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Surfactant-water systems with small layer rigidity

Phase stability, defects models and defects mobility in polyoxyethylene surfactant with water†

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Starting from recent experiments in non-ionic surfactants, we discuss various topics characteristic of low rigidity K_1 materials. (1) The stability of the lamellar and cubic phases is studied in a simple model involving K_1 , the saddle-splay constant K_2 , and entropy terms due to the chains. We expect the lamellar phase to have a large range of existence, and the cubic phase to be of small extent. (2) We compare to cubic phases stability in large K_1 materials. We discuss the mobility of edge dislocations on the basis of a new model of the core which involves stretching of the core layers in one dimension, and easy nucleation of pores in this region. The core extension is a characteristic length of low K_1 materials which is much larger than de Gennes' length for microemulsions with a similar low K_1 .

1. Introduction

Non-ionic polyoxyethylene surfactants with water have recently attracted the attention of physicists by a number of characters which differentiate them strongly from more usual ionic (like S.D.S.) or zwitter ionic surfactants (like lecithin). Let us indicate some of them. (i) Their binary phase diagrams have been studied in detail by Mitchell *et al.* [1]. The phase diagrams display the usual liquid-crystalline phases shown up by surfactants, but the extent of the lamellar L_α phase is quite large, while the temperature range of the cubic phase is relatively small, or even absent for small length aliphatic chains, as C_8EO_n and $C_{10}EO_n$ [1]. For $C_{12}EO_n$, the cubic phase appears for $n > 4$. (ii) The L_α phases of the compounds $C_{12}EO_5$ and $C_{12}EO_6$ show up, in the high temperature region just below the L_2 isotropic surfactant-water phase, curved regions observed by E.P.R. [2], whose density increases with temperature, with an activation energy of the order of 0.5 eV. These curved regions are related to the appearance, with seemingly the same energy of activation, of rectangular dislocation loops perpendicular to the layers (two screw segments and two edge segments) which gather in clusters and disorganize strongly the layers structure near the transition [3].

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Their thermodynamical stability has been analysed by Allain and Kléman [4]; it is related to the existence of an unusually small splay Frank modulus K_1 (which is of the order of 100 times smaller than in lecithin [5], i.e. of the same order of magnitude as in microemulsions); the phase transition is therefore probably not an example of a defects-driven transition, as described in [6], notwithstanding the presence of thermodynamical defects. (iii) The screw parts of these thermodynamic dislocation loops are visible by freeze-fracture experiments [3] and are at a distance apart of approximately 500 Å; the edge parts, according to the calculation of [4], are also approximately at the same distance, i.e. about ten layers apart. The usual non-thermodynamic defects, which are visible with the polarizing microscope (oily streaks, focal domains, long edge dislocations, etc.) anneal quickly (in a few hours or even less), which also contrasts with the behaviour of non-thermodynamic defects in other surfactants like lecithin [7], where defects take days to anneal if at all. The mobility of edge dislocations in these non-ionic surfactants has been measured [5]: it is of the same order of magnitude as in usual thermotropic smectics (like 8CB). The activation energy ($U_m \sim 0.5$ eV) is much smaller (in 8CB, $U_m \sim 1.8$ eV).

These peculiar aspects of non-ionic surfactants call for a re-evaluation of many physical properties in media with a low K_1 splay modulus and a low activation energy for the mobility of defects. In the next paragraph of this paper, we shall first address the question of the large stability range of the L_α phase and the quasi non-existence of the cubic phase; the very crude phenomenological model we develop in that purpose leads us to classify these non-ionic surfactants between the usual amphiphilic systems (K_1 large) and the systems which display micro-emulsions (K_1 small). The question of the stability and structure of cubic phases Q_α is today the subject of various studies [8, 10, 11]; this paragraph is by its own a contribution to this subject and discusses also in that respect the question of large K_1 systems.

The results are as follows: when K_1 is large, the stability of the cubic phase Q_α is best explained, as in Helfrich's theory [10], by a negative saddle-splay constant K_{24}^b (b for bilayer) which originates generally in a monolayer saddle-splay constant K_{24} which is itself negative. All our discussion is phenomenological, since there is no molecular model yet at hand which provides a negative K_{24} .

Helfrich [14], Lorenzen *et al.* [15] and Petrov and Bivas [16] have constructed theories which relate the material constants of the bilayer to those of the monolayers. Assuming that the monolayers are independent and add linearly their elastic contributions, they find $K_{24}^b = 2K_{24} + 2K_1 d_0 \sigma_0$ where d_0 is a layer thickness and σ_0 the spontaneous curvature. Their calculation also assumes $|d_0 \sigma_0| \ll 1$, so that the sign of K_{24}^b is always the same as the sign of K_{24} . This result is certainly true most of the time, and particularly when the material constants are large, although it does not take into account the chemical interactions which may arise when the monolayers are very close. But these short range interactions might be quite relevant when the material constants are small, and be at work in the 'frustration' model of [11].

For low K_1 materials, we derive the material constants in the frame of a simple model where the dominant term is the entropy of the chains. We show that K_1 is proportional to $k_B T$, and that K_{24} is itself small, but now positive. This would explain, as we argue, that the L_α phase is favoured in the higher temperature part of the phase diagram and is of large extent, while the Q_α phase, if it occurs, would show up at lower temperatures and be of a small extent. The Q_α phase would then be stabilized either by new features in the molecular interactions which would yield a large enough 'classical' negative K_{24} , or by a kind of 'frustration' effect, as depicted in [11], where

the conflicting forces acting on the monolayers and resulting from a positive K_{24} would compromise in a new geometry with an effective negative K_{24}^b .

In what concerns defects, we show in §3 that the core of an edge dislocation of the lamellar phase is extended along a plane normal to the layers, in low K_1 media. This model differs greatly from the usual models of the core in layered media, and might explain the easy annealing properties of such systems; we discuss in particular (§4) the process of easy glide of dislocations, which might occur by the nucleation of pairs of pores of opposite signs in the extended core (or in the terminology of metallurgists, by the nucleation of a double jog). The splitting of the core also results in a lateral extension of the layers in the core, which we can describe as an 'effective' extensional stress and which helps in the formation of these pairs of pores when a configurational force drives the dislocation in its glide plane. Let us recall that in usual lyotropics, climb is favoured rather than glide: it does not necessitate any breaking and reconstruction of the layer. Finally we complete this paper by a discussion of the low energy of activation for mobility processes, which we relate to the energy of nucleation of pores.

2. Some topics on the phase diagram of low K_1 materials and large K_1 materials compared

2.1. Generalities

The X-ray studies of cubic phases have shown that their structure has the overall topology of a minimal surface Σ with possibly many sheets ($\sigma_1 + \sigma_2 = 0$; σ_1 and σ_2 are the principal curvatures) which runs through all three-dimensional space in a periodic manner, without self-intersections [8]. The cubic symmetry groups of relevance for lyotropic systems and the corresponding arrangements of minimal surfaces have been classified by Scriven [9]. The *monolayers* of amphiphiles fold along surfaces of negative gaussian curvature $\sigma_1\sigma_2$ which are equidistant from Σ , on both sides; the final result is a structure made of connected infinite media for water (one or several) and for the amphiphiles. The two monolayers which are both sides of Σ form what we refer to as a *bilayer* in the sequel.

In Helfrich's model of the stability of the cubic phases, the bilayer is prior to the monolayer; the stability is due to the existence of a negative [10] saddle-splay coefficient K_{24}^b entering the free energy density $\rho f_{ss}^b = -K_{24}^b\sigma_1^b\sigma_2^b$ where σ_1^b and σ_2^b designate now some average made over the principal curvatures of the two monolayers, which are therefore parallel in first approximation. In Charvolin and Sadoc's model [11], the stability is presented as the result of a geometrical compromise, a 'defrustration', between stress elasticity which tends to keep the monolayers parallel, and curvature elasticity which acts separately on each of them and tends to curve them in a similar manner (by which it is meant that both monolayers curve spontaneously along a surface of spherical curvature, both of them with the aliphatic chains either inside this spherical shape, or outside), i.e. in opposite directions with respect to the middle surface Σ of the bilayer. It is then argued that in order to satisfy these contradictory requirements, monolayers take together a negative (hyperbolic) curvature, rather than the spherical one that each of them would take spontaneously.

Let us recall at this stage that the discussion of the curvature free energy of a monolayer is usually made either in terms of spontaneous mean curvature σ_0 , or in terms of gaussian curvature. This duality deserves some remarks, and a return to the definitions of the terms which are in use.

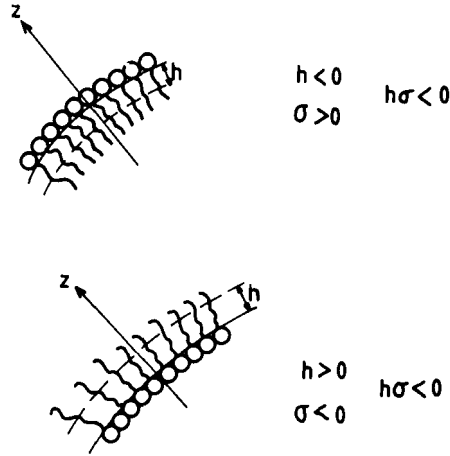


Figure 1. Definition of h (with sign) in a curved layer.

The *spontaneous mean curvature* is taken by convention to be positive if the monolayer curves spontaneously as a direct micelle (figure 1 (a)), and the inverse in the opposite case (figure 1 (b)). But in both cases the resulting spontaneous gaussian curvature σ_0^2 is positive, i.e. the monolayers curve spontaneously towards spherical surfaces, if the splay energy term

$$\varrho f_s = \frac{1}{2} K_1 (\sigma_1 + \sigma_2 - 2\sigma_0)^2 \tag{1}$$

is predominant. Since the sign of σ_0 is conventional, the sign of $\sigma_1 + \sigma_2$ has to be fixed with the same convention, i.e. the normal to the layers has to be oriented the same way for σ_0 and for σ_1, σ_2 .

Gaussian curvature appears in the saddle-splay term of the monolayer

$$\varrho f_{ss} = -K_{24} \sigma_1 \sigma_2. \tag{2}$$

A positive K_{24} favours positive gaussian curvature; the inverse is true if K_{24} is negative. No sign convention is necessary in defining $\sigma_1 \sigma_2$. Therefore hyperbolic spontaneous curvature can be explained phenomenologically only by the K_{24} term, which seems more general than the ϱf_s splay term.

In fact the two physical concepts of curvature are simply related, as we show below, at least in a model of the monolayer where the microscopic forces in play are short range and leading to a dense packing, for the polar heads, and entropic for the chains. Then K_{24} is necessarily positive. We assume that this is the model for low K_1 materials. It is also a model which is coherent with the ‘frustration’ model of the cubic phases alluded to above, if K_{24} is not too large, i.e. if the tendency towards positive gaussian curvature of the monolayers is not too strong and does not prevent the formation of hyperbolic curvature. For this condition

$$\lambda_{24} = (K_{24}/B)^{1/2} < d_0, \tag{3}$$

where d_0 is a typical layer thickness and B is a compressibility modulus which measures the steric forces of interaction between monolayers. If K_{24} is, on the other hand, large but still positive, we do not expect the cubic phases to be stable. Finally, a negative K_{24} can only be explained by more complex forces of interaction between molecules in the monolayer.

In the sequel we speculate that the stability of the cubic phases of usual lyotropic materials (K_1 large) is due to a negative K_{24} (on each monolayer), a condition which of course yields a negative K_{24}^b (we retrieve Helfrich's condition); in this case one expects a large domain of existence of the cubic phase, if other factors do not affect it. Conversely for low K_1 materials, a positive but small K_{24} obeying equation (3) might not prevent the cubic phase from existing if one believes in the 'frustrated' model of Charvolin *et al.* The domain of existence of Q_α should, however, be small, while the extent of the L_α phase should be rather large (as observed), as it is stabilized by the entropy contribution of the chains and possibly of the polar heads, whose length is comparable to the length of the chains, in the type of compounds we considered in the introduction.

2.2. Large K_1 materials and the role of saddle-splay

Cubic phases can be understood as a result of a strong K_1 ($\lambda = (K_1/B)^{1/2}$ comparable to d_0) and of a tendency towards negative gaussian curvature of the monolayers ($K_{24} < 0$), without any frustration originating in the competition of these tendencies.

Note Σ , the middle surface of the two monolayers, which sit at an effective distance $\pm h$ of Σ . h varies from point to point on Σ , and the elements of area $d\Sigma_\pm$, on the \pm monolayers, are related to $d\Sigma$, the element of area on Σ_\pm , by

$$d\Sigma_\pm = d\Sigma[1 \pm h(\sigma_1 + \sigma_2) + h^2\sigma_1\sigma_2 + (\nabla_\perp h)^2 + O(h^3)], \quad (4)$$

where ∇_\perp is the gradient along Σ .

$(\nabla_\perp h)^2$ is a short hand notation for

$$(\nabla_\perp h)^2 = \frac{1}{A^2} \left(\frac{\partial h}{\partial x_1} \right)^2 + \frac{1}{B^2} \left(\frac{\partial h}{\partial x_2} \right)^2,$$

where A, B, dx_1, dx_2 appear in the fundamental quadratic form of the surface

$$ds^2 = A^2 dx_1^2 + B^2 dx_2^2,$$

where this surface is spanned by a system of rectangular curvilinear coordinates. In general it is not possible, except in the case of minimal surfaces, to make $A = B$. If the minimal surface is the plane, we can take $A = B = \text{constant}$. In equation (6) the reader should understand that $(\partial/\partial x) = (1/R)(\partial/\partial x_1)$, $(\partial/\partial y) = (1/R)(\partial/\partial x_2)$ and $A = B = R$.

We now require the two monolayers to possess properties of mutual symmetry. This condition implies that the terms of odd order in equation (4) vanish, at least for the largest ones. Hence the mean curvature H must vanish

$$H = \sigma_1 + \sigma_2 = 0,$$

which means that Σ is either a plane or a minimal surface. If K_{24} is strongly negative, it is a minimal surface and this is the result we expected. However this condition does not mean that Σ_+ and Σ_- are symmetric with respect to Σ (symmetry in the usual sense implies congruence, and Σ_+ and Σ_- are not congruent, even if $H = 0$). For example, the mean curvatures H_+ and H_- are different; they read to the first order in h

$$H_+ = -H_- = \nabla_\perp h + O(h^2). \quad (5)$$

Similarly the gaussian curvatures G_+ and G_- read

$$G_{\pm} = G \left[1 \pm 2 \left(\frac{\partial \ln R}{\partial x} \frac{\partial h}{\partial x} - \frac{\partial \ln R}{\partial y} \frac{\partial h}{\partial y} \right) \pm \left(\frac{\partial^2 h}{\partial x^2} - \frac{\partial^2 h}{\partial y^2} \right) + O(h^2) \right], \quad (6)$$

where $R = |1/\sigma_1| = |1/\sigma_2|$ and $G = \sigma_1\sigma_2$. Equations (5) and (6) have been derived by taking into account the condition $H = 0$.

The gaussian curvatures $\Delta G_+ = G_+ - G_-$ and $\Delta G_- = G_- - G_+$ give opposite contributions to the free energy of the two monolayers, according to equation (2). Conversely both mean curvatures H_+ and H_- give positive contributions to the free energy. It is therefore tempting to make $H_+ = H_- = 0$ in order to reduce the energy. The monolayers are therefore themselves minimal surfaces, but to some correction which is of the second order (see equation (6)). The splay contribution vanishes to the same order. The only energy terms which enter significantly the stability problem of the cubic phases we are describing here are, therefore, the term of compression, and the saddle-splay term; they act in opposite directions if K_{24} is negative.

2.3. Low K_1 materials and the role of entropy

The presence of a cubic phase in a low K_1 material can of course also be justified in the model just proposed for large K_1 material in §2.2, with a negative K_{24} which can be small, since K_1 is itself small, and we do not reject this possibility at all; in some of our non-ionic surfactants C_mEO_n the polar heads and the aliphatic chains are of similar length, for $m \sim n$, and the saddle-splay terms coming from the contributions of both sides can compensate near zero, with a global negative sign. But we investigate here another possibility, in agreement with the model of frustration [11], with a small positive K_{24} coming from the entropy of the chains, and corresponding to some mean spontaneous curvature. More specifically, we show that the entropy contribution of the chains of a monolayer yields spontaneous curvature σ_0 , and a small positive K_{24} , while the entropy contribution of the chains of a bilayer always tends to hinder spontaneous curvature of the bilayer. In other words, we explain in this model the large stability in temperature of the L_α phase, rather than the stability of the Q_α phase which is anyway small.

Let us assume, as in the more complex models of Ben-Shaul and Gelbardt [17], that the area per polar head is not modified significantly when the layers are distorted. We do not expect any influence of the entropy of configuration in ordered phases like Q_α or L_α , contrary to the case of microemulsions. We therefore consider only the difference in entropy between the curved monolayer and the flat one in a model where we treat the chains as a two-dimensional perfect gas; this difference varies proportionally to the logarithm of the change in area of the chains

$$-T\Delta S_{\pm} = -\frac{k_B T}{a^2} \ln \frac{\Delta \Sigma_{\pm}}{\Delta \Sigma} \sim -\frac{k_B T}{a^2} \{ \pm h(\sigma_1 + \sigma_2) + h^2 \sigma_1 \sigma_2 + (\nabla_1 h)^2 \}, \quad (7)$$

where h is still some effective distance, but now measured from the surface of the polar heads to some position along the normal to Σ . Some caution has to be taken in the definition of the sign of h (see figure 1). We will now discuss a number of very simple conclusions which can be drawn from the consideration of equation (7).

A curved bilayer has always a smaller entropy than a planar one; entropy contributes then to the total free energy by a splay modulus

$$K_1^b \sim k_B T \frac{h_s^2}{a^2}, \quad (8)$$

which is of no consequence as long as the splay modulus of pure elastic origin is large compared to $k_B T$ (h_s denotes some physical length (related to h and to the distance between the monolayers) which describes this splay effect). However, if this not the case, the entropy term K_1^b favours greatly the L_α phase (if B is large). This is why the L_α phase is so large in non-ionic surfactants. We can even expect that the greater the h_s , the larger the domain of existence of the L_α phase. Experimentally, the L_α phase in $C_{12}EO_n$ has the largest extension for n small; there are neither cubic Q_α nor hexagonal H_α phases for $n < 4$. The extent of the L_α phase decreases when n increases, while correlatively the Q_α and H_α phases appear for $n = 4$, and increase equally with n . More generally, the extent of the L_α phase increases with the ratio m/n in C_mEO_n phases, which looks coherent with a possible correspondingly increasing effective length h_s .

Note that K_1^b (equation (8)) decreases with T , and might become smaller than the elastic contribution to the splay constant; when this happens, entropy no longer stabilizes the L_α phase, and a strong first order transition to Q_α or H_α phase can occur. These are phases of monolayers, whose spontaneous curvature is stabilized by entropy effects, with a small positive K_{24} , as we show now. It is interesting to notice that our argument predicts those phases at a lower temperature than the L_α phase, as is indeed observed.

Consider a monolayer, with chains obeying a perfect gas model, and a free energy density containing only splay and entropy terms

$$qf = \frac{1}{2}K_1(\sigma_1 + \sigma_2)^2 - \frac{k_B T}{a^2} \ln D, \quad (9)$$

with

$$D = 1 + h(\sigma_1 + \sigma_2) + h^2\sigma_1\sigma_2,$$

according to equation (7) (we discard the gradient terms). By minimizing qf with respect to σ_1 and σ_2 we find two spontaneous curvatures, which both are stable minima (but one of them leads to a smaller free energy density), viz.

$$\sigma_1 = \sigma_2 = \sigma_0 = -\frac{1}{2h} \left\{ 1 \pm \left(1 + \frac{2k_B T h^2}{K_1 a^2} \right)^{1/2} \right\}, \quad (10)$$

and an effective K_{24} which is positive, as expected for a positive gaussian curvature,

$$K_{24} = \frac{k_B T h^2}{a^2 D_0}, \quad (11)$$

where $D_0 = 4\sigma_0^2 h^2$. We believe that we have obtained with equations (8) and (9) the simplest model to obtain spontaneous positive curvature with here the chains outside (we have introduced entropy in the chains; our result resembles the Bancroft rule [19]).

We can improve the model of the monolayer by introducing an elastic contribution of the chains which supplements the elastic contribution K_1 of the polar heads and the entropic contribution K_{24} of the chains. This elastic contribution is estimated as

$$\delta qf = \frac{1}{2}K'_1(\sigma'_1 + \sigma'_2)^2,$$

where K'_1 is a splay constant of the chains, and σ'_1 and σ'_2 the curvatures of the surface Σ_n , at a distance h from the polar heads. We get easily

$$\delta qf = \frac{1}{2}K'_1(\sigma_1 + \sigma_2)^2 + hK'_1(\sigma_1 + \sigma_2)(\sigma_1^2 + \sigma_2^2). \quad (12)$$

The new free energy density $\varrho f + \delta\varrho f$ is more complex. In particular the minimization leads to an algebraic equation of the third order. It can be shown that, while the root of smaller energy in the simple case studied above leads always to $h\sigma_0 > 0$, a root of even smaller energy $h\sigma_0 < 0$ appears in this formulation, when K_1' is large enough. This root breaks the Bancroft rule. We have not studied this case in detail.

2.4. Microemulsions

We mention them for the sake of completeness. They are low K_1 materials thermodynamically stabilized by the entropy of configuration of the micellar shapes, and therefore not some form of disordered Q_a phases.

3. Model of the core of edge dislocations

3.1. Extension of the core

We reproduce here, in a somewhat shorter version, arguments which have been first given in [4]. The deformation field of an edge dislocation is represented in figure 2, according to [12,13]: the layers are practically equidistant outside two parabolae of shape

$$x^2 = \pm 4\lambda z, \quad (13)$$

where $\lambda = (K_1/B)^{1/2}$ is the de Gennes penetration length for smectics. The layers are at some angle α of the general direction of the layers inside the parabolae, with

$$\alpha \sim b(\lambda z)^{-1/2} \exp(-x^2/4z\lambda)$$

decreasing slowly along z , but large for $|z| < b^2/\lambda$. The curvature of the layers inside the parabolae can be considered as large; hence linear elasticity is not relevant in the region where the width of the parabola is smaller than d_0 , the layers repeat distance, i.e. within the distance $|z| < d_0^2/\lambda$. Since $|b| = nd_0$ ($n \geq 1$), the first condition $|z| < b^2/\lambda$ is satisfied for $|z| < d_0^2/\lambda$ and we expect an extension of the core along the z direction of the order of

$$\xi_z = d_0^2/\lambda. \quad (14)$$

This quantity is of the order of d_0 for usual values of K_1 ; in such a case the core is rather isotropic, with $\xi_x \sim \xi_z$, and the current model of a core split into two disclinations, with a semicircular folding of the layers (figure 2) is certainly valid. But when K_1 is of the order of $k_B T$, i.e. small as it is in the system we are considering,

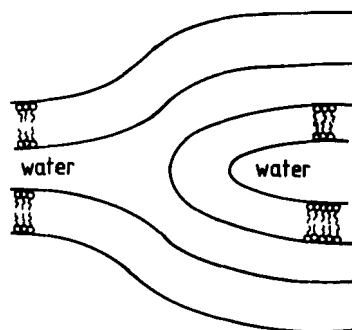


Figure 2. Schematic drawing of the deformation of the layers in the elastic region around an edge dislocation.

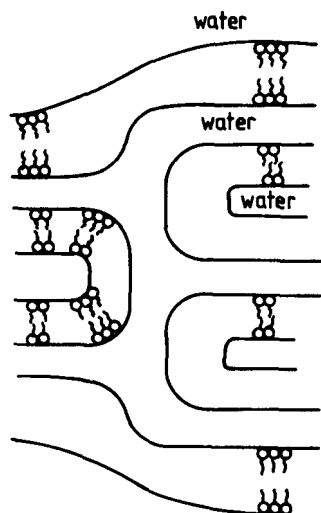


Figure 3. $\lambda \ll d_0$; core extended perpendicularly to the layers.

the core is extremely anisotropic ($\xi_z \sim 10\xi_x$, taking for λ the value measured in $C_{12}EO_6$), and can be modelled as in figure 3. This model is probably not the only possibility but it indicates a strong tendency for the layers to behave as if they were stretched in this region. Dislocations with extended cores of that type are observed in the roll systems of electro-hydrodynamical instabilities in nematics; these systems are formally similar to two-dimensional smectics, and are equivalent to a small λ smectic for a particular choice of the driving frequency [18].

3.2. Lateral extension and effective stress of the layers in the core

In studying the glide of an edge dislocation, we shall be led to consider the nucleation of pores in the extended core submitted to a shear stress $\Sigma_{13} = \sigma_{13}/d_0$ acting in the layers parts which are along Oz . If the surface of a pore is A , the work done by the stress in creating the pore is $\sigma_{13}A$ [22], a quantity which is subtracted from the activation energy U of the pore. If, furthermore, the layers are extended because their thermal fluctuations are damped in this region, the activation energy is no longer U but $U - \sigma_c A$, where σ_c is an effective stress which describes phenomenologically this stretching. It is therefore interesting to investigate the order of magnitude of this stretching, in the line of the theory proposed by Helfrich and Servuss [20] in their study of the undulations of membranes.

Consider first parallel fluid membranes in an overall undeformed smectic. We expect according to Helfrich and Servuss a mean square fluctuation of the layers $\langle |u^2| \rangle \sim \alpha d_0^2$, where α is some numerical coefficient of the order of 1/10. Most of the fluctuations which contribute to $\langle |u^2| \rangle$ have a long wavelength, in particular larger than the de Gennes wavelength ξ_x below which the layers are rigid [21],

$$\xi_x \sim a \exp \frac{2\pi\kappa}{k_B T}, \quad (15)$$

where $\kappa = K_1 d_0$ is the rigidity of one layer. Inserting $K_1 \sim 10^{-8}$ dyne/cm leads to $\xi_x \sim 20 \text{ \AA}$. Above this length the layers do not feel any stretching. Under this length, there is some stretching which can be estimated as the ratio $K_1 (\langle u^2 \rangle^{1/2} / \xi_x^2)$ (according

to linear elasticity we have $\sigma_{13} = K_1(\partial^3 u/\partial x^3)$, i.e. is of the order of 10^{-2} dyne/cm. This expression of σ_{13} is justified by the fact that there are no thermal effects for lengths below ξ_κ .

Since ξ_κ is rather small, according to de Gennes' theory this should lead to a disordered state rather than a lamellar state; this is however obviously not the case. An explanation can be sought in the fact that the entropy of the bilayers is larger when they are planar than when they are curved; as shown above this entropy factor has to be taken into account as long as $\kappa \lesssim k_B T$. Note that de Gennes' theory considers monolayers and not bilayers. The typical length for bilayers is ξ_z .

In order to estimate now the stretching due to the undulations whose wavelength seats between ξ_κ and ξ_z , we write the Fourier components of the layer displacement u as

$$\langle |u_q|^2 \rangle = \frac{k_B T}{V(q_\perp^4 K_1 + Bq_\parallel^2 + q_\perp^2 \Sigma)}, \tag{16}$$

where we use Σ , the stress density per unit volume, and K_1 , rather than the values related to surfaces, since we are considering a bulk specimen. We also introduce the layers compressibility modulus B . We integrate equation (16) in the ranges $(2\pi/\xi_z) < q_\perp < (2\pi/a)$ and $0 < q_\parallel < 2\pi/d_0$; we have, replacing integration on discrete modes by a volume integration,

$$\langle |u|^2 \rangle = \frac{k_B T}{2(2\pi)^2} \int \frac{q_\perp dq_\perp dq_\parallel}{q_\perp^4 K_1 + Bq_\parallel^2 + q_\perp^2 \Sigma}. \tag{17}$$

The integration on q_\parallel is straightforward and yields

$$\langle |u|^2 \rangle = \frac{k_B T}{2(2\pi)^2} \int q_\perp dq_\perp \frac{1}{B^{1/2}(q_\perp^4 K_1 + q_\perp^2 \Sigma)^{1/2}} \tan^{-1} \left[\left(\frac{B}{(q_\perp^4 K_1 + q_\perp^2 \Sigma)^{1/2}} \right) \frac{2\pi}{d_0} \right].$$

Since only small q_\perp are contributing, for which $q_\perp^4 K_1 d_0^2 \ll 2\pi B$ (this inequality is even true for the largest $q_\perp \sim 2\pi/\xi_\kappa$, since $K_1/B = \lambda^2 \ll d_0^2$), we approximate the \tan^{-1} by $\pi/2$ and get, for $\Sigma = 0$,

$$\langle |u|^2 \rangle \sim \frac{k_B T}{32\pi\kappa} (\lambda d_0) \ln \frac{\xi_z}{a}. \tag{18}$$

The essential result we get is that $\langle |u|^2 \rangle$ no longer scales like d_0^2 , but like λd_0 ; this difference does not matter when $\lambda \sim d_0$. But in our case it implies that the fluctuations of the layers are much less important than expected, and conversely, the effective stress at a scale smaller than ξ_z is relatively large, of the order of

$$\sigma_c \sim \frac{k_B T}{4\pi} \frac{1}{\langle |u|^2 \rangle} \simeq \frac{4\pi\kappa}{\lambda d_0} \sim 1 \text{ dyne/cm}. \tag{19}$$

Whether this value of σ_c is large enough to significantly decrease the activation energy for mobility of edge dislocations in climb is a question which we investigate below and to which we give a positive answer.

4. The mobility of an edge dislocation

As already stated, the usual mechanism of motion of edge dislocation in water-surfactant systems is by climb, i.e. the dislocation line moves in a layer, perpendicularly to its Burgers' vector. This is in strong contrast with the main mechanism

of motion of dislocations in solids, where glide is dominant. Climb is non-conservative, i.e. requires the displacement of matter by diffusion or by some flow process of molecules through the layers, while glide is conservative.

4.1. Climb

Topology (separation of water and hydrophobic media) favours easy climb, which can proceed by the addition in series of two mechanisms: (a) jump of amphiphilic molecules from one layer to the next near the tip of the supplementary layers which constitute the edge dislocation, and (b) diffusion along the layers. It is clearly this jump (through water, or by a flip-flop from one monolayer to the next) which is difficult and determines the activation energy, nothing else than the activation energy for self-diffusion D_{\parallel} through the layers. Any metallurgical model of climb would therefore foresee a mobility coefficient $m = V/\Sigma$, where V is the velocity of the configuration of the dislocation, and Σ the applied stress, of the form

$$m = \alpha \frac{D_{\parallel} V_m}{k_B T} \frac{1}{l}, \quad (20)$$

where V_m is a molecular volume, D_{\parallel} the self diffusion constant for motion perpendicular to the layers, l a molecular length, and α a numerical coefficient. The quantity $D_{\parallel} V_m/k_B T$ is akin to λ_p , the Helfrich coefficient of permeation. Equation (20) yields a mobility which is independent of the Burgers' vector. Models which consider that the permeation process takes place all along the layer, and not only at the tip, lead to a mobility proportional to the Burgers' vector. We need more experiments to reach a conclusion concerning which type of model is good, but it might well be that the truth is in between.

The mobility of edge dislocations in climb is measured by the 'lubrication wedge' method [23]; it yields in our non-ionic surfactants a value of λ_p of the order of 10^{-14} cm²/poise, as in a classical thermotropic S_A phase, for example 8CB, and an activation energy of the order of 0.4 eV, which is at least four times smaller than in 8CB. These values of λ_p are in contrast with those measured in lecithin, where λ_p is 10^{-15} times smaller. This difference is explained [5] as being due to the fact that the main process of permeation is through the channels offered by the screw dislocations when their density is sufficient (λ_p scales as cr_c^4/μ in this model; c is the density of screw dislocations per unit surface of layer, r_c the channel radius, and μ the viscosity through the channel). The activation energy which is measured is therefore the activation energy of the inverse viscosity (i.e. diffusivity) of the matter which flows through the channel. If it is water, as it can be in a lyotropic liquid crystal, and since r_c is much probably of the order of d_0 , i.e. larger than the size of a water molecule, we do expect to find a value akin to the value of pure water, except if the polar oxyethylene heads offer large obstacles (the question can be quite subtle, since OE has no affinity for water above the higher consolute point, which is explained this way). If the channel is an inverse channel, it is the surfactant itself which flows, but in a very anisotropic medium of aliphatic chains. The geometrical situation for diffusion would then be much akin to the flow through channels in a thermotropic smectic, where the activation energy is high. From the experimental results in lubrication [15] we therefore expect that most of the diffusion through layers goes through direct screw dislocations channels and direct pores and passages. The activation energy for self diffusion of water is ~ 0.15 eV [24].

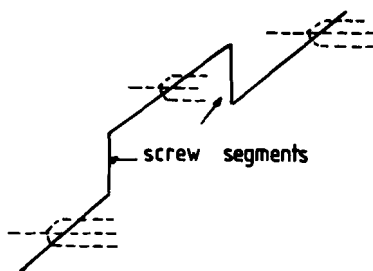


Figure 4. A double jog along the extended core.

4.2. Glide

In glide, the layers have to break and fuse again. This is most probably achieved in $C_{12}EO_5$ and $C_{12}EO_6$ by the activated nucleation of double jogs, formed of short segments of screw dislocations of opposite sign, which originate in the core region of the edge dislocation as pictured in figure 4. Since the cores of the screw dislocations are akin to pores, the activation energy is the energy of formation of these pores, U , decreased by the energy gain due to the effective stress σ_c of the layers in the region where the pores nucleate.

The gain in energy due to stretching is $\sigma_c A$, where A is a typical area for a pore. With $\sigma_c \sim 1$ dyne/cm and $A \sim \pi d_0^2$, we get $\sigma_c A \sim 0.3$ eV. This is probably an overestimated value, but it remains that the tendency to layers cohering which pre-exists in the extended core should make glide quite easy. In comparison with classical dislocation theory in metals, this situation is somewhat akin to climb in presence of an oversaturation of point defects; here the analogues of the point defects are the pores which nucleate easily on the stretched layers, since their energy of formation is decreased by the quantity $\sigma_c A$, i.e. $E = U - \sigma_c A$ [22].

5. Conclusion

Non-ionic surfactants in water offer a new type of lyotropic system with quite unusual features, which have been discussed in this paper at a very elementary level, assuming that some of these new features arise from a low K_1 layer rigidity (which remains to be explained with some molecular model). In this context, two ideas appear to be of relevance.

First, since $\kappa = K_1 d_0$ is small and comparable to $k_B T$, the entropy effects of the chains have to be taken into account. Their contribution should explain both the large extent in the phase diagram of the lamellar phase and the small extent of the cubic phase, whose stability might result either from the competition of mutually frustrating effects specific to low K_1 media, or of a negative K_{24} saddle-splay constant. Secondly, the penetration length $\lambda = (K_1/B)^{1/2}$ being small, the usual core model of edge dislocations has to be modified, and layers' stretching effects considered in the question of the mobility of the defects.

It is clear that any complete model of non-ionic surfactants has to go much farther than these very simple ideas, which none the less can be of some help in the difficult and vast question of systems with interfaces, and in particular point out to new questions relevant to more usual surfactants in water, and microemulsions.

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