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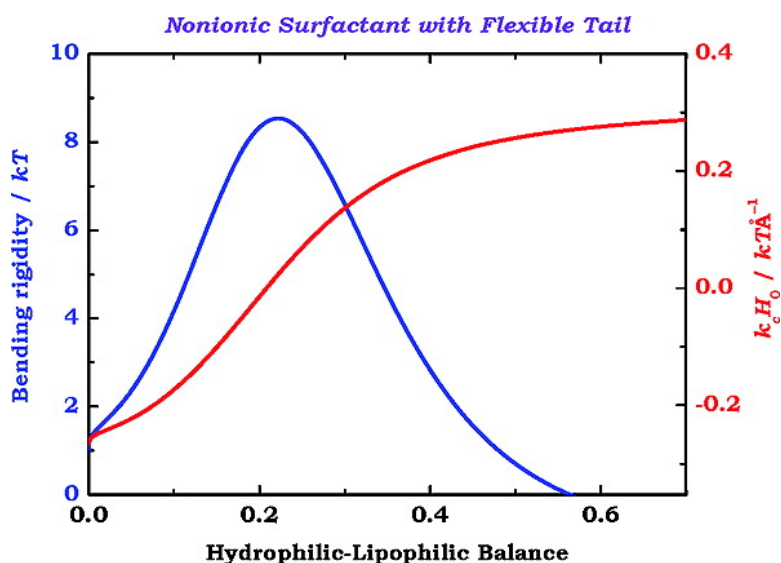
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# Bending Elasticity of Nonionic Surfactant Layers

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A novel approach to evaluate the bending elasticity of monolayers formed by nonionic surfactants with a rigid head group is introduced by means of considering head group repulsion as derived from the free energy of mixing rigid hydrophilic head groups with surrounding solvent molecules as well as contributions related to the hydrophobic tails. Explicit expressions for the spontaneous curvature ( $H_0$ ), bending rigidity ( $k_c$ ) and saddle-splay constant ( $\bar{k}_c$ ) have been derived for the constraint of constant chemical potential of free surfactant (thermodynamically open layers) as well as the constraint of constant aggregation number (thermodynamically closed layers). Most interestingly, it is demonstrated that  $k_c$  for thermodynamically open layers formed by a nonionic surfactant with rigid tail and head group always must be zero. However,  $k_c$  for surfactants with a flexible tail as a function of the head group-to-tail volume ratio is found to go through a maximum at some large, positive value of  $k_c$  and  $H_0 \approx 0$ . Eventually,  $k_c$  falls below zero as the head group volume increases above a certain value. Hence, we may conclude that nonionic surfactants with a rigid head group may form thermodynamically stable fluid layers or aggregates only insofar the hydrophobic part is flexible with respect to chain conformational degrees of freedom and the head group is not too voluminous. It is found that the head group repulsion contribution to  $k_c H_0$  is always positive whereas the corresponding contribution to  $\bar{k}_c$  may be positive or negative depending on whether the hydrophobic layer of the film is thicker or thinner than the hydrophilic layer.

## 1. Introduction

Amphiphilic molecules (surfactants, lipids, block copolymers, etc.) are composed of a hydrophilic and a hydrophobic part. In addition to the options available for conventional noncomposed substances that are dissolved in a solvent (i.e., forming a homogeneous nearly ideal mixture or separating into two distinct phases), amphiphilic molecules may also self-assemble to form a dispersion of thermodynamically stable aggregates. This may lead to the formation of structures with a conspicuously large variety with respect to size, shape, polydispersity and flexibility depending on molecular architecture and solution properties. Discrete aggregates such as rather small globular micelles, very long threadlike or wormlike micelles, or unilamellar vesicles have frequently been observed in dilute solutions whereas macroscopic aggregates arranged in a more or less ordered pattern make up lyotropic liquid-crystalline phases at high amphiphilic concentrations.<sup>1</sup>

The molecular architecture is of decisive importance for the aggregation behavior of surfactants in an aqueous solvent. The hydrophilic head groups may be charged (ionic surfactants) or uncharged (nonionic surfactants) and rigid or flexible whereas the hydrophobic tail is usually flexible for surfactants forming rather well-defined fluid structures, such as micelles or biological membranes. As a matter of fact, a flexible tail, such as an aliphatic hydrocarbon chain, seems to be a necessary prerequisite for nonionic surfactants with a rigid head group to self-assemble at all.

In recent years, it has become widely accepted that bending properties play a decisive role in the behavior of aggregates formed by the self-assembly of amphiphilic molecules. A quantitative description of the bending properties of surfactant films has been made possible by the introduction of the so-called

Helfrich expression<sup>2</sup>

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

which describes the free energy per unit area at a single point on the surface of a surfactant layer as an expansion to second order in mean and Gaussian curvatures:  $H \equiv 1/2(c_1 + c_2)$  and  $K \equiv c_1 c_2$ , respectively, where  $c_1$  and  $c_2$  are the principal curvatures at a single point on the surface.

The total free energy of a self-assembled interface may be obtained by integrating  $\gamma$  over the entire surface area of the film

$$E = \gamma_0 A + 2k_c \int_A (H - H_0)^2 dA + \bar{k}_c \int_A K dA \quad (2)$$

The first term in eq 2 is the free energy of stretching an interface with interfacial tension  $\gamma_0 \equiv \gamma(H = H_0, K = 0)$  to achieve a surface area  $A$  whereas the remaining two terms represent the work of bending the interface at constant  $A$ .

Three important parameters related to different aspects of bending a surfactant layer are introduced in eq 1—the spontaneous curvature ( $H_0$ ), the bending rigidity ( $k_c$ ), and the saddle-splay constant ( $\bar{k}_c$ ) and as a common notation, we refer to them as the bending elasticity constants.<sup>3,4</sup>

(i) The spontaneous curvature represents the sign and magnitude of the preferential curvature of a single surfactant layer. In the present work, we have defined  $H_0$  to be positive for a film that appears convexly curved from a position in the hydrophilic phase, such as ordinary surfactant micelles in water. It has recently been demonstrated that  $H_0$  is directly related to the transition between micelles and various bilayer structures.<sup>5</sup> Accordingly, micelles predominate as  $H_0 > (4\xi)^{-1}$ , where  $\xi$  is the monolayer thickness, whereas bilayers are expected to be present as  $H_0 < (4\xi)^{-1}$ .

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(ii) The bending rigidity quantifies the resistance against deviations from a uniform mean curvature  $H = H_0$ , which means that rigid and monodisperse objects with a uniform shape are expected to form at high values of  $k_c$  and more flexible, polydisperse, and geometrically heterogeneous structures may form at low values of  $k_c$ .<sup>3,5,6</sup> Most interestingly, the sign of  $k_c$  is a measure of the stability of an amphiphilic layer: stable layers may exist only for positive values of  $k_c$  when  $\gamma$ , according to eq 1, shows a minimum with respect to  $H$ .

(iii) The saddle-splay constant has the interesting property of largely influencing the topology of the surfactant layer (i.e., the number of handles or holes present in the interface) because it determines the sign and magnitude of the last term in eq 2. According to the Gauss–Bonnet theorem, the corresponding integral equals

$$\int_A K \, dA = 4\pi(1 - g) \quad (3)$$

where  $g$  is the number of handles or holes in the interface. For instance,  $g = 0$  for discrete aggregates formed by a geometrically closed surface, such as a micelle, and the integral in eq 3 then equals  $4\pi$ . Consequently, negative values of  $\bar{k}_c$  are expected to favor a collection of discrete aggregates with geometrically closed interfaces (micelles, vesicles, and microemulsion droplets) over connected structures (e.g., lamellar or hexagonal phases). Moreover, the quantity in eq 3 becomes negative for perforated or bicontinuous structures ( $g > 1$ ), which, as a consequence, must be favored by large, positive values of  $\bar{k}_c$ .<sup>3</sup>

The size distribution of a dilute dispersion of self-assembled interfaces may be derived by means of evaluating eq 2 for an appropriate geometrical shape. In accordance, we have in some recent papers investigated the thermodynamics and bending energetics of vesicles<sup>7</sup> and droplet microemulsions<sup>6</sup> as well as rodlike,<sup>8</sup> tablet-shaped,<sup>5</sup> and toruslike<sup>9</sup> micelles. It is found that the stretching free energy per molecule, as evaluated from eq 2, is constant whereas the bending free energy per molecule strongly decreases with increasing values of the aggregation number  $N$ . As a consequence, the concentration of free monomers (approximately equal to the critical aggregate concentration) is almost exclusively determined by the stretching free energy whereas the effect of bending becomes negligible in the limit of large  $N$  (i.e.,  $N \gg 1$ ). Likewise, as a result of the different behaviors with respect to  $N$ , the bending free energy largely determines the size and shape of self-assembled interfaces whereas the stretching free energy has no influence at all.

It has previously been demonstrated that the quantitative outcome of the bending elasticity constants largely depend on the constraints under which a surfactant layer is bent.<sup>10–12</sup> We may distinguish between two important cases: (i) surfactant layers for which the number of molecules is fixed during the process of bending (thermodynamically closed layers) and (ii) layers where molecules are exchanged with the surrounding environment (solvent) during the process of bending according to the constraint of constant chemical potentials (thermodynamically open layers). By considering the relevant latter case, equivalent to a system where full equilibrium with respect to all degrees of freedom has been achieved, the bending free energy is defined in a similar way as the conceptually related quantity of stretching free energy (equivalent to interfacial tension). It may be noted that in order

to treat thermodynamically open layers it is essential to take into account free energy contributions related to both heads and tails that may oppose one another in a balance yielding a minimum in molecular free energy with respect to the area per aggregated surfactant for a given curvature.<sup>12</sup>

Bending elasticity of (thermodynamically closed) nonionic surfactant layers has previously been investigated by means of considering the chain conformational free energy of flexible tails and head groups as calculated from a lattice model.<sup>13,14</sup> Moreover, Paunov et al. derived explicit expressions for the different bending elasticity constants for nonionic amphiphilic molecules with flexible head groups and tails by means of taking into account the free energy of mixing with solvent molecules as well as the elasticity free energy of the flexible chains.<sup>15</sup> In more general approaches, surfactant head groups have been modeled by means of considering pairwise interactions<sup>10,16</sup> whereas most attempts to calculate bending elasticity constants have been focused on charged amphiphilic layers,<sup>12,17–20</sup> occasionally including additional steric head group interactions.<sup>8,21</sup>

In accordance, we have recently derived relations that explicitly quantifies  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$  for a dilute dispersion (interaggregate interactions were neglected) of thermodynamically open layers with finite thickness formed by ionic surfactants in terms of molecular architecture, solution properties, and composition in a binary surfactant mixture for different cases of pure and mixed amphiphilic films.<sup>8,12,20</sup> The calculations were based on well-established contributions to the process of self-assembling amphiphilic molecules such as the Poisson–Boltzmann mean field theory for charged interfaces, the hydrophobic effect, and the conformational entropy of flexible hydrophobic chains. Accordingly, we demonstrated that  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$  are functions of molecular architecture (size and flexibility of the tail, charge number of the head group, etc.) as well as the Debye screening length, hydrophilic–hydrophobic interfacial tension, and composition in binary mixtures.

In this article, we have extended our approach and derived explicit expressions for the bending elasticity constants of single-component monolayers formed by nonionic surfactants with rigid head groups. More specifically, we have explored in detail the contribution to  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$  due to the repulsive interactions that arise as an effect of the entropy of mixing rigid hydrophilic head groups with surrounding solvent molecules.

An increasing number of attempts to determine bending elasticity constants experimentally have been carried out during recent years although there still exists a lack of quantitative agreement among different techniques.<sup>22–27</sup> Nevertheless, several qualitative systematic trends that relate the various bending

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elasticity constants to surfactant architecture may be induced from different experimental observations. For instance,  $H_0$  may be estimated by studying the size and type of microemulsion droplets or the aggregation number of surfactant aggregates. The bending rigidity is related to the stiffness/flexibility of a self-assembled interface so that monodisperse compact aggregates with uniform curvature, such as infinitely long cylinders, lamellar sheets, and cubic lamellar phases, are expected to be present at large values of  $k_c$  whereas more flexible, polydisperse aggregates with heterogeneous geometry, such as long wormlike micelles, vesicles, or a bicontinuous  $L_3$  phase, are expected to form at low  $k_c$  values. Moreover, the aggregates are predicted to become destabilized as  $k_c$  becomes negative. The saddle-splay constant may be estimated by studying transitions between aggregates of different topologies such as vesicles and lamellar sheets or planar lamellar and bicontinuous monolayers and bilayers.

One fruitful way to estimate the three bending elasticity constants qualitatively as well as quantitatively is to study the size, shape, persistence length, polydispersity, and so forth of self-assembled amphiphilic structures such as micelles, vesicles, and microemulsion droplets and to compare with theoretical predictions in accordance with eqs 1 and 2. Therefore, in recent works we have derived explicit expressions that directly relate  $H_0$ ,  $k_c$ , and  $\bar{k}_c$  to experimental properties such as the size, shape, and polydispersity of micelles,<sup>5</sup> vesicles,<sup>7</sup> and droplet microemulsions.<sup>6</sup> These properties are most suitably investigated with different scattering techniques such as small angle neutron and X-ray scattering as well as light scattering.

## 2. Molecular Thermodynamic Model for Calculating the Bending Elasticity of Surfactant Monolayers

In this article as well as in previous related papers,<sup>12,20</sup> we have chosen to define the bending elasticity constants as bare constants, i.e., as properties of a single surfactant monolayer where entropic effects due to undulations are not incorporated into  $H_0$ ,  $k_c$  and  $\bar{k}_c$ . Accordingly, it has been demonstrated that the three bending elasticity constants  $k_c$ ,  $\bar{k}_c$ , and  $k_c H_0$  (but not  $H_0$  itself) may be written as sums of different contributions.<sup>28</sup> Hence, for the case of nonionic surfactants we may write

$$k_c H_0 = (k_c H_0)_{\text{hb}} + (k_c H_0)_{\text{hg}} + (k_c H_0)_{\text{chain}} \quad (4)$$

$$k_c = k_c^{\text{hb}} + k_c^{\text{hg}} + k_c^{\text{chain}} \quad (5)$$

$$\bar{k}_c = \bar{k}_c^{\text{hb}} + \bar{k}_c^{\text{hg}} + \bar{k}_c^{\text{chain}} \quad (6)$$

The contributions due to the hydrophobic effect (hb) and chain conformational entropy of the hydrophobic tails (chain) have been treated in detail in earlier works by us on charged surfactant layers,<sup>12,20</sup> and a summary of our achievements is given in Appendix A. This article is mainly focused on deriving the contribution to the bending elasticity due to head group repulsion effects (hg) and the treatment of the self-assembly of nonionic surfactants with a rigid head group.

In our model, it is essential that the hydrophobic tails in an amphiphilic monolayer be subjected to geometrical packing constraints that relate the area per amphiphilic molecule at the hydrophobic–hydrophilic interface ( $a$ ) to the thickness of the hydrophobic part of the monolayer ( $\xi$ ) and the molecular tail volume ( $v_{\text{tail}}$ ). The following relation

$$\frac{1}{a} = \frac{\xi}{v_{\text{tail}}} \left( 1 - \xi H + \frac{\xi^2}{3} K \right) \quad (7)$$

have been derived from purely geometrical considerations.<sup>28–30</sup> In the present treatment, we have considered the surfactant layers to be an incompressible medium for which  $v_{\text{tail}}$  is a constant. However, the thickness of the hydrocarbon part of the surfactant layer  $\xi$  is, in general, curvature-dependent and may be written as a series expansion with respect to  $H$  and  $K$

$$\xi = \xi_p (1 + k'_\xi H + k''_\xi H^2 + k'''_\xi K) \quad (8)$$

where  $\xi_p$  is the thickness of the hydrophobic part of a planar monolayer and  $k'_\xi$ ,  $k''_\xi$ ,  $k'''_\xi$  are constants related to the curvature dependence of  $\xi$ .<sup>12,28</sup>

Equations 7 and 8 may be combined to give

$$\frac{1}{a} = \frac{1}{a_p} (1 + k'_a H + k''_a H^2 + k'''_a K) \quad (9)$$

where  $a_p$  is the area per surfactant molecule in a planar layer and  $k'_a$ ,  $k''_a$ , and  $k'''_a$  are three constants related to the curvature dependence of  $a$ .<sup>12,28</sup> The latter assume values that depend upon the constraints under which the amphiphilic layer is curved. For a thermodynamically closed monolayer  $k'_a = k''_a = k'''_a = 0$  whereas for a thermodynamically open layer they assume values that minimize the molecular free energy of the film for given values of  $H$  and  $K$ .<sup>12</sup> The two sets of constants are related as follows:  $k'_a = k'_\xi - \xi_p$ ,  $k''_a = k''_\xi - 2\xi_p k'_\xi$ , and  $k'''_a = k'''_\xi + \xi_p^2/3$ .<sup>28</sup>

It is possible to calculate the various bending elasticity constants from the pressure distribution in a surfactant layer.<sup>31–33</sup> This method might be useful when investigating single contributions to the bending elasticity. However, in the present work we have employed a more complicated model consisting of several free-energy contributions. Moreover, we primarily consider the relevant case of thermodynamically open surfactant layers by means of taking into account an equilibrium condition with respect to layer thickness (discussed below). In that case, the pressure distribution is not readily accessible; consequently, it is more convenient to calculate the various bending elasticity constants in a more straightforward way directly from the individual free-energy contributions as demonstrated in detail below. Nevertheless, the two methods are expected to give identical results for a self-consistent model such as the one that is employed in this article.

## 3. Free Energy of Surfactant Head Groups

A number of different effects related to the surfactant head groups may contribute to the free energy of an amphiphilic film. For instance, the hydrophobic–hydrophilic interface is shielded by the head groups, which is expected to reduce the hydrophobic free energy. This contribution is independent of curvature and may be incorporated into a single constant,  $\epsilon_{\text{hg}}^0$ . However, a large curvature-dependent contribution related to the head groups may arise as solvent molecules penetrate the amphiphilic layer and mix with the hydrophilic head groups. Hence, the hydrophilic head groups become diluted as the layer is increasingly positively curved, which is favorable from an entropic point of view

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(analogous to the increase in entropy upon expanding a gas), and the corresponding free energy may be quantified from the ideal free energy of mixing  $N$  head groups with  $N_w$  solvent molecules. Taking into account that the volume of a single head group ( $v_{hg}$ ) and a solvent molecule ( $v_w$ ) may be different, we may write the head group free energy as follows<sup>34–36</sup>

$$\frac{\varepsilon_{hg}}{kT} = \frac{\varepsilon_{hg}^\circ}{kT} + \frac{N_w}{N} \ln(1 - \phi_{hg}) + \ln \phi_{hg} = \frac{\varepsilon_{hg}^\circ}{kT} + \frac{v_{hg}}{v_w} \frac{1 - \phi_{hg}}{\phi_{hg}} \ln(1 - \phi_{hg}) + \ln \phi_{hg} \quad (10)$$

where  $\phi_{hg}$  is the volume fraction of head groups in the hydrophilic layer of the film.

In Appendix B, we demonstrate in detail how eq 10 is employed to derive the following expressions for the three bending elasticity constants

$$(k_c H_0)_{hg} = \frac{kT}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] (d - k'_a) \quad (11)$$

$$k_c^{hg} = \frac{kT}{4a_p} \left[ 1 + \frac{v_{hg}}{v_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right] (d - k'_a)^2 + \frac{1}{2a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] k''_a \quad (12)$$

$$\bar{k}_c^{hg} = -\frac{kT}{a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] \left( \frac{d^2}{3} - k'''_a \right) \quad (13)$$

where  $d$  is the thickness of the hydrophilic part of a surfactant monolayer within which head groups and solvent molecules are mixed.

The contribution to the bending elasticity constants due to the free energy of mixing head groups and solvent molecules has previously been derived by Paunov et al.<sup>15</sup> in a treatment of nonionic surfactants with flexible head groups. However, only the approximate case in the limit of infinite dilution ( $\phi_{hg}^p \rightarrow 0$ ) was considered. Moreover, it will be evident from our further analysis below that taking into account the hydrophobic effect and treating the surfactant layer as open in a thermodynamic sense is essential for the final outcome of the expressions of  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$ .

In the derivation of eqs 11–13, we have assumed the head groups to be sufficiently soft or flexible to enable them to fill the entire hydrophilic layer. However, we may take into account additional excluded volume effects for hard head groups in a simple way by means of defining the head group volume fraction in a strictly planar layer in the following manner

$$\phi_{hg}^p \equiv \frac{v_{hg}}{\alpha v_{tail}} \frac{\xi_p}{d} \quad (14)$$

Here we have introduced parameter  $\alpha$  in eq 14, which, strictly speaking, equals the volume fraction that is occupied by close-packed head groups in the hydrophilic part of a single monolayer. For instance,  $\alpha = \pi 3\sqrt{3} \approx 0.605$  for a single layer of close-packed spheres whereas  $\alpha = \pi 2\sqrt{3} \approx 0.907$  if the head groups are shaped as straight cylinders.  $\alpha = 1$  for soft head groups that are able to fill the entire hydrophilic layer. As a result,  $\phi_{hg}^p$  as

defined in eq 14 may be interpreted as an effective volume fraction. This is, of course, a rather crude approximation of treating excluded volume effects in the concentrated regime. However, because the shape of a surfactant head group dissolved in aqueous solution is usually not known in accurate detail it would hardly be meaningful to invoke more sophisticated approaches<sup>37,38</sup> in our model. Our aim is to include all essential contributions to the process of self-assembling amphiphilic molecules while still keeping our model as simple as possible.

In the present model, we have considered the hydrophobic–hydrophilic interface to be a starting reference where  $H$  and  $K$  are defined. However, in our derivation of eqs 11–13 (as well as the corresponding expressions for the hydrophobic effect and chain conformational entropy shown in Appendix A) we have taken full account of the fact that the hydrophobic effect is located in a different tangential plane (at the hydrocarbon–hydrophilic interface) than the head group contribution (acting in a hydrophilic layer with finite thickness  $d$ ). As a result, eqs 11–13, as well as all expressions for the various bending elasticity constants given throughout this article are independent of the particular choice of reference surface. In other words, the expressions obtained in eqs 11–13 are equivalent to the free-energy expression in eq 10 in a second-order curvature expansion.

It may finally be noted that the always positive quantity

$$1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) = 1 + \frac{v_{hg}}{v_w} \phi_{hg}^p \left( \frac{1}{2} + \frac{\phi_{hg}^p}{3} + \frac{\phi_{hg}^{p^2}}{4} + \dots \right) \quad (15)$$

appears in the expressions of all bending elasticity constants in eqs 11–13. This quantity simply equals the derivative of  $\varepsilon_{hg}$  with respect to  $\phi_{hg}$  for a planar layer. As a consequence,  $(k_c H_0)_{hg}$  and  $\bar{k}_c^{hg}$  become proportional to each other, which is a general result for all individual free energy contributions (cf. eqs A2 and A4 and eqs A7 and A9 in Appendix A).

#### 4. Bending Elasticity Constants for Thermodynamically Open Monolayers Formed by a Nonionic Surfactant with a Rigid Tail

**Spontaneous Curvature.** The additive quantity  $k_c H_0 = (k_c H_0)_{hb} + (k_c H_0)_{hg}$  for a nonionic surfactant with a rigid tail may simply be obtained by summing the contribution due to the hydrophobic effect in eq A2 with the head group repulsion contribution in eq 11, resulting in

$$\frac{k_c H_0}{kT} = \frac{d}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \frac{k'_a}{4a_p} \left( 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right) - \frac{a_p \gamma_{hb}}{kT} \quad (16)$$

$k_c H_0$  for a thermodynamically open film may be obtained by means of employing the equilibrium condition with respect to the area per amphiphilic molecule of a planar monolayer

$$\frac{d\varepsilon_p}{da} = \frac{kT}{a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \gamma_{hb} = 0 \quad (17)$$

where  $\varepsilon_p = \varepsilon_{hb} + \varepsilon_{hg}$  is the sum of the two expressions given in eqs A1 and 10 at planar geometry ( $H = K = 0$ ) and  $\gamma_{hb}$  is the hydrophobic–hydrophilic interfacial tension. As a result, the term

(34) Guggenheim, E. A. *Mixtures*; Clarendon Press: Oxford, U.K., 1952.

(35) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953; Chapter 12.

(36) Flory, P. J. *Faraday Discuss.* **1974**, 57, 7–29.

(37) Mansoori, G. A.; Carnahan, N. F.; Starling, K. E.; Leland, T. W., Jr. *J. Chem. Phys.* **1971**, 54, 1523–1525.

(38) Erpenbeck, J. J.; Luban, M. *Phys. Rev. A* **1985**, 32, 2920–2922.

proportional to  $k'_a$  in eq 16 cancels out, giving the rather simple expression

$$\frac{k_c H_0}{kT} = \frac{d\gamma_{hb}}{4} \quad (18)$$

It is noted that eq 18 assumes always positive values for surfactants with a head group of finite size ( $d > 0$ ). This result is typical for thermodynamically open layers, for which it is necessary to take into account opposing contributions that may generate a free energy minimum in accordance with eq 17.

The canceling of terms proportional to  $k'_a$  for thermodynamically open systems has also been seen to occur for monolayers formed by ionic surfactants,<sup>12</sup> and it is evident that this feature must always be present regardless of the particular model employed. It reflects the circumstance that the curvature dependence of  $a$  (cf. eq 9) may not per se contribute explicitly to the various bending elasticity constants because the particular values of  $k'_a$  (as well as  $k''_a$  and  $k'''_a$ ) are determined as a direct result of the equilibrium condition in eq 17.

**Bending Rigidity.** The bending rigidity of monolayers formed by a nonionic surfactant with a rigid tail is obtained by summing the contributions given in eqs A3 and 12, giving

$$\frac{k_c}{kT} = \frac{(d - k'_a)^2}{4a_p} \left( 1 + \frac{\nu_{hg}}{\nu_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right) + \frac{k''_a}{2a_p} \left( 1 - \frac{\nu_{hg}}{\nu_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) - \frac{a_p \gamma_{hb}}{kT} \right) \quad (19)$$

For a thermodynamically open monolayer, we may employ the equilibrium condition in eq 17, which implies that all terms proportional to  $k''_a$  cancel out and, as a result,

$$\frac{k_c}{kT} = \frac{(d - k'_a)^2}{4a_p} \left( 1 + \frac{\nu_{hg}}{\nu_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right) \quad (20)$$

The remaining constant  $k'_a$  may be obtained from the equilibrium condition  $d\xi/da = 0$  considering terms proportional to  $H$ . However, a less tedious procedure<sup>12</sup> to determine  $k'_a$  is simply to minimize  $k_c$  in eq 20 with respect to  $k'_a$ , giving  $k'_a = d$  and  $k_c = 0$ .

Interestingly,  $k_c = 0$  means that  $\gamma$  in eq 1 is a constant with respect to  $H$ , and as a consequence, a spontaneous curvature cannot be defined. In other words, we may conclude that thermodynamically stable self-assembled layers or aggregates may not be formed by nonionic surfactants with a rigid hydrophobic part (e.g., a steroid backbone or a fluorocarbon tail) attached to a rigid head group. This is consistent with the fact that surfactants usually are considered to be composed of a hydrophilic head group and a flexible hydrophobic tail.<sup>39</sup> Moreover, to our knowledge stable fluid micelles formed by nonionic surfactants with both a rigid tail and head group have never been reported. Nonionic surfactants with a rigid tail reported in the literature usually consist of a flexible hydrophilic head group. For instance, a surfactant consisting of a rather stiff phytosterol tail and a flexible polyoxyethylene head group was found to form micelles only insofar as the number of ethyleneoxide groups was larger than about 10.<sup>40</sup> Likewise, fluorinated nonionic surfactants exclusively

consist of a flexible head group, and very little is known about their association behavior in dilute aqueous solutions.<sup>41</sup>

It is a striking feature of thermodynamically open surfactant layers that the bending rigidity may vanish despite the fact that the individual contributions to  $k_c$  are large in magnitude (cf. eqs A3 and 12). This means that  $a$  in eq 9 will always respond to a change in curvature so as to give  $k'_a = d$  and a minimum value equal to  $k_c = 0$  where two contributions that both lack an explicit curvature dependence exactly cancel one another (cf. eqs A1 and 10). In contrast, electrostatics as calculated from the Poisson–Boltzmann theory gives rise to an explicit curvature dependence; consequently,  $k_c$  for ionic surfactants with rigid tails was found to assume small but positive values.<sup>12</sup> The chain conformational entropy of flexible head groups, not taken into account in the present work, may also give rise to such an explicit curvature dependence.

**Saddle-Splay Constant.** The sum of eqs A4 and 13 gives the following expression for the saddle-splay constant for a monolayer formed by a nonionic surfactant with a rigid tail

$$\frac{\bar{k}_c}{kT} = -\frac{d^2}{3a_p} \left[ 1 - \frac{\nu_{hg}}{\nu_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] + \frac{k'''_a}{a_p} \left( 1 - \frac{\nu_{hg}}{\nu_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) - \frac{a_p \gamma_{hb}}{kT} \right) \quad (21)$$

$\bar{k}_c$  for a thermodynamically open layer may be obtained by means of employing the equilibrium condition in eq 17. Similar to the cases of  $k_c H_0$  and  $k_c$ , terms including  $k'''_a$  are canceled, giving

$$\bar{k}_c = -\frac{\gamma_{hb} d^2}{3} \quad (22)$$

It becomes clear that the saddle-splay constant must always be a negative quantity that vanishes in the limit of  $d \rightarrow 0$ . The saddle-splay constant estimated in experiments<sup>22,25,26</sup> as well as theory<sup>12,20</sup> is usually found to assume negative values. This is expected for cases where  $\bar{k}_c$  is mainly determined by various mean-field free-energy contributions. Mean-field contributions act equivalently in all lateral directions and are expected to influence the curvature in a uniform way, leading to negative  $\bar{k}_c$  values. However, anisotropic specific interactions may cause curvature having opposite signs in different directions (i.e., a local saddlelike shape of the layer), leading to a positive value of  $\bar{k}_c$ .

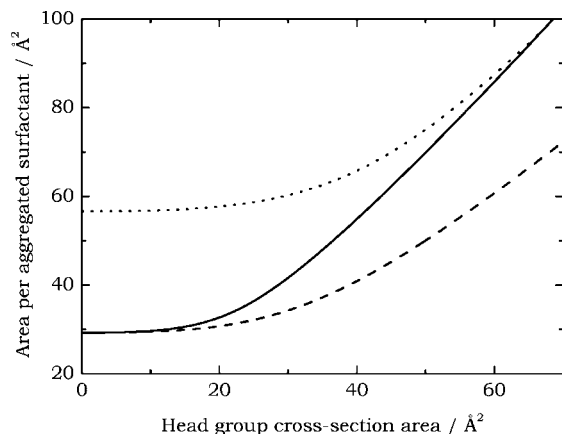
## 5. Bending Elasticity Constants for Thermodynamically Open Monolayers Formed by a Nonionic Surfactant with a Flexible Tail

As surfactants with flexible tails, such as aliphatic hydrocarbon chains, are dealt with, an additional free-energy contribution  $\epsilon_{chain}$  due to the restrictions in chain conformational entropy of the hydrophobic tails must be taken into account. We previously treated the chain conformational contribution to the various bending elasticity constants<sup>12,20</sup> using a planar approximation where explicit curvature dependencies of  $\epsilon_{chain}$  were neglected. The result is summarized in Appendix A (cf. eqs A7–A9). Although the chain conformational free-energy contribution is usually rather small in magnitude for surfactants and lipids with moderate chain lengths, it was found for the case of ionic surfactants that it has a large indirect impact and raises the magnitudes of  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$  for surfactants with flexible tails.<sup>12</sup>

(39) Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. *Surfactant and Polymers in Aqueous Solution*, 2nd ed.; John Wiley & Sons: Chichester, U.K., 2003.

(40) Folmer, B. M.; Svensson, M.; Holmberg, K.; Brown, W. J. *Colloid Interface Sci.* **1999**, *213*, 112–120.

(41) Kissa, E. *Fluorinated Surfactants*; Marcel Dekker: New York, 1994; Surfactant Science Series Vol. 50.



**Figure 1.** Equilibrium area per aggregated surfactant ( $a_p$ ) plotted against the head group cross-sectional area for a planar monolayer as calculated from the equilibrium condition in eq 24. The solid line corresponds to the case of single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ ), the dashed line refers to single-chain surfactants with head groups treated as soft spheres ( $\alpha = 1$ ), and the dotted line refers to double-chain surfactants with hard spherical head groups. The tail volumes of a single and a double chain were set equal to 350 and 700 Å<sup>3</sup>, respectively, the molecular volume of the solvent is  $v_w = 30$  Å<sup>3</sup>, the hydrophobic–hydrophilic interfacial tension is  $\gamma_{hb} = 50$  mJ/m<sup>2</sup>, and the parameters related to the chain conformational entropy contribution in eq A6 were  $\lambda = 0.03$  Å<sup>-2</sup> and  $\xi_0 = 8.54$  Å.

Below it will become evident that a similar result is also obtained for the case of nonionic surfactants.

Explicit curvature-dependent terms in  $\varepsilon_{\text{chain}}$  (cf. eq A5) have been taken into account in previous model calculations by us on ionic surfactants.<sup>8,12</sup> The results indicate that the rise in magnitudes of  $k_c H_0$  and  $k_c$  for surfactants with flexible tails become somewhat counteracted. Although this contribution was found to be on the order of the magnitude of  $kT$ , it has been neglected in this article for the sake of simplicity. As a result, we have been able to express the various bending elasticity constants with comparatively simple and explicit expressions. One possible way to take the curvature dependence of  $\varepsilon_{\text{chain}}$  into account, while still retaining the explicit form is to include it in the interfacial tension parameter  $\gamma_{hb}$  which then would become somewhat lower than its macroscopic value of 50 mJ/m<sup>2</sup>.

**Spontaneous Curvature.** Expressions for the various bending elasticity constants may be obtained by summing all contributions [ $k_c H_0 = (k_c H_0)_{hb} + (k_c H_0)_{\text{chain}} + (k_c H_0)_{hg}$ ] given in eqs A2, A7, and 11). As a result,

$$\frac{k_c H_0}{kT} = \frac{\xi_p + d}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \frac{\xi_p \gamma_{hb}}{4kT} - \frac{k'_\xi}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \frac{\gamma_{hb} a_p}{kT} + \frac{\xi_p}{kT} \frac{d\varepsilon_{\text{chain}}}{d\xi} \quad (23)$$

Minimizing the free energy per surfactant molecule for a planar monolayer (i.e.,  $\varepsilon_p = \varepsilon_{hb} + \varepsilon_{\text{chain}} + \varepsilon_{hg}$ ) in accordance with eqs A1 and 10 gives the following equilibrium condition

$$1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) - \frac{\gamma_{hb} a_p}{kT} + \frac{\xi_p}{kT} \frac{d\varepsilon_{\text{chain}}}{d\xi} = 0 \quad (24)$$

from which the equilibrium area per aggregated surfactant for a planar monolayer ( $a_p$ ) may be calculated. Accordingly,  $a_p$  for a nonionic surfactant with either one or two C<sub>12</sub> aliphatic chains is plotted as a function of the cross-sectional area of a spherical head group in Figure 1. It is seen that  $a_p$  significantly increases

for the case of treating the head groups as hard ( $\alpha = \pi/3\sqrt{3}$ ) rather than soft spheres ( $\alpha = 1$ ).

Combining eqs 23 and 24 gives the following expression

$$\frac{k_c H_0}{kT} = \frac{\xi_p + d}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \frac{\xi_p \gamma_{hb}}{4kT} \quad (25)$$

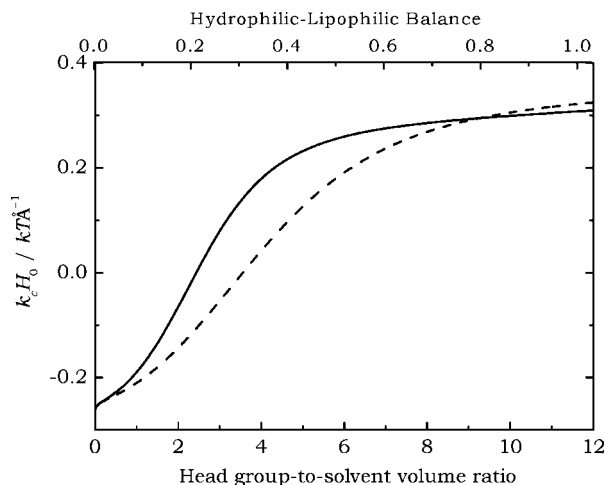
which is valid for a thermodynamically open monolayer. Notably, all terms proportional to  $k'_\xi$  have been canceled in eq 25 and so have all contributions including the detailed appearance of the chain conformational free energy  $\varepsilon_{\text{chain}}$ . As a matter of fact, eq 25 is identical to the expression expected for a surfactant monolayer that is bent at constant layer thickness in an analogous way as was recently obtained for charged surfactant layers.<sup>12</sup> This behavior may be rationalized as a result of the strong resistance toward changes in layer thickness imposed by the presence of chain conformational entropy. This gives the bending elasticity constants for surfactants with flexible tails an indirect, strong dependence on  $\xi_p$ , which is absent in the case of surfactants with rigid tails (cf. eqs 18 and 25). As a matter of fact, this huge influence on all bending elasticity constants appears despite the fact that we have, in a first approximation, employed the planar expression for  $\varepsilon_{\text{chain}}$  in eq A6. The cancelation of  $k'_\xi$  in eq 25 follows as a consequence of taking the equilibrium condition in eq 24 into account and is analogous to the cancelation of  $k'_a$  in the case of surfactants with rigid tails (cf. eq 18).

We may also note that because the equilibrium condition in eq 24 relates the three free-energy contributions taken into account, it is possible to write eq 25 in some alternative ways depending on which contribution is eliminated. We have chosen to eliminate the lesser known  $\varepsilon_{\text{chain}}$ , and as a result,  $k_c H_0$  as expressed by eq 25 may be quantified from readily accessible properties related to the chemical structure of surfactant and solvent such as the molecular volumes of the head, tail, and solvent, the thickness of hydrophilic and hydrophobic monolayer parts, and the hydrophobic–hydrophilic interfacial tension. The possibility of expressing the various bending elasticity constants in terms of experimentally available quantities rather than detailed values of the chain conformational free energy is, of course, an utmost valuable feature that follows from our present theoretical achievements.

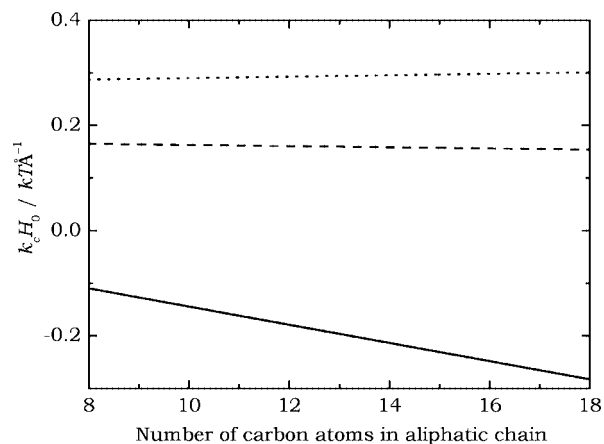
In accordance with eq 25,  $k_c H_0$  may be considered to be a sum of two contributions. The first term takes into account head group repulsion effects and is always positive (cf. series expansion in eq 15) and increases with an increasing head group-to-solvent volume ratio ( $v_{hg}/v_w$ ). The last term in eq 25 takes into account hydrophobic effects and is always negative with a magnitude that increases with increasing hydrophobic–hydrophilic interfacial tension ( $\gamma_{hb}$ ) as well as the thickness of the hydrophobic part of the monolayer ( $\xi_p$ ). It may be noted that eq 15 approaches unity in the limit of  $v_{hg} \rightarrow 0$ , which means that an entropic repulsive contribution to  $k_c H_0$  in eq 25 ( $= \xi_p/4a_p$ ) is still present for surfactants with infinitely small (pointlike) head groups.

$k_c H_0$  is found to increase from negative to positive values as  $v_{hg}/v_w$  (or the hydrophilic–lipophilic balance defined as  $HLB = v_{hg}/v_{\text{tail}}$ ) is increased at constant tail volume  $v_{\text{tail}}$ , where  $v_{hg}$  has been set equal to  $\pi d^3/6$ , which is valid for a spherical geometry of the head groups (cf. Figure 2). As expected, it is found that a more pronounced head group repulsion between hard spheres ( $\alpha = \pi/3\sqrt{3}$ ) raises  $k_c H_0$  as compared to the case of less repulsive soft head groups ( $\alpha = 1$ ), except at very large values of  $v_{hg}/v_w$  where the area per aggregated surfactant becomes substantially larger for the hard spheres (cf. Figures 1 and 2). However, the latter values correspond to head group volumes in the region





**Figure 2.** Bending rigidity times the spontaneous curvature ( $k_c H_0$ ) in eq 25 plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic–lipophilic balance ( $HLB = v_{hg}/v_{tail}$ ) for single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ ), solid line) and head groups treated as soft spheres ( $\alpha = 1$ ), dashed line). The thickness of the hydrophobic part of the monolayer  $\xi_p$  was calculated from eq 24 with a tail volume equal to  $v_{tail} = 350 \text{ Å}^3$ . The head group volume was set to  $v_{hg} = \pi d^3/6$  where  $d$  is the thickness of the hydrophilic shell.  $v_w$  and  $\gamma_{hb}$  were set equal to the same values as in Figure 1.



**Figure 3.** Bending rigidity times the spontaneous curvature ( $k_c H_0$ ) in eq 25 plotted against the number of carbon atoms in the aliphatic chain ( $n$ ) for single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ ) with diameter  $d = 4 \text{ Å}$  (solid line),  $6 \text{ Å}$  (dashed line), and  $8 \text{ Å}$  (dotted line). The thickness of the hydrophobic part of the monolayer  $\xi_p$  was calculated from eq 24. The tail volume was calculated according to  $v_{tail} = 27.4 + 26.9n \text{ Å}^3$  whereas  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  were set to the same values as in Figures 1 and 2.

where  $k_c < 0$  and stable surfactant aggregates cannot form (cf. Figure 4 further below).

$k_c H_0$  is plotted against the number of carbons in an aliphatic hydrocarbon chain ( $n$ ) in Figure 3 for a given volume of the head group, where the chain volume was calculated from the empirical relation<sup>42</sup>  $v_{tail} = 27.4 + 26.9n \text{ Å}^3$ . As a result,  $k_c H_0$  is seen to depend linearly on  $n$  mainly as a result of the linear behavior with respect to monolayer thickness shown in eq 25. Moreover,  $k_c H_0$  is found to decrease with increasing  $v_{tail}$  except at large values of  $v_{hg}$  where  $1 - v_{hg}/v_w(1 + \ln(1 - \phi_{hg}^p)/\phi_{hg}^p) > a_p \gamma_{hb}$  (cf. eq 25).

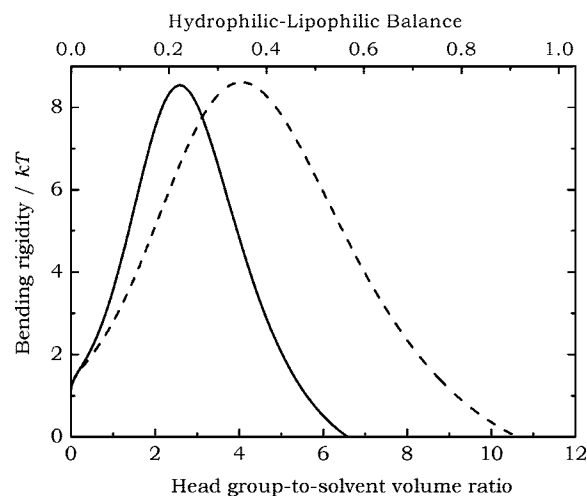
**Bending Rigidity.** The sum of the various contributions given in eqs A3, A8, and 12 gives the following contribution for the bending rigidity of a monolayer formed by a nonionic surfactant with a flexible tail

$$\frac{k_c}{kT} = \frac{\xi_p k'_\xi}{2a_p} \left( \frac{\gamma_{hb} a_p}{kT} - \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] \right) + \frac{(\xi_p + d - k'_\xi)^2}{4a_p} \left( 1 + \frac{v_{hg}}{v_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right) + \frac{k_\xi'^2}{2a_p} \left( \xi_p^2 \lambda + \frac{\gamma_{hb} a_p}{kT} - \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] \right) \quad (26)$$

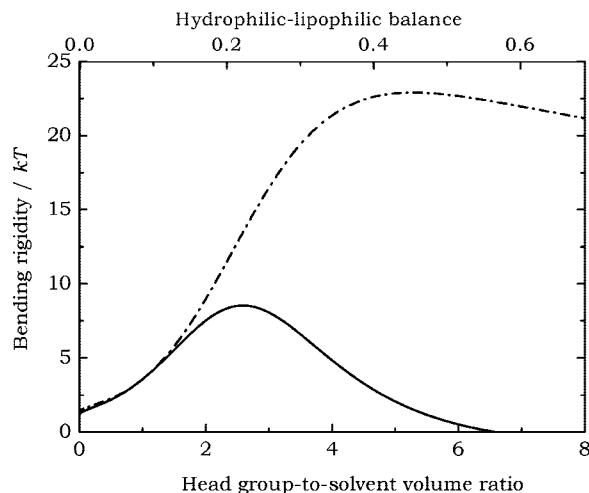
In the derivation of eq 26, we have employed the geometrical relations<sup>12,28</sup>  $k'_a = k'_\xi - \xi_p$  and  $k''_a = k''_\xi - 2\xi_p k'_\xi$  as well as the equilibrium condition in eq 24 and have eliminated  $k'_a$  and  $d\varepsilon_{chain}/d\xi$ , whereas  $d^2\varepsilon_{chain}/d\xi^2 = 2\lambda kT$  (cf. eq A6). It is seen that all terms including  $k''_\xi$  have been canceled as a result of employing eq 24, whereas  $k_c$  still depends on  $k'_\xi$ . For the case of a thermodynamically open monolayer,  $k'_\xi$  assumes the value that minimizes eq 26.<sup>12</sup> Hence, it directly follows from our approach that the bending rigidity must always be lower for an equilibrated thermodynamically open layer than for any other constraint (e.g., a thermodynamically closed layer). This result has also been demonstrated, independently, by Porte and Ligoure<sup>10</sup> and Safran.<sup>43</sup>

The bending rigidity for a thermodynamically open monolayer is plotted in Figure 4 against  $v_{hg}/v_w$  as well as HLB for a given tail volume. Notably, in contrast to the case of a nonionic surfactant with *rigid* tail,  $k_c$  in Figure 4 is found to assume comparatively large positive values for head groups of moderate size. The reasons for the different behaviors between surfactants with rigid and flexible tails are identical as previously discussed for  $k_c H_0$  (i.e., the resistance toward changes in layer thickness upon bending as a result of chain conformational entropy effects).

$k_c$  as shown in Figure 4 is found to reach an evident maximum indicating the HLB value where the surfactant monolayer assumes optimal stability. The maximum appears to be located very close to  $H_0 = 0$  irrespective of the choice of  $\alpha$  (cf. Figures 2 and 4). The bending rigidity is seen to decrease rapidly with the size of the head group as  $H_0 > 0$  and in regions with sufficiently large  $k_c H_0$  values, where micelles are expected to predominate,  $k_c$  is found to be very low. It has recently been demonstrated that elongated micelles is primarily promoted by low bending



**Figure 4.** Bending rigidity ( $k_c$ ) for a thermodynamically open monolayer in accordance with eq 26, plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic–lipophilic balance ( $HLB = v_{hg}/v_{tail}$ ) for single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ , solid line) and head groups treated as soft spheres ( $\alpha = 1$ , dashed line).  $\xi_p$  was calculated from eq 24 with  $v_{tail}$ ,  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  set to the same values as in Figures 1 and 2.



**Figure 5.** Bending rigidity ( $k_c$ ) for the case of bending a monolayer with constant monolayer thickness in accordance with eq 27 plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic-lipophilic balance (HLB =  $v_{hg}/v_{tail}$ ) for single-chain surfactants with head groups treated as hard spheres with  $\alpha = \pi/3 \sqrt{3}$  (dashed-dotted line). The solid line shows  $k_c$  as calculated from eq 26 and also plotted in Figure 4.  $\xi_p$  was calculated from eq 24 with  $v_{tail}$ ,  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  set to the same values as in Figures 1 and 2.

rigidities.<sup>5</sup> As a matter of fact, nonionic surfactants with comparatively large head groups have usually been found to be considerably elongated.<sup>44,45</sup> At sufficiently voluminous head groups  $k_c$  may fall below zero implying that the surfactant has become too hydrophilic in order to form stable aggregates. The reduction of  $k_c$  at large values of  $v_{hg}$  is much more pronounced for the case of treating the head groups as hard rather than soft spheres.

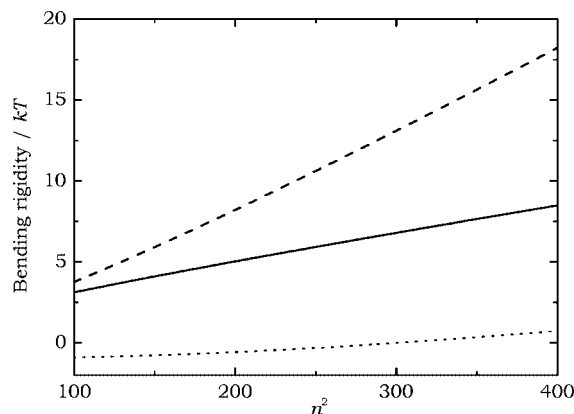
We may note that  $k_c$  still assumes positive values in the limit of  $v_{hg} \rightarrow 0$ , which means that the head group repulsion for pointlike head groups is sufficient for stable monolayers to form. However, it is possible that the contribution to  $k_c$  due to the explicit curvature dependence of  $\epsilon_{chain}$  in eq A5, which has been neglected in the present study, may reduce the bending rigidity so that  $k_c$  becomes negative at  $v_{hg} = 0$ .<sup>8,12</sup>

It is a striking result that  $k_c$  for a nonionic surfactant with a flexible tail may assume large, positive values insofar as the proportions between head and tail are well balanced, whereas  $k_c = 0$  for a nonionic surfactant with a rigid tail. This may explain the circumstance that it often seems necessary for a nonionic amphiphilic molecule to consist of a flexible hydrocarbon tail in order to form stable layers or aggregates.

It is found that  $k_c$  for a thermodynamically open layer is close to zero at moderate volumes of the head group. In accordance, eq 26 may be simplified so as to give the following expression

$$k_c = \frac{1}{4a_p} \left[ 1 + \frac{v_{hg}}{v_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right] (\xi_p + d)^2 \quad (27)$$

which is identical to the bending rigidity for a monolayer that is bent at constant layer thickness equal to  $\xi_p$  (cf. Figure 5). As the head group volume increases,  $k_c$  is found to sharply increase in magnitude as a result of the strong head group repulsions that causes the layer to become thicker as a response to an increasing



**Figure 6.** Bending rigidity ( $k_c$ ) for a thermodynamically open monolayer plotted against the square of the number of carbon atoms in the aliphatic chain ( $n^2$ ) for single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3 \sqrt{3}$ ) with diameter  $d = 4$  Å (solid line), 6 Å (dashed line), and 8 Å (dotted line).  $\xi_p$  was calculated from eq 24 with  $v_{tail}$ ,  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  set to the same values as in Figures 1–3.

curvature. As a result, the large values of  $k_c$  expected from eq 27 are substantially decreased by the negative terms in eq 26 that depend on  $v_{hg}$  (cf. Figure 5). This means that a reduction of  $k_c$  with increasing head group repulsion must be a general feature for thermodynamically open layers. It is obvious from the behavior observed in Figure 4 that the reduction of  $k_c$  becomes more enhanced as the repulsive effects increase in magnitude.

Eventually, as the head group repulsion becomes sufficiently strong, the bending rigidity may turn into negative values. Negative values of  $k_c$  imply that a maximum, rather than a minimum, is generated as the free energy per unit area in eq 1 is plotted against the mean curvature and, as a result, stable aggregates may no longer form. In physical terms, this means that the head group repulsion dominates the hydrophobic effect to the extent that the balance between the two contributions is no longer sufficient to generate a minimum in  $\gamma(H)$ .

The bending rigidity as calculated from our model shows almost linear behavior when plotted against the square of the number of carbon atoms in an aliphatic chain (cf. Figure 6), which is not surprising considering the appearance of eq 27. It is seen that  $k_c$  rises more steeply at head group volumes corresponding to values close to the maximum seen in Figure 4. The quadratic behavior of  $k_c$  with respect to layer thickness is consistent with recent measurements of the bending rigidity of bilayers formed by various nonionic diblock copolymers using single- and dual-micropipet techniques.<sup>46</sup>

Bending rigidity proportional to  $\xi^2$  has been found in some earlier theoretical works,<sup>47,48</sup> and it seems to be a general feature of fluid surfactant or lipid layers, although more complicated behaviors may be anticipated by taking into account chain conformational entropy effects of thermodynamically closed layers.<sup>33</sup> According to eq 27, the quadratic behavior may be rationalized as a consequence of the influence of lateral head group repulsion as a monolayer is bent at constant thickness. However, a solid plate with elastic behavior in accordance with Hooke's law<sup>49</sup> or a simple spring model with a spring constant inversely proportional to the layer thickness<sup>30</sup> gives  $k_c \propto \xi^3$ . This evidently shows that the behavior of the bending elasticity is expected to depend on the particular model that is employed and

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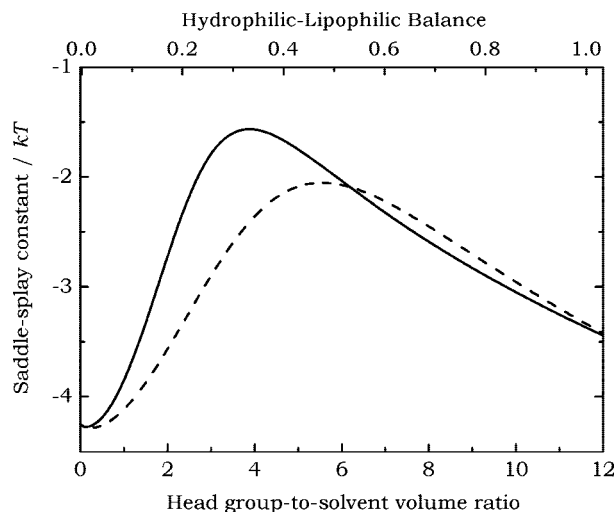
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**Figure 7.** Saddle-splay constant ( $\bar{k}_c$ ) according to eq 29 plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic-lipophilic balance (HLB =  $v_{hg}/v_{tail}$ ) for single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ , solid line) and head groups treated as soft spheres ( $\alpha = 1$ , dashed line).  $\xi_p$  was calculated from eq 24 with  $v_{tail}$ ,  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  set to the same values as in Figures 1 and 2.

fluid mono- and bilayers formed by amphiphilic molecules are not expected to be described accurately by simple models derived for solid plates.

**Saddle-Splay Constant.** The overall saddle-splay constant may be calculated as a sum of the different contributions in eqs A4, A9, and 13

$$\frac{\bar{k}_c}{kT} = \frac{\xi_p^2}{3a_p} \left( 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) - \frac{\gamma_{hb}a_p}{kT} \right) - \frac{d^2}{3a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] + \frac{1}{a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) - \frac{\gamma_{hb}a_p}{kT} + \xi_p \frac{d\varepsilon_{chain}}{d\xi} \right] k_{\xi}''' \quad (28)$$

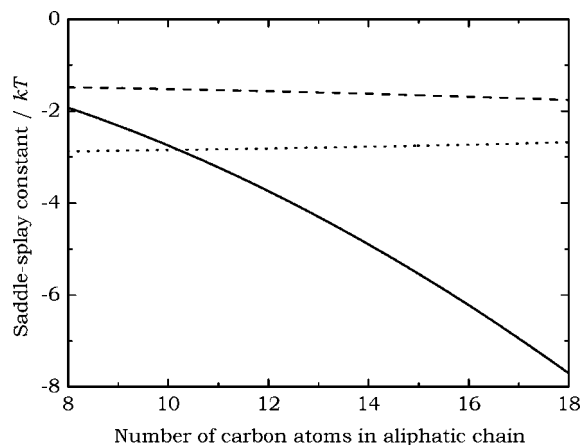
where  $k_a''' = k_{\xi}''' + \xi_p^2/3$ . For the case of a thermodynamically open layer, eq 28 may be rewritten so as to give

$$\frac{\bar{k}_c}{kT} = \frac{\xi_p^2}{3a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \frac{\xi_p^2 \gamma_{hb}}{3kT} \quad (29)$$

by means of employing the equilibrium condition in eq 24.

As for the case of  $k_c H_0$ , the expression in eq 29 exactly equals the saddle-splay constant for a monolayer that is bent at constant layer thickness, and it lacks explicit dependence on the chain conformational free energy. Moreover, analogous to  $k_c H_0$ , the saddle-splay constant may be considered to be a sum of two terms: one takes into account head group repulsion effects whereas the other is due to the hydrophobic effect. The latter term is always negative whereas the former contribution may be positive insofar as  $\xi_p > d$ . However, for sufficiently large hydrophobic-hydrophilic interfacial tensions ( $\gamma_{hb}$ ), the second term will be dominant and, for all practical purposes,  $\bar{k}_c$  is expected to be a negative quantity, similar to the case of surfactants with rigid tails (cf. eq 22).

The saddle-splay constant for a thermodynamically open monolayer is plotted against  $v_{hg}/v_w$  and HLB in Figure 7. At low head group volumes,  $\bar{k}_c$  is seen to increase with increasing  $v_{hg}$



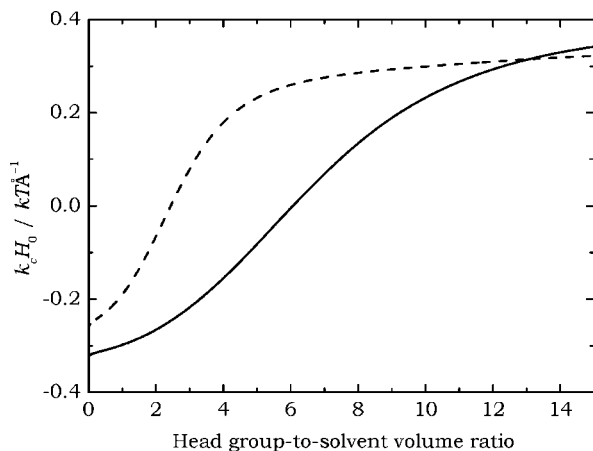
**Figure 8.** Saddle-splay constant ( $\bar{k}_c$ ) for a thermodynamically open monolayer plotted against the number of carbon atoms in the aliphatic chain ( $n$ ) for single-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ ) with diameter  $d = 4$  Å (solid line), 6 Å (dashed line), and 8 Å (dotted line).  $\xi_p$  was calculated from eq 24 with  $v_{tail}$ ,  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  set to the same values as in Figures 1–3.

as the head group repulsion term in eq 29 increases in magnitude. However, as  $v_{hg}$  becomes sufficiently large the head group repulsion will begin to influence the area per head group  $a_p$  significantly (cf. Figure 1) as well as the geometrically related monolayer thickness  $\xi_p$ . As a result,  $\xi_p$  is reduced and the positive head group term in eq 29 decreases in magnitude, causing  $\bar{k}_c$  to decrease with increasing  $v_{hg}$ . Eventually,  $\xi_p$  may fall below  $d$ , and both terms in eq 29 become negative quantities.

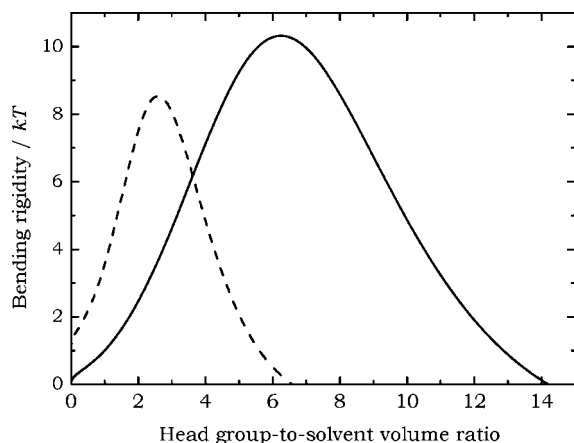
The saddle-splay constant for a nonionic surfactant with a given head group volume is plotted in Figure 8 against the number of carbon atoms in an aliphatic hydrocarbon chain. At small head group volumes  $\bar{k}_c$  is mainly determined by the contribution due to the hydrophobic effect, and it is seen to decrease with increasing chain length. At higher values of  $v_{hg}$ , the saddle-splay constant is seen to be less sensitive to changes in chain length because the two terms in eq 29 balance one another to a large extent. It is evident from the appearance of eq 29 that  $\bar{k}_c$  is expected to display a quadratic dependence on  $\xi_p$ .

## 6. Bending Elasticity Constants for Monolayers Formed by a Double-Chain Nonionic Surfactant

The various bending elasticity constants for thermodynamically open monolayers formed by a double-chain nonionic surfactant may be calculated from eqs 25, 26, and 29 with  $a_p = v_{tail}/\xi_p$  as calculated from the equilibrium condition in eq 24 (cf. Figure 1). In our calculations, we have set  $v_{tail}$  (double chain) =  $2v_{tail}$  (single chain). The resulting values of  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$  for a nonionic surfactant with two identical  $C_{12}$  aliphatic chains are shown in Figures 9–11 together with the corresponding quantities for a single-chain surfactant. The main difference between a double-chain and a single-chain surfactant with identical head groups is the reduction in head group repulsion in the former case as a result of increasing values of  $a_p$  (cf. Figure 1). As a result,  $k_c H_0$  is found to decrease in magnitude (cf. Figure 9) whereas much larger head group volumes are required before  $k_c$  starts decreasing with increasing values of  $v_{hg}$  (cf. Figure 10). As for a single-chain surfactant, it is found that the maximum in  $k_c$  seen in Figure 10 is approximately located at  $H_0 = 0$  (cf. Figure 9). The saddle-splay constant of a double-chain surfactant is found to be significantly lower than for the corresponding single-chain surfactant at low values of  $v_{hg}$  (cf. Figure 11). This may be rationalized as a result of larger values of  $a_p$  for the



**Figure 9.** Bending rigidity times the spontaneous curvature ( $k_c H_0$ ) for a thermodynamically open monolayer plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic–lipophilic balance (HLB =  $v_{hg}/v_{tail}$ ) for double-chain surfactants with head groups treated as hard spheres ( $\alpha = \pi/3\sqrt{3}$ , solid line). The tail volume was set to  $v_{tail} = 700 \text{ Å}^3$ .  $k_c H_0$  for the corresponding single-chain surfactant ( $v_{tail} = 350 \text{ Å}^3$ ) is also given (dashed line).  $\xi_p$  was calculated from eq 24 with  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  set to the same values as in Figures 1 and 2.



**Figure 10.** Bending rigidity ( $k_c$ ) for a thermodynamically open monolayer plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic–lipophilic balance (HLB =  $v_{hg}/v_{tail}$ ) for double-chain surfactants with  $\alpha = \pi/3\sqrt{3}$  (solid line).  $k_c$  for the corresponding single-chain surfactant is also given (dashed line).  $\xi_p$  was calculated from eq 24 with  $v_{tail}$  set to the same values as in Figure 9 and  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  being equal to what is given in Figures 1 and 2.

double-chain surfactant, implying lower magnitudes of the positive head group term in eq 29.

## 7. Bending Elasticity Constants for Thermodynamically Closed Monolayers

Up to this point, we have exclusively discussed thermodynamically open mono- and bilayers. However, it is also straightforward to derive expressions for the different bending elasticity constants for a thermodynamically closed monolayer by means of setting  $k'_a = k''_a = k'''_a = 0$  in the corresponding general expressions in eqs 16, 19, 21, 23, 26, and 28. Hence, for nonionic surfactants with a rigid tail we obtain the following expressions

$$\frac{k_c H_0}{kT} = \frac{d}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] \quad (30)$$

$$\frac{k_c}{kT} = \frac{d^2}{4a_p} \left( 1 + \frac{v_{hg}}{v_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right) \quad (31)$$

$$\bar{k}_c = -\frac{d^2}{3a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] \quad (32)$$

Since the quantity in eq 15 is always positive, it follows that  $k_c H_0$  is always positive whereas  $\bar{k}_c$  is negative for a thermodynamically closed monolayer. Moreover, the bending rigidity according to eq 31 must always be a positive quantity because  $k_c = 0$ , which is valid for a thermodynamically open layer, is the minimum attainable value. As a consequence, metastable aggregates may form out of nonionic surfactants with both rigid heads and tails if the solubility in solvent is so poor as to approximately fulfill the constraint of constant aggregation number.

For nonionic surfactants with flexible tails, we obtain

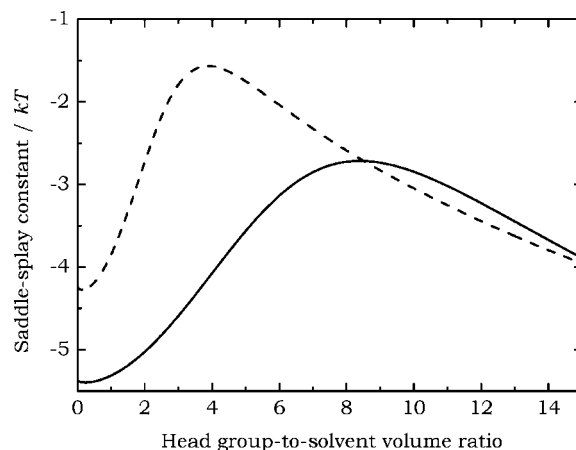
$$\frac{k_c H_0}{kT} = \frac{d}{4a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] + \frac{\xi_p^2}{4a_p} \frac{d\epsilon_{chain}}{d\xi} \quad (33)$$

$$k_c = \frac{d^2 kT}{4a_p} \left[ 1 + \frac{v_{hg}}{v_w} \frac{\phi_{hg}^p}{1 - \phi_{hg}^p} \right] + \frac{\xi_p^3}{a_p} \left[ \frac{d\epsilon_{chain}}{d\xi} + \frac{\xi_p}{4} \frac{d^2 \epsilon_{chain}}{d\xi^2} \right] \quad (34)$$

$$\bar{k}_c = -\frac{d^2}{3a_p} \left[ 1 - \frac{v_{hg}}{v_w} \left( 1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p} \right) \right] - \frac{\xi_p^3}{3kT a_p} \frac{d\epsilon_{chain}}{d\xi} \quad (35)$$

by means of setting  $k'_a = k'_\xi - \xi_p$ ,  $k''_a = k''_\xi - 2\xi_p k'_\xi$  and  $k'''_a = k'''_\xi + \xi_p^2/3$  equal to zero in eqs 23, 26, and 28, respectively.

It is interesting to compare the two cases of open and closed systems in a thermodynamic sense for surfactants with flexible tails. It is noted that the chain conformational free energy  $\epsilon_{chain}$



**Figure 11.** Saddle-splay constant ( $\bar{k}_c$ ) for a thermodynamically open monolayer plotted against the head group-to-solvent volume ratio ( $v_{hg}/v_w$ ) as well as the hydrophilic–lipophilic balance (HLB =  $v_{hg}/v_{tail}$ ) for double-chain surfactants with head groups treated as hard spheres with  $\alpha = \pi/3\sqrt{3}$  (solid line).  $k_c$  for the corresponding single-chain surfactant is also given (dashed line).  $\xi_p$  was calculated from eq 24 with  $v_{tail}$  set to the same values as in Figure 9 and  $v_{hg}$ ,  $v_w$ , and  $\gamma_{hb}$  are equal to what is given in Figures 1 and 2.



contributes explicitly to eqs 33–35 for the case of thermodynamically closed layers but not to eqs 23, 27, and 29 for open layers whereas the contribution due to the hydrophobic effect ( $\gamma_{\text{hb}}$ ) is present in the expressions for open layers but absent for closed layers. The absence of  $\gamma_{\text{hb}}$  in eqs 33–35 is a direct result of  $a$  being constant ( $k_a' = k_a'' = k_a''' = 0$ ) in the process of bending a thermodynamically closed surfactant monolayer (cf. eq 9). The explicit contribution to the bending elasticity constants that arises as an effect of chain conformational entropy  $\varepsilon_{\text{chain}}$  for thermodynamically closed layers has previously been treated in detail and extensively discussed by Szleifer, Ben-Shaul, and Gelbart.<sup>17,50</sup> However, it is obvious from our present treatment that the quantitative outcome of the different bending elasticity constants is expected to depend not only on the model but also on the particular constraints at which amphiphilic mono- and bilayers are bent.

## 8. Summary

The three bending elasticity constants  $k_c H_0$ ,  $k_c$ , and  $\bar{k}_c$  have been evaluated for monolayers formed by a nonionic surfactant according to a novel approach. Hence, it is demonstrated that the entropy of mixing rigid head groups with solvent molecules in a hydrophilic layer of finite thickness gives rise to a repulsive interaction among the hydrophilic head groups that may balance contributions due to the hydrophobic tails. In accordance, we have derived explicit expressions for the head group contribution to the various bending elasticity constants in terms of molecular volumes of head group and solvent as well as the thickness of the hydrophilic layer and the effective volume fraction of head groups therein. Among other things, it is demonstrated that the free energy of mixing head groups and solvent still contributes to all bending elasticity constants even in the limit where the head group volume approaches zero.

Most interestingly, we may conclude that nonionic surfactants with both a rigid tail and head group cannot form thermodynamically stable fluid layers ( $k_c = 0$ ) whereas  $k_c$  for the corresponding surfactant with a flexible tail may assume large, positive values insofar as the proportions between head and tail are well balanced. In other words,  $k_c$  is found to show a distinct maximum as a function of the head group volume located approximately where the spontaneous curvature equals zero. The combination of positive values of  $k_c H_0$  and small values of  $k_c$  suggests that considerably elongated micelles are expected to form in aqueous solutions of nonionic surfactants with a flexible tail, in agreement with experimental observations. Because the surfactant eventually becomes too hydrophilic,  $k_c$  may become negative, implying that self-assembled aggregates cannot exist in equilibrium anymore. Moreover,  $k_c$  is found to increase with the square of the layer thickness, in agreement with experiments.

The bending rigidity times the spontaneous curvature ( $k_c H_0$ ) for thermodynamically open monolayers formed by a nonionic surfactant with a flexible tail may be written as the sum of a positive contribution due to head group repulsion effects and a negative contribution originating from the hydrophobic tails. As a result,  $k_c H_0$  is seen to increase from negative to positive values with increasing head group volume. Likewise, the saddle-splay constant for the corresponding surfactant monolayer may be written as a sum of a hydrophilic and a hydrophobic contribution. The latter contribution is always negative whereas the head group contribution may assume both positive and negative values

depending on whether the hydrophobic layer is thicker or thinner than the hydrophilic layer.  $\bar{k}_c$  is found to be proportional to the square of the layer thickness

Both  $k_c H_0$  and  $\bar{k}_c$  for monolayers formed by a double-chain nonionic surfactant are found to assume lower values as compared to the corresponding single-chain surfactant with an identical head group. The bending rigidity of monolayers formed by a double-chain surfactant assumes positive values in a much wider regime of head group volumes as a result of decreased head group repulsion effects.

**Acknowledgment.** This work was supported by the Swedish Research Council.

## Appendix A: Contributions to the Bending Elasticity Constants Related to the Surfactant Tails

**Hydrophobic Free Energy.** The free energy per aggregated surfactant molecule due to the hydrophobic effect may be written as follows

$$\varepsilon_{\text{hb}} = \varepsilon_{\text{hb}}^0 + a\gamma_{\text{hb}} \quad (\text{A1})$$

where curvature-independent contributions have been incorporated into the single constant  $\varepsilon_{\text{hb}}^0$  and the macroscopic value of the hydrophobic–hydrophilic interfacial tension equals about  $\gamma_{\text{hb}} = 50 \text{ mJ m}^{-2}$  for a water–hydrocarbon interface at room temperature.<sup>51</sup> The following expressions

$$(k_c H_0)_{\text{hb}} = \frac{1}{4} \gamma_{\text{hb}} k_a' \quad (\text{A2})$$

$$k_c^{\text{hb}} = -\frac{1}{2} \gamma_{\text{hb}} k_a'' \quad (\text{A3})$$

$$\bar{k}_c^{\text{hb}} = -\gamma_{\text{hb}} k_a''' \quad (\text{A4})$$

for the hydrophobic contribution to the various bending elasticity constants have previously been derived by means of calculating  $\gamma = \varepsilon/a$  and collecting terms proportional to  $\varepsilon_0 = a_p(\gamma_p - \gamma_{\text{hb}}) \approx -a_p\gamma_{\text{hb}}$ , where  $\varepsilon_0$  is the sum of all curvature-independent contributions to  $\varepsilon$  and  $\gamma_{\text{hb}} \gg \gamma_p$  ( $\equiv \gamma[H = K = 0]$ ).<sup>28</sup>

**Chain Conformational Free Energy.** In general, any contribution to the free energy per aggregated surfactant may be written as a series expansion in curvature.<sup>28</sup> Hence, for the case of the unfavorable free energy due to the restrictions of chain conformations in a monolayer consisting of a surfactant with flexible tail we may write

$$\varepsilon_{\text{chain}} = \varepsilon_{\text{chain}}^p (1 + k_{\text{chain}}' H + k_{\text{chain}}'' H^2 + k_{\text{chain}}''' K) \quad (\text{A5})$$

where the planar part  $\varepsilon_{\text{chain}}^p$  primarily depends on the thickness  $\xi$  of the hydrocarbon part of the monolayer. The latter may be approximated by the following rather simple harmonic expression<sup>12</sup>

$$\frac{\varepsilon_{\text{chain}}^p}{kT} = \lambda(\xi - \xi_0)^2 + \frac{\varepsilon_{\text{chain}}^{\text{min}}}{kT} \quad (\text{A6})$$

which is found to agree very well with detailed statistical mechanics calculations for monolayer thickness fairly close to its optimum value  $\xi_0$ .<sup>52</sup>  $\xi_0$  has been found to be close to half the thickness of a fully stretched aliphatic chain.<sup>53,54</sup> For instance,  $\xi_0 = 8.54 \text{ \AA}$  and  $\lambda = 0.03 \text{ \AA}^{-2}$  for a  $\text{C}_{12}$  hydrocarbon chain

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according to detailed statistical mechanics calculations by Gruen and co-workers.<sup>53</sup> In a first approximation,  $\lambda$  can be assumed to be independent of surfactant tail length.

It has previously been demonstrated that the planar part of the chain conformational free energy ( $k'_{\text{chain}}$ ,  $k''_{\text{chain}}$ , and  $k'''_{\text{chain}}$  in eq A5 are set equal to zero) gives rise to the following contributions to the different bending elasticity constants<sup>12</sup>

$$(k_c H_0)_{\text{chain}} = -\frac{1}{4a_p} \frac{d\varepsilon_{\text{chain}}}{d\xi} \left( \frac{\partial \xi}{\partial H} \right)_K [H = K = 0] \quad (\text{A7})$$

$$k_c^{\text{chain}} = \frac{1}{4a_p} \frac{d^2 \varepsilon_{\text{chain}}}{d\xi^2} \left( \frac{\partial \xi}{\partial H} \right)_K^2 [H = K = 0] + \frac{1}{4a_p} \frac{d\varepsilon_{\text{chain}}}{d\xi} \left( \frac{\partial^2 \xi}{\partial H^2} \right)_K [H = K = 0] + \frac{k'_a}{2a_p} \frac{d\varepsilon_{\text{chain}}}{d\xi} \left( \frac{\partial \xi}{\partial H} \right)_K [H = K = 0] \quad (\text{A8})$$

$$\bar{k}_c^{\text{chain}} = \frac{1}{a_p} \frac{d\varepsilon_{\text{chain}}}{d\xi} \left( \frac{\partial \xi}{\partial K} \right)_H [H = K = 0] \quad (\text{A9})$$

### Appendix B: Derivation of the Head Group Repulsion Contribution to the Bending Elasticity Constants

The free energy per aggregated surfactant of mixing head group and solvent molecules in a hydrophilic layer is given in eq 10, where the volume fraction of head groups in the hydrophilic layer of the film equals

$$\phi_{\text{hg}} = \frac{\nu_{\text{hg}} V_{\text{hb}}}{\nu_{\text{tail}} V_{\text{hl}}} \quad (\text{B1})$$

The volumes of the hydrophobic and the hydrophilic layers equal  $V_{\text{hb}} = N\nu_{\text{tail}}$  and  $V_{\text{hl}} = N_w\nu_w + N\nu_{\text{hg}}$ , respectively, where the molecular volumes of the tail, head group, and solvent,  $\nu_{\text{tail}}$ ,  $\nu_{\text{hg}}$ , and  $\nu_w$ , respectively, are constants for incompressible media.

The volume ratio between a hydrophobic layer of thickness  $\xi$  and a hydrophilic layer of thickness  $d$  is curvature-dependent according to the following geometrical relation

$$\frac{V_{\text{hb}}}{V_{\text{hl}}} = \frac{\xi}{d} \left[ 1 - (\xi + d)H + d(\xi + d)H^2 + \frac{\xi^2 - d^2}{3}K \right] \quad (\text{B2})$$

By means of combining eqs 9, B1, and B2, we may write the volume fraction of head groups as a second-order expansion with respect to  $H$  and  $K$

$$\phi_{\text{hg}} = \phi_{\text{hg}}^p \left[ 1 - (d - k'_a)H + (k''_a + d(d - k'_a))H^2 + \left( k'''_a - \frac{d^2}{3} \right)K \right] \quad (\text{B3})$$

where  $\phi_{\text{hg}}^p \equiv \phi_{\text{hg}}(H = K = 0)$ . The head group free energy  $\varepsilon_{\text{hg}}$  in eq 10 is curvature-dependent as a result of the curvature

dependence of  $\phi_{\text{hg}}$  in eq B3, and the corresponding contribution to the various bending elasticity constants may be evaluated from the following definitions<sup>12,28</sup>

$$(k_c H_0)_{\text{hg}} = -\frac{1}{4a_p} \left( \frac{\partial \varepsilon_{\text{hg}}}{\partial H} \right)_K [H = K = 0] \quad (\text{B4})$$

$$k_c^{\text{hg}} = \frac{1}{4a_p} \left[ 2k'_a \left( \frac{\partial \varepsilon_{\text{hg}}}{\partial H} \right)_K [H = K = 0] + \left( \frac{\partial^2 \varepsilon_{\text{hg}}}{\partial H^2} \right)_K [H = K = 0] \right] \quad (\text{B5})$$

$$\bar{k}_c^{\text{hg}} = \frac{1}{a_p} \left( \frac{\partial \varepsilon_{\text{hg}}}{\partial K} \right)_H [H = K = 0] \quad (\text{B6})$$

so as to give eqs 11–13.

### Appendix C: List of Symbols

$a_p$	area per aggregated surfactant at the hydrophobic–hydrophilic interface of a planar monolayer
$d$	thickness of the hydrophilic part of a monolayer
$H$	mean curvature at the hydrophobic–hydrophilic interface
$H_0$	spontaneous curvature
$k$	Boltzmann's constant
$K$	Gaussian curvature at the hydrophobic–hydrophilic interface
$k_c$	bending rigidity of a monolayer
$\bar{k}_c$	saddle-splay constant of a monolayer
$k'_a$ , $k''_a$ , and $k'''_a$	constants related to the curvature dependence of $a$ as defined in eq 9
$k'_\xi$ , $k''_\xi$ , and $k'''_\xi$	constants related to the curvature dependence of $\xi$ as defined in eq 8
$N$	number of surfactant molecules in a monolayer
$N_w$	number of solvent molecules in the hydrophilic part of a monolayer
$T$	absolute temperature
$\nu_{\text{hg}}$	molecular volume of the surfactant head group
$\nu_{\text{tail}}$	molecular volume of the hydrophobic surfactant tail
$\nu_w$	molecular volume of solvent
$\alpha$	volume fraction of close-packed head groups in the hydrophilic part of a monolayer
$\varepsilon$	free energy per surfactant aggregated in a monolayer
$\varepsilon_{\text{chain}}$	chain conformational contribution to $\varepsilon$
$\varepsilon_{\text{hb}}$	hydrophobic contribution to $\varepsilon$
$\varepsilon_{\text{hg}}$	head group repulsion contribution to $\varepsilon$
$\lambda$	parameter related to the quadratic behavior of $\varepsilon_{\text{chain}}$ as defined in eq A6
$\gamma_{\text{hb}}$	hydrophobic–hydrophilic interfacial tension
$\xi_p$	thickness of the hydrophobic part of a planar monolayer
$\phi_{\text{hg}}^p$	volume fraction of head groups in the hydrophilic part of a planar monolayer

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