \quad (5)$$

where x is the distance between the center of the ion and the cylindrical surface. We note that the expression inside the brackets {} depends only on the ratio x/r_{DNA}. The integration is easily done at large distances away from the surface where the dispersion potential becomes proportional to r_{DNA}^2/x^5. In the small separation limit, when $x/r_{DNA} \to 0$, the dominating term is proportional to $1/x^3$. Here, we carry out the integration over y analytically, and the angle integration is done numerically. To compare with our previous results we choose the constant N such that $U_\pm (x = r_{ion}) = B_\pm/r_{ion}^3$. We then still have to estimate the dispersion coefficient $B_\pm$. The dielectric properties of polyelectrolytes and micelles will clearly be quite different from those of the surrounding water. This is all we really need to know to be sure that there will be substantial dispersion potentials of the same order of magnitude as those near oil−water interfaces. Here, to estimate the influence of ionic dispersion potentials we investigate various combinations of dispersion coefficients of the same order of magnitude as those that were used in our investigation of the surface tension of salt solutions. This will enable us to estimate the influence of dispersion potentials on ion concentrations and potentials at different concentrations.

III. Numerical Results

Conventional theories for the ion distribution and condensation near and at a polyelectrolyte (e.g., DNA) surface totally neglect dispersion potentials that act between ions and polyelectrolyte. We argue that this is one important reason there has been no satisfactory explanation for the Hofmeister effect. Here we will highlight the influence of ionic dispersion potentials by presenting a few numerical results.

The first issue that needs to be addressed is the influence of ionic dispersion potentials on the adsorption excess, which as we have already pointed out is related to thermal stability of polyelectrolytes. We show results for $r \times (c_0 - c_-[r])$ as a function of r. The area under the curves are of course related to the surface adsorption excess of co-ions, but also via global charge neutrality to the surface excess of the counterions. Figures 1 and 2 show the results for 1 and 0.1 molar concentrations. The influence of dispersion potentials increases with increasing concentration, since at higher concentrations the electrostatics is strongly screened while the dispersion potential is unaffected. At 0.1 M concentration the influence begins to be noticeable, at 1 M it cannot be neglected even for low estimates of the dispersion potential. At lower concentrations (say 0.01 M) the influence of ionic dispersion potentials is more or less negligible. Where exactly the transition occurs, of course, depends on the magnitude and sign of these dispersion potentials. However, at biological concentrations (around 0.15 M), or at the even higher concentrations considered by Tomac et al.[4] (1−5 M), the influence of dispersion potentials can no longer be neglected. This is consistent with the fact that Hofmeister effects are observed at high concentrations, but usually not at low concentrations. We also observe in Figure 2 that the co-ion
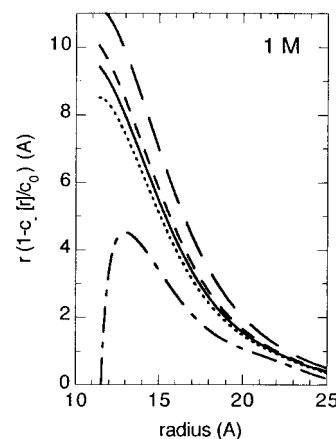

Figure 1. The function $r \times (1 - c_-[r]/c_0)$ as a function of r at 1 M concentration. Here the values for $B_\pm/10^{-50}$ N m^3 are 0 (solid line), 1 (dashed line), −1 (dotted line), 5 (long-dashed line), and −5 (dash−dotted line).
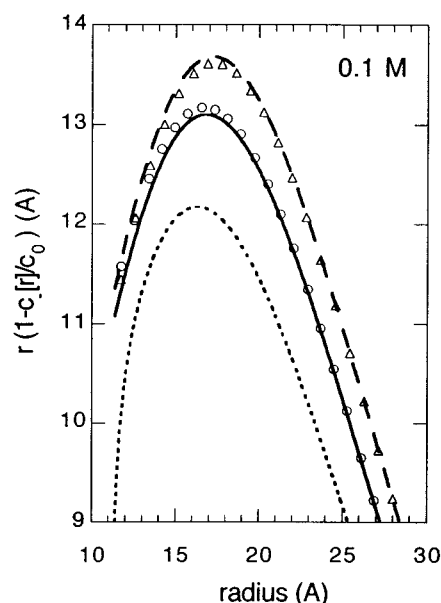

Figure 2. The function $r \times (1 - c_-[r]/c_0)$ as a function of r at 0.1 molar concentration. Here the values for $B_\pm/10^{-50}$ N m^3 are 0 (solid line), 5 (dashed line), and −5 (dotted line). We have also included the case when only one ionic species experiences a dispersion potential: $B_\pm = 5 \times 10^{-50}$ N m^3 and $B_- = 0$ N m^3 (triangles); $B_+ = 0$ N m^3 and $B_- = 5 \times 10^{-50}$ N m^3 (circles).

distribution at large distances does not depend on the dispersion potential that act on the co-ions. It depends on electrostatics, which are strongly influenced by dispersion potentials that act on the counterions. Close to the polyion surface dispersion potentials that act on the co-ions will become important and dominant.

In Figure 3 we show the ion concentrations (c_0 =1 M) for the cases $B_\pm = 0$ and $\pm 5 \times 10^{-50}$ N m^3. It is clear that both co-ion and counterion distribution are strongly influenced by dispersion potentials. In fact, there will be important influences near the interface even with much smaller dispersion potentials and at lower concentrations. There is for example a more than 50% change in the concentrations at the surface for $c_0 = 0.1$ M when an attractive dispersion coefficient $B_\pm = -1 \times 10^{-50}$ N m^3 is replaced with a repulsive dispersion potential with the same magnitude. In Figure 4 we present the potentials (ϕ) for the same parameters used as in Figure 3. Once again the influence of dispersion potential is evident.

Counterion Condensation on Polyelectrolytes

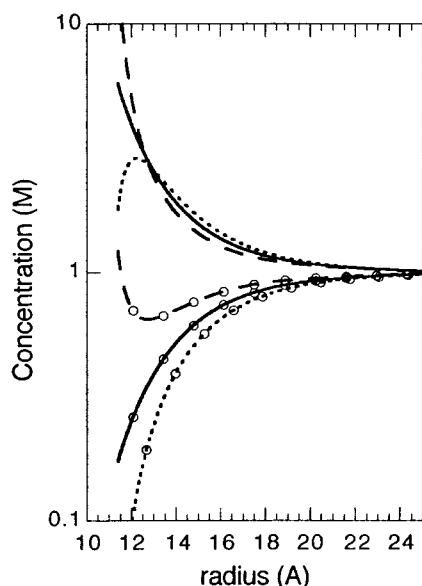*J. Phys. Chem. B, Vol. 106, No. 32, 2002* **7911**

Figure 3. The ionic concentrations as a function of radius away from the cylinder center. Three different cases are shown: no dispersion potentials (solid line); attractive dispersion potentials ($B_\pm = -5 \times 10^{-50}$ N m^3) (dashed); and repulsive dispersion potentials ($B_\pm = 5 \times 10^{-50}$ N m^3) (dotted). The co-ion concentrations have been marked with open circles.
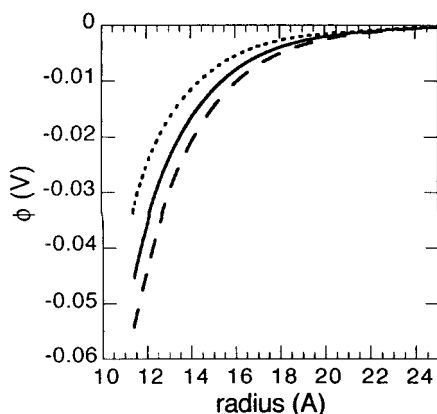

Figure 4. The electrostatic potentials for the same combinations of dispersion potentials and concentration as shown in Figure 3.

IV. Conclusions

The purpose of this paper has been to include the dispersion potentials acting on the surrounding ions in the calculation of the double layer around a charged cylinder. We have shown that these forces may have important influence on ion distributions outside polyelectrolytes. This supports the view that these (previously neglected) ionic dispersion potentials are one important reason behind the ion specific, or Hofmeister, series found for the thermal stability of nucleic acid complexes. Of course, there will also be influences from for example the different ion sizes, water structure, dissolved gas,[31] and the way dispersion forces are handled in the surface region. The purpose of this simplification is to demonstrate that the effects of including ionic dispersion potentials are very important. Although a large number of effects need to be included in a complete theory it is clear that one cannot neglect ionic dispersion potentials in any calculation of charge density around polyelectrolytes at biological concentrations (>0.15 M). Dispersion forces will often even be of the same order of magnitude as electrostatic potentials. One purpose of this work is to highlight the need for an analytical theory for ionic binding[5-7,32]

on polyions and micelles that takes ionic dispersion potentials into account. Another purpose of the present work is to strongly encourage further experiments that can provide more detailed information about the frequency dependent polarizability of ions in water. We argue that this is a key quantity to understand specific ion effects, and at the very least we have shown that it has a very important role. We conclude that any realistic calculation on this kind of system should include ionic dispersion potentials.

One of many possible steps beyond the present paper is to calculate the midpoint transition temperature of nucleic acid helices, which is experimentally known to be ion specific. To compare correctly analytically with Donnan equilibrium one needs to use the experimental Donnan coefficients. One must then do a thermodynamic conversion[33] to take into account partial molar volumes. The Donnan equilibrium depends on activity coefficients of the bulk electrolytes and these are ion specific too. Pailthorpe et al. did the thermodynamic conversion from constant pressure to constant density in their comparison between theory and experimental activity coefficients. They could fit their data properly taking account of measured partial molar volumes. The theory works for alkali halides in the sense that the assumed "hard" hydrated radii of the primitive model that emerges do make sense and are additive. However, they do not make sense for ions such as NO_3^-, SO_4^{2-}, Cs^+, and some others. The results for these ions are nonsensical because the hydrated radii that fit the measured activity coefficient over the entire concentration range are less than the bare ion radii. This can be accommodated by admitting an extra attractive ion specific potential.[33] We argue that the obvious candidate is the ionic dispersion potential.

References and Notes

(1) Manning, G. S. *Quart. Rev. Biophys.* **1978**, *11*, 179.
(2) Record, M. T., Jr.; Anderson, C. F.; Lohman, T. M. *Quart. Rev. Biophys.* **1978**, *11*, 103.
(3) Record, M. T., Jr.; Zhang, W.; Anderson, C. F. *Adv. Protein Chem.* **1998**, *51*, 281.
(4) Tomac, S.; Sarkar, M.; Ratilainen, T.; Wittung, P.; Nielsen, P.; Nordén, B.; Gräslund, A. *J. Am. Chem. Soc.* **1996**, *118*, 5544.
(5) Anderson, C. F.; Record, M. T., Jr. *Biophys. Chem.* **1980**, *11*, 353.
(6) Mohanty, A. U.; Ninham, B. W.; Oppenheim I. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 4342.
(7) Evans, D. F.; Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344.
(8) Hayter, J. B. *Langmuir* **1992**, *8*, 2873.
(9) Lyubartsev, A. P.; Laaksonen, A. *J. Chem. Phys.* **1999**, *111*, 11207.
(10) Kjellander, R.; Lyubartsev, A. P.; Marcelja, S. *J. Chem. Phys.* **2001**, *114*, 9565.
(11) Collins, K. D.; Washabaugh. M. W. Q. *Rev. Biophys.* **1985**, *18*, 323.
(12) Baldwin, R. L. *Biophys. J.* **1996**, *71*, 2056.
(13) Grigorjev, P. A.; Bezrukov. S. M. *Biophys. J.* **1994**, *67*, 2265.
(14) Kim, H.-K.; Tuite, E.; Nordén, B.; Ninham, B. W. *Eur. J. Phys. E* **2001**, *4*, 411.
(15) Weissenborn, P. K.; Pugh, R. J. *J. Colloid Interface Sci.* **1996**, *184*, 550.
(16) Boström, M.; Williams, D. R. M.; Ninham, B. W. *Langmuir* **2001**, *17*, 4475.
(17) Dubois, M.; Zemb, Th.; Fuller, N.; Rand, R. P.; Parsegian. V. A. *J. Chem. Phys.* **1998**, *108*, 7855.
(18) Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Brady, J.; Evans, D. F. *J. Phys. Chem.* **1996**, *90*, 1637.
(19) Ninham, B. W.; Yaminsky, V. *Langmuir* **1997**, *13*, 2097.
(20) Netz, R. R. *Eur. Phys. J. E* **2001**, *5*, 189.
(21) Boström, M.; Williams, D. R. M.; Ninham, B. W. *Phys. Rev. Lett.* **2001**, *87*, 168103.

Boström et al.

(22) Lo Nostro, P.; Lopes, J. R.; Ninham, B. W.; Baglioni, P. *J. Phys. Chem. B* **2002**, *106*, 2166.

(23) Senear, D. F.; Batey, R. *Biochem.* **1991**, *30*, 6677.

(24) Misra, V.; Hecht, J.; Sharp, K.; Friedman, R.; Honig, B. J. *Mol. Biol.* **1994**, *238*, 264.

(25) Marky, N. L.; Manning, G. S. *J. Am. Chem. Soc.* **2000**, *122*, 6057.

(26) Podgornik, R.; Rau, D. C.; Parsegian, V. A. *Biophys. J.* **1994**, *66*, 962.

(27) Zubay, G. L. *Biochemistry*, 4th ed.; McGraw-Hill: Dubuque, 1998.

(28) Mahan, G. D. *J. Chem. Phys.* **1982**, *76*, 493.

(29) Wolf, A. V.; Brown, M. G.; Prentiss, P. G. *CRC Handbook of Chemistry and Physics*, 52nd ed.; The Chemical Rubber Co., Cleveland, 1971; D181-D226.

(30) Gu, Y.; Li, D. J. *Colloid Int. Sci.* **1999**, *217*, 60.

(31) Alfridson, M.; Ninham, B. W.; Wall, S. *Langmuir* **2000**, *16*, 10087.

(32) Belloni, L. *Colloids Surf. A: Physicochem. Eng. Aspects* **1998**, *140*, 227.

(33) Pailthorpe, B. A.; Ninham, B. W.; Mitchell, D. J. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 115.