Curvature Elasticity of Pure and Mixed Surfactant Films

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We present here the first theoretical account of the dependence of curvature elastic energies of surfactant layers on area per head group and alkyl carbon number in pure films, and on composition in mixed cases. Treating explicitly the chain conformational statistics, we show that the bending constant can be decreased by an order of magnitude upon halving of the carbon number or upon replacement of as few as one-half of the long chains by the short ones.

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Recently much interest has been focused on the bending elasticity of amphiphilic layers such as those encountered in vesicles and red blood cells,[1] microemulsions,[2,3] and lamellar systems.[4] It is now widely appreciated that the curvature energy (k) of these interfacial films plays a crucial role in the determination of the size and shape distributions of aggregates[3] and the relative stabilities of competing phases.[2,5] In particular, one can distinguish between systems whose films have bending constants of tens of k_BT and those for which k is approximately equal to k_BT. Notable among the former class are the phospholipid membranes whose curvature energies have been measured by many investigators.[6-11] While controversy still remains concerning the exact values of k, there is consensus that k in these systems is on the order of tens of k_BT. In lamellar and fluid microemulsion phases of single-chain-surfactant, short-chain-alcohol, oil, and water systems, on the other hand, ESR,[4] light,[12,13] x-ray,[14] and direct mechanical[15] experiments indicate that the interfacial bending energy is as small as k_BT. Here the thermal (undulation) fluctuations dominate many properties of the film[12-16] and it becomes crucial to understand the basis for such dramatic lowering of k.

Previous theories[17-19] have developed both phenomenological and microscopic approaches to the role of the alkyl-chain elasticity in determining the curvature force constants of surfactant layers. While properly focusing attention on these important contributions to bending energies, no attempt was made to provide *a priori* relations between k and area per molecule, chain length, and mixed-layer composition. In the present Letter we pursue the premise that the curvature elasticity of surfactant films is dominated by the "tails"—rather than the "heads"—of the constituent amphiphiles. More specifically, our calculations suggest that the bending energy arises primarily from the loss of conformational entropy associated with the hydrophobic chains. Using a simple statistical thermodynamic theory of chain packing at interfaces, we demonstrate first that the value of k depends sensitively on the area per molecule, decreasing dramatically with increasing area. Furthermore, we show that the bending energy for pure (one-component) films is a strongly increasing function of chain length (alkyl carbon number). For *mixed* films—such as those which arise in long-chain-surfactant, short-chain-alcohol systems—we find that k can be even lower than that for the pure film of short chains. Finally we show, without any empirical or adjustable parameters, that the k associated with the tails varies from tens of k_BT down to k_BT as n drops from ≈ 12 to ≈ 6 in pure films or as one adds enough short chains in the *mixed* systems. These predictions are consistent with preliminary suggestions from synchrotron x-ray scattering experiments on lamellae formed from sodium dodecyl sulfate (SDS) and alcohols of decreasing chain length.[20]

Consider the basic quadratic expression for the free energy per unit area of film which is characterized by the principal curvatures c_1 and c_2: $f/a = \frac{1}{2}k(c_1+c_2-c_0)^2+\bar{k}c_1c_2$. Here f is the free energy per molecule, a is the (head group) area per molecule, and c_0 is the "spontaneous" curvature. k and $\bar{k}$ correspond to the "splay" and "saddle splay" modes discussed in the classic Frank theory[21] of curvature deformations in bulk liquid crystals. We shall be concerned here only with the case of *bi*layers. (*Mono*layers are discussed at length elsewhere.[22]) In addition, as already mentioned above, we focus attention on the *tails* since the contribution to the bending energy from the heads is expected in general to be smaller and—in any case—we are interested here in determining the dependence of k on chain lengths and composition.

The tail contribution k_{tail} (henceforth simply k) is calculated from the curvature free energy via extension of the mean-field theory developed earlier to treat chain packing in micelles and bilayers.[23] We need only specify the bent film geometry (small c_1,c_2) and determine the chain conformational statistics by minimizing the free energy subject to the constraint of uniform average density of tail segments. The total area available to the chains at a distance x from the "midplane" surface is given by $A(x)=A(0)[1+(c_1+c_2)x+c_1c_2x^2]$ with $x=\pm l$ corresponding to the "external" (E) and "internal" (I) surfaces of the bilayer. Let $\phi_E(x,\alpha)dx$ be the volume [in units of a segment (CH_2) volume] occupied by an E chain in the interval $x,x+dx$ when it has configuration α. Here α refers both to the internal conformation of the (semiflexible) chain and to its overall position and orientation with respect to the interface. For an arbitrary bilayer deformation, there are $N_{E(I)}$ molecules whose heads originate at the surface of the external (internal) half: $N_E+N_I=N$, with $y_{E(I)}=N_{E(I)}/N$. Then the constraint of uniform segment density can be written as

$$y_E\sum_\alpha P_E(\alpha)\varphi_E(x,\alpha)+(1-y_E)\sum_\beta P_I(\beta)\varphi_I(x,\beta)=A(x)/N\equiv a(x), \tag{1}$$

where $P_E(\alpha)$ is the probability that an E chain will have configuration α [and similarly for $P_I(\beta)$]. Note that Eq. (1) collects contributions (i.e., segments) from chains in *both* the outer (E) and inner (I) halves of the film: Interdigitation of the chains plays an important role in bending of the bilayer.

The probability distribution functions P are then found by our minimizing the chain free energy

$$f_t=y_E\left\{\sum_\alpha P_E(\alpha)\epsilon(\alpha)+k_BT\sum_\alpha P_E(\alpha)\ln P_E(\alpha)\right\}+(1-y_E)\left\{\sum_\beta P_I(\beta)\epsilon(\beta)+k_BT\sum_\beta P_I(\beta)\ln P_I(\beta)\right\}, \tag{2}$$

subject to the packing constraints (1). [Here $\epsilon(\alpha)$— $\approx\frac{1}{2}$ kcal/mole per gauche bond—is the internal energy associated with the conformation α]. This constrained variational calculation yields directly

$$P_E(\alpha)=Z_E^{-1}\exp\left\{-\left[\epsilon(\alpha)+\int_{-l}^{+l}dx\,\Pi(x)\varphi_E(x,\alpha)\right](k_BT)^{-1}\right\} \tag{3}$$

(with Z_E the normalization constant, or "partition function") and similarly for $P_I(\beta)$. $\Pi(x)$ denotes the set of Lagrange multipliers conjugate to the constraint conditions specified by Eq. (1): Physically, they describe the lateral pressures acting on each chain, due to the interchain repulsions arising from excluded volume.

The key result from the above mean-field analysis is that the single quantity $\Pi(x)$ specifies completely all of the conformational statistics and thermodynamics of the surfactant chains.[23] Furthermore, this lateral pressure profile is determined in turn by the *geometry* of the amphiphilic layer, i.e., by the $a(x)$ defining the available cross-sectional area (per chain) as a function of distance along the normal. For convenience of computation, we discretize x space by dividing up the bilayer into M shells of finite thickness: The summations over chain configurations are evaluated as described elsewhere.[23] Then Eq. (1) reduces to M coupled (nonlinear) algebraic relations which are solved directly for the Π_i's, the lateral pressures which must be applied to "squeeze" an "isolated" chain—one constrained by the interface—into one whose segments are packed at constant density.

We only present here our results for k, suppressing the more problematic saddle-splay constant $\bar{k}$.[22] Also, our calculations refer to curvature free energies for which the area per molecule is held constant (implying that y_E varies with curvature). As discussed elsewhere,[22] this k is an upper bound to the bending energy which would ensue if the area per molecule were dependent on radius of curvature R. In Fig. 1 is displayed the dependence of k on area per molecule a, for two different pure chain bilayers ($n=6$ and $n=12$) and for one mixed (equimolar 6/12) system. This plot illustrates how k is a strongly decreasing function of a, e.g., for $a=30\rightarrow 36$ Å^2 in the

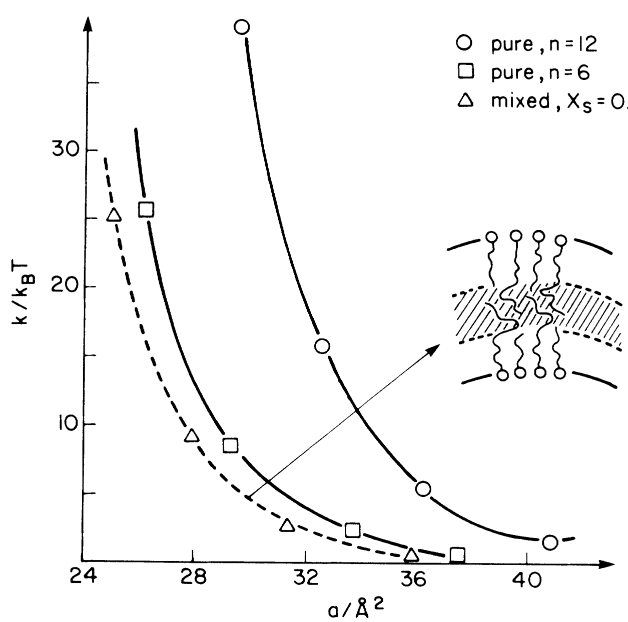

FIG. 1. Bending energy k vs area per molecule for two single-component bilayer systems and for their equimolar mixture.

$n=12$ case, we have $k=(38\rightarrow 5)k_BT$. Such dramatic lowering of k is easily understood in terms of the decreased loss of conformational entropy associated with bending a significantly less confined chain. It is also consistent with the experimental observation[24] that bending energies are small (of order few k_BT) for pure films of nonionic surfactant (e.g., the alkyl polyglycol ethers) whose bulky head groups demand large areas per molecule (>50 Å^2). Note that the $n=6$ curve in Fig. 1 lies considerably below that for $n=12$. This reflects the strong dependence of k on (alkyl carbon number) n which is shown more explicitly in Fig. 2, for two different values of a. In each case, the bending energy is a monotonically increasing function of chain length. For one-component bilayers with $a=27$ Å^2, for example, k is almost ten times bigger for $n=12$ than for $n=6$: In general, in fact, one finds $k\sim n^x$ with $x\approx 2.5$. As far as actual *magnitudes* are concerned, our results suggest that measurements of bending energies for short-chain surfactant systems would give k values as small as a few k_BT.

At least as interesting as the n dependence of k is its variation with mole fraction in *mixed* systems, appropriate to the experimental situation in which short-chain cosurfactants (e.g., alcohols) are added to bilayer systems. Returning to Fig. 1 we see, from how closely the equimolar curve follows that for $n=6$, that replacing as few as half of the long chains by short ones is sufficient to reduce k from its $n=12$ to its $n=6$ value. This is because the short chains act as effective "spacers," setting the longer ones far enough apart so that their "ends" are dangling essentially "free." These ends are in fact interdigitated, comprising a middle portion of the bilayer —see inset of Fig. 1—in which the chains are only marginally constrained by one another (i.e., larger effective area per molecule). Accordingly, the curvature energy associated with the mixed film is determined largely by the bending of the small-area ($n=6$) portion of each monolayer.

The dramatic decrease of k upon replacement of long chains by short ones is illustrated more directly in Fig. 3 where we plot k vs X_S, the mole fraction $N_S/(N_S+N_L)$ for an average area per molecule of 30 Å^2. Again we note the "saturation" effect: A one-to-one ratio of short to long chains ($X_S=\frac{1}{2}$) is sufficient to reduce the bending energy by an order of magnitude, as discussed above. We note also—see dotted curve—that the decrease of k with X_S in the mixed case is faster than that with n in the pure film. This behavior has indeed been observed in recent spin probe[4] and x-ray synchrotron[20] measurements in SDS-pentanol ($n_L=12$, $n_S=5$) mixtures. In the *real* systems, of course, X_S can never be made to exceed ≈ 0.8 since the limit of a pure short-chain layer is not physically possible. Somewhat more remarkable than the decrease of k with X_S is the fact that (for $X_S>0.3$ in the example of Fig. 3) the mixed bilayer is even easier to bend than a pure film composed only of its short-chain species, i.e., $k(X_S>0.3)<k(X_S=1)$. This feature was already noted in Fig. 1, where the curve of k vs a for a 50-50 mixture of $n=6/12$ lies everywhere below that for the pure $n=6$ case.

We close with mention of a simple approximation in

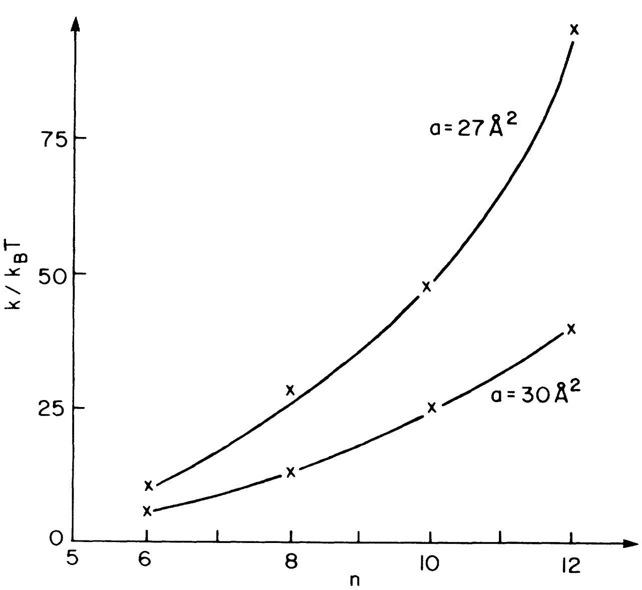

FIG. 2. k vs alkyl carbon number n, for two values of the area per molecule.

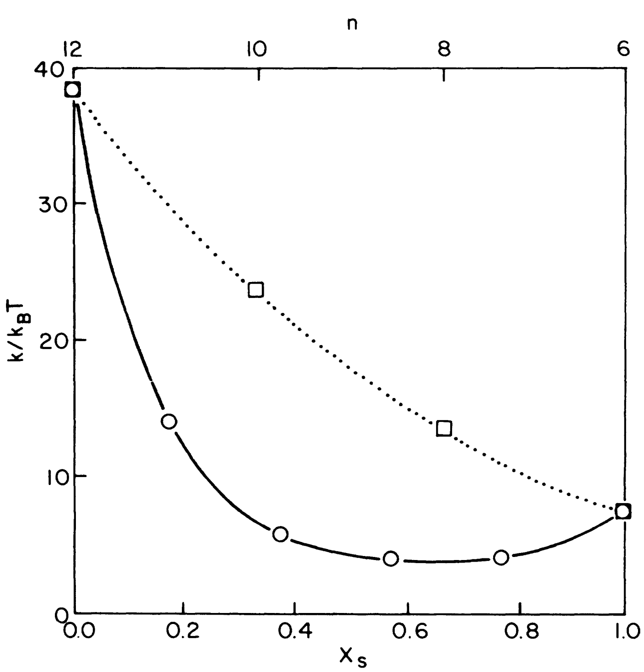

FIG. 3. k vs X_S, the mole fraction of short chains in a mixture of $n=12$ and $n=6$ components; the upper abscissa labels refer to the dotted curve, which shows the values of k for different *pure* bilayers.

which interdigitation is neglected and a bent bilayer is treated as a pair (E/I) of stretched/compressed monolayers. A cylindrical deformation, say, at constant area per molecule a, implies average chain lengths of

$$\left.\begin{matrix} l_E \\ l_I \end{matrix}\right\} = 1 \pm \tfrac{1}{2}(l_p/R),$$

where $l_p = v/a = l(R=\infty)$ with v the chain volume. Simple scaling arguments, confirmed by model calculations,[25] show that the free energy of a (small a) *planar* layer varies as l^2/n. Substituting $l_{E,I}(R)$ for l, adding the contributions for the two ($\not{F} \rightarrow \pm$) monolayers, and evaluating the R^{-2} coefficient, we find $k \sim l_p^4/an$. With use of $l_p = v/a \sim n/a$, this yields $k \sim n^3/a^5$, in qualitative agreement with the numerical results discussed above.

We conclude, then, by reiterating our finding that the elasticity of packed chains is the dominant contributing factor to the bending energy of surfactant films. For one-component bilayers we have shown that the curvature elastic constant can vary from $k_B T$ to tens of $k_B T$ as either the alkyl (carbon) number is increased or the area per molecule is decreased. More significantly—related to the role of short-chain alcohol and other cosurfactant additives in stabilizing model membrane and microemulsion systems—we have demonstrated that addition of relatively few short chains is sufficient to lower the bending energy dramatically (even beyond that of the pure, short-chain film). All of these effects can be straightforwardly understood in terms of the conformational packing entropy associated with the excluded volume of semiflexible chains at curved interfaces.

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