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SPHEROCYLINDRICAL AND DISK-LIKE AGGREGATES IN SINGLE COMPONENT AND MULTICOMPONENT AMPHIPHILIC SYSTEMS

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Abstract The formation of spherocylindrical and disk-like aggregates in amphiphilic-water systems is considered on the basis of a simple molecular model. This model explicitly takes into account the liquid crystal properties of the amphiphilic monolayer (its bending elasticity), as well as the "two dimensional" entropy of mixing in the monolayer's plane (in case of multicomponent monolayers). The results obtained in this work could be of significance in the preliminary selection of mixtures that give lyotropic nematic phases.

INTRODUCTION

It is well established that in solution some amphiphilic substances form nematic liquid crystal phases. The building blocks of those lyotropic mesophases have rod-like (spherocylindrical) or disk-like (lamellar) shape. When the amount of amphiphile exceeds some critical value (commonly refered as Critical Micelle Concentration - CMC) in the solution, its molecules group into aggregates (or building blocks) called micelles. Their spontaneous aggregation depends upon the balance of hydrophilic-hydrophobic interactions between the molecules in the solution. It is widely accepted that just above the CMC the shape of micelles is spherical. Further increase of concentration leads to a change of the shape into an aspherical one (spherocylindrical or disk-

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like). Depending on the specific interactions between such aspherical aggregates they can form nematic phases of calamitic or discotic type.

The problem of the shape of micelles and their alignment into nematic structures has been discussed by many authors[1-9]. Most of them use the packing approach of Israelachvili et al.[1]. The main point of this model is that monomers and micelles (aggregates) are considered as different "chemical" species between which "chemical" reactions take place:

$$NA_1 \rightleftarrows A_N$$

where A_1 represents a monomer amphiphilic molecule and A_N represents a N-micelle (e.g. a micelle built up of N amphiphilic molecules). When thermodynamic equilibrium between the reacting species is reached the equilibrium condition is fulfiled, so one can write:

$$N\mu^{mono} = \mu^{micelle}$$

As far as diluted solutions are considered the chemical potential of the monomers and this of the micelles has the same form as the chemical potential of an ideal gas:

$$\mu^{mono} = \mu^{o1} + k_B T \ln(X_1)$$

$$\mu^{micelle} = N\mu^{oN} + k_B T \ln(X_N/N)$$

where X_1 is the number (concentration) of monomers, and (X_N/N) is the number (concentration) of N-micelles in the volume (system). Combining the above expressions one gets the basic equation of the Israelachvili model[1]:

$$\mu^{o1} + k_B T \ln(X_1) = \mu^{oN} + (k_B T/N) \ln(X_N/N) \qquad (1)$$

Here μ^{o1} is the standard chemical potential of a monomer in solution when the monomer concentration $X_1=1$, and μ^{oN} is the

standard chemical potential of an amphiphilic molecule in a N-micelle when the concentration of N-micelles $(X_N/N)=1$.

To proceed further on from the basic equation (1) one must know the dependence of the standard chemical potential μ^{oN} on the aggregation number N. Usually[1-12] this information is derived from a model and most of the papers[1-6,11,12] use the model of Israelachvili et al.[1]. According to this model the hydrophobic hydrocarbon chains behave like an isotropic liquid. Upon bending, such a monolayer adjusts the surface to volume ratio, required for a molecule, by changing its thickness (chain length). The anisotropic alignment of the hydrophobic chains, normal to the oil-water interface of the amphiphilic monolayer, is taken into account only through the restriction that the monolayer thickness is less than the maximum length of a chain in all-trans conformation, L_o. Because there is no work done to bend the monolayer starting from a flat state until its thickness reaches the maximum chain length L_o, such a monolayer of amphiphilic molecules does not possess bending elasticity in the Israelachvili model[10]. But in reality the chains of amphiphilic molecules are not passive participants in the process of aggregate formation.

It is well known that when amphiphilic molecules form lamellar, hexagonal and micellar phases their hydrocarbon chains are in a "liquid crystal" state characterized by the existence of long range orientational order in their alignment. When the long range order in a liquid crystal is perturbed, elastic torques appear tending to restore the initial molecular (chain) orientation[13]. Analyzing the stability of nonspherical aggregates (micelles) one must take into account this intrinsic feature of liquid crystals - their bending elasticity.

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The importance of chain contribution to the phase polymorphism of lyotropic liquid crystals is not well appreciated in the literature. In the recent works of some authors[5,7,11,12,22] the significance of chains is revealed on the basis of statistical mechanical modelling of the hydrophobic core of micelles. That is why in the work of McMullen et al.[5] the Israelachvili model has been extended to account indirectly for this monolayer property via an elastic response to the chain stretching. When bent, such a monolayer tends to restore its initial configuration because bending changes the optimal length of the hydrophobic chains.

In case of spherocylindrical (or disk-like) micelles one has to consider a "chemical" reaction of the form:

$$NA_1 \rightleftarrows A_N^{sc}$$

where A_N^{sc} represents a spherocylindrical aggregate ("chemical species") in equilibrium with monomers. Therefore one can write:

$$N\mu^{mono} = \mu_N^{sc}$$

or:

$$\begin{aligned} N(\mu^{ol} + k_B T \ln(X_1)) &= N^s\mu^{os} + N^c\mu^{oc} + k_B T \ln(X_N/N) \\ N^s + N^c &= N \end{aligned} \tag{2}$$

where N^s and N^c are the number of molecules in the spherical caps and in the cylindrical part of a spherocylindrical aggregate respectively, and (X_N/N) is the number (concentration) of spherocylindrical micelles. If the micelles under considerations are "uniformly" symmetrical, e.g. spherical or cylindrical (but not spherocylindrical), equation (2) transforms into (1). This equation determines

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the number of molecules in the micelle (or the aggregation number). Due to the "uniform" symmetry of spherical and cylindrical micelles such aggregates are homogeneous (i.e. each molecule in the aggregate feels similar environment) and the thermodynamics of "chemical" reactions determines all the parameters of such micelles (i.e. their aggregation numbers). In case of a spherocylindrical micelle, such an aggregate is not a homogeneous but rather a heterogeneous system (i.e. molecules in the cylindrical part and those in the spherical caps feel different environments, due to the different local curvature). Because the exchange of molecules between the monomer pool and a micelle is slower than the exchange of molecules between the cylindrical part of the micelle and its semi-spherical caps (fast and free lateral diffusion of molecules over all the aggregate) the intraaggregate equilibrium is reached well before the monomer-micelle equilibrium, so one can consider that micelle as a relatively closed system. It is this fact that permits one to apply the concept of "chemical" species and "chemical" reactions to the process of micelle formation. The thermodynamics of chemical reactions determines the equilibrium between monomers and micelles but it can say nothing for the intraaggregate equilibrium. We need a new idea and this is the idea to consider the pool of spherocylindrical micelles as a two phase disperse system: the first disperse subphase consists of all cylindrical parts of the spherocylindrical aggregates and the second disperse subphase consists of their semi-spherical caps. It is important to note that both subphases are equivalently dispersed (the number of spheres is equal to the number of cylinders). We have already mentioned the slow exchange of molecules between the monomer pool and a micelle. Combined with the fact that the monomer

concentration above CMC is almost constant this leads to the conclusion that the term $\ln(X_N/N)$ does not change or changes slowly and as far as the intraaggregate equilibrium is considered it can be omitted. In that case the intraaggregate equilibrium is reached when a thermodynamical equilibrium between both subphases is met (e.g. $\mu^{os}=\mu^{oc}$). That is why we shall require latter on: the chemical potential of an amphiphilic molecule in the cylindrical part of a spherocylindrical micelle to be equal to the chemical potential of such a molecule in the spherical caps. When the intraaggregate equilibrium is reached, $\mu^{oc}=\mu^{os}=\mu^{osc}$ and equation (2) can be rewritten in the form:

$$\mu^{ol} + k_B T \ln(X_1) = \mu^{osc} + (k_B T/N)\ln(X_N/N) \qquad (3)$$

We like to stress now that equations (3) and (1) are identical. When formation of nonspherical aggregates is considered in the literature[1-6] the starting point is a small spherical aggregate. If the packing of amphiphilic molecules in such small aggregates is not optimal the aggregates start to grow when the amphiphile concentration is further increased. In all models cited above the driving force for this growth is the chemical potential difference between a molecule in the aggregate ends (region of strong local curvature) and a molecule in the central part of the aggregate[6]. The bigger the aggregate the smaller the relative number of molecules in the strongly curved edge region is. Therefore the free energy per molecule in the aggregate is lower. The process of growth is counteracted by the dilution entropy of the solution, which favours small aggregates. If there is no free energy difference between the molecules in the different parts of a nonspherical aggregate, no driving force for the aggregate growth

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exists[6]. Thus, the free energy difference is essential for the formation of finite size nonspherical aggregates using the Israelachvili model[1].

But we have already mentioned that the amphiphilic molecules are free to move over all the aggregate, and some of them can escape from the strongly curved region of the nonspherical aggregate into the rest of it, decreasing in such a way the free energy per molecule in the strongly deformed region. This process would continue until the chemical potential of molecules in all points of a nonspherical aggregate becomes constant, i.e. the intra-aggregate equilibrium is reached. To our knowledge no attempts by other authors have been made to fulfil such a condition when modelling nonspherical micelles. When aggregates consisting of two or more types of amphiphilic molecules are considered, homogeneous distribution of the cosurfactant over all the aggregates is usually supposed[6]. But due to the different packing conditions for molecules of different wedge symmetry (shape) at points of different local curvature, it is natural to assume heterogeneous surfactant - cosurfactant distribution in a nonspherical aggregate. Indeed, this hypothesis has been proven by the fine experiment of Hendrikx, Charvolin and Rawiso[14]. This problem will be discussed in more detail further on. In a recent paper of Gelbart et al.[2] the partitioning of cosurfactant molecules between regions of different local curvature is taken into account. But in that paper[2] the aggregates are considered as a mixture (sum) of surfactant and alcohol molecules, while an alternative and more consistent (from our point of view) approach would be to consider them as a two dimensional "solution" of cosurfactants (two dimensional "solutes") in a two dimensional "solvent" (the

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surfactant itself). With this idea in mind one can correctly account for the effects due to the entropy of mixing between the surfactant-cosurfactants in a single aggregate.

Obviously, we need a proper model that takes explicitly into account the intrinsic liquid crystal properties of an amphiphilic monolayer (its bending elasticity), as well as the entropy of mixing in the monolayer's plane (in case of multicomponent aggregates). Using such a model one can properly analyze the conditions for formation of thermodynamically stable nonspherical aggregates in amphiphilic systems.

THE MODEL

The model proposed by Petrov and Derzhanski[15] is suitable for our purposes because it takes into account explicitly the elastic properties of amphiphilic monolayers which consist of identical molecules (single component monolayers). According to this model[15] the elastic free energy per molecule (in a monolayer of similar molecules), f, is given by the expression:

$$f(\alpha,c_1,c_2)=(k_H/2)((A_H/H)-1)^2 + (k_C/2)((A_C/C)-1)^2 \qquad (4)$$

where:

$$A_H= \alpha\,(1+(c_1+c_2)d/2+c_1c_2d^2/4) = \alpha\,\alpha_H$$
$$A_C= \alpha\,(1+(c_1+c_2)d/4+c_1c_2d^2/16) = \alpha\,\alpha_C \qquad (4a)$$

α is the area per molecule in a monolayer measured at a surface passing through the chain ends, c_1,c_2 are the principal curvatures of the same surface at a given point, d is the doubled monolayer thickness and α_H and α_C are abbreviations for the expressions in the square brackets. The constants H and C are the equilibrium cross sections of

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hydrophilic heads and hydrophobic parts of molecules, A_H and A_C are the respective actual areas in the deformed monolayer, and k_H and k_C determine the strength of interaction between hydrophilic heads and hydrophobic chains of molecules respectively. Roughly speaking, one can distinguish two layers of interactions in a monolayer (two contributions to the monolayer free energy, $f=f_H+f_C$): the first is formed by the heads ($f_H=(k_H/2)((A_H-H)/H)^2$) interacting elastically (H is the area per head at equilibrium, k_H is the head elastic constant) and a second one formed by the chains ($f_C=(k_C/2)((A_C-C)/C)^2$) interacting elastically (C is the area per chain at equilibrium, k_C is the chain elastic constant). Upon bending, the heads are stretched apart and the chains are compressed or vice versa thus simulating an elastic behaviour for the monolayer itself. As we have already mentioned McMullen et al.[5] have extended the Israelachvili model to account for the chain elasticity adding a term in the form: $f_C=(k_C/2)((L/L_o)-1)^2$. This expression can be related to the chain contribution in (4) via the equality $A_CL=CL_o=v$, if v (the volume of a hydrophobic chain) is considered to be constant. Using (4) one can write the chemical potential per molecule, μ, as a function of monolayer stress, σ, ($\sigma=\frac{\partial f}{\partial \alpha}$) and its principal curvatures c_1 and c_2 (according to (4a) α_H and α_C depends on c_1 and c_2):

$$\mu(\sigma,c_1,c_2) = \frac{k_H+k_C}{2} + \frac{(\sigma + \frac{k_H}{H}\alpha_H + \frac{k_C}{C}\alpha_C)^2}{2(\frac{k_H}{H^2}\alpha_H^2 + \frac{k_C}{C^2}\alpha_C^2)} \qquad (5)$$

The expressions (4) and (5) are valid for a single component

monolayer (e.g. build-up of identical amphiphilic molecules).

The model[15] has been generalized[16,17], i.e. expressions for the free energy per molecule, and expressions for the chemical potentials of the monolayer components have been obtained for a multicomponent monolayer containing small amount of dopant amphiphilic molecules (cosurfactants). The idea of this generalization is to consider such a mixed monolayer as a "two-dimensional solution" of dopants (cosurfactants) in the "two-dimensional solvent" - the monolayer formed from the others amphiphilic molecules. According to the terminology accepted in this paper, a monolayer build-up of only one kind of amphiphilic molecules (e.g. monolayer which does not incorporate cosurfactant) will be denoted as a single component system. For example, the binary mixture - amphiphile plus water - is a single component system. The ternary system - amphiphile$_1$ plus amphiphile$_2$ plus water - is a two-component one, because it consists of two different kinds of amphiphilic molecules.

To derive the generalized formulae for the chemical potentials of different monolayer components one can proceed in the following way. Starting from the expression (5) for the chemical potential of a single component monolayer one can make the assumption that, when a dopant (cosurfactant) molecule is added to it, its Gibbs free energy can be calculated using (5), but instead of parameters H and C one must substitute $(H_o+(H_1-H_o)/N)$ and $(C_o+(C_1-C_o)/N)$, where N is the number of "solvent" (surfactant) molecules. This assumption means that when one adds a dopant molecule with a bigger (smaller) equilibrium head or chain cross section the equilibrium of the layer of heads or chains would be shifted. One can expand the so substituted expression (5)

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with respect to N^{-1} and the result can be presented in the form:

$$\mu = \mu_o + (\mu_1 - \mu_o)/N \tag{5a}$$

If one adds more dopant molecules (say N_1) the last term in (5a) should be multiplied by N_1 and this procedure would be correct if the dopant molecules are distinguishable. Because they are not one must add a term of the form $k_B T n.\ln(\frac{n}{e})$, where $n=N_1/(N_o+N_1)$ is the dopant concentration, and e is the base of natural logarithm. This last term accounts for the entropy of mixing due to dopant partitioning in the monolayer plane. The final expressions[16,17] for the free energy per molecule, f, in a two-component monolayer (surfactant plus cosurfactant), as well as those for the chemical potentials of the "solvent", μ_o, and of the "dopant" (cosurfactant), μ_1, are presented below:

$$f(\sigma,c_1,c_2,n) = \frac{k_H+k_C}{2} + \frac{\sigma^2-(\frac{k_H}{H_o}\alpha_H + \frac{k_C}{C_o}\alpha_C)^2}{2(\frac{k_H}{H_o^2}\alpha_H^2 + \frac{k_C}{C_o^2}\alpha_C^2)} + k_B T n.\ln(\frac{n}{e}) +$$

$$+ n\left\{\frac{\sigma^2 - (\frac{k_H}{H_o}\alpha_H + \frac{k_C}{C_o}\alpha_C)^2}{\frac{k_H}{H_o^2}\alpha_H^2 + \frac{k_C}{C_o^2}\alpha_C^2} \frac{\frac{k_H\Delta H}{H_o^2 H_o}\alpha_H^2 + \frac{k_C\Delta C}{C_o^2 C_o}\alpha_C^2}{\frac{k_H}{H_o^2}\alpha_H^2 + \frac{k_C}{C_o^2}\alpha_C^2} + \right.$$

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$$+\left[\frac{\left(\frac{k_H}{H_o}\alpha_H+\frac{k_C}{C_o}\alpha_C\right)\left(\frac{k_H\Delta H}{H_oH_o}\alpha_H+\frac{k_C\Delta C}{C_oC_o}\alpha_C\right)}{\frac{k_H}{H_o^2}\alpha_H^2+\frac{k_C}{C_o^2}\alpha_C^2}\right] \tag{6}$$

$$\mu_o(\sigma,c_1,c_2,n)=\frac{k_H+k_C}{2}+\frac{(\sigma+\frac{k_H}{H_o}\alpha_H+\frac{k_C}{C_o}\alpha_C)^2}{2(\frac{k_H}{H_o^2}\alpha_H^2+\frac{k_C}{C_o^2}\alpha_C^2)}-k_BTn \tag{7}$$

$$\mu_1(\sigma,c_1,c_2,n)-\mu_o(\sigma,c_1,c_2,n)=k_BT\ln(n)-$$

$$-\frac{(\sigma+\frac{k_H}{H_o}\alpha_H+\frac{k_C}{C_o}\alpha_C)^2}{2(\frac{k_H}{H_o^2}\alpha_H^2+\frac{k_C}{C_o^2}\alpha_C^2)}\times \tag{8}$$

$$\times\left[\frac{\frac{k_H\Delta H}{H_o^2H_o}\alpha_H^2+\frac{k_C\Delta C}{C_o^2C_o}\alpha_C^2}{\frac{k_H}{H_o^2}\alpha_H^2+\frac{k_C}{C_o^2}\alpha_C^2}-\frac{\frac{k_H\Delta H}{H_oH_o}\alpha_H+\frac{k_C\Delta C}{C_oC_o}\alpha_C}{(\sigma+\frac{k_H}{H_o}\alpha_H+\frac{k_C}{C_o}\alpha_C)}\right]$$

$$\Delta H=H_1-H_o \qquad \Delta C=C_1-C_o$$

Here σ is the lateral stress of the monolayer, H_o and C_o are the "geometrical" parameters of the "solvent" (surfactant) and H_1 and C_1 are those of the dopant (cosurfactant).

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SPHEROCYLINDRICAL AGGREGATES

The conditions for the formation of thermodynamically stable spherocylindrical aggregates in single component and multi-component amphiphilic systems are considered elsewhere[9] in detail. Here we describe only the method and the basic conclusions that we shall need when discussing the differences between the spherocylindrical and disk-like aggregates (micelles). Intending to apply our model to the case of spherocylindrical aggregates, we consider these aggregates as formed from an amphiphilic monolayer coated on a cylinder (length L and radius r) and on two semispheres (radius r) attached to the cylinder's ends, fig.1. When r→0,

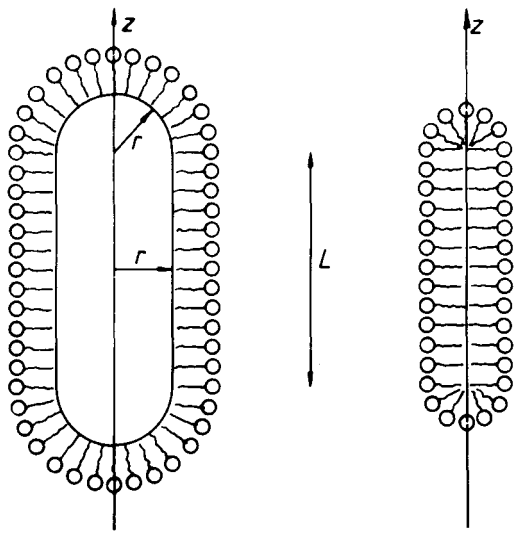

FIGURE 1. A monolayer coated on a spherocylindrical body of radius r (left); A spherocylindrical aggregate (micelle), r→0 (right); z is the axis of axial symmetry.

the structure of the amphiphilic monolayer coated on this geometrical body corresponds to the structure of a sphero-

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cylindrical aggregate. The system of such aggregates decomposes into two subsystems: the first consisting of their cylindrical parts (labelled "c"), and the second consisting of their semispherical caps (labelled "s"). The free energy of the whole system is a sum of the free energies of both subsystems and therefore its variation can be written in the form:

$$\delta F = \sigma^s \delta A^s + \mu_\alpha^s \delta N_\alpha^s + \sigma^c \delta A^c + \mu_\alpha^c \delta N_\alpha^c, \quad N_\alpha^s + N_\alpha^c = N_\alpha \qquad (9)$$

Here A^s and A^c are the sphere and cylinder subsystems' monolayer areas, respectively. Due to the fact that the variations δA^s and δA^c are independent, and $\delta N = 0$ (we have already mentioned that as far as the intraaggregate equilibrium is considered the pool of micelles can be treated as a closed system with fixed number of molecules), it follows that the condition for thermodynamic equilibrium ($\delta F=0$) is fulfilled only if:

$$\sigma^s=0, \ \sigma^c=0, \ \mu_\alpha^s=\mu_\alpha(\sigma^s,\frac{1}{r},\frac{1}{r},n^s)=\mu_\alpha(\sigma^c,\frac{1}{r},0,n^c)=\mu_\alpha^c \qquad (10)$$

When $\alpha=0$ the chemical potential is given by (7) and when $\alpha=1$ by (8) at $\sigma=0$. The equilibrium condition for a single component system is reduced to a single equation without free parameters and therefore it holds only when the model parameters confirm some restrictions[9]: physically, this means that only very special amphiphilic substances whose molecular "shape" parameters obey the above equation can form spherocylindrical micelles. In the general case, equation (10) is not satisfied. This means that semispherical caps and cylindrical parts of spherocylindrical aggregates cannot exist in thermodynamic equilibrium, i.e. stable spherocylindrical aggregates cannot form in such

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amphiphilic systems. Since $\mu=f-\sigma\alpha$, $\mu=f$ when $\sigma=0$ and this leads to $f^s \neq f^c$. As can be seen, when $f^s>f^c$ the total free energy of the amphiphilic system is minimal if N^s is minimal. This happens to be the case with maximal (i.e., infinite) length of spherocylindrical aggregates (hexagonal phase). When $f^s<f^c$ the formation of spherical aggregates (micelles) is energetically favourable. Only in the special case, when the condition for equilibrium (10) is met, stable spherocylindrical aggregates are formed in the system. In that case $f^s = f^c$ and the system's free energy does not depend on the length of aggregates - spherocylindrical aggregates of different length may coexist. This means also that the standard chemical potential per molecule, μ^{osc}, does not depend on the aggregation number N. But the actual aggregation number is determined according to equation (3). As Israelachvili et al.[1] have demonstrated in this case the size distribution of micelles is very broad, so such a system is highly polydisperse.

In a two-component system we have some freedom. The equilibrium condition:

$$\begin{aligned} \mu_0^s(\sigma^s=0,n^s) &= \mu_0^c(\sigma^c=0,n^c) \\ \mu_1^s(\sigma^s=0,n^s) &= \mu_1^c(\sigma^c=0,n^c) \end{aligned} \tag{11}$$

has a simple solution for the dopant concentration in the cylindrical part of the aggregate, n^c, and in the spherical caps, n^s, when the "solvent" - "solute" pair is properly selected[9]. It is worthwhile to point out that in our model the local cosurfactant-surfactant molar ratio is different in the spherical and in the cylindrical parts of the aggregates ($n^s/n^c \neq 1$). This difference is a consequence of the different local curvature of the monolayer, which leads to different "packing" conditions for the dopant in both

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parts of the aggregate. This effect is an intrinsic property of the model and is a consequence of the interplay between the liquid crystal properties (bending elastic energy) of the monolayer and the entropy of mixing (in the monolayer's plane).

If the mean dopant concentration, n^*, in the system is inbetween n^c and n^s, (that means $n^s<n^*<n^c$ if $n^s<n^c$ or $n^s>n^*>n^c$ if $n^s>n^c$) then the mixed system will form spherocylindrical aggregates of length L, determined by the expression:

$$L = \frac{d}{2} \frac{n^s - n^*}{n^* - n^c} \frac{\dfrac{2k_H}{H_o} + \dfrac{k_C}{C_o}}{\dfrac{4k_H}{H_o} + \dfrac{k_C}{C_o}} \frac{\dfrac{16k_H}{H_o^2} + \dfrac{k_C}{C_o^2}}{\dfrac{4k_H}{H_o^2} + \dfrac{k_C}{C_o^2}} \tag{12}$$

The length of the aggregate depends explicitly on the surfactant parameters (H_o and C_o) and it depends implicitly on the cosurfactant parameters (H_1 and C_1) via the concentrations n^s and n^c. The dependence of the aggregate length on the cosurfactant concentration, n^*, allows one to change practically this parameter. Here we should point out that in single component amphiphilic systems the spherocylindrical aggregates, when formed (very exotic case, as mentioned before), are polydisperse, while in two-component amphiphilic systems they are monodisperse (the size of a two-component spherocylindrical aggregate is determined by the expression (12)). In this case equation (3) determines the relative proportion of amphiphilic molecules in the monomer pool, X_1, and those in the micelles of length L_o, X_N. If the dopant concentration n^* is out of the range determined by the points n^s and n^c no more spherocylindrical

aggregates can exist. Spheres or infinite cylinders are formed instead depending on the relation between n^*, n^c and n^s. If $n^*<n^c<n^s$ or $n^s<n^c<n^*$ then infinite cylinders are formed while if $n^*<n^s<n^c$ or $n^c<n^s<n^*$ then spherical micelles exist.

DISK-LIKE AGGREGATES

Let us now derive the condition for the formation of thermodynamically stable disk-like aggregates. We shall consider an appropriate geometrical body formed by two circles of

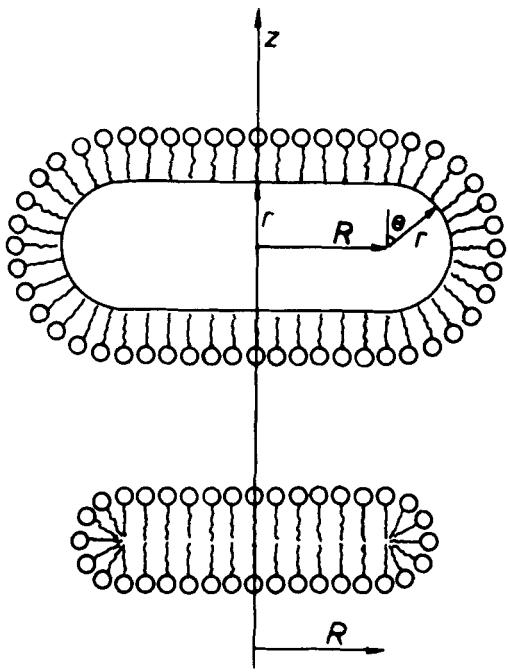

FIGURE 2. A monolayer coated on a disk-like body (up, see text); A disk-like aggregate (micelle) of radius R, r→0 (down); z is the axis of axial symmetry.

radius R at a distance r from each other touching a torus of radii R and r respectively, fig.2. Applying the same

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approach we shall imagine the disk-like aggregates as made of a monolayer coated on the body. When $r \to 0$ the body vanishes and the monolayer structure corresponds to the proposed structure of a disk-like aggregate (micelle). Taking into account that the system of aggregates decomposes into two subsystems: the first consisting of the flat portions of the micelles (labelled "m") and the second consisting of their circular rims (labelled "e"), one can write the variation of the total free energy in the form:

$$\delta F = \sigma^m \delta A^m + \mu_\alpha^m \delta N_\alpha^m + \gamma^e \delta l^e + \mu_\alpha^e \delta N_\alpha^e, \quad N_\alpha^m + N_\alpha^e = N_\alpha \tag{13}$$

Here A^m is the total area of the disks and l^e is the total length of the disk perimeters. At equilibrium $\delta F=0$, because of the independence of the variations δA^m and δl^e, and when the system has a fixed number of molecules of each kind ($\delta N_\alpha=0$), the following relations must hold:

$$\sigma^m = 0, \quad \gamma^e(R,\sigma^m,n^m) = 0, \tag{14}$$

$$\mu_\alpha^m(\sigma^m,n^m)=\mu_\alpha(\sigma^m,0,0,n^m)=\mu_\alpha(\sigma^e,\frac{1}{r},\frac{\sin(\theta)}{R+r\sin(\theta)},n^e)=\mu_\alpha^e(\sigma^e,n^e)$$

It is shown in[16,17] that the last two equations in (14) determine the edge energy function $\gamma(R,\sigma^m,n^m)$, therefore the only restrictive condition to fulfil remains:

$$\gamma^e(R,\sigma^m=0,n^m) = 0 \tag{15}$$

The dopant (cosurfactant) concentration is zero ($n^m=0$) for a single component amphiphilic system, so equation (15) reduces to the relation:

$$\gamma^e(R,0,0) = 0 \tag{16}$$

This equation determines the radius, R, of a thermodynamically stable disk-like aggregate. Using equation (14) and the expression (5) for the chemical potential as a function

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of the monolayer curvature one can write the following relation:

$$\mu^m(0,0) = \mu\left(\sigma^e, \frac{1}{r}, \frac{\sin(\theta)}{R+r\sin(\theta)}, 0\right) = \mu^e(\sigma^e) \qquad (17)$$

This expression describes the condition for thermodynamic equilibrium between the molecules in the flat part of the disk and the molecules building its circular rim. Due to the different local curvature sensed by the molecules (oriented in different ways with respect to the disk normal) the subsystem of molecules building the disk edge is heterogeneous. According to equation (17) the monolayer stress in the edge, σ^e, is a function of the molecular orientation angle, θ. So, the molecules with different orientations with respect to the disk normal feel different environments in the circular rim. Nevertheless equation (17) ensures thermodynamic equilibrium in that case as well. Equation (17) permits one to calculate the monolayer lateral stress σ^e in the edge region as a function of disk radius, R. Integrating this function along the length of the semicircle, formed by the intersection of the edge and the plane perpendicular to the disk and containing its axis, we obtain the total tangential force $\gamma^*(R)$ acting when the edge is cut. As mentioned above, when $r\to 0$ we get the structure of a disk-like aggregate and that is why we interpret $\lim\gamma^*(R,r^{-1})\big|_{r\to 0}$ as an edge energy of the aggregate. It is easy to see that the edge energy depends on the disk radius:

$$\gamma(R)=\frac{d}{4}S\int_0^{\pi}\left[\sqrt{(B_2+2C_2z\sin(\theta)+D_2z^2\sin^2(\theta))} - (A_1+B_1z\sin(\theta))\right]d\theta \qquad (18)$$

Here:

$$A_1 = \frac{\frac{2k_H}{H_o} + \frac{k_C}{C_o}}{\frac{k_H}{H_o} + \frac{k_C}{C_o}}, \qquad B_1 = \frac{\frac{4k_H}{H_o} + \frac{k_C}{C_o}}{\frac{k_H}{H_o} + \frac{k_C}{C_o}}, \qquad B_2 = \frac{\frac{4k_H}{H_o^2} + \frac{k_C}{C_o^2}}{\frac{k_H}{H_o^2} + \frac{k_C}{C_o^2}}$$

$$C_2 = \frac{\frac{8k_H}{H_o^2} + \frac{k_C}{C_o^2}}{\frac{k_H}{H_o^2} + \frac{k_C}{C_o^2}}, \qquad D_2 = \frac{\frac{16k_H}{H_o^2} + \frac{k_C}{C_o^2}}{\frac{k_H}{H_o^2} + \frac{k_C}{C_o^2}}, \qquad z = \frac{d}{4R}, \qquad S = \frac{k_H}{H_o^2} + \frac{k_C}{C_o^2}$$

are some expressions of the model parameters. The equation (18) leads to elliptical integrals and this makes the analysis too complicated. That is why we shall use here an approximation that simplifies (18) neglecting the Θ dependence (i.e. $\Theta = \pi/2$). So we obtain:

$$\gamma(R) = \frac{\pi}{4}\, dS\left(\sqrt{B_2 + 2C_2 z + D_2 z^2} - (A_1 + B_1 z)\right) \tag{19}$$

Using (19) one can solve (16) and can obtain the values of z at which the edge energy vanishes. They are solutions of the following equation:

$$(B_2 - A_1^2) + 2(C_2 - A_1 B_1)z + (D_2 - B_1^2)z^2 = 0 \tag{20}$$

Its solution is:

$$R = \frac{d}{4} \frac{(D_2 - B_1^2)}{-(C_2 - A_1 B_1) \pm ((C_2 - A_1 B_1)^2 - (B_2 - A_1^2)(D_2 - B_1^2))^{1/2}} \tag{21}$$

Considering, for the sake of simplicity, only the case $k_H = k_C = k$ we can analyze the influence of molecular asymmetry (shape) on the radius of disk-like aggregates. In this case

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(21) reads:

$$R = \frac{d}{4}\frac{3(q^2-4)}{5-2q^2}\left\{1 \pm \left(1 - \frac{3(2-q^2)(4-q^2)}{(5-2q^2)^2}\right)^{1/2}\right\}^{-1}$$

$$q=H_o/C_o \qquad (22)$$

Equation (20) has a solution of physical meaning only if the molecular asymmetry, q, is in the range $(\sqrt{2},2)$. When $q\to\sqrt{2}$ disks degenerate into infinite lamellae while in the case $q\to 2$ they degenerate into spherical micelles.

In case of a two-component amphiphilic system the condition for the formation of thermodynamically stable disk-like aggregates is given by (14). The restrictions imposed on the chemical potentials of the "solute" and the "solvent" molecules determine two implicit functions:

$$n^e(R,n^m) \qquad (23)$$

$$\sigma^e(R,n^m) \qquad (24)$$

The first of them reflects the local increase (or decrease) of dopant (cosurfactant) concentration in the edge region due to the different local curvature there, and the difference in the molecular asymmetry, H/C, of the surfactant and cosurfactant. As mentioned before, this effect is an intrinsic property of the model and it is analogous to the partitioning of a substance between two different phases. These are the edge region and the flat part of disks. They are different due to the different local curvature in both parts of disk-like aggregates. The effect of cosurfactant-surfactant separation in disk-like aggregates has been observed experimentally by Hendrikx, Charvolin and Rawiso[14]. These authors have found that: the charged soap molecules (which repel each other due to the

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charge, and are therefore characterized by bigger effective heads) concentrate in the edge region, while the molecules of the noncharged long chain alcohol concentrate in the flat part of the aggregates. This is in accordance with the predictions of our model whereby the amphiphilic molecules with bigger heads concentrate in the edge region, and those with smaller heads in the flat part of the disks. Once more we use the function (24) to determine the dependence of the edge energy on the disk radius, R, and on the dopant concentration in the flat part of the aggregate, n^m. The main requirement for thermodynamic equilibrium is given by (15) but now the edge energy $\gamma(R,n^m)$ has two parameters. At zero concentration this equation reduces to that for a single component system. When the dopant concentration is increased, the aggregate radius (at which the edge energy vanishes) will increase or decrease depending on the dopant asymmetry, H_1/C_1.

DISCUSSION

Comparing disk-like to spherocylindrical aggregates one can conclude that the formation of disks is more probable because it is easier to satisfy the condition for their thermodynamic equilibrium. But in a real amphiphilic system, transitions between all kinds of aggregates are possible. This possibility will shift the equilibrium towards the more favourable units. In order to determine which type of aggregates will be formed in a real amphiphilic system when the molecular asymmetry of its components are known, one has to compare the free energy per molecule in both cases. The aggregates with the lower free energy per molecule will be thermodynamically favourable and therefore they will be

formed in the system. In the case of single component system one can see that when the molecular asymmetry, H/C, is in the range: $\sqrt{2}<H/C<2$, infinite spherocylinders[9], as well as disk-like aggregates of finite radius, R, can be formed. The free energy per molecule can be calculated according to (6) with n=0. The result (if $k_H=k_C=k$) is:

$$f^d - f^c = \frac{2k^3}{H^3 C}\left(\frac{H^2}{C^2} - 2\right), \quad f^d > f^c \quad \text{if} \quad \frac{H}{C} > \sqrt{2} \tag{25}$$

It is obvious that when disk-like aggregates can be formed ($H/C>\sqrt{2}$) their energy per molecule is higher than that of infinite spherocylinders. Therefore a real amphiphilic system will prefer a hexagonal phase (with infinite spherocylinders) rather than a nematic one (with finite disk-like aggregates).

On the basis of above considerations one can conclude that disk-like aggregates cannot be formed in a single component amphiphilic system. But a lyotropic nematic (discotic) phase has been observed already in a single component amphiphilic system[18]. This discrepancy between the model predictions and the experiment can be explained in several ways:

1. The discotic nematic phase is formed due to the inter-aggregate interactions which are not taken into account in our model. But such an explanation seems to us unplausible because the investigations of other authors[3] have shown that the interaggregate interactions only increase the growth of the disks or rods without changing the trend for their stability.

2. The structure of disk-like aggregates, forming the nematic phase, differs[19] from that accepted in our work and therefore our conclusions cannot apply to the real amphi-

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philic system in consideration.

3. The amphiphilic substance, forming the discotic nematic phase, is an ionic detergent and is partially dissociated in solution. The system is a mixture of charged and neutral molecules. The electrical repulsion between charged heads leads to an increased separation between them and therefore they must be described by a bigger head cross section in terms of our model. So, the system consists of two kinds of molecules, each kind possessing different molecular asymmetry. Hence, it is rather a two-component amphiphilic system and not a single-component one.

4. Lemaire and Bothorel[20] have demonstrated that there are two minima in the interaction energy profile for parallel oriented hydrocarbon chains. The first minimum corresponds to the gel state chain-cross-section, and the second one corresponds to the liquid crystal state of the chains. Petrov[21] has pointed out that due to the strong deformation of the monolayer in the edge region and the related elastic stresses, it is possible for the chains to undergo a transition from the liquid crystal minimum to the gel minimum. In this case the molecules in the flat part of the disk and those in the edge region must be described by different model parameters. Here again the system is effectively two-component. Let H be the equilibrium cross section of the head, and C_1 ,C_2 be the respective cross sections of the hydrophobic parts in the gel (C_1) and in the liquid crystal (C_2) state respectively. Using the expressions for the chemical potentials (4,5), we can write the condition for thermodynamic equilibrium in this case:

$$\begin{aligned} \mu^m(H,C_2) &= \mu^e(H,C_1) \\ \mu^c(H,C_2) &= \mu^s(H,C_1) \end{aligned} \tag{26}$$

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The results obtained modifying the model in this way are analogous to those obtained before. The only difference is that the free energy per molecule in a disk-like aggregate can be higher or lower than that of an infinite spherocylinder depending on the molecular asymmetry in both minima (H/C_1 and H/C_2). Indeed, if C_1 is the equilibrium cross-section of the chains in the edge region (molecules in gel minimum), and C_2 is that in the flat part of the disk (molecules in the liquid crystal minimum) we have ($k_H=k_C=k$):

$$f^d = \frac{k}{2}\frac{(H - C_2)^2}{H^2 + C_2^2}, \qquad f^c = \frac{k}{2}\frac{(H - 2C_1)^2}{H^2 + 4C_1^2} \tag{27}$$

It is easy to see that the difference:

$$f^d - f^c = kH\frac{(H^2 - 2C_1C_2)(2C_1 - C_2)}{(H^2 + C_2^2)(H^2 + 4C_1^2)} \gtrless 0 \tag{28}$$

can be positive or negative, depending on the relationship between the equilibrium cross-sections of the chains in gel and in liquid crystal minima. When $(H^2-2C_1C_2)(2C_1-C_2)<0$, disk-like aggregates are of lower elastic free energy than infinite cylinders. Obviously Petrov's hypothesis permits us to coordinate the experimental facts with the conclusions made on the basis of our model.

CONCLUSION

The model proposed here reveals the role of the bending elasticity of amphiphilic monolayers when micelles of different shape are formed, and especially the significance of the shape asymmetry (the existence of regions of different local curvature). Our model takes into account explicitly the redistribution of amphiphilic components

between regions of different local curvature, due to the different effective molecular shape of these components - an effect predicted earlier by us[16,17] and Fromherz[23], and later on experimentally observed by other authors[14]. We would like to underline some possibilities for further development of this model. At present it does not consider the entropy of mixing when the number of aggregates in the amphiphilic system changes. Since infinite aggregates are entropically unfavourable[1], the involvement of this factor can change some of the conclusions made here[2-6]. A work to reveal the role of mixing entropy in our model is in progress now. The results obtained in this work could help in the preliminary selection of mixtures that form lyotropic nematic liquid crystal phases.

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