

On the Stability of Lyotropic Lamellar Liquid Crystals and the Thicknesses of Their Lamellae

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The stability of lamellar lyotropic liquid crystals was investigated using a thermodynamic formalism. The interfacial tension γ was expressed in terms of the thicknesses δ_1 and δ_2 of the two kinds of lamellae. For given thicknesses, the system might be stable if $\gamma \geq 0$. In addition, the derivatives $\partial f / \partial \delta_i$ of the excess free energy f , due to van der Waals, hydration, steric, electrostatic, and undulation interactions, must be negative for the lamellar structure to be stable. The thermodynamic conditions employed show that the domain of existence of the lamellar phase is restricted to narrow ranges of layer thicknesses and parameters of interaction. The effect of the bending modulus and of the ionic strength on the stability was examined. The thicknesses of the two kinds of lamellae were calculated using equilibrium and mass balance equations. It was shown that the nonlinearity of these equations could be responsible for the observed deviations from the "ideal dilution law". A comparison between the calculated and experimental results was made.

Introduction

Lyotropic liquid crystals are composed of a surfactant, a cosurfactant (typically a medium chain length alcohol), water, and oil. It is well-known that, in relatively narrow ranges of composition and temperature, a lamellar structure that exhibits a long-range translational order along one direction (L_a) can be formed.¹ It was also shown that the lamellar phase could preserve its orientational order upon its dilution with water.¹ This was initially supposed to be a consequence of the repulsion between the charged interfaces formed by ionic surfactants. However, it was subsequently found that the lamellar phase can be hyperswollen by adding large amounts of an oil–cosurfactant mixture, a system for which the electrostatic interactions do not play a role;² a hyperswelling in water was also observed for nonionic surfactants.³

It was first suggested by Helfrich⁴ that the confinement of the thermal undulations of uncharged phospholipid bilayers by the neighboring bilayers, in a lipid/water lamellar liquid crystal, leads to a long-range repulsive force, which can be responsible for the extensive swelling of the lipid bilayers in water.⁵ However, for most bilayers, their high bending modulus K_C provides a small contribution of the entropic confinement (which is inversely proportional to K_C) to the free energy; hence only a limited swelling can occur.⁶ It was shown by Safinya et al.⁷ that the addition of pentanol to an uncharged lipid (dimyristoylphosphotidylcholine)/water multilayer decreases the rigidity of the bilayers and consequently the equilibrium separation distance increases from $d \approx 40$ to $d \geq 200$ Å.

It is then tempting to attribute the high swelling (distances over 5000 Å)² of uncharged lyotropic liquid

crystals to a low value of the interface bending modulus, which provides a large entropic confinement repulsion. However, the matter is more complex in this case than in that of lipid bilayers. The lipid bilayers are generally formed before their swelling in water, and as a first approximation one can consider that the total area and the thickness of the bilayers remain constant during the formation of the lamellar liquid crystal for any water dilution. In this case, even for strong repulsions between the layers, the system remains stable. Indeed, Palmer and Schmitt⁸ observed that charged lipid bilayers swelled indefinitely in distilled water but collapsed steadily upon exposure to solutions of progressively higher ionic strength.

In contrast, the lyotropic liquid crystals are self-assembled after the mixture of the constituents is allowed to equilibrate for a long time (typically, days), and there are additional contributions to the free energy due to the formation of the lamellae. In this case, a strong repulsion between layers will increase the free energy of the lamellar phase and as a result a nonlamellar phase may be formed. It was observed experimentally that the addition of salt, which screens the electrostatic interactions, and hence reduces repulsion, to a dilute ionic surfactant/cosurfactant/water system, can stabilize the lamellar phase.⁹ Dilute lamellar phases typically occur in relatively narrow ranges of temperature and composition, and the addition of a cosurfactant or the increase of temperature (which by decreasing the bending modulus enhances the long-range undulating repulsion between layers, thus increasing the free energy) can lead to a phase transition.

The domains of existence of the lamellar liquid crystals can be in principle identified by calculating the free energies of the various possible phases. Because of the difficulty in performing such a calculation, a first purpose of this paper is to employ the thermodynamic formalism developed by Ruckenstein¹⁰ to extract some information about the domain of stability of the lamellar phase.

A second goal is to determine the widths of the water and oil lamellae and to explain the deviation from the so-called "ideal dilution law". In a crude model, one can

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assume that the entire surfactant and cosurfactant is adsorbed on the interface and hence the total area of the interface, S , for a system of volume V is proportional to the volume fraction of surfactant and cosurfactant, ϕ . Because for planar interfaces $V = Sd/2$, the repeat distance d (the sum of the thicknesses of the hydrophobic and hydrophilic layers) becomes inversely proportional to ϕ . Consequently, the product between d and ϕ should be independent of ϕ . This behavior is sometimes called the "ideal dilution law". However, it was well established that deviations from the ideal dilution law occur frequently,¹ the area per headgroup of surfactant being variable during swelling, and dependent on the surfactant/cosurfactant ratio.

These deviations were accounted by Strey et al.,³ who carried out experiments with the binary water- $C_{12}E_5$ system, by noting that the amplitude of the thermal undulations increased with the repeat distance d . If one considers the total area of the interface a constant S which depends only on the number of surfactant molecules, the projection S_0 of the total area on a plane perpendicular to d will decrease with increasing d . Hence, the apparent area per surfactant molecule, which is defined as the ratio between S_0 and the total number of surfactant molecules, decreases with increasing d , while the ideal dilution law implies that the apparent area per surfactant molecule is a constant. The excess area, defined as $\Delta S = S - S_0$, was related to the bending modulus of the interface,³ and the experimental results for the deviations from the ideal dilution law were used to determine K_C .^{3,11} However, it should be noted that there are binary systems for which the deviations from the ideal dilution law occur in the opposite directions. For instance, in the binary systems of fatty acid alkali soaps/water, the apparent area per headgroup increases with water dilution, because of the incorporation of water in the interface.¹

In the second part of the paper, it will be shown that the partition of the alcohol between the phases can explain the deviations from the ideal dilution law for a water/oil/surfactant/cosurfactant lyotropic lamellar liquid crystal.

I. Thermodynamic Stability of Lyotropic Liquid Crystals

I.1. Thermodynamic Equations. We briefly describe the thermodynamic formalism of Ruckenstein.¹⁰ Let us consider a liquid crystal of volume V per unit area, in equilibrium, and denote by δ_1 the average thickness of the water layer and by δ_2 the average thickness of the oil layer. The Helmholtz free energy of the system can be written as the sum of a free energy F_0 of a hypothetical system in which the lamellae are treated as bulk, planar, phases and a free energy F_1 , which accounts for the smallness of the lamellae, the interactions between them, and their thermal undulations. One can write

$$dF_0(\delta_1, \delta_2, V, N_i) = 2\gamma d\left(\frac{V}{\delta_1 + \delta_2}\right) + \sum \mu_i dN_i - p_1 d\left(\frac{V\delta_1}{\delta_1 + \delta_2}\right) - p_2 d\left(\frac{V\delta_2}{\delta_1 + \delta_2}\right) \quad (1a)$$

where γ is the interfacial free energy between the two kinds of lamellae, μ_i is the chemical potential of species i (at pressure p_1 in the layers of thickness δ_1 and pressure p_2 in the layers of thickness δ_2), and N_i is the number of

molecules of species i in the volume V , and

$$dF_1(\delta_1, \delta_2, V) = d\left(f(\delta_1, \delta_2) \frac{V}{\delta_1 + \delta_2}\right) \quad (1b)$$

where f is the free energy per unit area of one pair of lamellae 1 and 2, due to their thinness, interaction between them, and their thermal undulation ($V/(\delta_1 + \delta_2)$ is the number of pairs of lamellae). It should be emphasized that the pressures p_1 and p_2 are not equal to the external pressure because they are defined on the basis of the free energy F_0 .

However, at thermodynamic equilibrium one can write

$$dF_0 + dF_1 \equiv dF(N_i, V) = \sum \mu_i^* dN_i - p dV \quad (2)$$

where p is the external pressure and μ_i^* is the chemical potential of species i at the pressure p . By equating the coefficients of dV , dN_i , $d\delta_1$, and $d\delta_2$ from eqs 1 and 2, after some algebra the following equations are obtained¹⁰

$$p_1 = p + \frac{\partial f}{\partial \delta_1} \quad (3a)$$

$$p_2 = p + \frac{\partial f}{\partial \delta_2} \quad (3b)$$

$$2\gamma = -f + \delta_1 \frac{\partial f}{\partial \delta_1} + \delta_2 \frac{\partial f}{\partial \delta_2} \quad (3c)$$

$$\mu_i^*(p) = \mu_i(p_i) \quad (3d)$$

The free energy per unit area for a pair of successive lamellae, which includes the effect of thermal undulations, is computed as follows. Let us denote by $U(x_1, x_2)$ the interaction potential between planar water and oil lamellae of thicknesses x_1 and x_2 , which include the van der Waals, hydration, steric, and electrostatic interactions

$$U(x_1, x_2) = f_{\text{vdw}} + f_{\text{hydration}} + f_{\text{steric}} + f_e \quad (4)$$

The first quantitative method to account for the undulation repulsion between membranes, due their mutual confinement, was developed by Helfrich,⁴ which showed that the entropic contribution to the free energy, due to the confinement of the thermal fluctuations by the neighboring lamellae, for membranes interacting via a hard-wall potential, is given by $\Delta F \propto (kT)^2/K_C\sigma^2$, where k is the Boltzmann constant, T is the absolute temperature, K_C is the bending modulus, and σ is the root-mean-square fluctuation of the position of the membrane. There have been a number of theoretical attempts to extend the Helfrich theory to bilayers interacting via arbitrary potentials.^{12–15} Here we will employ a variational procedure developed recently by the authors.¹⁵ The free energy is composed of the energy of interaction between lamellae, averaged over the distance distributions, and an entropic term, due to the confinement of one interface by its neighbors. Denoting with $P_1(x_1)$ and $P_2(x_2)$ the distribution of distances through the water and oil lamellae, respectively, and considering that the free energy due to the entropic confinement of the membranes is inversely

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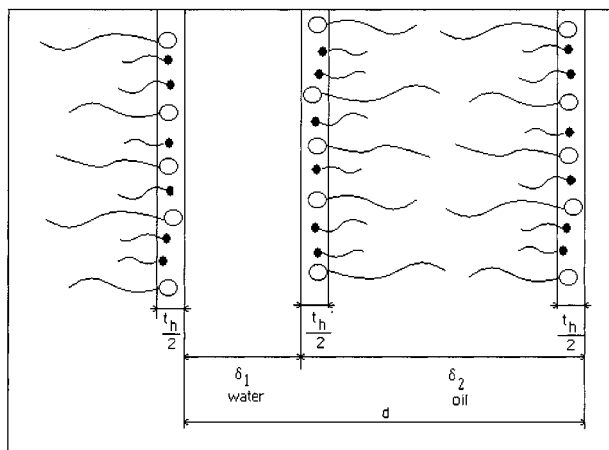


Figure 1. A sketch of a lyotropic lamellar liquid crystal, composed of water, oil, a surfactant (open circles), and cosurfactant (full circles). The distribution of the surfactant and cosurfactant between the water and oil phases and interface is discussed in section II.

proportional to the root-mean-square fluctuations of the distribution of the distances, $(\sigma_1)^2$ and $(\sigma_2)^2$, through water and oil, respectively, one can write, using Derjaguin approximation, that

$$f(\delta_1, \delta_2, \sigma_1, \sigma_2) = \int dx_1 dx_2 P_1(x_1) P_2(x_2) U(x_1, x_2) + \frac{(kT)^2}{64K_C\sigma_1^2} + \frac{(kT)^2}{64K_C\sigma_2^2} \quad (5)$$

where x_1 and x_2 are the fluctuating thicknesses of the water and oil layers, respectively.

In a first approximation one might consider that σ_1 and σ_2 are independent of each other. The energy is increased by distributions with large values of σ , because in this case a larger part of the interface is in a region of stronger repulsive interactions; on the other hand the entropic term decreases when the σ values are large. Consequently, there are optimum values of σ_1 and σ_2 for which the free energy is minimum. The following asymmetric truncated Gaussian function will be employed for the distance distributions ($i = 1, 2$)¹⁵

$$\begin{aligned} P_i(x_i) &= 0 \\ x_i &< 0 \\ P_i(x_i) &= \frac{1}{C_a} \exp\left(-\frac{(x_i - \delta'_i)^2}{2\sigma_i^2}\right) \\ 0 &< x_i < \delta'_i \\ P_i(x_i) &= \frac{1}{C_a} \exp\left(-\frac{(x_i - \delta'_i)^2}{2(\alpha\sigma_i)^2}\right) \\ x_i &> \delta'_i \end{aligned} \quad (6)$$

where α is an asymmetry coefficient of the distribution; in the calculations, the value $\alpha = 1.4$, suggested by Monte Carlo simulations,¹⁶ will be employed. The constant C_a and the position δ'_i of the maximum of the distribution can be calculated as a function of the average distance δ_i through normalization and distance averaging, respec-

tively. Then, the minimization of $f(\delta_1, \delta_2, \sigma_1, \sigma_2)$ of eq 5 with respect to σ_1 and σ_2 provides the free energy f for any values of δ_1 and δ_2 .

I.2. The Interaction Potential $U(x_1, x_2)$. Let us consider the contributions to the interaction potential $U(x_1, x_2)$, for fixed x_1 and x_2 thicknesses of the planar water and oil layers, respectively (see Figure 1). In the hypothesis of pairwise additivity, the van der Waals excess interaction for a pair of lamellae in a periodic multilayer is given by (see Appendix A)

$$\begin{aligned} f_{\text{vdW}} = & -\frac{A_{\text{eff}}}{12\pi} \left\{ \frac{1}{(x_2 - t_h)^2} + \sum_{n=1}^{\infty} \left(\frac{1}{(n(x_1 + x_2) - x_2 + t_h)^2} + \frac{1}{(n(x_1 + x_2) + x_2 - t_h)^2} - \frac{2}{(n(x_1 + x_2))^2} \right) \right\} \equiv \\ & -\frac{A_{\text{eff}}}{12\pi} \left\{ \frac{1}{(x_1 + t_h)^2} + \sum_{n=1}^{\infty} \left(\frac{1}{(n(x_1 + x_2) - x_1 - t_h)^2} + \frac{1}{(n(x_1 + x_2) + x_1 + t_h)^2} - \frac{2}{(n(x_1 + x_2))^2} \right) \right\} \quad (7) \end{aligned}$$

where $A_{\text{eff}} = A_{11} + A_{22} - 2A_{12}$ is an effective Hamaker constant. In the calculation of the van der Waals attraction, the headgroups of thickness t_h of the surfactant will be considered as belonging to the water layer, since their dielectric properties are closer to water than to hydrocarbon. The van der Waals energy in eq 7 is symmetric in the distances $(x_1 + t_h)$ and $(x_2 - t_h)$ and can be interpreted as an interaction between lamellae (the terms under the sum) plus a contribution, the first term, due to the thinness of the lamellae; this term will be called effective self-energy (the true van der Waals self-energy is given by eq A.1 in Appendix A). When one of the thicknesses x_1 or $x_2 \rightarrow \infty$, the corresponding sum vanishes; however, the effective self-energy of the finite layer provides a negative contribution to the free energy. It will be shown later that this contribution is essential for the stability of the lamellar phase.

The second contribution to the energy comes from the hydration repulsion between the interfaces of the water layers, which is given by

$$f_{\text{hydration}} = A_H \exp\left(-\frac{x_1}{\lambda_H}\right) \quad (8)$$

The interaction parameters A_H and λ_H were determined for various lipid bilayers;¹⁷ λ_H is typically between 1 and 3 Å, while A_H was found within a rather broad range, around 10^{-1} J/m².

The third contribution to the free energy comes from the steric repulsion in the oil layers between the hydrocarbon tails of the surfactant adsorbed on the interface. Extending the simple formula suggested by de Gennes¹⁸ for the steric force between long-chain polymer-covered surfaces, to relatively short chains, one can write

$$f_{\text{steric}} = C \frac{2L(kT)}{s^3} \left[\frac{4}{5} \left(\left(\frac{2L}{x_2 - t_h} \right)^{5/4} - 1 \right) + \frac{4}{7} \left(\left(\frac{x_2 - t_h}{2L} \right)^{7/4} - 1 \right) \right] \quad (9)$$

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for $(x_2 - t_h) < 2L$ and

$$f_{\text{steric}} = 0$$

for $(x_2 - t_h) \geq 2L$, where $x_2 - t_h$ represents the actual thickness of the hydrocarbon lamella, L is the maximum length of the surfactant tail, and s is the separation distance between the headgroups of the surfactant along the interface. The proportionality coefficient C can be determined from a comparison with experimental data and was shown to be of the order of unity;¹⁹ here it will be taken as unity.

The electrostatic contribution to the energy, in the presence of an electrolyte, depends on the behavior of the surface charge density, σ_e , when two surfaces approach each other. Assuming that the surface charge density remains constant, an excellent approximation for the electrostatic contribution to the energy is given by²⁰

$$f_e(x_1) = \frac{2nkT}{\kappa} \left\{ 2y_0 \ln \left(\frac{B + y_0 \coth\left(\frac{\kappa x_1}{2}\right)}{1 + y_0} \right) - \ln(y_0^2 + \cosh(\kappa x_1) + B \sinh(\kappa x_1)) + \kappa x_1 \right\} \quad (10)$$

where $y_0 = \tanh(e\psi_0/kT)$ and $B = (1 + y_0^2 \operatorname{cosech}^2(\kappa x_1/2))^{1/2}$.

In the above expressions, n is the concentration of the 1:1 electrolyte, $\kappa = (2e^2 n / \epsilon \epsilon_0 kT)^{1/2}$ is the reciprocal Debye length, e is the protonic charge, ϵ_0 is the permittivity constant, ϵ is the dielectric constant, and ψ_0 is the surface potential when the plates are infinitely far apart, which is related to the surface charge density via the expression $\sigma_e = (4ne/\kappa) \sinh(e\psi_0/2kT)$.

The electrostatic contribution to the energy when the only ions present in the solution are those of the counterions of the surfactant molecules, hence in the absence of an added electrolyte, is calculated by integrating the electrostatic pressure from infinity to the distance x_1 . Denoting the surface charge $\sigma_e = a_d e / A$, where a_d is the degree of dissociation and A is the area per surfactant molecule adsorbed on the interface, the electrostatic energy per unit area is given by (see Appendix B)

$$f_e(x_1) = - \frac{2\epsilon\epsilon_0(kT)^2}{e^2} \int_{\infty}^{x_1} K^2(x) dx \quad (11a)$$

where

$$\frac{Kx}{2} \tan\left(\frac{Kx}{2}\right) = \frac{a_d x e^2}{4A\epsilon\epsilon_0 kT} \quad (11b)$$

The case $a_d = 0$ corresponds to a noncharged interface ($f_e = 0$).

1.3. Necessary Conditions for Stability. In a system with a fixed number of layers, such as the phospholipid bilayers, the equilibrium position (corresponding to the minimum of the free energy, F , of the whole system) is obtained when the free energy per unit area for the pair water/bilayer, f , is a minimum. This is no longer true when the number of pairs of layers is variable. In this case, at thermodynamic equilibrium one should use eq 3c. From this equation, if the interactions between lamellae are known, one can calculate the surface tension γ as a function

of δ_1 and δ_2 . While γ can be very small ($\sim 10^{-5}$ N/m), it cannot be negative, because then the interface will become unstable and a different phase (microemulsion, cubic, hexagonal, etc.) will be generated. Consequently, a necessary condition for the stability of the lamellar phase is

$$2\gamma = -f + \delta_1 \frac{\partial f}{\partial \delta_1} + \delta_2 \frac{\partial f}{\partial \delta_2} \geq 0 \quad (12a)$$

When the lamellar liquid crystal is in equilibrium with an excess phase i (either water or oil) and one assumes that the concentrations of the surfactant and cosurfactant are the same in the excess phase and in the lamellae of the same kind, the equality of the chemical potentials leads (because of eq 3d) to $p = p_i$, which when used in eqs 3a or 3b provides the condition for equilibrium with an excess phase i , $\partial f(\delta_1, \delta_2) / \partial \delta_i = 0$. After the lamellar phase reaches the equilibrium with an excess phase, δ_i can no longer increase, since this will always increase the total free energy of the system. Consequently, the lamellar phase might exist only in the regions where

$$\begin{aligned} \partial f(\delta_1, \delta_2) / \partial \delta_i &\leq 0 \\ i &= 1, 2 \end{aligned} \quad (12b)$$

The domains in which $\partial f(\delta_1, \delta_2) / \partial \delta_i > 0$ correspond to unstable lamellar phases; in such cases, an excess phase will separate until thicknesses of the lamellae, which satisfy the conditions $\partial f(\delta_1, \delta_2) / \partial \delta_i = 0$, will be reached.

We will present now detailed calculations for a model lyotropic lamellar liquid crystal, using for the interaction parameters typical values from the literature: the thickness of the headgroups $t_h = 8$ Å;⁶ the effective Hamaker constant $A_{\text{eff}} = 1.0 \times 10^{-20}$ J;^{6,15} A recent comparison with experiment of the force per unit area and of the root-mean-square fluctuation of the separation distance between two neutral phospholipid bilayers as a function of the average separation distance provided the following values for the parameters involved in the hydration force: the decay length $\lambda_H \cong 1.5$ Å and the preexponential factor $A_H \cong 0.035$ J/m².¹⁵ There are no experimental results for the lamellar lyotropic liquid crystals; however one can expect a comparable value for the decay length but a smaller one for the preexponential factor, because the former is due to the structure of water and the latter to the headgroup of the surfactant and the presence of cosurfactant. Here we will employ $\lambda_H = 1.5$ Å and $A_H = 0.02$ J/m². A value of $L = 8$ Å for the length of the surfactant tails and a value of $s = 7$ Å for the distance between the headgroups along the interface will be used. First, the surface charge will be set equal to zero, which corresponds to nonionic surfactants.

The elastic bending modulus K_C for lipid bilayers was found to be of the order of 10×10^{-20} J.⁶ For the lyotropic lamellar liquid crystals, the additional presence of a cosurfactant at the interface should lead to smaller values. Various experimental measurements²¹ provided values ranging between 0.08 and 5×10^{-20} J.

Figure 2 presents $(-f)$ (the negative of the excess free energy per pair of layers), as a function of the average thicknesses of the layers, δ_1 and δ_2 , for $K_C = 5 \times 10^{-20}$ J. From conditions (12a) and (12b), one can see that the lamellar phase cannot exist for positive values of f . To simplify the figure, we set $f = 0$ in Figure 2 when f was positive. In the case considered, the free energy has a minimum for $\delta_1 = 22$ Å and $\delta_2 = 39$ Å. Since both

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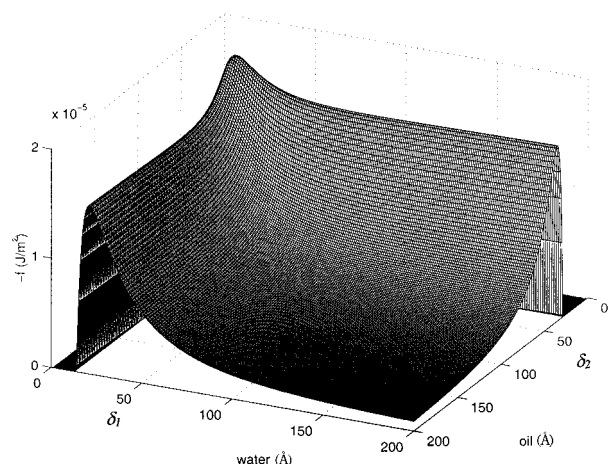


Figure 2. The negative of the excess free energy ($-f$) vs the thicknesses of water (δ_1) and oil (δ_2) layers. The interaction parameters are given in the text.

derivatives are vanishing for these values of δ_1 and δ_2 , this point represents a triple point, where the lamellar phase is in thermodynamic equilibrium with both water and oil excess phases. Since eq 3c assigns a unique value to the interfacial tension ($2\gamma = -f$), the triple point can be reached only for certain concentrations of the constituents. There are however points in the vicinity of this minimum, where both derivatives of f are nonpositive and hence the lamellar phase might be stable for lower values of the interfacial tension than for the value at the triple point.

In Figure 3, the derivatives of the free energy with respect to δ_1 (Figure 3a) and δ_2 (Figure 3b) are plotted as functions of the distances δ_1 and δ_2 for the same parameters as in Figure 2. The lamellar phase might exist only in the regions where the derivatives are negative, which are the flat regions in parts a and b of Figure 3 (to simplify the figures, we set the values of the derivatives equal to zero in the regions where they are negative). One can see from the two-dimensional projections (Figure 3c) that condition (12b) is very restrictive, since most of the δ_1, δ_2 plane is inaccessible to the lamellar phase.

As already noted, when $\partial f / \partial \delta_i$ vanishes, the system is in equilibrium with an excess phase of kind i , and consequently the thickness of layer i cannot increase any longer. Figure 3c reveals that the above vanishing does not occur if at least one of the thicknesses is sufficiently small. This can be easily understood in terms of the interaction between lamellae of the same kind. While the repulsive interaction depends only on the separation between lamellae, the van der Waals attraction increases with their thickness (see eq 9). Therefore, thick lamellae of one kind are bound, because of increased van der Waals attraction, and the system cannot be swollen any longer in the other kind of liquid, while a system with thin lamellae of one kind might be unbound and hence be swollen in the other kind of liquid.

In a lipid/water system, the thickness of the bilayers is constant, and the unbinding transition can occur, in principle, by varying the Hamaker constant or temperature.²² For lyotropic lamellar liquid crystals, hyperswelling in a liquid of one kind might also occur if the lamellae of the other kind are thin enough and hence unbound. However, thin lamellae might lead to a positive contribution to the free energy (since the repulsive forces overcome at short distances the van der Waals attraction), and hence the lamellar phase can become unstable.

To complete the analysis, we present in Figure 4 the domains in which both conditions (12a) and (12b) are fulfilled for various values of K_C , namely, (10, 5, 3, and 2) $\times 10^{-20}$ J. The figure indicates that outside the marked region the lamellar phase is certainly unstable; however, inside the marked region, the lamellar phase might compete for stability with another unknown phase, which might have a lower free energy.

Figure 4 indicates that the domains that might be accessible to the lamellar phase in the δ_1, δ_2 plane are rather narrow. For high values of K_C , hence low undulation repulsion, it is possible to generate lamellar liquid crystals when both kinds of lamellae are thin. This occurs because, if the undulation repulsion is negligible, there is always an absolute minimum of f at small thicknesses, since both the hydration repulsion through water and steric repulsion through oil have shorter ranges than the van der Waals attraction. Conditions (12a) and (12b) limit the existence of a lamellar phase only to a narrow region in the vicinity of this minimum, and further addition of water or oil will lead to the separation of an excess phase. However, there are other regions which are in principle accessible to the lamellar phase; they correspond to systems with thin lamellae of one kind and thick lamellae of the other kind, the effective self-van der Waals energy of the thin lamellae ensuring the thermodynamic stability of the system.

When K_C decreases, the undulation repulsion increases, and this has two consequences. On one hand, to maintain stability, the thickness of the thin lamellae should increase in order to diminish the effect of repulsion. This in turn increases their attraction and, hence, stimulates their binding. On the other hand, the repulsion between the thin lamellae increases, and this favors swelling. The results presented in Figure 4 show that, in a relatively broad range for K_C , it is possible to obtain a lamellar phase, if the lamellae of one kind are thin enough to be unbound. However, the contribution to the free energy due to their thinness (the self-energy) should remain sufficiently negative, to counteract the positive free energy due to the repulsion between them. When K_C further decreases, the undulation repulsion might become so large that no thin layers of one kind can provide enough effective self-energy for the formation of a stable lamellar liquid crystal. Indeed, for $K_C = 1 \times 10^{-20}$ J, the undulation repulsion between layers becomes so strong that the lamellar phase was found unstable in all the domains of the δ_1, δ_2 plane investigated ($\delta_1 \leq 200$ Å, $\delta_2 \leq 200$ Å).

Let us now consider the same system in the presence of an 1:1 electrolyte, with $K_C = 10 \times 10^{-20}$ J and the surface charge density, at large separation distance δ_1 , $\sigma_e = 1/200 \text{ Å}^2 = 0.08 \text{ C/m}^2$. A higher bending modulus was selected to take into account the effect of the charge on the rigidity of the interfaces. In Figure 5 we present the region of stability of the lamellar phase, for various electrolyte concentrations. For $n = 0.5$ M, it is possible to obtain a lamellar phase with thin oil lamellae ($\delta_2 \approx 30$ Å) and thick water layers ($\delta_1 > 40$ Å), and also with thin water layers ($\delta_1 \approx 40$ Å) and thick oil layers ($\delta_2 > 170$ Å). In the latter case, the oil layers were thick enough for their attraction to overcome the electrostatic repulsion. When the electrolyte concentration was decreased, the electrostatic repulsion increased, and no lamellar phase containing thin water lamellae could be formed. However, a lamellar phase with thick water lamellae could be generated, when the thickness of the oil layers was sufficiently small to provide, via their self-energy, the required negative contribution to the free energy. Our calculations indicated that the thickness of the (thin) oil lamellae was almost

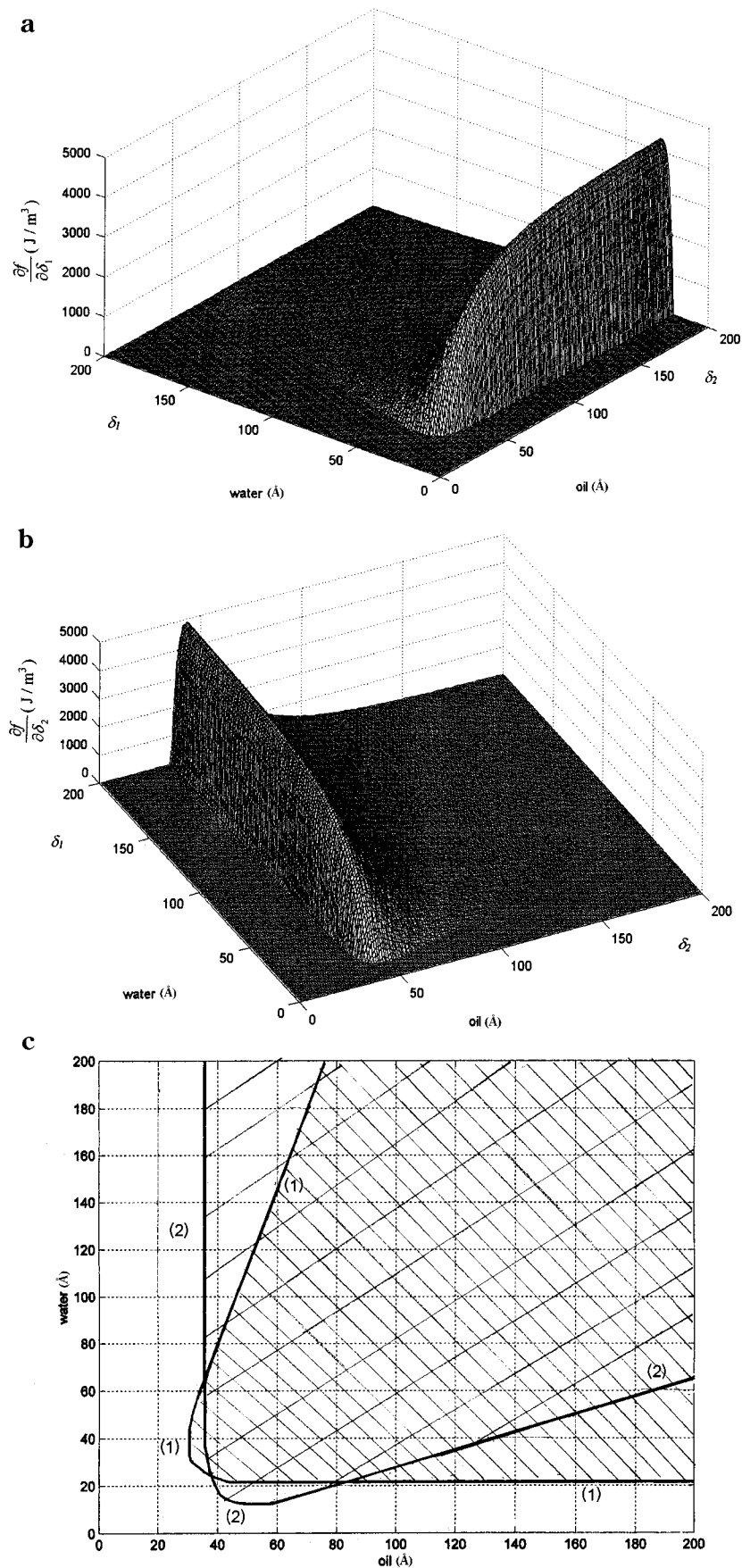


Figure 3. (a) The derivative of f with respect to δ_1 . The lamellar phase cannot exist in the regions where the derivative is positive. (b) The derivative of f with respect to δ_2 . The lamellar phase cannot exist in the regions where the derivative is positive. (c) The contour plot of the derivatives of f with respect to δ_1 and δ_2 , respectively. At line 1, $\partial f / \partial \delta_1 = 0$ and at line 2, $\partial f / \partial \delta_2 = 0$ (inside each of the marked domains delimited by lines 1 and 2, an excess phase separates). The intersections of the line 1 and 2 are triple points, where the lamellar phase is in equilibrium with both excess phases.

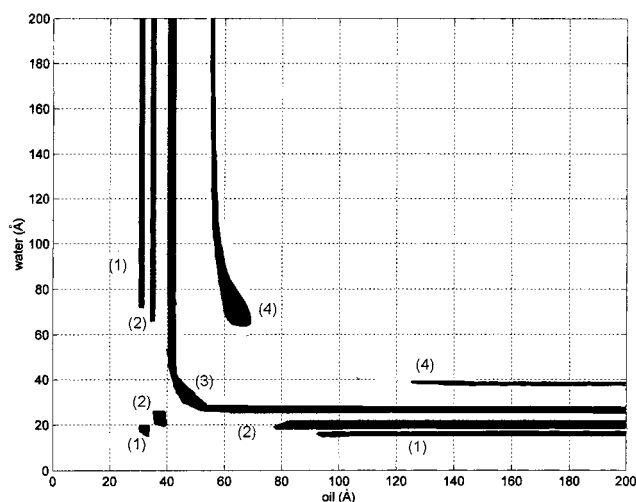


Figure 4. Domains in which the lamellar phase fulfills the conditions (12a) and (12b) and might be stable, for (1) $K_C = 10 \times 10^{-20}$ J, (2) $K_C = 5.0 \times 10^{-20}$ J, (3) $K_C = 3.0 \times 10^{-20}$ J, and (4) $K_C = 2.0 \times 10^{-20}$ J. For $K_C < 1.0 \times 10^{-20}$ J, no domain of stability was found in the region investigated in the δ_1, δ_2 plane ($\delta_1 \leq 200$ Å, $\delta_2 \leq 200$ Å).

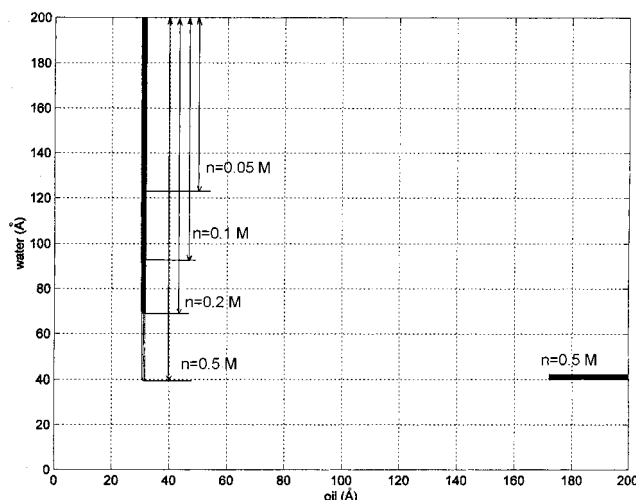


Figure 5. Possible domains of stability of the lamellar phase for charged lyotropic liquid crystals, in the presence of electrolyte: (1) $n = 0.5$ M; (2) $n = 0.2$ M; (3) $n = 0.1$ M; (4) $n = 0.05$ M. No domain of stability for the lamellar phase was found in the region investigated for $n < 0.01$ M.

independent of the electrolyte concentration n ($\delta_2 \approx 30$ Å), while the minimum thickness of the water lamellae was strongly dependent on n ($\delta_1 > 40$ Å for $n = 0.5$ M, $\delta_1 > 70$ Å for $n = 0.2$ M, $\delta_1 > 90$ Å for $n = 0.1$ M and $\delta_1 > 120$ Å for $n = 0.05$ M). A further decrease of the electrolyte concentration increased the free energy and provided negative values for the interfacial tension calculated with eq 3c and, hence, made the system unstable. For $n = 0.01$ M, no region of stability was found in the δ_1, δ_2 plane investigated (200×200 Å).

Most challenging are the systems that have ionic surfactants and are free of electrolyte. In this case it is possible to obtain a swollen phase, by the addition of a mixture of cosurfactant and oil.^{2,23,24} The thickness of the water lamellae, evaluated from the composition of the liquid crystal and the repeat distance, is about 17 Å.² If

one assumes that the surface charge is $\sigma_e = 1e/200\text{Å}^2$, then the osmotic pressure due to counterions exceeds by 1 order of magnitude the van der Waals attraction, and the system cannot be stable. However, at the distances involved, the dielectric constant of water should be much smaller than that of the bulk water, since the water molecules are polarized by the headgroups of the surfactant adsorbed on the interface. In addition, while the dissociation increases the entropy and thus decreases the free energy, the repulsion between the surfaces generates a positive free energy, which can dominate. For this reason, the degree of dissociation which optimizes the free energy is expected to depend on the distance between the interfaces. When the latter distance is small, the dissociation can be low, because the dissociation will generate too strong a repulsion. A theory for the interaction between layers at low separations will be presented in a separate publication. Here a comparison between the results of the present calculations and experiment will be used to evaluate the degree of dissociation.

Stable lamellar liquid crystals can be obtained for $K_C = 10 \times 10^{-20}$ J and a surface charge $\sigma_e = 1e/50000\text{Å}^2$. In this case, $a_d \approx 10^{-3}$ and the domain in which the lamellar phase might be stable corresponds to a thickness between 17 and 19 Å of the water lamellae; the system, however, can swell indefinitely in oil, the self-energy of the water lamellae providing the necessary negative contribution to the free energy.

In summary, information about the interactions between layers allowed one to identify the domains where the lamellar phase is unstable. A positive derivative of f with respect to δ_1 or δ_2 implies that the region is inaccessible to a lamellar phase. In this case, a water or oil phase will separate until the allowed values for δ_1 and δ_2 will be reached. In addition, a negative surface tension indicates that another phase (cubic, hexagonal, microemulsion, etc.) is stable. It should be, however, emphasized that when $\gamma > 0$, a phase other than the lamellar one may be the thermodynamically stable one.

It is generally believed that an extreme swelling is a consequence of a strong repulsion between layers and hence that a low bending modulus favors swelling. This is not, however, always accurate, because a high repulsion can lead to a large positive contribution to the free energy that makes the lamellar phase unstable.

II. The Distribution of the Components in the Lamellar Liquid Crystal

II.1. Uncharged Lyotropic Lamellar Liquid Crystals. A common procedure to evaluate the thicknesses of the water and oil layers was to assume that all the molecules of surfactant and cosurfactant are adsorbed on the interface, where they occupy constant areas. While very simple, this procedure is not always accurate, because the cosurfactant is also present in the water and particularly in the oil phase.²³ Larche et al. explained the deviation from the ideal dilution law by taking into account the distribution of the cosurfactant (pentanol) between the interface and the oil (decane) phase.²³

A more complete procedure to compute the average thicknesses of the water and oil layers will be presented below. It is based on eq 3c, mass balances of components, and phase equilibrium equations. The calculations indicated that the interfacial tension of lamellar liquid crystals is very low, of the order of 10^{-5} N/m. It will be shown that $\gamma = 0$ is always an excellent approximation of eq 3c.

(23) Larche, F. C.; El Qebbaj, S.; Marignan, J. *J. Phys. Chem.* **1986**, 90, 707.

(24) Safinya, C. R.; Roux, D.; Smith, G. S.; Sinha, S. K.; Dimon, P.; Clark, N. A.; Bellocq, A. M. *Phys. Rev. Lett.* **1986**, 57, 2718.

For an uncharged lyotropic lamellar liquid crystal, the equilibrium concentrations are given by the expressions²⁵

$$X_i^S = X_i^W \frac{f_i^W}{f_i^S} e^{\gamma \tau_i a / kT} e^{-(\mu_i^{0,S} - \mu_i^{0,W}) / kT} \quad (13)$$

where a is the area occupied at the interface by a molecule of water, $\tau_i a$ is the area occupied at the interface by a molecule of species i , X_i^S is the surface fraction occupied by species i ($X_i^S = \tau_i N_i^S / N$, where N_i^S is the number of molecules of species i at the interface and N the total number of molecules of water which completely cover the interface, in the absence of surfactant and cosurfactant), X_i^W is the mole fraction of species i in the aqueous phase, μ_i^W and μ_i^S are the standard chemical potentials in the water phase and at the interface, respectively, and f_i^W and f_i^S are the activity coefficients in the water phase and at the interface, respectively. At room temperature ($T = 300$ K), and for $\gamma \approx 10^{-5}$ N/m and $a = 10 \text{ \AA}^2$, one obtains $\gamma a / kT \approx 2 \times 10^{-4}$ and the exponential involving γ can be approximated by unity. We will assume that the activity coefficients are unity in water, and the activity coefficients at the interface are computed using the expression

$$\ln f_i^S = \left(\frac{\partial \left(\frac{\Delta G^E}{kT} \right)}{\partial N_i^S} \right)_{T,P,N_{j \neq i}^S} \quad (14)$$

where for the excess free energy ΔG^E the following expression for ternary mixtures was employed²⁶

$$\frac{\Delta G^E}{kT} = H_{12}^S N_1^S X_2^S + H_{13}^S N_1^S X_3^S + H_{23}^S N_2^S X_3^S \quad (15)$$

where H_{ij}^S is the interaction parameter for the pair i - j at the interface.

We assume that no surfactant is present in the oil phase, and the main problem to be solved is to determine the relation between the concentrations of alcohol in the water and oil phases. A theory for the partition of the alcohol between oil and water, at chemical equilibrium, which takes into account the self-association of alcohol in the oil phase, is detailed in Appendix C. The equation that relates the mole fraction of the alcohol in the oil phase to the mole fraction of the alcohol in the water phase has the form

$$X_A^O = \frac{N_A^O}{N_O^O + N_A^O} = \frac{\frac{X_A^W}{(X_A^W)_{\text{SAT}}}}{1 + K_X \left(1 - \frac{X_A^W}{(X_A^W)_{\text{SAT}}} \right)^2} \quad (16)$$

where the subscripts stand for the type of molecule (A for alcohol and O for oil), the superscripts stand for the phase (O for oil and W for water), K_X is the self-association equilibrium constant, and $(X_A^W)_{\text{SAT}}$ is the saturation concentration of alcohol in water (see Appendix C).

Equations 13–16 with $\gamma = 0$ and mass balances can be used to determine the distribution of molecules between the interface and the water and oil phases. In what follows,

we will examine the swelling of the quaternary mixture C_{12}E_6 /pentanol/water/decane. The changes in the standard chemical potentials of the components between the water phase and interface, $\Delta \mu_i = \mu_i^{0,W} - \mu_i^{0,S}$, and the values of the pair interaction parameters H_{ij}^S can be determined in principle from the fit of eq 13 to experimental data regarding the oil/water interfacial tension at low concentrations of surfactant and cosurfactant. The earlier calculations of Ruckenstein and Rao²⁵ provided the values $\Delta \mu_S = 6500$ cal/mol for C_{12}E_6 and $\Delta \mu_W = -718$ cal/mol for water. For pentanol we selected the value $\Delta \mu_A = 3000$ cal/mol, which is compatible with the experimental data for the lowering of the oil/water interfacial tension by alcohol.²⁷ The surface interaction parameters H_{ij}^S for different pair of molecules were taken as 0.5,²⁵ the value $K_X = 94.2$ was selected for the association constant of pentanol in oil,²⁸ and $(X_A^W)_{\text{SAT}}$ was taken as 4.1×10^{-3} .²⁸

We denote by N_S , N_A , N_W , and N_O the total number of molecules of surfactant, cosurfactant, water, and oil, and by V_S , V_A , V_W , and V_O their volumes per molecule. The volumes and the area occupied on the interface were estimated from the density of alkanes and the earlier calculations of Nagarajan and Ruckenstein.²⁹ The values employed were $V_W = 30 \text{ \AA}^3$, $V_O = 320 \text{ \AA}^3$, $V_S = 650 \text{ \AA}^3$, $V_A = 180 \text{ \AA}^3$, $a = 10 \text{ \AA}^2$, $\tau_S = 3.4$ and $\tau_A = 1.0$. By denoting N_S^S , N_A^S , and N_W^S the number of molecules of surfactant, cosurfactant, and water, respectively, adsorbed on the interface, and with N_A^O the number of cosurfactant molecules in the oil phase, the system of equations to be solved is

$$X_S^S = \frac{(N_S - N_S^S)}{(N_W + N_S + N_A - N_W^S - N_S^S - N_A^S - N_A^O)} \times \frac{f_S^W}{f_S^S} e^{-(\mu_S^{0,S} - \mu_S^{0,W}) / kT} \quad (17a)$$

$$X_A^S = \frac{(N_A - N_A^S - N_A^O)}{(N_W + N_S + N_A - N_W^S - N_S^S - N_A^S - N_A^O)} \times \frac{f_A^W}{f_A^S} e^{-(\mu_A^{0,S} - \mu_A^{0,W}) / kT} \quad (17b)$$

$$X_W^S = \frac{(N_W - N_W^S)}{(N_W + N_S + N_A - N_W^S - N_S^S - N_A^S - N_A^O)} \times \frac{f_W^W}{f_W^S} e^{-(\mu_W^{0,S} - \mu_W^{0,W}) / kT} \quad (17c)$$

$$\frac{N_A^O}{N_O + N_A^O} = \frac{\frac{1}{(X_A^W)_{\text{SAT}}} \frac{(N_A - N_A^S - N_A^O)}{(N_W + N_S + N_A - N_W^S - N_S^S - N_A^S - N_A^O)}}{1 + K_X \left(1 - \frac{1}{(X_A^W)_{\text{SAT}}} \frac{(N_A - N_A^S - N_A^O)}{(N_W + N_S + N_A - N_W^S - N_S^S - N_A^S - N_A^O)} \right)^2} \quad (17d)$$

(27) Aveyard, R.; Briscoe, B. J. *J. Chem. Soc., Faraday Trans.* **1972**, 68, 478.

(28) Nagarajan, R.; Ruckenstein, E. *Langmuir* **2000**, 16, 6400.

(29) Nagarajan, R.; Ruckenstein, E. *J. Colloid Interface Sci.* **1979**, 71, 580.

(25) Ruckenstein, E.; Rao, I. V. *J. Colloid Interface Sci.* **1987**, 117, 104.

(26) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*; McGraw-Hill: New York, 1987.

where the surface fractions are given by

$$X_S^S = \frac{\tau_S N_S^S}{\tau_S N_S^S + \tau_A N_A^S + N_W^S} \quad (17e)$$

$$X_A^S = \frac{\tau_A N_A^S}{\tau_S N_S^S + \tau_A N_A^S + N_W^S} \quad (17f)$$

$$X_W^S = \frac{N_W^S}{\tau_S N_S^S + \tau_A N_A^S + N_W^S} \quad (17g)$$

The activity coefficients on the interface are calculated using the expressions

$$f_S^S = \exp \left(H_{SA}^S (X_A^S - X_A^S X_S^S) + H_{SW}^S (X_W^S - X_W^S X_S^S) - H_{AW}^S (X_A^S X_S^S) \frac{\tau_S}{\tau_W} \right) \quad (17h)$$

$$f_A^S = \exp \left(H_{SA}^S (X_S^S - X_S^S X_A^S) \frac{\tau_A}{\tau_S} + H_{AW}^S (X_W^S - X_W^S X_A^S) - H_{SW}^S (X_W^S X_S^S) \frac{\tau_A}{\tau_S} \right) \quad (17i)$$

$$f_W^S = \exp \left(H_{SW}^S (X_S^S - X_S^S X_W^S) \frac{1}{\tau_S} + H_{AW}^S (X_A^S - X_A^S X_W^S) \frac{1}{\tau_S} - H_{SA}^S (X_S^S X_A^S) \frac{1}{\tau_S} \right) \quad (17j)$$

The following mass balance relations complete the system of equations

$$N_S = N_S^S + N_S^W \quad (17k)$$

$$N_A = N_A^S + N_A^W + N_A^O \quad (17l)$$

$$N_W = N_W^S + N_W^W \quad (17m)$$

where it was assumed that no oil is present at the interface or in the water phase and also that no water or surfactant is present in the oil phase.

The repeat distance d and the average thicknesses of the layers, δ_1 (water) and δ_2 (oil) can be obtained from the relation between the total interface area and total volume

$$d = \frac{2(N_S V_S + N_A V_A + N_W V_W + N_O V_O)}{a(\tau_S N_S^S + \tau_A N_A^S + N_W^S)} \quad (18a)$$

$$\delta_1 = d \frac{N_S^W V_S + N_A^W V_A + N_W^W V_W}{N_S V_S + N_A V_A + N_W V_W + N_O V_O} \quad (18b)$$

$$\delta_2 = d \frac{N_O^O V_O + N_A^O V_A + N_S^S V_S + N_A^S V_A + N_W^S V_W}{N_S V_S + N_A V_A + N_W V_W + N_O V_O} \quad (18c)$$

where it was considered that the interface (including the polar headgroups) belongs to the oil layer.

In Figure 6 the repeat distance (Figure 6a) and the thickness of the oil lamellae (Figure 6b) are plotted as functions of ϕ (the ratio between the volume of surfactant + cosurfactant and the total volume), for fixed volume

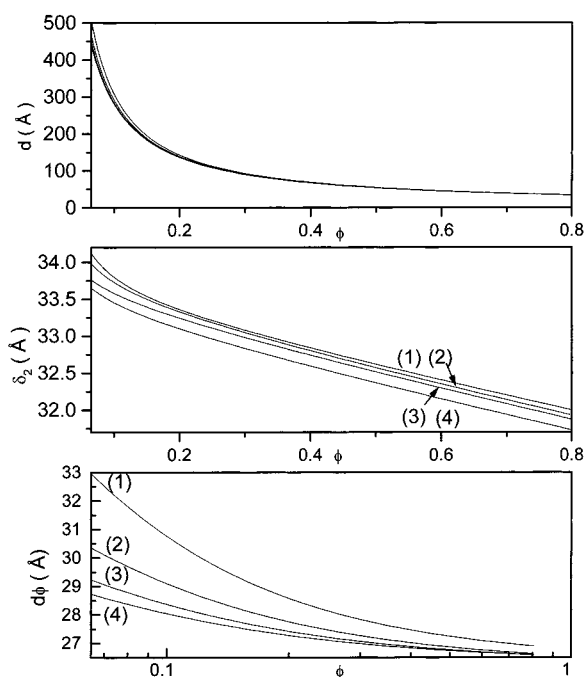


Figure 6. The repeat distance d (a), the thickness of the oil layer δ_2 (b), and the product $d\phi$ (c) vs ϕ (volume ratio of surfactant and cosurfactant) for various volume ratios r between surfactant and cosurfactant, for the quaternary system $C_{12}E_6$ /pentanol/water/decane described in text: (1) $r = 1.0$; (2) $r = 2.0$; (3) $r = 3.0$; (4) $r = 4.0$.

ratios, r , between surfactant and cosurfactant. The initial volumes of water and oil were taken each as 10% of the total volume of the system; further, the system was diluted by addition of water and the new equilibrium values were calculated, using eqs 17a–m and 18a–c.

One can see that the thickness of the oil layers does not remain constant upon dilution. This is a consequence of the nonlinearity of the system of eqs 17, which takes into account the partition of the alcohol between oil, water, and interface and the dependence of the surface activity coefficients on the surface concentrations of all the components. Figure 6c, in which the product between the repeat distance d and ϕ as a function of ϕ is plotted, clearly shows that there are deviations from the ideal dilution law; during the water dilution, alcohol and surfactant molecules leave the interface, and this shrinks its area.

II.2. Charged Lyotropic Lamellar Liquid Crystals.

In the case of a charged system, two changes in the system of eqs 17 must be made.^{30,31} First γ should be replaced in eq 17a, for the surfactant, by $\gamma + \int_{\psi=0}^{\psi_0} \sigma d\psi$. Second, the mole fraction of the surfactant in water, X_S^W , should be replaced in the same equation by the mole fraction of the surfactant in water, in the vicinity of the interface (X_S^W)*. Assuming that the surfactant in the aqueous phase is totally dissociated, the concentration of surfactant near the interface (X_S^W)* can be related to the average surfactant concentration in the water phase, X_S^W , by using the equilibrium and mass balance relations

$$kT \ln(X_S^W)^* + e\psi_0 = kT \ln(X_S(x)) + e\psi(x) \quad (19a)$$

with

(30) Ruckenstein, E.; Krishnan, R. *J. Colloid Interface Sci.* **1980**, *76*, 201.

(31) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, 1987.

$$\frac{1}{\delta_1} \int_{-\delta_1/2}^{\delta_1/2} X_S(x) dx = X_S^W \quad (19b)$$

where $X_S(x)$ is the local concentration of the surfactant in the water phase.

One thus obtains

$$(X_S^W)^* = (X_S^W) \frac{\delta_1 \exp\left(-\frac{e\psi_0}{kT}\right)}{\int_{-\delta_1/2}^{\delta_1/2} dx \exp\left(-\frac{e\psi(x)}{kT}\right)} \quad (20)$$

In the absence of electrolyte, both integrals $\int_{\psi=0}^{\psi_0} \sigma d\psi$ and $\int_{-\delta_1/2}^{\delta_1/2} dx \exp(-e\psi(x)/kT)$ can be carried out analytically (see Appendix B), and eq 17a is replaced by

$$X_S^S = A' \exp\left(\frac{aB'}{kT}\right) \frac{(N_S - N_S^S)}{(N_W + N_S + N_A - N_W^S - N_S^S - N_A^S - N_A^O)} \frac{f_S^W}{f_S^S} e^{-(\mu_S^{O,S} - \mu_S^{O,W})/kT} \quad (17a')$$

where

$$A' = \frac{K\delta_1 \cos^2\left(\frac{K\delta_1}{2}\right)}{\left(\cos\left(\frac{K\delta_1}{2}\right) \sin\left(\frac{K\delta_1}{2}\right) + \frac{K\delta_1}{2}\right)} \quad (21a)$$

and

$$B' = \frac{8\epsilon\epsilon_0(kT)^2}{e^2\delta_1} \left(\frac{K\delta_1}{2} \tan\left(\frac{K\delta_1}{2}\right) - \frac{1}{2} \ln\left(1 + \tan^2\left(\frac{K\delta_1}{2}\right)\right) - \frac{K^2\delta_1^2}{8}\right) \quad (21b)$$

with K the solution of

$$\frac{K\delta_1}{2} \tan\left(\frac{K\delta_1}{2}\right) = \frac{\sigma_e\delta_1 e}{4\epsilon\epsilon_0 kT} \quad (21c)$$

The calculated results in the absence of electrolyte will be now compared with the experimental results obtained regarding a lamellar lyotropic liquid crystal SDS (sodium dodecyl sulfate)/pentanol/water/dodecane swollen in a mixture of dodecane and pentanol.²⁴ The weight fraction water/surfactant was 1.552; from the dilution line in the phase diagram, we calculated that the initial concentration of pentanol in the oil-free system was 29 wt % and the concentration of pentanol in the dodecane-based diluant was 8 wt %. The experimental values for the repeat distance were obtained from the X-ray diffraction spectrum (Figure 2 in ref 24) for various dodecane concentrations.

In the calculations, we used $\Delta\mu_S = 6960$ cal/mol for SDS²⁵ and, as in section II.1, $\Delta\mu_W = -718$ cal/mol for water and $\Delta\mu_A = 3000$ cal/mol for pentanol. The area occupied on the surface was considered $\tau_{SA} = 34$ Å² for SDS and $\tau_{AA} = 10$ Å² for pentanol.²⁵ The values $V_S = 480$ Å³ and $V_O = 380$ Å³ were employed.²⁹ A very low surface charge, $\sigma_e = 1e/50000$ Å², as suggested by the stability analysis of section I, was employed. In Figure 7 the calculated repeat distance (curve 1) is compared with the experimental result of Safinya et al.²⁶ Curve 2 represents the repeat distance

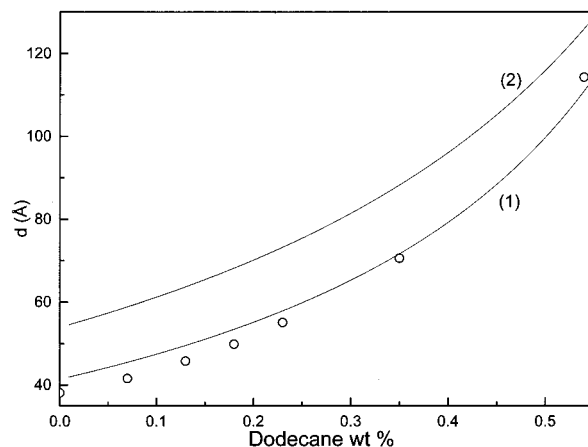


Figure 7. The repeat distance, as a function of dodecane weight fraction, for a quaternary system SDS/pentanol/water/dodecane: curve 1, computed using eqs 17 and 18; curve 2, computed by assuming that the entire surfactant and cosurfactant are adsorbed on the interface. The circles represent the experimental result of Safinya et al.²⁴

calculated using a very simple model, in which the entire surfactant and cosurfactant was assumed to be adsorbed on the interface, and the total area of the interface was calculated as $N_{STSA} + N_{ATA}a$. It is of interest to note that this simple evaluation provides a smaller value for the total area (larger repeat distance) than the more involved calculation in which the partition of surfactant and alcohol between phases was taken into account. The apparent paradox (less adsorbed surfactant/alcohol molecules and larger area in the latter case) is explained by the fact that eqs 17 predict that about 25% of the sites of the interface are occupied by water molecules.

III. Conclusions

In the first part of the paper, a thermodynamic formalism developed earlier¹⁰ was used to obtain information about the domains of stability of the lamellar phase. It was shown that, for a set of interaction parameters between layers and bending modulus of the interface, only certain thicknesses are allowed for the water and oil layers.

In the second part, using the equilibrium relations for the various components present in the water and oil phases and on the interface and coupling them with mass balances, one could calculate the thicknesses of the water and oil layers as functions of the component concentrations. It was shown that the deviation from the ideal dilution law can be accounted for by the partition of the components between phases. A comparison between the calculated and experimental results was made.

Appendix A: Van Der Waals Free Energy for a Multilayer, Formed by Alternating Water and Oil Planar Lamellae

A complete expression for the van der Waals interaction energy can be obtained, in the hypothesis of pairwise additivity, by adding the self-energy of the planar layers

$$\begin{aligned} f_{1,1} &= -\frac{A_{11}}{12\pi} \frac{1}{X_1^2} \\ f_{1,2} &= -\frac{A_{22}}{12\pi} \frac{1}{X_2^2} \end{aligned} \quad (A.1)$$

(where A_{11} and A_{22} are Hamaker constants and X_1 and X_2 are the thicknesses of the layers) to the interaction energy between all the pair of layers, computed as for layers separated by vacuum. The van der Waals interaction between two planar layers of thickness X_1 and X_2 , separated by a distance d , is given by³¹

$$f_{12} = -\frac{A_{12}}{12\pi} \left(\frac{1}{d^2} + \frac{1}{(d+X_1+X_2)^2} - \frac{1}{(d+X_1)^2} - \frac{1}{(d+X_2)^2} \right) \quad (\text{A.2})$$

The total van der Waals energy (per pair of successive water and oil layers and unit area) is computed by adding all the interactions between each of the layers of the pair and all the layers in the system to their interaction and their self-energies. When two layers are in contact, it was considered that a small (but finite) distance e , which is related to the closest approach between molecules, separates the layers.

By rearranging the terms and taking the limit $e \rightarrow 0$, the excess van der Waals energy, dependent on the thicknesses X_1 and X_2 , acquires the form

$$\begin{aligned} f_{\text{vdW}} &= -\frac{A_{\text{eff}}}{12\pi} \left\{ \frac{1}{(X_2)^2} + \sum_{n=1}^{\infty} \left(\frac{1}{(n(X_1+X_2)-X_2)^2} + \frac{1}{(n(X_1+X_2)+X_2)^2} - \frac{2}{(n(X_1+X_2))^2} \right) \right\} \\ &\equiv -\frac{A_{\text{eff}}}{12\pi} \left\{ \frac{1}{(X_1)^2} + \sum_{n=1}^{\infty} \left(\frac{1}{(n(X_1+X_2)-X_1)^2} + \frac{1}{(n(X_1+X_2)+X_1)^2} - \frac{2}{(n(X_1+X_2))^2} \right) \right\} \end{aligned} \quad (\text{A.3})$$

where $A_{\text{eff}} = A_{11} + A_{22} - 2A_{12}$ is an effective Hamaker constant.

Appendix B. Electrostatic Interaction in a Electrolyte-free Lamellar Liquid Crystal

In this Appendix, equations will be derived for the double layer interaction between two charged, planar surfaces in an electrolyte-free system. We assume that the potential $\psi(x)$ obeys the Poisson–Boltzmann equation

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{\epsilon \rho_0}{\epsilon \epsilon_0} \exp\left(-\frac{e\psi(x)}{kT}\right) \quad (\text{B.1})$$

where ρ_0 is the concentration of counterions at the middle distance between the planes, x is the position coordinate, with $x=0$ at the middle distance, ϵ is the dielectric constant of water, and ϵ_0 is the permittivity constant. The solution of this equation, for the boundary conditions

$$\psi(0) = 0, \quad \frac{\partial \psi(x)}{\partial x} \Big|_{x=0} = 0$$

is³²

$$\psi(x) = \frac{2kT}{e} \ln(\cos(Kx)) \quad (\text{B.2})$$

where K is given by

$$\frac{K\delta_1}{2} \tan\left(\frac{K\delta_1}{2}\right) = \frac{\sigma_e \delta_1 e}{4\epsilon \epsilon_0 kT} \quad (\text{B.3})$$

δ_1 being the distance between the planes and σ_e the surface charge density. From (B.1) and (B.2), the following relation between ρ_0 and K is obtained

$$\rho_0 = \frac{2\epsilon \epsilon_0 kT}{e^2} K^2 \quad (\text{B.4})$$

The osmotic pressure between the charged plates is given by³²

$$p = \rho_0 kT = \frac{2\epsilon \epsilon_0 (kT)^2}{e^2} K^2 \quad (\text{B.5})$$

The integral $\int_{\psi=0}^{\psi_0} \sigma_e d\psi$ can be obtained by combining (B.2) and (B.3)

$$\begin{aligned} \int_{\psi=0}^{\psi_0} \sigma_e d\psi &= \int_{K=0}^K \sigma_e \frac{d\psi}{dK} dK = \\ &= \frac{8\epsilon \epsilon_0 (kT)^2}{e^2 \delta_1} \left(\frac{K\delta_1}{2} \tan\left(\frac{K\delta_1}{2}\right) - \frac{1}{2} \ln\left(1 + \tan^2\left(\frac{K\delta_1}{2}\right)\right) - \frac{K^2 \delta_1^2}{8} \right) \end{aligned} \quad (\text{B.6})$$

where K is the solution of eq B.3 for the surface charge density, σ_e , and ψ_0 is the surface potential (at $x = \delta_1/2$).

It will be assumed that the surfactant molecules in the aqueous phase are completely dissociated and that their presence in the water phase does not affect the potential given by eq B.2, since their concentration is very low. The condition of equilibrium and the mass balance of the surfactant in the water phase lead to the following expression for the concentration $(X_S^w)^*$ of surfactant ions near the interface, as a function of the average concentration of the surfactant in the water phase

$$(X_S^w)^* = X_S^w \frac{K\delta_1 \cos^2\left(\frac{K\delta_1}{2}\right)}{\left(\cos\left(\frac{K\delta_1}{2}\right) \sin\left(\frac{K\delta_1}{2}\right) + \frac{K\delta_1}{2}\right)} \quad (\text{B.7})$$

Appendix C: Distribution of Alcohol between Water and Oil Phases

In what follows, we provide the derivation of an equation, which relates the concentration of alcohol in water and the oil phases, on the basis of a model developed earlier.²⁸ Let us assume that N_O^0 molecules of oil and N_A^0 molecules of alcohol are present in the oil phase. Denoting by N_{jA}^0 the number of aggregates containing j molecules of alcohol, the mole fraction of the aggregates of size j is given by

$$X_{jA}^0 = \frac{N_{jA}^0}{N_O^0 + \sum_j N_{jA}^0} \quad (\text{C.1})$$

The association equilibrium for alcohol aggregates is written

(32) Cowley, A. C.; Fuller, N. L.; Rand, R. P.; Parsegian, V. A. *Biochemistry* **1978**, *17*, 3163.

$$A_1 + A_j \leftrightarrow A_{j+1} \quad (\text{C.2})$$

where the association equilibrium constant is considered to be independent of j . Denoting by K_x the stepwise association equilibrium constant, the mole fraction of alcohol aggregates of size j is given by

$$X_{jA}^0 = \frac{(K_x X_{1A}^0)^j}{K_x} \quad (\text{C.3})$$

Since the summation over all mole fractions should remain finite, $K_x X_{1A}^0 < 1$ and

$$\begin{aligned} \sum_j X_{jA}^0 &= \frac{X_{1A}^0}{(1 - K_x X_{1A}^0)} \\ \sum_j j X_{jA}^0 &= \frac{X_{1A}^0}{(1 - K_x X_{1A}^0)^2} \end{aligned} \quad (\text{C.4})$$

The true mole fraction of oil is then

$$\begin{aligned} X_O^0 &= \frac{N_O^0}{N_O^0 + \sum_j N_{jA}^0} = 1 - \frac{\sum_j N_{jA}^0}{N_O^0 + \sum_j N_{jA}^0} = \\ &= 1 - \frac{\sum_j j X_{jA}^0}{1 - K_x X_{1A}^0} = \frac{(1 - K_x X_{1A}^0 - X_{1A}^0)}{(1 - K_x X_{1A}^0)} \end{aligned} \quad (\text{C.5})$$

from where one obtains

$$\sum_j N_{jA}^0 = N_O^0 \frac{X_{1A}^0}{(1 - K_x X_{1A}^0 - X_{1A}^0)} \quad (\text{C.6})$$

and further

$$\begin{aligned} N_{1A}^0 &= X_{1A}^0 (N_O^0 + \sum_j N_{jA}^0) = \\ &= N_O^0 X_{1A}^0 \frac{1 - K_x X_{1A}^0}{1 - K_x X_{1A}^0 - X_{1A}^0} \end{aligned} \quad (\text{C.7})$$

The ratio between the total number of alcohol molecules and the number of alcohol monomers is given by

$$\frac{N_A^0}{N_{1A}^0} = \frac{\sum_j j X_{jA}^0}{X_{1A}^0} = \frac{1}{(1 - K_x X_{1A}^0)^2} \quad (\text{C.8})$$

Using eqs C.7 and C.8, the mole fraction of alcohol can be calculated as a function of the mole fraction of monomers

$$X_A^0 = \frac{N_A^0}{N_O^0 + N_A^0} = \frac{X_{1A}^0}{1 - 2K_x X_{1A}^0 + K_x(K_x + 1)(X_{1A}^0)^2} \quad (\text{C.9})$$

The latter equation can be inverted as

$$X_{1A}^0 = \frac{1 + 2K_x X_A^0 - \sqrt{1 + 4K_x X_A^0 - 4K_x (X_A^0)^2}}{2K_x X_A^0 (1 + K_x)} \quad (\text{C.10})$$

The standard chemical potential of the monomeric alcohol in oil is considered equal to that of the monomers of alcohol in alcohol and is related to the chemical potential of the pure alcohol, μ_A , and the concentration of monomers in pure alcohol via

$$\mu_A = \mu_{1A}^0 + kT \ln(X_{1A}^0)^* \quad (\text{C.11})$$

The monomeric mole fraction in pure alcohol is obtained from eq C.10 in the limit $X_A^0 \rightarrow 1$

$$(X_{1A}^0)^* = \frac{1}{1 + K_x} \quad (\text{C.12})$$

By equating the chemical potential of alcohol in the oil phase to the chemical potential of alcohol in the water phase, one obtains

$$\frac{X_A^w}{(X_A^w)_{\text{SAT}}} = \frac{X_{1A}^0}{(X_{1A}^0)^*} = (1 + K_x) X_{1A}^0 \quad (\text{C.13})$$

where $(X_A^w)_{\text{SAT}}$ is the saturation concentration of alcohol in water when the water phase coexists with a pure alcohol phase. At 25 °C, the solubility of alcohol in water is given by the expression³³

$$\ln(X_A^w)_{\text{SAT}} = 1.40 - 1.38n_C \quad (\text{C.14})$$

where n_C is the number of carbon atoms. The stepwise association equilibrium constant K_x for aliphatic alcohols ranging from propanol to decanol can be computed using the empirical expression²⁸

$$K_x = 92(n_C)^{-0.47} e^{3000((1/T) - (1/323))} \quad (\text{C.15})$$

Because K_x and $(X_A^w)_{\text{SAT}}$ are known, a relation between the molar fraction of alcohol in water and oil, X_A^w and X_A^0 , respectively, can be established. Using eqs C.13 and C.9, one obtains

$$X_A^0 = \frac{N_A^0}{N_O^0 + N_A^0} = \frac{\frac{X_A^w}{(X_A^w)_{\text{SAT}}}}{1 + K_x \left(1 - \frac{X_A^w}{(X_A^w)_{\text{SAT}}}\right)^2} \quad (\text{C.16})$$

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(33) Tanford, C. *The hydrophobic effect*; John Wiley & Sons: New York, 1980.