Specific Ion Effects in Common Black Films: The Role of the Thermal Undulation of Surfaces

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It has long been demonstrated that the traditional double layer theory does not provide an accurate description for the repulsion between colloidal particles at small separations and high ionic strengths. Recent experiments on black films revealed that the traditional theory seems to be inadequate even for large separation distances and moderate ionic strengths. These results raise doubts about the validity of the DLVO approximations. It is argued here that the results can be, however, understood within the framework of the traditional theory if one accounts for the thermal undulation of the film interfaces, and a new treatment to account for the thermal undulations is suggested.

1. Introduction

When two charged particles immersed in an electrolyte approach each other, the overlap of their ionic atmospheres (the double layers) generates a repulsive force. The traditional Derjaguin–Landau–Verwey–Overbeek (DLVO) theory assumes that the stability of charged colloids is a consequence of a balance between this double layer repulsion and the attractive van der Waals interactions.1

The first theoretical description of the double layers assumed that the ions interact via a mean potential, which obeys the Poisson equation.2 Such a simple theory is clearly only approximate and sometimes predicts ionic concentrations in the vicinity of the surface that exceed the available volume.3 There were a number of attempts to improve the model, by accounting for the variation of the dielectric constant in the vicinity of the surface,4 for the volume-exclusion effects of the ions,5 or for additional interactions between ions and surfaces, due to the screened image force potential,6 to the van der Waals interactions of the ions7 with the system, or to the change in hydration energy when an ion approaches the interface.8

It is clear that the DLVO theory is incomplete, a simple example being the stability of neutral lipid bilayers,9 or of the water films involving nonionic surfactants,10 where there is no double layer to provide the required repulsion. Another example is provided by the specific ion effects, namely, the different behaviors of systems immersed in different electrolytes of the same valence. Various electrolytes have been classified long ago by Hofmeister in an empirical series, based on their efficiency in protein precipitation.11 More recently, it was shown that, in a certain pH range, amphoteric latex particles coagulated when the concentration of CsNO3 exceeded about 0.3 M but remained stable even at 3.0 M of KNO3.12 Since the DLVO theory of double layer forces accounts only for the ion valency and concentration, it cannot explain why different results were obtained when Cs was replaced by K.

Experiments regarding the force between mica surfaces revealed that the traditional DLVO theory provides good agreement at large separations but fails at low separations and high electrolyte concentrations.13 For some electrolytes, even at relatively low ionic strengths (10−2 M) there is an additional strong repulsion at low separations between surfaces. All of the above experiments can be understood qualitatively if one assumes an additional short-range repulsion between surfaces. It was suggested that such a repulsion, the hydration force, is provided by the organization of water in the vicinity of the surface (the “hydration” of the surfaces).14 However, there is no agreement regarding the microscopic origin of the hydration repulsion. Some models assume that the hydrogen bonding of water near a surface is responsible for this repulsion and that the ions do not play any role.15 Another model considers that, when two surfaces approach each other, the electrolyte ions are losing their hydrating molecules and this unfavorable free energy process generates a repulsion, hence that the hydrated electrolyte ions are vital to the hydration force.16 The local interaction between dipoles (surface–water and water–water dipoles) was also proposed to explain the hydration repulsion.17 Since the dipole interactions are electrostatic, this hydration and the double layer should be coupled into a single force.18 In this case,
while a repulsion is present even in the absence of electrolyte ions, the force can depend on the electrolyte concentration via the Poisson equation,\(^\text{18}\) and particularly because of the charge recombination on the surface, which, while decreasing the surface charge, generates new surface dipoles.\(^\text{17}\)

A common feature of the experiments discussed above is that the hydration repulsion is short ranged. In contrast, recent experiments with AOT-based black films (thin water films with surfactant monolayers adsorbed at the water/air interfaces) showed that the traditional double layer theory is not accurate even at large distances, of the order of 100 Å.\(^\text{19}\) Indeed, different cations (Cs and Li) led to different dependencies of the thickness of the film on the applied pressure, for electrolyte concentrations exceeding 0.05 M. For concentrations between 0.05 and 0.2 M CsCl, the results could be explained in terms of the DLVO interactions, when a surface potential of about 0.1 V was employed in the calculations. However, this implies that the surface charge density doubles when the electrolyte concentration increases from 0.05 to 0.2, whereas a decrease of the surface charge density because of charge recombination is expected to occur. When Li replaced Cs, the equilibrium thickness of the film increased by as much as 10 Å, and the slope of pressure vs distance plot decreased, suggesting an increase in the Debye decay length. Sentencet and Benattar\(^\text{19}\) pointed out that the difference is too large to be explained by different Stern layers.\(^\text{3}\) The difference is also too large to be accounted for by additional interactions between ions and surfaces, such as ion-dispersion\(^\text{7}\) or ion-hydration interactions.\(^\text{8}\) It was shown that when the interfaces interact through thermal undulations, the free energy due to the change in area is smaller than that due to bending. However, for much larger wavelengths, the bending free energy becomes much smaller. Consequently, for \(\lambda > 4\) Å, the bending at constant area becomes favorable thermodynamically. Since the wavelengths of the thermal undulation of AOT interface are in general much larger than 4 Å (the distance between two neighboring AOT molecules on the surface being about 7–8 Å),\(^\text{22}\) in what follows it will be assumed that the interfaces bends at constant area.

It was shown that when the interfaces interact through a harmonic potential, the entropic contribution to the free energy due to the finite confinement is inversely proportional to the mean square fluctuation, \(\sigma^2\), of the distribution of distances between interfaces.\(^\text{23}\) In a seminal paper, Helfrich conjectured that for a hard-wall interaction between membranes, the entropic confinement contribution has the same functional form as for a harmonic potential and that \(\sigma\) is proportional to the average intersurface distance \(d\).\(^\text{23}\) This conjecture leads to a supplementary pressure, due to the confinement of the thermal undulations, \(P_\text{conf} \sim \langle d\rangle\).\(^\text{22}\) This law is valid at large separations, for elastic membranes interacting via short-range potentials, such as the neutral lipid bilayers;\(^\text{24}\) however, it is not accurate at small separations, where experiments and Monte Carlo simulations\(^\text{25}\) showed that \(\sigma\) depends exponentially on \(d\).

The approach proposed here combines a Boltzmann-like distribution of the film thicknesses\(^\text{27}\) with the minimization of the total Gibbs free energy.\(^\text{28}\) One of the undulating interfaces is assumed flat and rigid (denoted 1 in Figure 1), while the other (2 in Figure 1) is considered to be composed of many flat pieces of finite area \(A\), which behave independently of each other and are Boltzmannian distributed in the potential created by the rigid interface. As shown below, the intersurface distance distribution based on this model coincides, for a harmonic interaction, with the exact result obtained from the partition function of two undulating membranes. The model is extended to cases involving nonharmonic interactions for which analytic solutions are not available.

\[
U_{\text{ST}} = \int_0^d dx \int dy \left( \frac{1}{2} K_c \left( \frac{\partial u(x,y)}{\partial x} + \frac{\partial u(x,y)}{\partial y} \right)^2 \right)
\]

where \(\gamma\) is the surface tension.

While the exact value for the bending modulus of an AOT layer between air and water is not known, experiment provided a value of the order of 1 KT for AOT monolayers between water and oil.\(^\text{21}\) These values are not very accurate; indeed for water/decane, the neutron spin–echo experiments provided 5.0 KT, while the small-angle neutron scattering led to 0.5 KT.\(^\text{21}\) Assuming that \(K_c = 1\) KT and \(\gamma = 0.025\) N/m,\(^\text{29}\) the bending energy \((1a)\) and the surface tension energy \((1b)\) become equal for a mode with \(\lambda = (K_c/\gamma)^{1/2} \sim 4\) Å. At smaller wavelengths, the free energy due to bending is smaller than that due to curvature. However, for much larger wavelengths, the bending free energy becomes much smaller. Consequently, for \(\lambda > 4\) Å, the bending at constant area becomes favorable thermodynamically. Since the wavelengths of the thermal undulation of AOT interface are in general much larger than 4 Å (the distance between two neighboring AOT molecules on the surface being about 7–8 Å),\(^\text{22}\) in what follows it will be assumed that the interfaces bends at constant area.

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\int dy \frac{\gamma \alpha^2}{4 \lambda^4} (1b) \]

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2. Elastic Interfaces Interacting via a Nonlinear Potential

Let us first summarize the results obtained for a thermal undulating membrane interacting with a rigid, flat surface via a harmonic potential, \( U_\text{h}(u) = (1/2)Bu^2 \). The total energy, per unit area, is given by

\[
U_h = \int \! dx \, dy \left( \frac{1}{2} K_C \left( \frac{\partial^2 u(x,y)}{\partial x^2} + \frac{\partial^2 u(x,y)}{\partial y^2} \right)^2 + \frac{1}{2} K_B u^2(x,y) \right) \tag{2}
\]

where \( u(x,y) \) denotes the displacement of a point of coordinates \( (x,y) \) of the membrane, along the normal to the \( (x,y) \) plane, from the position of the potential minimum, \( u_0 = 0 \). \( K_C \) is the bending modulus of the membrane and \( K_B \) is the constant of the harmonic potential of interaction between the undulating membrane and the rigid surface.

Denoting by \( \tilde{u}(q_x, q_y) \) the Fourier transform of \( u(x,y) \), the average energy of each undulation mode obtained from the equipartition principle is given by\(^{20,23} \)

\[
\langle \tilde{u}^2 \rangle = \frac{1}{2} K_C q_x^2 + \frac{1}{2} K_B \tag{3}
\]

Therefore for the mean square fluctuations one obtains

\[
\sigma^2 = \langle u^2 \rangle = \sum_{q_x, q_y} \langle \tilde{u}^2 \rangle = \frac{kT}{(2\pi)^2} \int_0^{\infty} \frac{2\pi q dq}{K_C q^4 + B} = \frac{kT}{8(K_C B)^{1/2}} \tag{4}
\]

and the distribution of distances is Gaussian

\[
\rho(u) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{u^2}{2\sigma^2}\right) \tag{5}
\]

This distribution of thicknesses is formally identical with the Boltzmannian distribution of distances between the fixed, rigid membrane (1 in Figure 1) and a collection of planar pieces of membranes of area \( A \), independent of each other, but free to move in the potential \((1/2)Bu^2 \) (see Figure 1).

\[
\rho(u) = \left( \frac{AB}{2\pi kT} \right)^{1/2} \exp\left(-\frac{ABu^2}{2kT} \right) \tag{6}
\]

if the area \( A \) is selected as\(^{27} \)

\[
A = \frac{kT}{B\sigma^2} = 8\left(\frac{K_C}{B}\right)^{1/2} \tag{7}
\]

An alternate procedure to calculate the distribution of an elastic membrane in a harmonic potential has as starting point the direct integration of the partition function of the canonical ensemble in Fourier space\(^{21} \)

\[
Z = \int \prod u du \left( \exp\left(-\beta \sum_{q_x, q_y} \frac{1}{2} \tilde{u}^2(K_C q^4 + B) \right) \right) = \prod_{q_x, q_y} \left( \frac{2\pi kT}{K_C q^4 + B} \right)^{1/2} \tag{8}
\]

The difference in the free energies of a free membrane (which formally corresponds to \( B = 0 \)) and that interacting with the rigid wall via the harmonic potential \((1/2)Bu^2 \) is given by

\[
\Delta F = kT \frac{1}{(2\pi)^2} \int_0^{\infty} dq \, 2\pi q \ln \left[ \frac{K_C q^4 + B}{K_C} \right]^{1/2} = \frac{kT}{8} \left( \frac{B}{K_C} \right)^{1/2} \tag{9}
\]

The entropic term of the free energy (per unit area) due to the confinement is obtained by subtracting the interaction energy per unit area from eq 9, a result which is essentially due to Helfrich\(^{23} \)

\[
\Delta F_{\text{ent}} = kT \frac{B}{8(K_C)} \left( \frac{1}{2} \right) - \frac{1}{2} B \langle u^2 \rangle = \frac{(kT)^2}{128K_C \sigma^2} \tag{10}
\]

Let us now assume that the functional form for the entropic contribution, eq 10, holds even when the membrane is subjected to an arbitrary potential, \( U(u) \), with a minimum at \( u = 0 \). Therefore, the Gibbs free energy of the membrane per unit area at a constant external pressure \( \Pi \) is given by

\[
G(A) = \int_0^\infty \rho(u)(U(u) + \Pi u) du + \frac{(kT)^2}{128K_C \sigma^2} \tag{11a}
\]

where

\[
\rho(u) = \frac{1}{N} \exp\left(-\frac{U(u) + \Pi u}{kT} \right) \tag{11b}
\]

with the normalization factor \( N \) given by

\[
N = \int_0^\infty \rho(u) du \tag{11c}
\]

The average distance between the membrane and the rigid surface is obtained from

\[
\langle d \rangle = d_0 + \frac{1}{N} \int_0^\infty u \rho(u) du \tag{11d}
\]

where \( d_0 \) is the distance between the position of the potential minimum \( u = 0 \) and the rigid surface. The mean square fluctuation of the membrane is given by

\[
\langle d^2 \rangle = d_0^2 + \frac{1}{N} \int_0^\infty u^2 \rho(u) du \tag{11e}
\]
\[ o^2 = \frac{1}{N} \int_{u} (u - ((d) - d_0)^2) \rho(u) \ du \]  

(11e)

The above integrations are performed over the entire range allowed for \( u \).

By employing eqs 11b–e, the Gibbs free energy eq 11a becomes a function of \( A \) alone for any value of the external pressure \( \Pi \), and consequently the value of \( A \) can be obtained from the minimization of \( G \). For the harmonic potential \( U_{h}(u) = (1/2)Bu^2 \), eq 11a can be integrated

\[ G(A) = \int_{-\infty}^{+\infty} \rho(u) \left( \frac{1}{2} Bu^2 + \Pi u \right) du + \frac{(kT)^2}{128K_C} \int_{-\infty}^{+\infty} u^2 \rho(u) du = \frac{kT}{2A} + \frac{KTBA}{128K_C} \]  

(12)

where the Boltzmannian distribution of the independent pieces of area \( A \) (eq 5) was taken into account. Minimization of \( G \) with respect to \( A \) recovers the relation between the area \( A \) and the elastic parameters of the membrane, eq 7, obtained by employing the equipartition principle (eq 4).

The main assumption in this approach is that the functional form of the entropic term is given by eq 10. This constitutes a very good approximation when most of the membrane is confined near the minimum of the enthalpy (the equilibrium position). This assumption is probably acceptable even when parts of the membrane wander far from the equilibrium position, since the Helfrich law (based on eq 10) seems to be obeyed at large separations.\(^{10,24}\)

### 3. Long-Range Interactions in Black Films

Let us now return to the long-range interactions between AOT-based black films at moderately high electrolyte concentrations (0.05–0.2 M CsCl and LiCl).\(^ {19}\) It has been long known that the DLVO theory is not accurate for univalent electrolytes above about 0.05 M.\(^ {14}\) It is also clear that the differences between the hydration behavior of the Li and Cs ions should lead to different interactions of the ions with the interfaces and to different rates for their recombination with the surface charges. Furthermore, the different polarizabilities of the ions should lead to different van der Waals interactions between ions and the rest of the system. In addition, the excluded volume effects are more important for the much strongly hydrated Li\(^+\) than for Cs\(^+\). There is no doubt that all of the above corrections to the DLVO theory, as well as many others, should be included in a complete theory. However, the purpose of this article is not to provide a set of parameters which lead to an excellent agreement with experiment but to show that the traditional DLVO theory can still provide a reasonable accurate description of the experiments, when the thermal undulations of the interfaces are taken into account. Therefore, the specific ion effects will be taken into account in what follows only via the ability of different ions to modify the bending modulus of the interface. There are no reliable data for the bending modulus of AOT interfaces between air and water, and it is not known how the bending modulus depends on the electrolyte concentration. However, there is experimental evidence that the addition of salt (NaCl) can decrease drastically the bending modulus of the AOT film, possibly because of the decrease of the surface charge density at high ionic strength.\(^ {29}\)

The concentration of AOT in all experiments was 2.5 \( \times 10^{-3} \) M, which roughly corresponds to its critical micelle concentration (cmc) in the absence of an electrolyte. When an electrolyte is added, the cmc concentration is lowered. For the ionic strengths employed in the experiments of Sentenac and Bennat,\(^ {19}\) the surface tension reached saturation well before 2.5 \( \times 10^{-3} \) M.\(^ {19}\) It will be therefore assumed that in all those experiments, the amount of AOT adsorbed did not change and that each surfactant molecule occupies in average an area of 60 Å\(^2\), which is in agreement with the values (40–70 Å\(^2\)) reported in the literature.\(^ {22}\)

The concentration of Na cation, resulting from the dissociation of AOT, will be neglected, since it is at least a few times lower than the concentration of the electrolyte cation. The reassociation of the AOT adsorbed on the surface with the electrolytes cations is taken into account via the association–dissociation equilibrium, which leads to a surface charge density \( \sigma_s \) given by\(^ {30}\)

\[ \sigma_s = - \frac{e \Gamma}{1 + \frac{C_e}{K_D} \exp\left(-\frac{e\psi_s}{kT}\right)} \]  

(13)

where \( e \) is the protonic charge, \( \Gamma \) is the surfactant surface density (1 molecule/60 Å\(^2\) \( \approx 2.77 \times 10^{-4} \) mol/m\(^2\)), \( C_e \) is the bulk electrolyte concentration (assumed completely dissociated), \( K_D \) is the dissociation constant, and \( \psi_s \) the surface potential. While specific ion effects can be introduced by employing different dissociation constants for AOT–Li and AOT–Cs, here the same value will be used for both, \( K_D = 0.5 \) M, implying that the most important contribution to specificity is due to the different bending moduli of the interfaces.

Let us first calculate the free energy of interactions between two planar, nonundulating interfaces. The potential obeys the Poisson–Boltzmann equation

\[ \nabla^2 \psi = \frac{2eC_e}{\epsilon \epsilon_0} \sinh\left(\frac{e\psi}{kT}\right) \]  

(14a)

with the boundary conditions

\[ \frac{d\psi}{dz}\bigg|_{z=d/2} = - \frac{\sigma_s}{\epsilon \epsilon_0} \]  

(14b)

and

\[ \frac{d\psi}{dz}\bigg|_{z=0} = 0 \]  

(14c)

where \( z \) is measured from the middle distance between the planar (nonundulating) interfaces separated by a distance \( d \), \( \epsilon \) is the dielectric constant, and \( \epsilon_0 \) is the vacuum permittivity.

After the solution of the Poisson–Boltzmann equation is obtained, the total double layer free energy per unit area is obtained by adding the electrostatic

\[ F_e(d) = \frac{1}{2} \int_{-d/2}^{d/2} \epsilon \epsilon_0 (\nabla \psi)^2 dz \]  

(15a)

entropic

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Figure 2. The enthalpy $H$ and its harmonic approximation $U_{\text{h}}$ in the vicinity of the minimum, for planar, rigid surfaces separated by a distance $d$ ($C_{\text{el}} = 0.1 \text{ M}$, $\Pi = 1 \times 10^4 \text{ N/m}^2$, $T = 3.3 \times 10^{-4} \text{ mol/m}^2$, $K_C = 0.5 \text{ M}$, $b_0 = -3.08 \times 10^{-12}$, $b_1 = -6.28 \times 10^{-14}$, $b_2 = 8.28 \times 10^{-10}$, $b_3 = 6.13 \times 10^{-12}$, and $T = 300 \text{ K}$). $\rho_1$ is the distribution of the intersurface distances for interfaces with bending modulus $K_C = 2 \text{ K T}$ interacting via the potential $U_h$. This distribution coincides with the Boltzmann distribution of finite pieces of area A, $\rho_2$ is the Boltzmann distribution of the pieces of area A, but now the enthalpy $H$ and not its harmonic approximation $U_{\text{h}}$ is the thermodynamic potential, $\rho_3$ is calculated using for A the value obtained from the minimization of the Gibbs free energy (eq 11a).

$$F_{\text{ent,ions}}(d) = 2C_{\text{el}}kT \int_{-\infty}^{d} \left[ \frac{\psi'(\sigma)}{kT} \sinh \left( \frac{\psi(\sigma)}{kT} \right) + 1 - \cosh \left( \frac{\psi(\sigma)}{kT} \right) \right] d\sigma$$

and chemical contributions

$$\Delta F_{\text{ch}}(d) = -2 \int_{\sigma(\infty)}^{\sigma(d)} \psi(\sigma) d\sigma$$

where $\psi(\sigma)$ is the surface potential and $\sigma(\infty)$ is the surface charge at infinite separation.

For the van der Waals interaction between nonundulating AOT interfaces, whose hydrocarbon chains are about 7 A long, the Padé approximant, calculated on the basis of the Lifshitz theory by Donners et al., will be used

$$U_{\text{vdW}}(d) = \frac{1}{d^2} \left( b_1 + b_2 d + b_3 d^2 \right)$$

where $d$ is the thickness of the water layer and the empirical parameters $b_i$ are assumed equal to those provided by Donners et al. for dodecane films with thickness of 9 A (in SI units): $b_1 = -3.08 \times 10^{-12}$, $b_2 = -6.28 \times 10^{-14}$, $b_3 = 8.28 \times 10^{-10}$, $b_4 = 6.13 \times 10^{-12}$, and $b_5 = -9.00 \times 10^{-23}$.

The enthalpy per unit area, $H$, between the surface 1 and one of the flat surfaces of area A is given by

$$H(u) = [F_{\text{el}}(d) - F_{\text{el}}(\infty)] + F_{\text{ent,ions}}(d) - F_{\text{ent,ions}}(\infty) + \Delta F_{\text{ch}}(d) + U_{\text{vdW}}(d) + \Pi u$$

where $d = d_0 + u$, $d_0$ being the distance between the rigid membrane and the local position of the minimum of the enthalpy. The enthalpy defined by eq 17 has an absolute minimum ($H = -\infty$) for $d = 0$, due to the divergence of the van der Waals attraction. However, the black film (before rupture) is in a metastable state, with the intersurface distances distributed around the local minimum of the enthalpy and all the intersurface distances larger than $d_{\text{min}}$ (see Figure 2). The integration over $u$ in eqs 11 are therefore performed in the range corresponding to $d_{\text{min}} < d < \infty$ ($d_{\text{min}} - d_0 < u < \infty$). When, because of thermal undulations, one region of one of the interfaces is separated from the corresponding region of the other interface by distances smaller than $d_{\text{min}}$, the black film ruptures. Details of this process are provided elsewhere.

In Figure 2 the enthalpy $H$ of the system, per unit area, for a nonundulating interface is plotted as a function of the separation distance $d$ for $C_{\text{el}} = 0.1 \text{ M}$ and $\Pi = 1 \times 10^4 \text{ N/m}^2$, the other parameters having the values given above. When both interfaces are rigid, their separation distance $d_0$ corresponds to the local minimum of the enthalpy. If the bending modulus is large, the separation between the interfaces is distributed in the vicinity of this minimum, where the enthalpy can be well approximated by the harmonic potential $U_h$. The distribution of the separation distances $\rho_1$ was calculated using this harmonic approximation and eq 5, for a bending modulus $K_C = 2 \text{ K T}$ ($T = 300 \text{ K}$). As already noted, the distribution is identical to a Boltzmann distribution of independent pieces of interfaces of area A, given by eq 7. A further improvement in calculating the distribution of the intersurface distances, proposed previously, was to use the harmonic approximation of the entropy, $U_h$, but employing the real enthalpy $H$ for the Boltzmann distribution ($\rho_2$ in Figure 2). A new better approximation is to consider the value of $A$ as a parameter which minimizes the Gibbs free energy, eq 11a (curve $\rho_3$ in Figure 2). The differences between $\rho_2$ and $\rho_3$ are in general significant only for small values of $K_C$ (flexible interfaces) and large separation distances.

The bending moduli of the AOT films in the presence of various electrolytes are not known. Experiment showed that at low AOT concentrations, the surface tension

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A reasonable agreement with experiment was of the right order of magnitude for the water/oil AOT whose values were changed from 0.5 to 5 parameter modified was the unknown bending modulus, approach to account for the thermal undulations. The only compared with the calculations involving the traditional emphasize the importance of membrane flexibility. The presence of these more rigid structures (hydrated ions) in the vicinity of the surface is not bound to the hydrated ions; hence the interface can more easily undulate in the “free” water. On the other hand, the Cs ions can approach closer to the interface binding of some water molecules. The presence of these more rigid structures (hydrated ions) in the vicinity of the interface attenuates the undulations. On this ground, one expects the AOT interfaces to be more flexible in the presence of Li ions. Another possibility is that different recombination constants for Cs and Li lead to different surface charging and hence to different bending moduli. However, in this article the same dissociation constant was employed in both cases, to emphasize the importance of membrane flexibility.

In Figure 3, the experimental results of ref 19 are compared with the calculations involving the traditional DLVO theory for the interactions between parallel (non-undulating) interfaces, combined with the present approach to account for the thermal undulations. The only parameter modified was the unknown bending modulus, whose values were changed from 0.5 to 5 kT, which are of the right order of magnitude for the water/oil AOT interfaces.21 A reasonable agreement with experiment was obtained for $K_c$ in the range 0.5–5 kT even though the other corrections to the traditional DLVO interactions (which are clearly non-negligible) were completely disregarded. It is of interest to note that the calculations at low ionic strengths seem to be better explained by a larger bending modulus, which is expected on intuitive grounds because the higher charged interface should be also more rigid. Consequently, the specific ion effects could be explained in terms of a change in interface flexibility within the traditional DLVO theory.

4. Conclusions

It is well-known that the traditional interactions of the DLVO theory are not accurate at high electrolyte interactions, particularly at small separation distances. Recent experiments on AOT-based black films apparently suggested that the traditional theory is also not valid at moderate ionic strengths and large separations. In this paper, it was argued that the experiments can be understood in terms of the traditional theory, when the thermal undulations of the interfaces are taken into account.

A new approach to account for the thermal undulations of elastic interfaces interacting via arbitrary potentials was suggested. For interfaces interacting via a harmonic potential, the distribution of distances between interfaces is formally identical to a Boltzmann distribution of many independent pieces of area A, where A is related to the bending modulus and to the constant of the interaction potential. Assuming that the distribution remains Boltzmannian in a nonharmonic potential, and that the entropic term due to undulation confinement remains proportional to $\sigma^{-2}$, as for a harmonic potential, the value of A can be obtained via the minimization of the Gibbs free energy of the system.

On the basis of this approach, it was shown that the experiments on AOT-based black films, which apparently disagree drastically with the DLVO theory, can still be understood in the traditional framework, if the bending modulus of the AOT-based interfaces depends on the kind of electrolyte used Li or Cs. One of the reasons for this explanation is that such a long-range departure from the classical theory was observed in thin films with flexible charged interfaces34 and not between rigid interfaces.13 It should be emphasized that, without any doubt, there are many differences between the double layers formed in LiCl and CsCl electrolytes, particularly at high ionic strengths, which are completely disregarded here. The dissociation constant of Li–AOT is probably different from that of Cs–AOT. In addition, the dependence of the bending modulus on the electrolyte concentration for the two types of electrolytes is unknown. The purpose of this paper was not to provide a set of parameters, which can describe the experiment, but merely to suggest that the DLVO theory, the traditional workhorse of colloid science, still provides reasonable results, when the undulations of the interfaces are taken into account.

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