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1 AUTHOR:

Magnus Bergstrom

Uppsala University

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Bending Elasticity of Charged Surfactant Layers: The Effect of Layer Thickness

L. Magnus Bergström*

Department of Pharmacy, Pharmaceutical Physical Chemistry, Box 580, Uppsala University, SE-751 23 Uppsala, Sweden

The bending properties of charged one-component surfactant films of finite thickness have been theoretically investigated. It is demonstrated that finite thickness effects are of crucial importance for layers formed by an ionic surfactant with a flexible hydrophobic tail, whereas the influence on layers formed by a surfactant with a rigid tail is less pronounced. As a matter of fact, in the former case, the spontaneous curvature and mean and Gaussian bending constants all become significantly modified as compared to an infinitely thin surface and assume identical values as if the surfactant layer were bent at constant layer thickness. As a result, the spontaneous curvature is found to decrease, whereas the magnitudes of the mean and Gaussian bending constants both increase with increasing layer thickness as well as with increasing hydrophobic−hydrophilic interfacial tension. All of these trends are consistent with experimental observations. In addition, it is demonstrated that separating the hydrophilic−hydrophobic interface and the surface of charge a certain distance from each other tends to increase the spontaneous curvature and the mean bending constant, whereas the Gaussian bending constant becomes increasingly negative. It is also found that the work of bending a bilayer into a geometrically closed vesicle is substantially raised to large positive values for surfactants with flexible aliphatic chains, whereas the corresponding quantity is negative for surfactants with rigid tails, indicating that stable bilayer structures may only be formed by the former surfactant. Furthermore, each of the bending elasticity constants for monolayers formed by a double-chain ionic surfactant are found to assume lower values as compared with layers formed by the corresponding single-chain surfactant.

1. Introduction

It has been well-established for many years that charged surfactant layers of arbitrary curvature such as a micelle, a microemulsion droplet, or a vesicle may be stabilized by a balance of two opposing forces: the hydrophobic effect tends to decrease the interfacial area per surfactant (a), whereas electrostatics tends to increase a.[1,2] Later on it was also realized that an additional contribution may arise as an effect of conformational entropy imposed on the more or less flexible tails of a surfactant consisting of one or more aliphatic chains.[3,4] This contribution gives rise to an extra repulsion between surfactants aggregated in a dense layer that is necessary for yielding reasonable aggregation numbers for small spherical micelles formed by surfactants with an aliphatic chain.[5] Additional contributions, such as steric headgroup repulsion, may also play an important role, in particular for nonionic surfactants the film stability of which is completely dependent on the presence of such interactions.

Moreover, since the early works by Israelachvili and Tanford it has become widely accepted that the free energy of a nonplanar surfactant layer is influenced, independently of a, on the curvature of the layer. This curvature dependence may be taken into account in an explicit manner by writing the free energy per unit area γ of a surfactant layer as an expansion to second order with respect to the mean and Gaussian curvatures, $H \equiv (c_1 + c_2)/2$ and $K \equiv c_1 c_2$, respectively, i.e.[6]

$$\gamma(H,K) = \gamma_0 + 2k_c(H - H_0)^2 + \bar{k}_c K \tag{1}$$

Here, c_1 and c_2 are the two principal curvatures at a single point on the aggregate surface most conveniently defined at the interface that divides the hydrophobic and hydrophilic regions from each other. In the present context, we have defined c_1 and c_2 to be positive for a film that appears convexly curved from a position in the hydrophilic phase, like ordinary surfactant micelles in water. Equation 1 is generally referred as to the Helfrich expression and it defines three parameters related to different aspects of curving a surfactant film of given area in an arbitrary manner. The three parameters, which are formally defined as

$$H_0 = H \text{ at } \left(\frac{\partial\gamma}{\partial H}\right)_K = 0 \tag{2}$$

$$k_c \equiv \frac{1}{4}\left(\frac{\partial^2\gamma}{\partial H^2}\right)_K \quad [H = H_0, K = 0] \tag{3}$$

$$\bar{k}_c \equiv \left(\frac{\partial\gamma}{\partial K}\right)_H \quad [H = K = 0] \tag{4}$$

play rather different roles as to determine the size and shape of a surfactant monolayer.[7−9] The spontaneous curvature H_0 determines the sign and magnitude of the preferable curvature of the surfactant film. The mean bending constant k_c determines the stiffness or rigidity of the film, i.e., its resistance against deviations from a uniform mean curvature of H_0, and it must assume positive values for a surfactant film to be stable. The Gaussian bending constant $\bar{k}_c$ has the interesting property of

* To whom correspondence should be addressed. Tel: +46 18 471 43 69. Fax: +46 18 471 42 23. E-mail: magnus.bergstrom@farmaci.uu.se.
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determining the topology of the surfactant film, e.g., whether planar layers ($\bar{k}_c < 0$) or a bicontinuous structure with several handles or holes ($\bar{k}_c > 0$) predominates. In addition, effects resulting from the process of stretching the surfactant layer are incorporated in the parameter γ_0. In the present paper, we will generally refer to H_0, k_c, and $\bar{k}_c$ as the bending elasticity constants.

The free energy of a single surfactant layer of arbitrary size and shape may be calculated, once the three bending elasticity constants are known, by simply integrating γ in eq 1 over the entire surface area A, i.e.

$$E \equiv \int_A \gamma \, dA$$
$$= \gamma_0 A + 2k_c \int_A (H - H_0)^2 \, dA + \bar{k}_c \int_A K \, dA \qquad (5)$$

where γ_0 is given by a constraint of fixed overall surfactant concentration.[10] In other words, a surfactant film or aggregate will assume the size and shape that minimizes the free energy (including dispersion effects) for a given set of values of H_0, k_c, and $\bar{k}_c$. As a consequence, it would be possible to predict the size and shape of a surfactant film if H_0, k_c, and $\bar{k}_c$, which all depend on the structure of the surfactants making up the aggregates as well as on the solution state, were quantitatively estimated from a detailed molecular model.

Expressions for the bending elasticity constants for a charged surface have been evaluated by Lekkerkerker[11] and, independently, Mitchell and Ninham[12] from the nonlinear Poisson–Boltzmann theory. Later on, different aspects of the bending properties of charged surfaces such as coupling effects between two charged monolayers in a bilayer,[13,14] dependence on surfactant concentration[15] and undulation effects[16] have been further investigated. In addition, the bending elasticity constants for charged mono- and bilayers have been calculated from various detailed molecular models.[17–20] However, previous approaches either treat a surfactant layer as an infinitely thin surface or, in some other way, neglect effects that arise as a result of the layer having a finite thickness where the surfactant tails are imposed to geometrical packing constraints. Nevertheless, other aspects of the film having a finite thickness have occasionally been taken into account, for example in the treatment of coupling effects in bilayers. The bending rigidity of bilayers was found to be proportional to the square of the bilayer thickness as a result of compressibility effects.[21] An even stronger increase of k_c with layer thickness was suggested for mono and bilayers with fixed number of surfactants as a result of chain conformational entropy effects, whereas $\bar{k}_c$ was found to become increasingly negative with increasing layer thickness.[22]

Moreover, it has become a trend to redefine the different bending elasticity constants so as to incorporate various entropic effects such as thermal undulations[23] or dispersion effects.[9] Rather than redefining the various bending elasticity constants, we have in the present paper always chosen to define H_0, k_c, and $\bar{k}_c$ as bare constants, i.e., as properties of a single rigid surfactant film where thermal undulations or dispersion effects may be explicitly taken into account whenever these aspects are investigated.[10,24–26]

An increasing number of attempts to experimentally determine bending elasticity constants have been carried out during recent years. Unfortunately, a lack of quantitative agreement between different techniques still exists.[27] Nevertheless, several qualitative systematic trends of how the various bending elasticity constants are related to surfactant architecture may be deduced from the experimental observations. The spontaneous curvature is closely related to the aggregation number of surfactant aggregates or the droplet size of microemulsions and, according to a large number of observations, H_0 is expected to increase with, for instance, decreasing size of the hydrophibic tail, increasing headgroup size or decreasing electrolyte concentration.[28] The mean bending constant (rigidity) is related to the stiffness/flexibility of a surfactant film and by measuring interfacial tension, droplet size, and polydispersity of microemulsions,[29–31] or the persistence length of wormlike micelles[32–38] estimates of the magnitude of k_c may be obtained. It has been found that k_c is comparatively large for ionic surfactant systems and decreases with increasing electrolyte concentration. The magnitude of k_c has also been observed to strongly increase with increasing surfactant hydrocarbon chain length. For instance, k_c was recently found to increase with the square of the thickness of bilayers formed by various nonionic diblock copolymers.[39] The Gaussian bending constant may be estimated from the study of the transition between a lamellar ($\bar{k}_c < 0$) and a bicontinuous microemulsion phase ($\bar{k}_c > 0$), and it is generally found that $\bar{k}_c$ increases with decreasing spontaneous curvature.[7,40,41]

In contrast to the various theoretical approaches mentioned above, geometrical packing constraints have been taken into account in our recent derivations of expressions for the bending elasticity constants in binary surfactant mixtures.[42] More recently, these expressions were utilized in order to calculate H_0, k_c, and $\bar{k}_c$ for charged thermodynamically open one-component surfactant layers from a detailed model.[10] Effects due to the hydrophobic effect, chain conformational entropy, electrostatics, and residual

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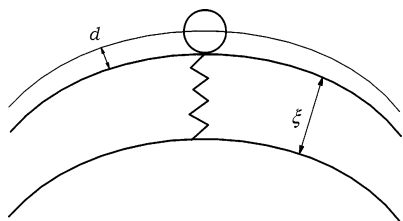(42) Bergström, M. *J. Chem. Phys.* **2003**, *118*, 1440–1452.

Figure 1. Schematic representation of a curved surfactant monolayer. In our model, the surfactant film is considered as consisting of a hydrophobic inner shell of thickness ξ with the charged headgroups located on a surface located a distance d outside the hydrophobic−hydrophilic interface. The area occupied by a single surfactant at the hydrophobic−hydrophilic interface is denoted a, whereas a_{el} denotes the corresponding area at the surface of charge.

headgroup repulsion were investigated. However, one of the drawbacks of such computer calculations carried out in ref 10 is that it is not possible to separate finite thickness effects from effects that are due to the treatment of the layer as an open system in the thermodynamic sense. Therefore, we have in the present paper investigated our molecular model in more detail for a pure film of finite thickness formed by a monovalent ionic surfactant with either rigid or flexible tail. As a result, the crucial effects of taking into account geometrical packing constraints are demonstrated. In our model, we have followed the well-established picture suggested by Tanford,[2] Gruen,[43] and others and considered the surfactant layer as consisting of a hydrocarbon region of finite thickness with the surface of charge located somewhat outside the hydrophobic−hydrophilic interface [cf. Figure 1]. In a forthcoming paper, we will extend our approach so as to include charged mono and bilayers formed in various binary surfactant mixtures.

2. Hydrophobic Free Energy and Geometrical Packing Constraints

We have previously demonstrated that $k_c H_0$, k_c, and $\bar{k}_c$ (but not H_0 itself) are all additive quantities that may be written as sums of several contributions.[42]

A large contribution to the bending elasticity constants appear as a result of an unfavorable hydrophobic/hydrophilic interfacial tension together with a curvature dependent area per aggregated surfactant as obtained by minimizing the monolayer free energy with respect to a for given values of H and K. As a result, we may write $1/a$ as a second-order expansion with respect to curvature, i.e.

$$\frac{1}{a} = \frac{1}{a_p}(1 + k_a' H + k_a'' H^2 + k_a''' K) \tag{6}$$

where a_p is the area per surfactant in a planar film and k_a', k_a'', and k_a''' are constants related to the curvature dependence of a. In accordance, we have been able to derive the following relations for the corresponding contribution to the bending elasticity constants[42]

$$(k_c H_0)_{hb} = \frac{1}{4}\gamma_{hb}k_a' \tag{7}$$

$$k_c^{hb} = -\frac{1}{2}\gamma_{hb}k_a'' \tag{8}$$

(43) Gruen, D. W. R. *Prog. Colloid Polym. Sci.* **1985**, *70*, 6−16.

$$\bar{k}_c^{hb} = -\gamma_{hb}k_a''' \tag{9}$$

where γ_{hb} is the hydrophobic−hydrophilic interfacial tension. The macroscopic interfacial tension for a hydrocarbon−water interface at room-temperature equals about 50 mJ/m². We have previously chosen to refer to this contribution as due to geometrical packing constraints since the hydrophobic part of a surfactant layer formed in a hydrophilic solvent, in the absence of any additional hydrophobic component, is subjected to packing constraints that relates a with the thickness ξ of the hydrophobic part of the monolayer, i.e.

$$\frac{1}{a} = \frac{\xi}{v}\left(1 - \xi H + \frac{\xi^2}{3}K\right) \tag{10}$$

where the volume v of the hydrophobic surfactant tail is a constant for an incompressible surfactant film. In the most general case, ξ may also exhibit a curvature dependence which may be taken into account by writing it in the form of a Taylor expansion to second order, i.e.

$$\xi = \xi_p(1 + k_\xi' H + k_\xi'' H^2 + k_\xi''' K) \tag{11}$$

where $\xi_p = v/a_p$ is the thickness of a planar layer. The values of the bending constants k_ξ', k_ξ'' and k_ξ''' depend on the constraints at which the surfactant film is curved. For example, at constant chemical potentials, in the case of a thermodynamically open film, they usually assume some nonvanishing finite values that are the results of a minimization of the monolayer free energy with respect to ξ at different curvatures, whereas at the constraint of constant film thickness $k_\xi' = k_\xi'' = k_\xi''' = 0$. An additional constraint that is worth mentioning in this context is the bending of a thermodynamically closed film for which the number of aggregated surfactants is kept constant. In this case, $k_a' = k_a'' = k_a''' = 0$ in order to keep the overall hydrophobic−hydrophilic interface area, as well as the aggregation number, of the surfactant film constant. As a matter of fact, these two sets of constants may be inter-related by means of employing the condition for geometrical packing constraints in eq 10 giving $k_a' = k_\xi' - \xi_p$, $k_a'' = k_\xi'' - 2\xi_p k_\xi'$ and $k_a''' = k_\xi''' + \xi_p^2/3$.[42]

3. Electrostatic Free Energy

Analogous to the curvature dependent quantities in eqs 6 and 11, we may also write the electrostatic free energy per charge of a surfactant layer in the form[42]

$$\epsilon_{el} = \epsilon_{el}^p(1 + k_{el}' H + k_{el}'' H^2 + k_{el}''' K) \tag{12}$$

where the different constants in eq 12 are formally defined as

$$\epsilon_{el}^p \equiv \epsilon_{el}(H = K = 0) \tag{13}$$

$$k_{el}' \equiv \frac{1}{\epsilon_{el}^p}\left(\frac{\partial \epsilon_{el}}{\partial H}\right)_K \quad [H = K = 0] \tag{14}$$

$$k_{el}'' \equiv \frac{1}{2\epsilon_{el}^p}\left(\frac{\partial^2 \epsilon_{el}}{\partial H^2}\right)_K \quad [H = K = 0] \tag{15}$$

$$k_{el}''' \equiv \frac{1}{\epsilon_{el}^p}\left(\frac{\partial \epsilon_{el}}{\partial K}\right)_H \quad [H = K = 0] \tag{16}$$

Moreover, the following relations have been demonstrated to be valid for the electrostatic contribution to the bending elasticity

constants for a surfactant monolayer consisting of an ionic surfactant with charge number z[42]

$$(k_cH_0)_{el} = -\frac{z}{4a_p}\left(\frac{\partial \epsilon_{el}}{\partial H}\right)_K \quad [H = K = 0] \tag{17}$$

$$k_c^{el} = \frac{z}{2a_p}k_a'\left(\frac{\partial \epsilon_{el}}{\partial H}\right)_K \quad [H = K = 0]$$
$$+ \frac{z}{4a_p}\left(\frac{\partial^2 \epsilon_{el}}{\partial H^2}\right)_K \quad [H = K = 0] \tag{18}$$

$$\bar{k}_c^{el} = \frac{z}{a_p}\left(\frac{\partial \epsilon_{el}}{\partial K}\right)_H \quad [H = K = 0] \tag{19}$$

The electrostatic free energy of a charged surface, with an adjacent layer of pointlike counterions, immersed in a polar medium has been shown to be most accurately described by the (nonlinear) Poisson−Boltzmann (PB) mean field theory[44] and, as a result, the electrostatic contribution to the bending elasticity constants as given in eqs 17−19 may be investigated in more detail.

Within the PB theory the electrostatic free energy shows a significant explicit curvature dependence and ϵ_{el}/kT may be written as a series expansion to second order in curvature, i.e.

$$\frac{\epsilon_{el}}{kT} = h_0 + h_1H_{el} + h_2H_{el}^2 + h_3K_{el} \tag{20}$$

where k is Boltzmann's constant, T is the absolute temperature, and H_{el} and K_{el} are the mean and Gaussian curvatures of an infinitely thin charged surface. The coefficients in eq 20 have been derived, independently, by Lekkerkerker[11] and Mitchell and Ninham[12] giving

$$h_0 = 2\left[\ln(S + \sqrt{S^2+1}) - \frac{\sqrt{S^2+1}-1}{S}\right] \tag{21}$$

$$h_1 = -\frac{4}{\kappa S}\ln\left(\frac{1 + \sqrt{S^2+1}}{2}\right) \tag{22}$$

$$h_2 = \frac{2}{\kappa^2 S}\left(1 - \frac{2}{S^2} + \frac{2}{S^2\sqrt{S^2+1}}\right) \tag{23}$$

$$h_3 = -\frac{2}{\kappa^2 S}D_1\left(\ln\left(\frac{1 + \sqrt{S^2+1}}{2}\right)\right) \tag{24}$$

The coefficients h_0, h_1, h_2, and h_3 are all functions of the reduced charge density

$$S \equiv \frac{2\pi l_B}{\kappa a_{el}} \tag{25}$$

where a_{el} is the area per surface charge and κ is the inverse Debye screening length. The Bjerrum length is defined as

$$l_B \equiv \frac{e_{el}^2}{4\pi\epsilon_0\epsilon_r kT} \tag{26}$$

where e_{el} denotes the elementary charge and ϵ_0 and ϵ_r are the permittivity in a vacuum and the dielectric constant, respectively. l_B equals about 7.15 Å for an aqueous medium at 25 °C. The

(44) Evans, D. F.; Wennerström, H. *The Colloidal Domain*; Wiley-VCH: New York, 1994; Chapter 3.

Debye function occurring in eq 24 is defined as

$$D_1(x) = \int_0^x \frac{t}{e^t - 1}\,dt \tag{27}$$

The electrostatic contribution to the bending elasticity constants in eqs 17−19 may be derived from eqs 20−24 for a surfactant monolayer with a curvature dependent area per surfactant [cf. eq 6] and with the surface of charge located a distance d outside the hydrophobic−hydrophilic interface [cf. Figure 1]. This is done in detail in Appendix A and the results are

$$\frac{1}{kT}\left(\frac{\partial \epsilon_{el}}{\partial H}\right)_K \quad [H = K = 0] = 2(k_a' - 2d)q - \frac{2a_p}{\pi l_B}\ln\left(\frac{S_p}{2q}\right) \tag{28}$$

$$\frac{1}{kT}\left(\frac{\partial^2 \epsilon_{el}}{\partial H^2}\right)_K \quad [H = K = 0]$$
$$= 2(k_a' - 2d)^2p - 4(k_a' - 2d)k_a'q + 4k_a''q$$
$$- \frac{4a_p}{\pi l_B}\left[(k_a' - 2d)pq - k_a'\ln\left(\frac{S_p}{2q}\right) - \frac{a_p}{4\pi l_B}\left(S_p - \frac{2pq}{S_p}\right)\right] \tag{29}$$

$$\frac{1}{kT}\left(\frac{\partial \epsilon_{el}}{\partial K}\right)_H \quad [H = K = 0]$$
$$= 2(k_a'' - d^2)q - \frac{a_p}{\pi l_B}\left[\kappa^{-1}D_1\left(\ln\left(\frac{S_p}{2q}\right)\right) + 2d\ln\left(\frac{S_p}{2q}\right)\right] \tag{30}$$

where $S_p \equiv 2\pi l_B/\kappa a_p$ is the reduced charge density for a strictly planar surface and we have, for the sake of simplicity, introduced the parameters

$$p \equiv \frac{S_p}{\sqrt{S_p^2 + 1}} \tag{31}$$

$$q \equiv \frac{S_p}{\sqrt{S_p^2 + 1} + 1} \tag{32}$$

both of which assume values in the range between zero and unity as $0 \leq S_p < \infty$.

In addition to terms that are valid for an infinitely thin surface, and that has been previously derived in refs 11 and 12, eqs 28−30 include contributions (terms involving k_a', k_a'', and k_a''') that arise as a consequence of the reduced charge density being curvature dependent, i.e., $S \equiv S(H, K)$. This follows directly from the fact that a depends on H and K, mainly as result of geometrical packing constraints [cf. eqs 6 and 10]. In addition, the location of the surface of charge somewhat outside the hydrophobic−hydrophilic interface has a significant effect on eqs 28−30 and, as a consequence, on the bending elasticity constants. Throughout the present paper we have set this distance equal to $d = 3$ Å which is a typical value used for surfactants consisting of an anionic sulfate headgroup.

4. General Expressions for the Bending Elasticity Constants of Monolayers Formed by a Single Monovalent Ionic Surfactant

Spontaneous Curvature. As was previously mentioned, the spontaneous curvature H_0 is not itself an additive quantity and may therefore not be subdivided into different contributions. However, the product k_cH_0 may be so and the corresponding electrostatic contribution for a one-component surfactant film consisting of a monovalent ionic surfactant may simply be obtained by inserting eq 28 in eq 17 with $z = 1$, which gives

$$\frac{(k_c H_0)_{el}}{kT} = \frac{1}{2\pi l_B}\ln\left(\frac{S_p}{2q}\right) - \frac{q}{2a_p}(k'_a - 2d) \quad (33)$$

We may note that, according to eq 33, $(k_c H_0)_{el}$ is made up of two terms. The first term ($= kT\ln(S_p/2q)/2\pi l_B = -h_1 kT/4a_p$) is the result of the process of bending an infinitely thin film at constant surface charge density and is identical to the expression previously derived by Lekkerkerker[11] and Mitchell and Ninham.[12] The second term ($= -(k'_a - 2d)qkT/2a_p$) is the result of the surfactant layer having a finite thickness with the surface of charge located a distance d outside the hydrophobic−hydrophilic interface.

In addition to electrostatics, an unfavorable interfacial tension between the hydrophobic part of the monolayer and the hydrophilic solvent also contributes to $k_c H_0$ in accordance with eq 7 and, as a result, we obtain the following expression for the sum of the two contributions

$$\frac{k_c H_0}{kT} = \frac{1}{2\pi l_B}\ln\left(\frac{S_p}{2q}\right) + \left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right)\frac{k'_a}{4} + \frac{dq}{a_p} \quad (34)$$

We may note that the constant k'_a, the magnitude of which is determined by the constraints imposed on the monolayer during the process of bending, is present in eq 34. $k_c H_0$ is plotted against the Debye-length κ^{-1} in Figure 2 for a few different cases. From a comparison between the two curves for a thermodynamically closed film ($k'_a = 0$), it is seen that $k_c H_0$ equals the contribution for an infinitely thin surface as $d = 0$, whereas it becomes considerably raised as the surface of charge is located at an increasingly large distance outside the hydrophobic−hydrophilic interface. The two cases of equilibrated monolayers formed by surfactants with either rigid or flexible tail will be further discussed below.

Mean Bending Constant. According to eqs 18, 28, and 29, we can write the electrostatic contribution to k_c for a monolayer formed by a monovalent ionic surfactant ($z = 1$) as

$$\frac{k_c^{el}}{kT} = \frac{\kappa^{-1}}{2\pi l_B}\left(1 - \frac{2(p-q)^2}{pq}\right) - \frac{pq}{\pi l_B}(k'_a - 2d) +$$
$$\frac{p}{2a_p}(k'_a - 2d)^2 + \frac{q}{a_p}k''_a \quad (35)$$

The first term in eq 35 may be interpreted as the contribution from bending an infinitely thin film and is identical to what has previously been derived.[11,12] This term vanishes at $S_p = p = q = 0$ and approaches $\kappa^{-1}/2\pi l_B$ at $S_p \gg 1$ ($p = q = 1$). The remaining terms appear as a result of the surfactant layer having a finite thickness. We may add the hydrophobic contribution to k_c as given by eq 8, and, as a result

$$\frac{k_c}{kT} = \frac{\kappa^{-1}}{2\pi l_B}\left(1 - \frac{2(p-q)^2}{pq}\right) - \left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right)\frac{k''_a}{2} -$$
$$\frac{pq}{\pi l_B}(k'_a - 2d) + \frac{p}{2a_p}(k'_a - 2d)^2 \quad (36)$$

The mean bending constant is plotted against the Debye screening length κ^{-1} in Figure 3 for the same cases that were treated in Figure 2 for $k_c H_0$. Analogous to the latter case, k_c is raised for a surfactant layer with the surface of charge located somewhat outside the hydrophobic−hydrophilic interface.

Gaussian Bending Constant. The electrostatic contribution to the Gaussian bending constant for a one-component charged surfactant layer with $z = 1$ may be obtained by inserting eq 30 in eq 19, i.e.
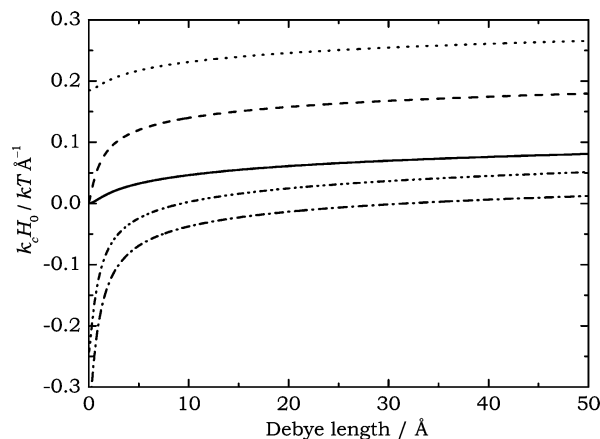

Figure 2. Mean bending constant multiplied with the spontaneous curvature ($k_c H_0$) as a function of the Debye-length (κ^{-1}) for some different constraints: (i) An infinitely thin surface, i.e., eq 34 with $k'_a = 0$ and $d = 0$ (solid line). (ii) Constant area per aggregated surfactant at the hydrophobic−hydrophilic interface ($k'_a = 0$) outside which the surface of charge is located a distance $d = 3$ Å (dashed line). (iii) A thermodynamically equilibrated monolayer composed of surfactants with rigid tails in accordance with eq 42 (dotted line). (iv) A thermodynamically equilibrated monolayer composed of surfactants with flexible tails in accordance with eq 53 (dash−dotted line). (v) A thermodynamically equilibrated monolayer composed of surfactants with flexible C_{12} tails according to detailed model calculations in ref 10 (dash−dot-dotted line). The hydrophobic interfacial tension was set equal to $\gamma_{hb} = 50.7$ mJ/m^2 and the Bjerrum-length $l_B = 7.15$ Å valid for a temperature of $T = 298$ K. a_p was set to 30 Å (i, ii, and iv) and $\xi_p = 11.7$ Å (iv) as obtained from detailed model calculations for an ionic surfactant with a C_{12} hydrocarbon chain [ref 10].
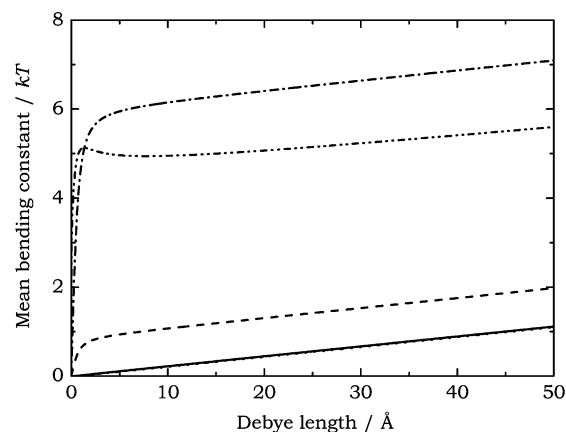

Figure 3. Mean bending constant (k_c) plotted against the Debye length (κ^{-1}) for some different constraints: (i) An infinitely thin surface, i.e., eq 36 with $k'_a = k''_a = 0$ and $d = 0$ (solid line). (ii) Constant area per surfactant at the hydrophobic−hydrophilic interface ($k'_a = k''_a = 0$) outside which the surface of charge is located a distance $d = 3$ Å (dashed line). (iii) A thermodynamically equilibrated monolayer composed of surfactants with rigid tails in accordance with eq 45 (dotted line). (iv) A thermodynamically equilibrated monolayer composed of surfactants with flexible tails in accordance with eq 58 (dash−dotted line). (v) A thermodynamically equilibrated monolayer composed of surfactants with flexible C_{12} tails in accordance with detailed model calculations in ref 10 (dash−dot-dotted line). γ_{hb}, a_p, and ξ_p assume the same values as given in Figure 2.

$$\frac{\bar{k}_c^{el}}{kT} = -\frac{\kappa^{-1}}{\pi l_B}D_1\left(\ln\left(\frac{S_p}{2q}\right)\right) - \frac{2d}{\pi l_B}\ln\left(\frac{S_p}{2q}\right) + \frac{2q}{a_p}(k'''_a - d^2) \quad (37)$$

$\bar{k}_{el}$ may be divided into a contribution from the bending of an infinitely thin charged monolayer[11,12] and a contribution that is
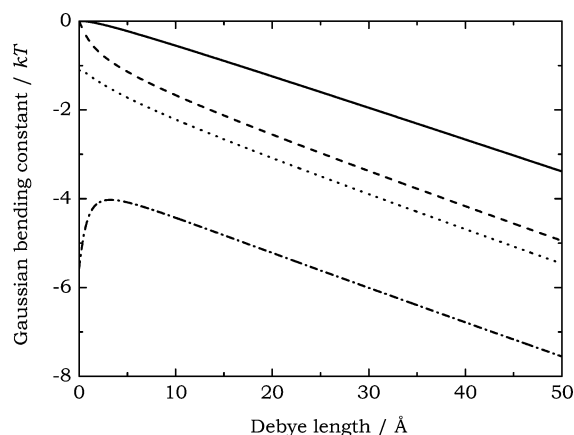
Figure 4. Gaussian bending constant ($\bar{k}_c$) plotted against the Debye length (κ^{-1}) for some different constraints: (i) An infinitely thin surface, i.e., eq 38 with $k_a''' = 0$ and $d = 0$ (solid line). (ii) Constant area per surfactant at the hydrophobic–hydrophilic interface ($k_a''' = 0$) outside which the surface of charge is located a distance $d = 3$ Å (dashed line). (iii) A thermodynamically equilibrated monolayer composed of surfactants with rigid tails in accordance with eq 46 (dotted line). (iv) A thermodynamically equilibrated monolayer composed of surfactants with flexible tails in accordance with eq 59 (dash–dotted line). γ_{hb}, a_p, and ξ_p assume the same values as given in Figure 2.

due to effects of the monolayer having a finite thickness. The former contribution vanishes at $S_p = 0$ and otherwise assumes negative values. Adding the hydrophobic contribution as given in eq 9 yields

$$\frac{\bar{k}_c}{kT} = -\frac{\kappa^{-1}}{\pi l_B} D_1\left(\ln\left(\frac{S_p}{2q}\right)\right) - \frac{2d}{\pi l_B}\ln\left(\frac{S_p}{2q}\right) - \left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right)k_a''' - \frac{2q}{a_p}d^2 \quad (38)$$

In Figure 4, we have plotted $\bar{k}_c$ against κ^{-1} for some different constraints and it is seen that $\bar{k}_c$ decreases, i.e., becomes more negative, with an increasing distance d between the hydrophobic–hydrophilic interface and the surface of charge.

5. Bending Elasticity Constants for Thermodynamically Open Monolayers Formed by an Ionic Surfactant with Rigid Hydrophobic Part

Constants related to the curvature dependence of the area per surfactant at the hydrophobic–hydrophilic interface (k_a', k_a'', and k_a''') are present in the expressions for the bending elasticity constants given in eqs 34, 36, and 38. The values of these constants depend on the actual constraints imposed during the bending process. For example, bending a layer for which the number of aggregated surfactants is kept constant implies that $k_a' = k_a'' = k_a''' = 0$ as already mentioned above [cf. Figures 2–4]. However, in many situations, it is more realistic to treat the surfactant layer as a thermodynamically open system which may exchange molecules with the surrounding solvent phase in order to keep the chemical potential of free surfactant constant during the bending process. In the simplest conceivable case only the hydrophobic effect together with electrostatics contribute to the free energy per aggregated molecule of self-assembling free surfactant monomers, where the free energy contribution of bringing surfactant tails from an aqueous solution to the corresponding hydrophobic liquid bulk phase, as given by Tanford,[2] is independent of a and may thus be incorporated in a single constant, i.e., $\epsilon(a) = \text{constant} + a\gamma_{hb} + \epsilon_{el}$. Already Tanford[2] realized that these two contributions are sufficient for

generating a minimum of ϵ with respect to a leading to the following condition for thermodynamic equilibrium in the surfactant layer

$$\frac{d\epsilon}{da} = \gamma_{hb} + \frac{d\epsilon_{el}}{da} = 0 \quad (39)$$

eq 39 is expected to be valid for ionic surfactants with rigid hydrophobic parts, e.g., bile salts with a hydrophobic cholesterol backbone, that do not give rise to any additional free energy contributions associated with the surfactant tails and for which the optimal value of a is sufficiently large for residual headgroup and tail repulsion effects to be neglected. For the case of a planar layer, for which $H = K = 0$ and $\epsilon_{el}/kT = h_0$ (cf. eqs 20 and 21), eq 39 may be rewritten so as to give

$$\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p} = \frac{\gamma_{hb}}{kT} - \frac{\kappa}{\pi l_B}\left(\sqrt{S_p^2 + 1} - 1\right) = 0 \quad (40)$$

from which we may deduce the following expression for the dependence of a_p with Debye length and interfacial tension

$$a_p = \sqrt{\frac{4\pi l_B kT}{\gamma_{hb}(\pi l_B \gamma_{hb}/kT + 2\kappa)}} \quad (41)$$

In the limit of large Debye lengths, i.e., $\kappa^{-1} \gg 2kT/\pi l_B \gamma_{hb}$, eq, 41 reduces to $a_p = 2kT/\gamma_{hb}$. For a hydrocarbon surfactant layer in an aqueous solvent at room temperature ($\gamma_{hb} = 50$ mJ/m² and $l_B = 7.15$ Å), the approximate expression holds true for κ^{-1} values much larger than 0.7 Å.

Spontaneous Curvature. By inserting the equilibrium condition given in eq 40 in eq 34 we now obtain an expression for $k_c H_0$ for an equilibrated monolayer composed of surfactants with rigid hydrophobic tails where residual headgroup and tail repulsions have been neglected. As a result

$$\frac{k_c H_0}{kT} = \frac{1}{2\pi l_B}\ln\left(\frac{\gamma_{hb}\pi l_B \kappa^{-1}}{2q^2 kT}\right) + \frac{\gamma_{hb} d}{2kT} \quad (42)$$

It is most interesting to note that the only terms left in eq 42 either comes from the explicit curvature dependence of ϵ_{el} in eq 20 or from the effect of the surface of charge being located a distance d outside the hydrophobic–hydrophilic interface, whereas all terms proportional to k_a' have been canceled. The latter terms appears in eq 34 as a result of the fact that both $a\gamma_{hb}$ and ϵ_{el} have an implicit curvature dependence which is directly related to the curvature dependence of a in accordance with eq 6. However, this curvature dependence of a, which is obtained by means of minimizing the free energy of the surfactant layer at different curvatures, is a direct consequence of the presence of an explicit curvature dependence in the equations for the electrostatic free energy and, as a consequence, terms depending on k_a' may not contribute with a net result to eq 42. It is also interesting to note that, because of this canceling effect, the presence of any additional free energy contributions due to residual headgroup or tail repulsion may not contribute in an explicit manner to $k_c H_0$ as long as these contributions lack any explicit curvature dependence. However, $k_c H_0$ may be indirectly influenced as the value of a_p may depend on these additional contributions. Equation 42 is plotted against the Debye screening length in Figure 2, and it is seen that $k_c H_0$ is significantly raised as compared with the case of a thermodynamically closed surfactant layer for which $k_a' = 0$. We may also note that, according to eq 42, $k_c H_0$ increases with increasing hydrophobic–

hydrophilic interfacial tension γ_{hb}. This may be rationalized as an effect of large values of γ_{hb} tending to decrease the area per aggregated surfactant a, implying that the electrostatic contribution to k_cH_0 increaaes.

Mean Bending Constant. A similar procedure for the mean bending constant, i.e., inserting the equilibrium condition given in eq 40 in eq 36, implies that all terms proportional to k_a'' are canceled for the very same reasons that caused terms depending on k_a' to cancel in the expression for k_cH_0 om eq 36. As a result

$$\frac{k_c}{kT} = \frac{\kappa^{-1}}{2\pi l_B}\left(1 - \frac{2(p-q)^2}{pq}\right) - \frac{pq}{\pi l_B}(k_a' - 2d) + \frac{\gamma_{hb}p}{4qkT}(k_a' - 2d)^2 \quad (43)$$

However, terms depending on k_a' are still present in eq 43 and an expression for k_a' may be derived from the equilibrium condition in eq 39 by considering terms proportional to the mean curvature H. A more straightforward procedure to determine k_a' for the equilibrium case, and which gives an identical result, is to simply minimize eq 43 with respect to k_a'. As a result we obtain

$$k_a' = 2d + \frac{2q^2kT}{\gamma_{hb}\pi l_B} \quad (44)$$

which always must be a positive number, i.e., the area per aggregated surfactant a decreases as the surfactant layer is increasingly bent with a positive curvature. Equation 44 may now be inserted in eq 43 to give

$$\frac{k_c}{kT} = \frac{\kappa^{-1}}{2\pi l_B}\left(1 - \frac{2(p-q)^2}{pq}\right) - \frac{pq^3 kT}{\gamma_{hb}(\pi l_B)^2} \quad (45)$$

Evidently, k_c is lowered by the last term in eq 45 and becomes smaller than for an infinitely thin film. This must always be the case since k_c has been minimized with respect to k_a'. This aspect may be formulated in terms of the principle that the constraint of keeping the chemical potential of free surfactant constant has the general property of softening a surfactant film. The lowering of k_c for equilibrated surfactant layers has previously been demonstrated by Porte and Ligoure[19] as well as Safran,[9] although the latter author was defining the bending elasticity constants in a different manner and, as a result, arrived at the rather trivial conclusion that k_c vanishes at the critical micelle concentration. In Figure 3, it is seen that the lowering of k_c is negligibly small for an infinitely thin layer but, since eq 45 is independent of theseparation d between the hydrophobic−hydrophilic interface and the surface of charge, k_c may be significantly reduced for films where such a separation is present [cf. Figure 1]. Moreover, it is evident from eq 45 that the magnitude of the reduction of k_c decreases with increasing hydrophobic−hydrophilic interfacial tension γ_{hb}.

Gaussian Bending Constant. As eq 40 is inserted in eq 38 all terms proportional to k_a''' are canceled in the expression for $\bar{k}_c$ in a similar manner as k_a' and k_a'' were for k_cH_0 and k_c in eq 42 and 43, respectively, and, as a result

$$\frac{\bar{k}_c}{kT} = -\frac{\kappa^{-1}}{\pi l_B}D_1\left(\ln\left(\frac{\gamma_{hb}\pi l_B\kappa^{-1}}{2q^2 kT}\right)\right) - \frac{2d}{\pi l_B}\ln\left(\frac{\gamma_{hb}\pi l_B\kappa^{-1}}{2q^2 kT}\right) - \gamma_{hb}d^2 \quad (46)$$

In Figure 4, we have plotted the Gaussian bending constant according to eq 46 and we note that $\bar{k}_c$ becomes slightly more negative than the corresponding quantity for a thermodynamically

closed surfactant layer. In analogy with the expression for k_cH_0 residual headgroup or chain repulsions would not give rise to any additional terms in eq 46 insofar an explicit dependence on K is absent in the corresponding free energy expressions. $\bar{k}_c$ may, however, be indirectly influenced as a result of a_p becoming modified as these contributions are taken into account. It is also evident from the appearance of eq 46 that $\bar{k}_c$ decreases only slightly with increasing γ_{hb}.

6. Bending Elasticity Constants for Thermodynamically Open Monolayers Formed by an Ionic Surfactant with Flexible Hydrophobic Part

Chain Conformational Free Energy. The big majority of amphiphilic molcelues of technical and biological importance, for instance, membrane phospholipids, are made up of one or two more or less flexible aliphatic chains. The flexibility of the hydrophobic part of a surfactant gives rise to an additional free energy contribution ϵ_{chain} as a result of chain conformational entropy effects that must be taken into account. The chain conformational free energy has been quantitatively estimated for different geometries by Gruen[3,45] and Ben-Shaul and co-workers[46] using mean field single-chain models, and it has been demonstrated that this contribution may be written as a function of only the layer thickness for a given geometry, i.e., $\epsilon_{chain} \equiv \epsilon_{chain}(\xi)$.

As a first approximation, we may assume that any explicit curvature dependence is absent in the expression for ϵ_{chain}. As a result, it is straightforward to show that chain conformational free energy contributes to k_cH_0 with the expression

$$(k_cH_0)_{chain} = -\frac{1}{4a_p}\frac{d\epsilon_{chain}}{d\xi}\left(\frac{\partial\xi}{\partial H}\right)_K \quad [H = K = 0] \quad (47)$$

in a similar manner as electrostatics in eq 17. An expression for the chain conformational free energy contribution to k_c may, likewise, be derived so as to give

$$k_c^{chain} = \frac{1}{4a_p}\frac{d^2\epsilon_{chain}}{d\xi^2}\left(\frac{\partial\xi}{\partial H}\right)_K^2[H = K = 0]$$
$$+ \frac{1}{4a_p}\frac{d\epsilon_{chain}}{d\xi}\left(\frac{\partial^2\xi}{\partial H^2}\right)_K[H = K = 0]$$
$$+ \frac{k_a'}{2a_p}\frac{d\epsilon_{chain}}{d\xi}\left(\frac{\partial\xi}{\partial H}\right)_K[H = K = 0] \quad (48)$$

whereas the corresponding expression for the Gaussian bending constant equals

$$\bar{k}_c^{chain} = \frac{1}{a_p}\frac{d\epsilon_{chain}}{d\xi}\left(\frac{\partial\xi}{\partial K}\right)_H \quad [H = K = 0] \quad (49)$$

To obtain the equilibrium condition that arises from the minimization of the free energy of the film it appears most convenient to minimize $\epsilon = \text{constant} + a\gamma_{hb} + \epsilon_{el} + \epsilon_{chain}$ with respect to film thickness ξ, rather than area per surfactant a, giving

$$\frac{d\epsilon}{d\xi} = \left(\gamma_{hb} - \frac{d\epsilon_{el}}{da}\right)\frac{da}{d\xi} + \frac{d\epsilon_{chain}}{d\xi} = 0 \quad (50)$$

(45) Gruen, D. W. R. *J. Phys. Chem.* **1985**, *89*, 153−163.
(46) Ben-Shaul, A.; Szleifer, I.; Gelbart, W. M. In *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*; Degiorgio, V., Corti, M., Eds.; North-Holland: Amsterdam, 1985; pp 404−428.

The following relations are valid for a planar monolayer with $H = K = 0$, $d\epsilon_{el}/da = 2q/a_p$ and $da/d\xi = -\xi_p/a_p$, and eq 50 may thus be rewritten so as to become

$$\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p} - \frac{\xi_p}{a_p kT}\frac{d\epsilon_{chain}}{d\xi} = 0 \qquad (51)$$

Spontaneous Curvature. Now we may write the sum of the three contributions in eqs 7, 33, and 47 as

$$\frac{k_c H_0}{kT} = \frac{1}{2\pi l_B}\ln\left(\frac{S_p}{2q}\right) - \left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right)\frac{\xi_p}{4} +$$
$$\left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p} - \frac{\xi_p}{a_p kT}\frac{d\epsilon_{chain}}{d\xi}\right)\frac{k'_\xi}{4} + \frac{dq}{a_p} \qquad (52)$$

where it has also been taken into account that $d\xi/dH = \xi_p k'_\xi$ at $H = 0$, in accordance with eq 11. Moreover, by taking the equilibrium condition in eq 51 into account, as well as setting $S_p = 2\pi l_B/\kappa a_p$, we may simplify eq 52 so as to give

$$\frac{k_c H_0}{kT} = \frac{1}{2\pi l_B}\ln\left(\frac{\pi l_B \kappa^{-1}}{a_p q}\right) - \frac{\xi_p}{4}\left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right) + \frac{dq}{a_p} \qquad (53)$$

in the expression of which all terms proportional to k'_ξ have been canceled.

As a matter of fact, eq 53 is identical to what is obtained when $k'_a = -\xi_p$ is inserted in eq 35. In other words, the chain conformational entropy contribution to ϵ does not give rise to any additional terms in eq 53, insofar any explicit dependence on H is absent in the expression for ϵ_{chain}, but it may have a huge indirect impact on $k_c H_0$ which is identical to the effect of bending the surfactant layer at constant layer thickness ($k'_\xi = 0$). Most interestingly, the detailed appearance of the curvature independent $\epsilon_{chain}(\xi)$ have no effect whatsoever on eq 53, although it may influence the magnitude of $k_c H_0$ by largely determining the final value of ξ_p.

$k_c H_0$ according to eq 53 is plotted in Figure 2 and is found to be brought down significantly as compared with the corresponding case where chain conformational free energy were not taken into account [cf. eq 42]. This is consistent with experimental observations that surfactants with stiff tails, e.g., bile salts, usually form small and highly curved micelles whereas surfactants with aliphatic chains more often form larger aggregates.[28] We have also included $k_c H_0$ as recently calculated from a detailed model[10] in Figure 2. It is somewhat larger than the corresponding quantity given by eq 53 since an explicit dependence on H for ϵ_{chain}, consistent with the fact that the magnitude of ϵ_{chain} depends on geometry,[45] was included in these calculations. In Figure 5, we have plotted eq 53 for some different values of ξ_p, and it is seen that $k_c H_0$ dramatically decreases from positive to negative values as the layer thickness, corresponding to an increased surfactant chain length, increases from 10 to 20 Å.

Notably, terms proportional to $\xi_p/4$ is present in eq 53, whereas the corresponding terms are absent in eq 42. Hence, we may conclude that the thickness of the surfactant film have a strong influence on $k_c H_0$ for layers of surfactants with flexible tails whereas ξ_p have no effect whatsoever on the bending properties of films composed of surfactants with rigid tails. Evidently, the hydrophobic contribution (γ_{hb}) combined with the finite thickness effect tends to lower $k_c H_0$ whereas the corresponding repulsive electrostatic effects ($\propto 2q/a_p$) tends to raise $k_c H_0$. Similar positive terms must be added to eq 53 as residual headgroup repulsion effects are taken into account, and, in accordance, detailed model
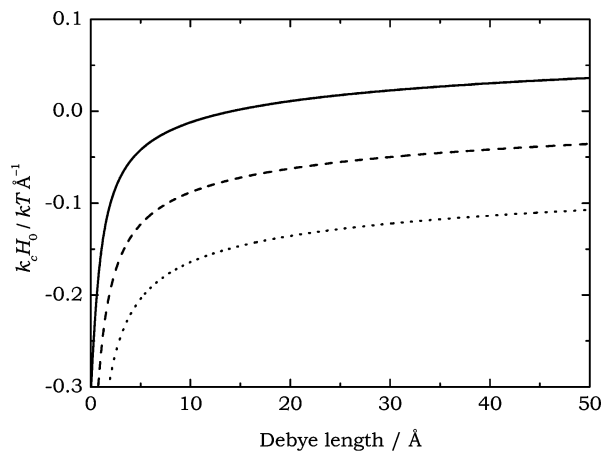

Figure 5. Mean bending constant multiplied with the spontaneous curvature ($k_c H_0$) in accordance with eq 53 as a function of the Debye-length (κ^{-1}) for $\xi_p = 10$ Å (solid line), $\xi_p = 15$ Å (dashed line) and $\xi_p = 20$ Å (dotted line). The hydrophobic interfacial tension was set equal to $\gamma_{hb} = 50.7$ mJ/m², the Bjerrum length $l_B = 7.15$ Å and $a_p = 30$ Å.

calculations have demonstrated that $k_c H_0$ increases with increasing headgroup cross-section area.[10]

It may finally be noted that a_p becomes rather insensitive to the hydrophobic−hydrophilic interfacial tension γ_{hb} when the chain conformational entropy contribution is included. As a result, we expect $k_c H_0$ to decrease with increasing γ_{hb}, i.e., the opposite trend as compared to the case of surfactants with rigid tails [cf. eq 42].

Mean Bending Constant. The sum of the various contributions to the mean bending constant given in eqs 8, 35, and 48 equals

$$\frac{k_c}{kT} = \frac{\kappa^{-1}}{2\pi l_B}\left(1 - \frac{2(p-q)^2}{pq}\right) - \frac{pq}{\pi l_B}(k'_\xi - \xi_p - 2d) + \frac{p}{2a_p}(k'_\xi -$$
$$\xi_p - 2d)^2 + \frac{(\xi_p k'_\xi)^2}{4a_p kT}\frac{d^2\epsilon_{ch}}{d\xi^2} + \frac{1}{2}\left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right)k'_\xi(k'_\xi + \xi_p) \qquad (54)$$

where we have employed the geometrical relations $k'_a = k'_\xi - \xi_p$ and $k''_a = k''_\xi - 2\xi_p k'_\xi$ as well as the equilibrium condition in eq 51. It is found that all terms proportional to k''_ξ are canceled in eq 54 in a similar manner as terms involving k'_ξ were in the expression for $k_c H_0$ in eq 53.

The remaining constant k'_ξ may be determined from the equilibrium condition including terms proportional to H or by simply minimizing eq 54 with respect to k'_ξ and, as a result, we obtain

$$k'_\xi = \frac{2pqa_p/\pi l_B + 2p(\xi_p + 2d) - \xi_p(\gamma_{hb}a_p/kT - 2q)}{2p + \xi_p^2(d^2\epsilon_{chain}/d\xi^2)/kT + 2\gamma_{hb}a_p/kT - 4q} \qquad (55)$$

To quantitatively estimate k_c in eq 54 we now need a detailed expression for $\epsilon_{chain}(\xi)$. From statistical mechanical model calculations of the chain conformational free energy by Gruen[3,45] and by Ben-Shaul and co-workers,[4,46] it has been demonstrated that ϵ_{chain} has a minimum at some finite thickness of the monolayer, usually close to half the length of a fully extended aliphatic chain, and is sharply raised as the minimum value is receded. The simplest way to incorporate these physical aspects, but still completely sufficient for our present purposes, is to write ϵ_{ch} as a quadratic polynomial function, i.e.

$$\frac{\epsilon_{\text{chain}}}{kT} = \lambda(\xi - \xi_{\text{min}})^2 + \frac{\epsilon_{\text{chain}}^{\text{min}}}{kT} \tag{56}$$

where ξ_{min} is the value of ξ that minimizes eq 56 and $\epsilon_{\text{chain}}^{\text{min}} \equiv \epsilon_{\text{chain}}(\xi = \xi_{\text{min}})$. λ is a positive constant that is a measure of the steepness of the function, i.e., the minimum of eq 56 becomes increasingly well defined with increasing values of λ. This constant may be estimated, for instance, from the expressions for ϵ_{chain} provided by Gruen[45] for a C_{11} aliphatic chain giving $\lambda \approx 0.05$ Å^{-2}, the number of which is expected to be fairly independent of the number of carbons in an aliphatic chain. From eq 56, it follows

$$\frac{1}{kT}\frac{d^2\epsilon_{\text{chain}}}{d\xi^2} = 2\lambda \tag{57}$$

which may be inserted in eq 55.

k'_ξ according to eqs 55 and 57 is plotted versus λ in Figure 6, and we see that the former quantity rapidly decreases with increasing λ. For the expected value of $\lambda = 0.05$ Å^{-2}, we note that k'_ξ is of the order of magnitude of 1 Å and decreases with increasing ξ_p. Since $k'_a = k'_\xi - \xi_p$ and $\xi_p > k'_\xi$, a must increase with increasing curvature, i.e., the opposite trend as compared with monolayers formed by surfactants with rigid tails. This is a result of the tendency of chain conformational free energy to keep the monolayer thickness fairly constant as seen by the comparatively low values of k'_ξ.

In Figure 7, we have plotted the mean bending constant according to eqs 54, 55, and 57, and we note that it virtually coincides with the corresponding expression obtained for the special case of bending the surfactant monolayer at constant thickness ($k'_\xi = 0$), i.e.

$$\frac{k_c}{kT} = \frac{\kappa^{-1}}{2\pi l_B}\left(1 - \frac{2(p-q)}{pq}\right) + \frac{pq}{\pi l_B}(\xi_p + 2d) + \frac{p}{2a_p}(\xi_p + 2d)^2 \tag{58}$$

Notably, neither of the contributions due to the hydrophobic effect (including γ_{hb}) or chain conformational entropy, but only electrostatics, contributes to the appearance of eq 58. However, detailed model calculations have shown that strong steric headgroup repulsions dramatically reduces k_c.[10] From eq 58 it becomes clear that this effect is mainly a result of a decreased $\xi_p = v/a_p$ with increasing headgroup cross-section area.

The mean bending constant according to eq 58 is plotted in Figure 3 together with k_c as calculated from a detailed model.[10] Since an explicit curvature dependence proportional to H^2 for the chain conformational free energy contribution were included in those calculations, k_c becomes somewhat lower than expected from eq 58. Moreover, it is seen that k_c dramatically increases in magnitude with increasing ξ_p corresponding to an increasing aliphatic chain length of the surfactant tail [cf. Figure 7]. As a matter of fact, a significant increase in rigidity of surfactant layers in e.g. microemulsions and wormlike micelles with increasing surfactant tail length has been observed with a number of different experimental techniques.[27]

The rigidities given in Figure 7 are the minimized values valid for an equilibrated surfactant monolayer. For a thermodynamically closed film k_c is expected to be significantly larger mainly as a result of large magnitudes of k_c^{chain}. For instance, k_c^{chain} was found from detailed model calculations to be close to 40 kT at $a = 30$ Å^2 for a monolayer bent with the constraint of fixed number of surfactants.[22]
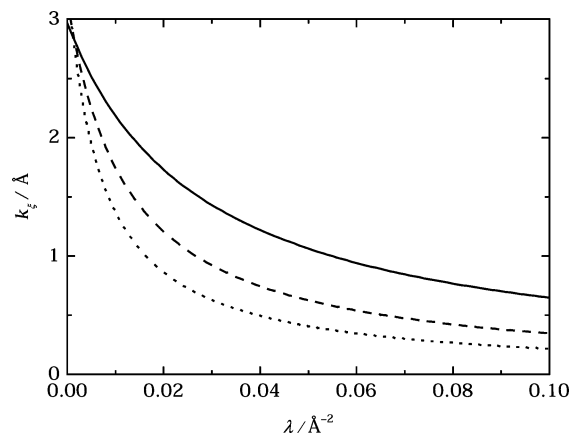

Figure 6. k'_ξ according to eqs 55 and 57 plotted against λ for $\xi_p = 10$ Å (solid line), $\xi_p = 15$ Å (dashed line), and $\xi_p = 20$ Å (dotted line). p and q were set equal to unity corresponding to $S_p \gg 1$. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.

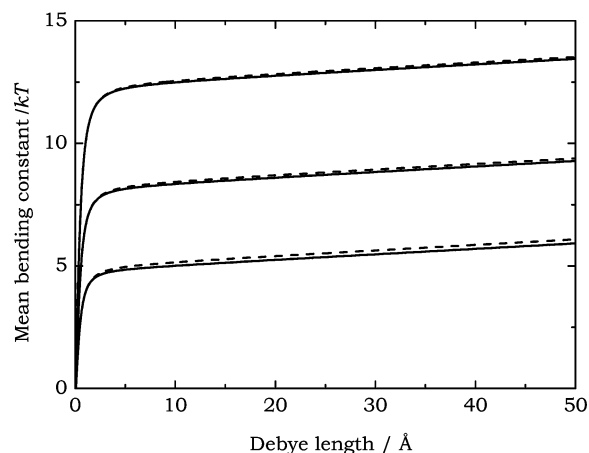**Figure 7.** Mean bending constant (k_c) in accordance with eqs 54, 55, and 57 with $\lambda = 0.05$ Å^{-2} (solid lines) as well as according to eq 58 (dashed lines) plotted against the Debye length (κ^{-1}) for $\xi_p = 10$ Å (lower lines), $\xi_p = 15$ Å (middle lines), and $\xi_p = 20$ Å (upper lines). γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.

Gaussian Bending Constant. The overall Gaussian bending constant may be obtained by summing up eqs 9, 37, and 49, i.e.

$$\frac{\bar{k}_c}{kT} = -\frac{\kappa^{-1}}{\pi l_B}D_1\left(\ln\left(\frac{\pi l_B \kappa^{-1}}{a_p q}\right)\right) - \frac{2d}{\pi l_B}\ln\left(\frac{\pi l_B \kappa^{-1}}{a_p q}\right)$$
$$-\left(\frac{\gamma_{\text{hb}}}{kT} - \frac{2q}{a_p}\right)\frac{\xi_p^2}{3} - \frac{2q}{a_p}d^2 \tag{59}$$

where we have set $S_p = 2\pi l_B/a_p\kappa$ and $k'''_\xi = k'''_\xi + \xi_p^2/3$ as well as employed the equilibrium condition in eq 51. It is found that all terms including k'''_ξ have been canceled and, as a result, eq 59 is identical to the expression obtained when setting $k'''_\xi = 0$ in eq 38, valid for monolayers bent at constant layer thickness. In Figure 4, it is shown that the magnitude of the always negative $\bar{k}_c$ becomes larger for monolayers composed of surfactants with a flexible hydrophobic tail.

The Gaussian bending constant according to eq 59 is plotted in Figure 8 against the Debye length for some different layer thicknesses and $\bar{k}_c$ is seen to decrease, i.e. becoming increasingly negative, with increasing layer thickness. We also expect eq 59 to become modified as steric headgroup repulsion effects are introduced. Additional positive terms proportional to $\xi_p^2/3$ must then be present, implying that $\bar{k}_c$ increases with increasing
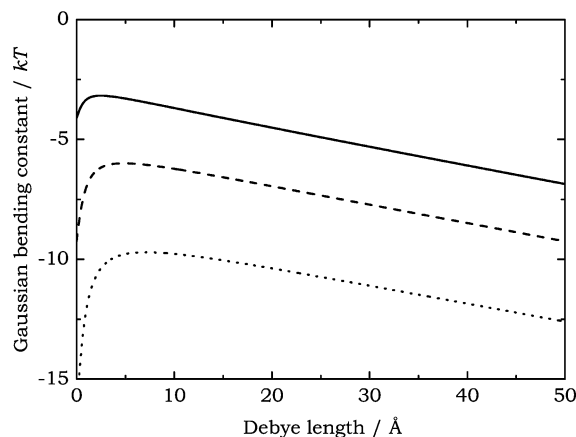
Figure 8. Gaussian bending constant ($\bar{k}_c$) plotted against the Debye length (κ^{-1}) in accordance with eq 59 for $\xi_p = 10$ Å (solid line), $\xi_p = 15$ Å (dashed line), and $\xi_p = 20$ Å (dotted line). γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.
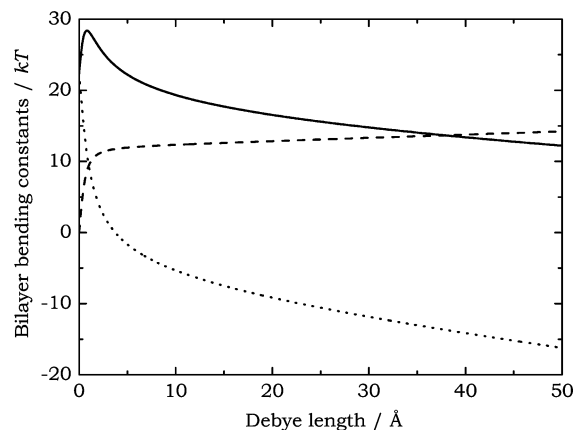

Figure 9. Bilayer bending constant $k_{bi} = 2k_c^{bi} + \bar{k}_c^{bi}$ (solid line), k_c^{bi} (dashed line), and $\bar{k}_c^{bi}$ (dotted line) for a bilayer composed of an ionic surfactant with flexible tail plotted against the Debye length (κ^{-1}) for $\xi_p = 11.7$ Å. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.

headgroup repulsion in agreement with results according to recent model calculations.[10]

From eq 59 we also see that $\bar{k}_c$ is expected to strongly decrease with increasing interfacial tension γ_{hb} for the case of surfactants with flexile tails, i.e., a much more pronounced dependence on γ_{hb} than expected for surfactants with rigid tails [cf. eq 46].

7. Bending Elasticity Constants for Bilayers Formed by a Monovalent Ionic Surfactant

We have already seen that it is straightforward to calculate the free energy of a single surfactant aggregate from the Helfrich expression in eq 1 by means of carrying out the integration in eq 5. It becomes particularly simple if the aggregate is composed of geometrical parts with uniform curvatures since we then only need to multiply γ in eq 1 with the overall interfacial area of the aggregate for each geometrical part.[10] In this manner, an arbitrarily curved surfactant bilayer may be regarded as composed of two monolayers the mean curvatures of which have opposite signs. Moreover, since coupling effects between two charged monolayers in a bilayer have been proven to be negligibly small at such large surface charge densities that is provided by ionic surfactants,[14] we may write the free energy of a single bilayer as the sum of contributions from the two monolayers. As a result, the free energy per unit area of the bilayer may be written in the form of a Helfrich-expression, i.e.

$$\gamma_{bi}(H,K) = \gamma_0^{bi} + 2k_c^{bi}(H - H_0^{bi})^2 + \bar{k}_c^{bi}K \qquad (60)$$

where the bending elasticity constants for the bilayer may be expressed in terms of the corresponding constants for a single monolayer, i.e., $k_c^{bi} = 2k_c$, $\bar{k}_c^{bi} = 2\bar{k}_c - 8\xi_p k_c H_0$ and $H_0^{bi} = 0$.[22,40,47] Accordingly, we may easily obtain expressions for k_c^{bi} and $\bar{k}_c^{bi}$ for the various cases treated above. For instance, an expression of the Gaussian bending constant for the case of an equilibrated bilayer formed by a monovalent ionic surfactant with flexible chain may be derived from eqs 53 and 59 so as to give

$$\frac{\bar{k}_c^{bi}}{kT} = -\frac{2\kappa^{-1}}{\pi l_B}D_1\left(\ln\left(\frac{\pi l_B \kappa^{-1}}{a_p q}\right)\right) - \frac{4(\xi_p + d)}{\pi l_B}\ln\left(\frac{\pi l_B \kappa^{-1}}{a_p q}\right)$$
$$+ \frac{4\xi_p^2}{3}\left(\frac{\gamma_{hb}}{kT} - \frac{2q}{a_p}\right) - \frac{4qd}{a_p}(2\xi_p + d) \qquad (61)$$

We may note that, in addition to the negative terms originating from the expression for $\bar{k}_c$ of a monolayer, an always positive term ($= 4\gamma_{hb}\xi_p^2/3kT$) due to the monolayer spontaneous curvature in eq 53 is present in eq 61. In accordance, $\bar{k}_c^{bi}$ may occasionally assume positive values provided γ_{hb} and ξ_p assume sufficiently large values. Notably, all terms in eq 61 are of the same order of magnitude equal to a few kT units.

Furthermore, it is well-known that the curvature free energy of a geometrically closed spherical bilayer vesicle assumes a constant value equal to $4\pi k_{bi}$,[48,49] where the effective bilayer bending constant k_{bi} is defined as

$$k_{bi} \equiv 2k_c^{bi} + \bar{k}_c^{bi} = 2(2k_c + \bar{k}_c - 4\xi_p k_c H_0) \qquad (62)$$

In Figure 9, we have plotted k_{bi}, together with k_c^{bi} and $\bar{k}_c^{bi}$, according to eqs 58, 61, and 62. It is seen that k_{bi} has a maximum at some very short Debye length ($\kappa^{-1} \approx 1$ Å) and deceases with increasing κ^{-1} above this maximum value whereas $\bar{k}_c^{bi}$ rapidly decreases from positive to negative values with increasing Debye length. The size of bilayer vesicles is directly related to k_{bi}, and from the behavior in Figure 9, we expect that the vesicle size increases with increasing electrolyte concentration (decreasing Debye length) as well as with increasing surfactant tail length.[25] Moreover, the positive values of $\bar{k}_c^{bi}$ below about $\kappa^{-1} = 4$ Å indicate that a transition from a conventional lamellar phase of planar bilayers to a bicontinuous minimal surface structure may be generated at high electrolyte concentrations.

The bilayer bending constant for surfactants with rigid tails may likewise be deduced from eqs 42, 45, and 46. Since the magnitude of k_c is close to zero whereas $k_c H_0$ is large and positive, k_{bi} becomes negative with a comparatively large magnitude [cf. Figure 10]. It has previously been demonstrated that vesicles formed as k_{bi} assumes negative values are stabilized by higher order terms in the Helfrich expression. As a result, these vesicles must be very small, i.e., in the same order of magnitude as the bilayer thickness.[25] As a matter of fact, the comparatively large values of $k_c H_0$ indicate that rather small micelles, with a large curvature, is preferentially formed by ionic surfactants with rigid tails.

(47) Ljunggren, S.; Eriksson, J. C. *Langmuir* **1992**, *8*, 1300.

(48) Helfrich, W. *J. Phys. France* **1986**, *47*, 321−329.
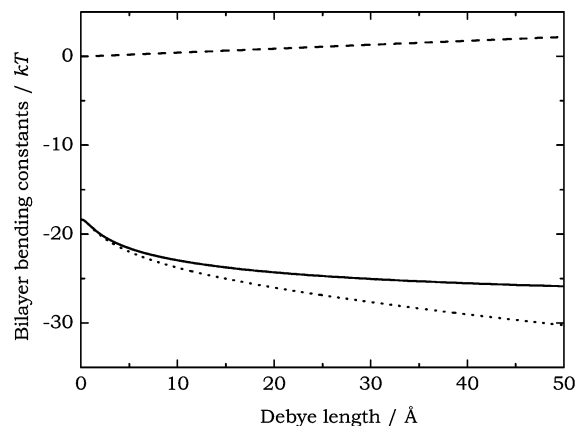(49) Bergström, M.; Eriksson, J. C. *Langmuir* **1996**, *12*, 624−634.

Figure 10. Bilayer bending constant $k_{bi} = 2k_c^{bi} + \bar{k}_c^{bi}$ (solid line), k_c^{bi} (dashed line), and $\bar{k}_c^{bi}$ (dotted line) for a bilayer composed of an ionic surfactant with rigid tail plotted against the Debye length (κ^{-1}) for $\xi_p = 11.7$ Å. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.
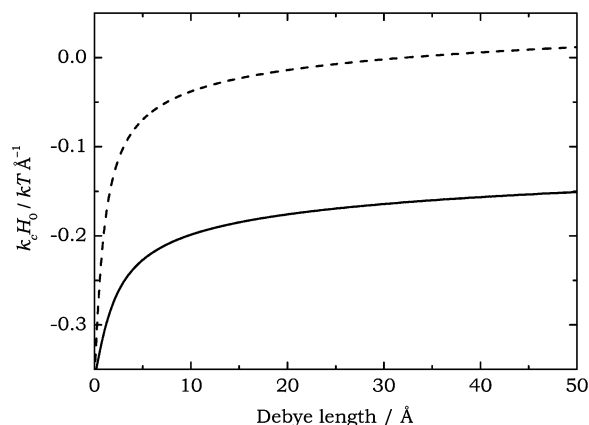

Figure 11. Mean bending constant multiplied with the spontaneous curvature (k_cH_0) in accordance with eq 53 as a function of the Debye length (κ^{-1}) for $\xi_p = 11.7$ Å. a_p was set equal to 60 Å (solid line), which corresponds to a double-chain surfactant, and $a_p = 30$ Å (dashed line) corresponding to a single-chain surfactant. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.

8. Bending Elasticity Constants for Monolayers and Bilayers Formed by a Double-Chain Ionic Surfactant

The equations derived above are valid for any monovalent ionic surfactant regardless of the number of chains that are attached to each headgroup. Nevertheless, the final values of the bending elasticity constants are expected to be influenced by the detailed architecture of the surfactant since a_p is largely dependent on, for instance, the number of tails. For a surfactant with two identical flexible chains, a_p approximately equals twice the value of the corresponding single-chain surfactant. The reason for this is that a_p to a large extent is determined by chain conformational entropy effects and, as a result, depends only slightly on surface charge density and electrolyte concentration as confirmed by detailed model calculations.[10,49,50]

As a result, the various bending elasticity constants for the case of double-chain surfactants may be obtained from eqs 53, 58, and 59, respectively, by simply setting a_p(double-chain) = $2a_p$(single-chain). In Figures 11−13, we have plotted k_cH_0, k_c, and $\bar{k}_c$ vs the Debye length for monolayers formed by an ionic single as well as a double-chain surfactant. We note that k_cH_0 is significantly reduced for a double-chain surfactant which is
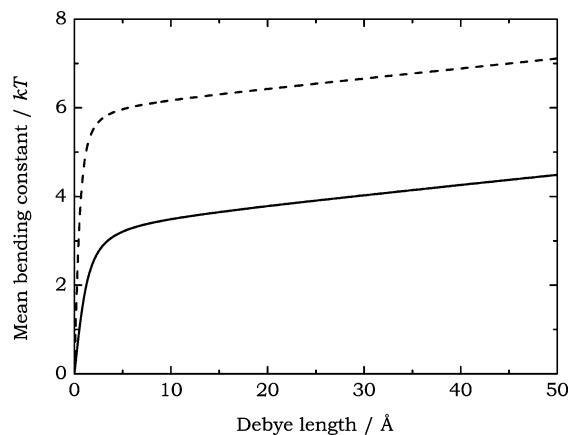
(50) Bergström, M. *Langmuir* **1996**, *12*, 2454−2463.

Figure 12. Mean bending constant (k_c) in accordance with eq 58 plotted against the Debye length (κ^{-1}) for $\xi_p = 11.7$ Å. a_p was set equal to 60 Å (solid line), which corresponds to a double-chain surfactant, and $a_p = 30$ Å (dashed line), corresponding to a single-chain surfactant. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.
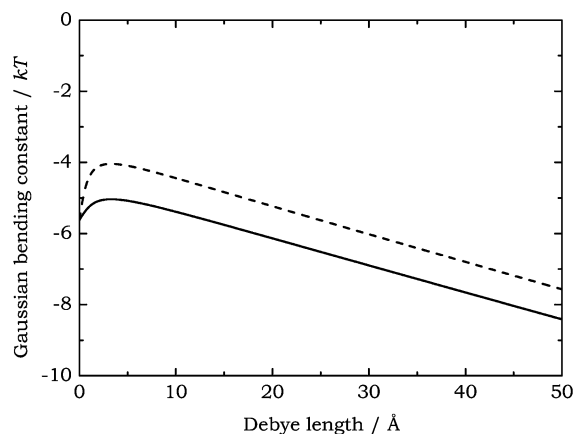

Figure 13. Gaussian bending constant ($\bar{k}_c$) in accordance with eq 59 plotted against the Debye length (κ^{-1}) for $\xi_p = 11.7$ Å. a_p was set equal to 60 Å (solid line), which corresponds to a double-chain surfactant, and $a_p = 30$ Å (dashed line), corresponding to a single-chain surfactant. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.

consistent with the well-known experimental fact that double-chain surfactants, such as biological phospholipids, form comparatively large aggregates with low curvature [cf. Figure 11]. The mean bending constant is found to be substantially lower for a double-chain surfactant [Figure 12] whereas the Gaussian bending constant is slightly reduced; that is, it becomes more negative than for the corresponding single-chain surfactant [Figure 13]. The latter effect is a consequence of the reduction of the term proportional to $\xi_p^2/3$ in eq 59 as a_p is raised.

Figure 14 shows the bilayer bending constant $k_{bi} = 2(2k_c + \bar{k}_c - 4\xi_p k_cH_0)$ for bilayers formed by a double-chain surfactant. k_{bi} is found to be slightly higher than for the corresponding single-chain surfactant at Debye lengths larger than about 2 Å, although it is indicated by the values of k_cH_0 that the latter type of surfactant preferentially forms structures with a high spontaneous curvature rather than bilayers with $H \approx 0$. We also note that the bilayer Gaussian bending constant $\bar{k}_c^{bi}$ assumes negative values at large Debye lengths that switches to positive values below about $\kappa^{-1} = 37$ Å for the particular case shown in Figure 14. Hence, we expect the double-chain surfactant to possess a larger tendency of forming bicontinuous bilayer phases at small Debye lengths than the corresponding single-chain surfactant.
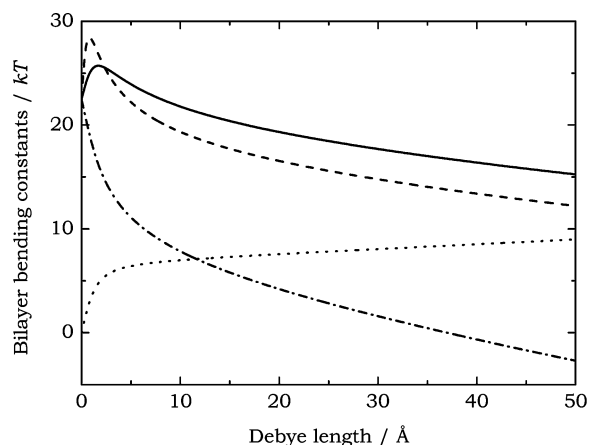
Figure 14. Bilayer bending constant $k_{bi} = 2k_c^{bi} + \bar{k}_c^{bi}$ for a bilayer composed of an ionic surfactant with flexible tail plotted against the Debye length (κ^{-1}) for $\xi_p = 11.7$ Å. a_p was set equal to 60 Å (solid line), which corresponds to a double-chain surfactant, and $a_p = 30$ Å (dashed line) corresponding to a single-chain surfactant. We have also included k_c^{bi} (dotted line) and $\bar{k}_c^{bi}$ (dash−dotted line) for a bilayer composed of a double-chain ionic surfactant. γ_{hb}, a_p, and l_B assume the same values as given in Figure 5.

9. Summary

Recently, it has been demonstrated that geometrical packing constraints may have a profound influence on the bending properties of surfactant mono- and bilayers.[42] In the present paper, we have utilized the general expressions derived in ref 42, together with the Poisson−Boltzmann (PB) theory of charged surfaces immersed in an aqueous solvent, to evaluate the bending elasticity constants for films formed by a single monovalent ionic surfactant with either rigid or flexible tail. As a result, we were able to investigate the effect of layer thickness on the bending properties of charged surfactant films. We demonstrate that explicit contributions, in addition to the conventional expressions for each of the bending elasticity constants k_cH_0, k_c, and $\bar{k}_c$ as obtained for an infinitely thin surface, appear as a result of the surfactant layer having a finite thickness.

For an infinitely thin surface, only electrostatics as derived from the PB theory contributes to the bending elasticity constants, and it is found that the spontaneous curvature H_0 and the mean bending constant k_c both are positive quantities, whereas the Gaussian bending constant $\bar{k}_c$ always assumes negative values. The magnitudes of all bending elasticity constants increase with increasing Debye screening length corresponding to a decreasing electrolyte concentration.

Most interestingly, the finite thickness effects are found to be largely dependent on whether chain conformational entropy is included in the calculations (surfactants with flexible chains) or not (surfactants with rigid tails). In the latter case, where only the hydrophobic effect and electrostatics have been taken into account in the treatment, k_cH_0 is found to increase as compared to an infinitely thin layer whereas k_c and $\bar{k}_c$ both decrease only slightly. On the other hand, just from the fact that the chain conformational free energy contribution foremost depends on layer thickness, and only indirectly on the area per surfactant, finite thickness effects are found to have a large impact on the bending elasticity constants for surfactants with flexible chains. As a matter of fact, the resulting expressions for each of k_cH_0 and $\bar{k}_c$ exactly coincide, whereas k_c virtually coincides, with the case of bending the surfactant layer at constant layer thickness. All bending elasticity constants become largely dependent on layer thickness: k_cH_0 decreases, k_c increases, and $\bar{k}_c$ becomes increasingly negative with increasing layer thickness in agreement

with experimental observations. The considerable increase of k_c as chain conformational entropy effects are taken into account enables us to conclude that layers or aggregates composed of a single ionic surfactant with a flexible tail must be comparatively rigid structures with large persistence lengths, for which thermal undulations are expected to be of less importance.

In addition to the large influence on the bending elasticity constants that chain conformational entropy may have, we also found that k_cH_0, k_c, and $\bar{k}_c$ all depend in a very different manner on the hydrophobic−hydrophilic interfacial tension γ_{hb}, depending on whether the surfactant has a rigid or flexible tail. γ_{hb} is found to have a stronger influence on k_cH_0 and $\bar{k}_c$ in the latter case and it is even demonstrated that k_cH_0 decreases with increasing γ_{hb} in the case of flexible tails whereas the opposite trend holds true for a surfactant with rigid tail. As a matter of fact, these dramatic effects on the bending properties of surfactant layers imposed by the presence of physical processes that take place in the interior of the hydrocarbon part of a layer of finite thickness, rather than at the surface, clearly demonstrates that it is not possible to incorporate the corresponding free energy contribution in a single interfacial tension parameter as has frequently been done, for instance, in the dressed micelle model.[51]

The location of the surface of charge at a distance d outside the hydrophobic−hydrophilic interface enhances the finite thickness effects on k_c and $\bar{k}_c$ the magnitudes of which increases with increasing d. Likewise, k_cH_0 was found to become considerably raised as d increases. It is also found that each of the constants k_cH_0, k_c, and $\bar{k}_c$ are reduced for monolayers composed of a double-chain surfactant as compared to the corresponding single-chain surfactant monolayer.

The bending properties of bilayers were also investigated, and it was found that the curvature energy in terms of the effective bilayer bending constant $k_{bi} = 2k_c^{bi} + \bar{k}_c^{bi}$ is raised as a result of finite thickness effects to large positive values for surfactants with flexible tails, whereas k_{bi} becomes negative for bilayers composed of surfactants with rigid tails. The large negative values of k_{bi}, as well as high positive values of k_cH_0, in the latter case, strongly suggests that surfactants with rigid tails preferentially form small micelles rather than large bilayer structures. As a matter of fact, a pronounced flexibility of the tails of amphiphilic molecules appears to be a prerequisite for the formation of stable bilayer structures such as biological lipid membranes. Moreover, the Gaussian bilayer bending constant $\bar{k}_c^{bi}$ for single-chain surfactants may assume positive values only at some very small Debye lengths whereas the change from negative to positive values was seen to occur at much larger κ^{-1} values for bilayers composed of a double-chain surfactant, indicating that the latter has a stronger tendency to form some kind of bicontinuous bilayer structure rather than planar membranes at high electrolyte concentrations.

Appendix A. Derivation of the Electrostatic Contribution to the Bending Elasticity Constants from the Poisson−Boltzmann Theory

Consider a surfactant film consisting of a hydrophobic innershell with the charged headgroups located on a surface somewhat outside the hydrophobic−hydrophilic interface [cf. Figure 1]. By means of changing variables from H_{el} and K_{el}, defined at the surface of charge, to H and K defined at the hydrophobic−hydrophilic interface eq 20 may be rewritten as

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(51) Evans, D. F.; Wennerström, H. *The Colloidal Domain*; Wiley-VCH: New York, 1994; Chapter 4.

$$\frac{\epsilon_{el}}{kT} = g_0 + g_1 H + g_2 H^2 + g_3 K \qquad (A1)$$

Setting eqs 20 and A1 equal to one another for a planar surface ($H_{el} = K_{el} = H = K = 0$) immediately gives $g_0 = h_0$. Likewise, inserting the proper values for cylindrical geometry, $H = 1/2R$, $H_{el} = 1/2R_{el}$, and $K = K_{el} = 0$ in eqs 20 and A1, as well as multiplying with R_{el}^2, gives

$$R_{el}^2 h_0 + \frac{h_1}{2} R_{el} + \frac{h_2}{4} = R_{el}^2 g_0 + \frac{g_1}{2} \frac{R_{el}^2}{R} + \frac{g_2}{4} \frac{R_{el}^2}{R^2} \quad (A2)$$

where R and R_{el} are the radial distances to the hydrophobic−hydrophilic interface and the surface of charge, respectively. Equation A2 may be rewritten so as to yield

$$h_1 R + h_1 d + \frac{h_2}{2} =$$
$$g_1 R + g_1 2d + \frac{g_2}{2} + \frac{g_1 d^2 + g_2 d}{R} + \frac{g_2 d^2}{2R^2} \quad (A3)$$

where $d = R_{el} - R$. $g_1 = h_1$ and

$$g_2 = h_2 - 2dh_1 = \frac{2}{\kappa^2 S}\left(1 - \frac{2}{S^2} + \frac{2}{S^2\sqrt{S^2+1}}\right) + \frac{8d}{\kappa S}\ln\left(\frac{1+\sqrt{S^2+1}}{2}\right) \qquad (A4)$$

may now be identified from eq A3, where the last equality in eq A4 follows from the definitions of h_1 and h_2 in eqs 22 and 23, respectively. Repeating the same procedure for spherical geometry ($H = 1/R$, $K = 1/R^2$ and $H_{el} = 1/R_{el}$, $K_{el} = 1/R_{el}^2$) gives

$$h_1 R + h_1 d + h_2 + h_3 = g_1 R + g_1 2d + g_2 + g_3 + \frac{g_1 d^2 + 2d(g_2 + g_3)}{R} + \frac{(g_2 + g_3)d^2}{R^2} \qquad (A5)$$

and by means of combining eqs A4 and A5 we may identify $g_1 = h_1$ as well as

$$g_3 = h_3 + dh_1 = -\frac{2}{\kappa S}\left[\kappa^{-1}D_1\left(\ln\left(\frac{1+\sqrt{S^2+1}}{2}\right)\right) + 2d\ln\left(\frac{1+\sqrt{S^2+1}}{2}\right)\right] \quad (A6)$$

from the definitions of h_1 and h_3 in eqs 22 and 24.

A comparison between eqs 12 and A1 enables us to identify $g_0 = \epsilon_{el}^p/kT$. It is, however, important to stress that the coefficients g_1, g_2, and g_3, in contrast to the corresponding coefficients in eq 12, are not true constants with respect to H and K. This immediately follows since g_1, g_2, and g_3 are all functions of the reduced charge density S which depends strongly on curvature. As a consequence, we may write

$$S(H,K) = S_p(1 + k'_S H + k''_S H^2 + k'''_S K) \qquad (A7)$$

where $S_p = 2\pi l_B/\kappa a_p$ is the reduced charge density for a strictly planar surface and k'_S, k''_S, and k'''_S are constants with respect to H and K.

It now follows from eq A1 that

$$\frac{1}{kT}\left(\frac{\partial\epsilon_{el}}{\partial H}\right)_K = \frac{1}{kT}\frac{d\epsilon_{el}}{dS}\left(\frac{\partial S}{\partial H}\right)_K = \frac{dh_0}{dS}\left(\frac{\partial S}{\partial H}\right)_K + h_1 \quad (A8)$$

$$\frac{1}{kT}\left(\frac{\partial^2\epsilon_{el}}{\partial H^2}\right)_K = \frac{1}{kT}\frac{d^2\epsilon_{el}}{dS^2}\left(\frac{\partial S}{\partial H}\right)_K^2 + \frac{1}{kT}\frac{d\epsilon_{el}}{dS}\left(\frac{\partial^2 S}{\partial H^2}\right)_K$$
$$= \frac{d^2 h_0}{dS^2}\left(\frac{\partial S}{\partial H}\right)_K^2 + \frac{dh_0}{dS}\left(\frac{\partial^2 S}{\partial H^2}\right)_K + 2\frac{dh_1}{dS}\left(\frac{\partial S}{\partial H}\right)_K + 2h_2 - 4dh_1 \qquad (A9)$$

$$\frac{1}{kT}\left(\frac{\partial\epsilon_{el}}{\partial K}\right)_H = \frac{1}{kT}\frac{d\epsilon_{el}}{dS}\left(\frac{\partial S}{\partial K}\right)_H = \frac{dh_0}{dS}\left(\frac{\partial S}{\partial K}\right)_H + h_3 + dh_1 \quad (A10)$$

where we have employed the relations $g_0 = h_0$, $g_1 = h_1$, $g_2 = h_2 - 2dh_1$, and $g_3 = h_3 + dh_1$ already demonstrated above. From eqs 21 and 22, it follows

$$\frac{dh_0}{dS} = 2\frac{\sqrt{S^2+1}-1}{S^2} \qquad (A11)$$

$$\frac{d^2 h_0}{dS^2} = \frac{2}{S}\left(\frac{1}{\sqrt{S^2+1}} - \frac{dh_0}{dS}\right) \qquad (A12)$$

$$\frac{dh_1}{dS} = -\frac{4}{\kappa\sqrt{S^2+1}(\sqrt{S^2+1}+1)} - \frac{h_1}{S} \quad (A13)$$

whereas

$$\left(\frac{\partial S}{\partial H}\right)_K[H = K = 0] = S_p k'_S \qquad (A14)$$

$$\left(\frac{\partial^2 S}{\partial H^2}\right)_K[H = K = 0] = 2S_p k''_S \qquad (A15)$$

$$\left(\frac{\partial S}{\partial K}\right)_H[H = K = 0] = S_p k'''_S \qquad (A16)$$

follows directly from eq A7. By means of employing eqs A11−A16, we may now rewrite eqs A8−A10 so as to give

$$\frac{1}{kT}\left(\frac{\partial\epsilon_{el}}{\partial H}\right)_K[H = K = 0] = 2qk'_S - \frac{4}{\kappa S_p}\ln\left(\frac{S_p}{2q}\right) \quad (A17)$$

$$\frac{1}{kT}\left(\frac{\partial^2\epsilon_{el}}{\partial H^2}\right)_K[H = K = 0] = 2pk'^2_S + 4q(k''_S - k'^2_S) - \frac{8pq}{\kappa S_p}k'_S$$
$$+ \frac{8}{\kappa S_p}\ln\left(\frac{S_p}{2q}\right)(k'_S + 2d) + \frac{4}{(\kappa S_p)^2}\left(S_p - \frac{2pq}{S_p}\right) \qquad (A18)$$

$$\frac{1}{kT}\left(\frac{\partial\epsilon_{el}}{\partial K}\right)_H[H = K = 0] = 2qk'''_S - \frac{2S_p}{(\kappa S_p)^2}D_1\left(\ln\left(\frac{S_p}{2q}\right)\right)$$
$$- \frac{4d}{\kappa S_p}\ln\left(\frac{S_p}{2q}\right) \qquad (A19)$$

where p and q are defined in eqs 31 and 32.

The constants k'_S, k''_S, and k'''_S defined in eq A7, may be further investigated for a one-component surfactant layer formed by a

monovalent ionic surfactant, by means of writing the reduced charge density as

$$S(H,K) = \frac{2\pi l_B}{\kappa a_{el}} = \frac{2\pi l_B}{\kappa a}\frac{a}{a_{el}} \qquad (A20)$$

where the ratio between the area per surfactant at the surface of charge a_{el} and the corresponding quantity a defined at the hydrophobic−hydrophilic interface depends on curvature in the following manner:

$$\frac{a_{el}}{a} = 1 + 2dH + d^2K \qquad (A21)$$

The combination of eqs 6, A7, A20, and A21 enables the identification of the following relations:

$$k'_S = k'_a - 2d \qquad (A22)$$

$$k''_S = k''_a - 2dk'_a + 4d^2 \qquad (A23)$$

$$k'''_S = k'''_a - d^2 \qquad (A24)$$

which may be inserted in Eqs. A17-A19 to finally give

$$\frac{1}{kT}\left(\frac{\partial \epsilon_{el}}{\partial H}\right)_K[H = K = 0] = 2(k'_a - 2d)q - \frac{2a_p}{\pi l_B}\ln\left(\frac{S_p}{2q}\right) \quad (A25)$$

$$\frac{1}{kT}\left(\frac{\partial^2 \epsilon_{el}}{\partial H^2}\right)_K[H = K = 0] = 2(k'_a - 2d)^2p - 4(k'_a - 2d)k'_aq$$

$$+ 4k''_aq - \frac{4a_p}{\pi l_B}\left[(k'_a - 2d)pq - k'_a\ln\left(\frac{S_p}{2q}\right) - \frac{a_p}{4\pi l_B}\left(S_p - \frac{2pq}{S_p}\right)\right] \quad (A26)$$

$$\frac{1}{kT}\left(\frac{\partial \epsilon_{el}}{\partial K}\right)_H[H = K = 0] = 2(k'''_a - d^2)q$$

$$- \frac{a_p}{\pi l_B}\left[\kappa^{-1}D_1\left(\ln\left(\frac{S_p}{2q}\right)\right) + 2d\ln\left(\frac{S_p}{2q}\right)\right] \quad (A27)$$

Appendix B. List of Symbols

a = area per aggregated surfactant at the hydropbobic-hydrophilic interface

a_{el} = area per aggregated surfactant at the surface of charge

a_p = area per aggregated surfactant for a planar monolayer

d = distance between the hydrophobic−hydrophilic interface and the surface of charge

$D_1(x)$ = Debye function

e_{el} = elementary charge

H = mean curvature at the hydrophobic−hydrophilic interface

H_{el} = mean curvature at the surface of charge

H_0 = spontaneous curvature

k = Boltzmann's constant

K = Gaussian curvature at the hydrophobic−hydrophilic interface

K_{el} = Gaussian curvature at the surface of charge

k_{bi} = bilayer bending constant

k_c = mean bending constant of a monolayer

k_c^{bi} = mean bending constant of a bilayer

$\bar{k}_c$ = Gaussian bending constant of a monolayer

$\bar{k}_c^{bi}$ = Gaussian bending constant of a bilayer

k'_a, k''_a, and k'''_a = constants related to the curvature dependence of a as defined in eq 6

k'_ξ, k''_ξ and k'''_ξ = constants related to the curvature dependence of ξ as defined in eq 11

l_B = Bjerrum length

p = parameter related to S_p and defined in eq 31

q = parameter related to S_p and defined in eq 32

S = reduced surface charge density

S_p = reduced surface charge density for a planar monolayer

T = absolute temperature

υ = volume of the surfactant hydrophobic tail

z = charge number

ϵ = free energy per surfactant aggregated in a monolayer

ϵ_{chain} = chain conformational contribution to ϵ

ϵ_{el} = electrostatic contribution per charge to ϵ

ϵ_0 = permittivity in a vacuum

ϵ_r = dielectric constant

κ = inverse of the Debye screening length

λ = parameter related to the quadratic behavior of ϵ_{chain} as defined in eq 56

γ_{hb} = hydrophobic−hydrophilic interfacial tension

ξ = monolayer thickness

ξ_p = thickness of a planar monolayer