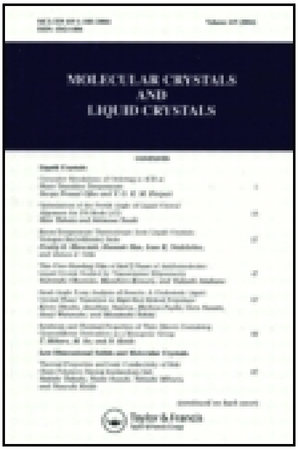

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From Micelles to Liquid Crystals

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FROM MICELLES TO LIQUID CRYSTALS

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Abstract Recent characterizations of aggregates of amphiphilic molecules in nematic phases of some amphiphiles/water phase diagrams gives new insight into the aggregation process. Thermodynamical models are being re–considered. We shall present some developments proposed to account for observations in the system sodium decyl sulfate / decanol / water.

INTRODUCTION

Up to a recent date the study of the aggregation of amphiphilic molecules in presence of water was approached along two distinct directions: the study of diluted micellar phases without any long range order and that of concentrated liquid crystalline phases with long range translational order. Systematic investigations of phases in the intermediate concentration range presenting a long range orientational order only, i.e. nematic phases, introduce a new link between these two domains and make possible a more coherent approach of the growth and organization of aggregates of amphiphilic molecules. We shall examine thermodynamical descriptions and phase diagrams in parallel.

Only the broadlines of micellar growth and organization will be considered. This manuscript is a brief presentation of the problem and should be considered as a guide giving access to references. We shall oversimplify the developments of the existing approaches to put in light their physical content and to emphasize the ideas which we believe to be at the basis of our understanding of this problem.

AMPHIPHILIC MOLECULES

They contain a hydrophobic paraffinic chain which is attached on a hydrophilic polar group.

We have studied the aggregation of two particular molecules
sodium decyl sulfate, $CH_3-(CH_2)_9-OSO_3Na$ and
decanol, $CH_3-(CH_2)_9-OH$.

FORMATION OF MICELLES

When the first molecules are put in presence of water only a few of them are dissolved in bulk water, because of the hydrophoby of their chains, and most of them build a film at the surface, where they can have their chain far from the contact with the water. There is a chemical exchange between these two situations which can be expressed writing the equality of the chemical potentials per molecule,

$$\tilde{\mu}_1^o + \log X_1 = \tilde{\mu}_{film} - \gamma a + \log X_{film} \quad , \qquad (1)$$

where $\tilde{\mu}_1^o$ and $\tilde{\mu}_{film}$ are the standard chemical potentials of molecules in the bulk and in the film, γ is the superficial tension, and a the mean area per molecule at the surface. The logarithmic terms are the mixing entropies of the molecules in the solution and in the film, X_1 and X_{film} are the molar fractions of molecules in both states. When the surface of the water is saturated the right member keeps constant, therefore the number of monomers can not increase, and the added molecules should precipitate. However, a more favorable situation is possible which is the formation of micellar aggregates dispersed in water, where the chains are clustered together and partially protected from the contact with water by the interface of polar heads. A new chemical exchange takes place between the monomers and the aggregates of s molecules which is expressed by the following equality of the chemical potentials[1],

$$\tilde{\mu}_1^o + \log X_1 = \tilde{\mu}_s^o + \frac{1}{s} \log \frac{X_s}{s} \qquad (2)$$

where X_s is the molar fraction of molecules in aggregates of s molecules — different s values should be considered to give account of the polydispersity but we shall ignore this effect in this simple presentation —. The formation of the aggregates is possible because the entropic loss associated with the clustering of the molecules is counterbalanced by an energetic gain in $\tilde{\mu}_s^o$ as the chains are no longer in contact with water. The molar fraction of molecules in aggregates with s molecules is then given by the following equation

$$X_s = s\,[X_1 . e^{(\tilde{\mu}_1^o - \tilde{\mu}_s^o)}]^s \, , \qquad (3)$$

from which we can estimate the critical micellar concentration (CMC) at which this aggregation starts

$$X_{CMC} = X_1 \sim e^{-(\tilde{\mu}_1^o - \tilde{\mu}_s^o)} . \qquad (4)$$

GROWTH OF MICELLES, IDEAL SOLUTION[1,2]

As the micelles do not interact, their growth is controlled by intramicellar terms only.

The first term is a constraint associated with the hydrophoby of the chains. It imposes them to keep a tail to tail organization so that one dimension of the aggregate must remain close to twice the molecular length. The spherical micelles can therefore grow only as prolate spheroids —rods— or oblate ones —disks—.

The second term is composed of the interfacial and chain energies to be put in $\tilde{\mu}_s^o$. The classical models consider that the *paraffinic medium is homogeneous,* and that its energy — g_{chain} — *is constant,* independent of the shape of the aggregate. We are therefore led to consider the interfacial energy only. It can be written as $\gamma a + c/a$ where γa is associated with the superficial tension and c/a with the interactions between polar heads and ions. For given c and γ this energy goes through a minimum for $a = a_o = \sqrt{(c/\gamma)}$.

The third term is the geometry of the molecule: volume v and length l. It intervenes as follows. When a_0 = v/l the molecule is analogous to a cylindrical rod and the aggregate will grow as a lamellar disk; when a_0 = 2 v/l the molecule is "pie" — shaped and the aggregate will grow as a cylindrical rod; when a_0 = 3 v/l the molecule has the shape of a cone and the aggregate will stay spherical[2].

In the first models[1,2] the third constraint is obeyed in the main body of the aggregate only so that if we want to grow finite aggregates with such molecules we cannot stay at the minimum of the energy as the lamellar body of the disk or the cylindrical body of the rod, which is at the minimum as $a = a_0$, must be closed by a cylindrical rim or two hemispherical caps, where $a > a_0$ and are therefore far from the minimum. If we call δ the energy difference between the rim or caps and the bodies of molecules the chemical potential per molecule can be written as:

$$\tilde{\mu}^{o}_{body} + \frac{\delta}{s^{p}} + \frac{1}{s} \log \frac{X_s}{s} , \qquad (5)$$

where p = 1 for rods - as the relative number of molecules in the caps decreases with increasing length of the aggregate - and p = 1/2 for disks - as the relative number of molecules in the rim decreases as the ratio of the perimeter of the disk over the surface of the disk which is proportional to the total number of molecules s-.The growth of the aggregate is now governed by the competition between the two last terms. In the case of rods the complete calculations show that a compromise is possible as the two terms vary as s^{-1}. *Finite rods are stable* and they grow as the concentration increases. In the case of disks no compromise is possible, the energy term being always dominant because of large δ values and slow $s^{-1/2}$ decrease. *Finite disks are not stable* and, immediately, *infinite lamellae* are to be formed to eliminate the rim. Another way to eliminate the rim consists in closing the lamellae upon themselves in the shape of a bag, or *vesicle*, this requires a curvature energy but may be entropically favorable if the vesicles are small.

GROWTH OF MICELLES, NON IDEAL SOLUTION[3,4,5]

The problem of growth of micelles in non ideal solution was approached by considering the entropic change introduced by the excluded volume between aggregates. In a second virial approximation the contribution per molecule is the product of the number of pairs and the excluded volume per pair divided by the number of molecules s per aggregate. With the classical expressions for the excluded volume for rods and disks[3] the chemical potential of one molecule in an aggregate of s molecules can now be written as

$$\tilde{\mu}^{o}_{body} + \chi_o + \frac{1}{s^p}(\delta + \chi) + \frac{1}{s}\log\frac{X_s}{s}\ , \tag{6}$$

where the new entropic term $\chi_o + \chi s^{-p}$ has the same s dependence as the energetic term δs^{-p} associated with the end effects, and $p = 1$ for rods and $p = 1/2$ for disks. Therefore its role consists in *enhancing the growth* of the aggregate without modifying the above scheme of stability. This is also valid when the development is pushed to higher orders.

ONSET OF ORDER[5]

It is intuitively evident that as the rods elongate and become more numerous with the increasing concentration they should become organized with at least some orientational order of the nematic type. To take this effect into account we must introduce an orientational entropy term, σs^{-1} per molecule. The expression for the chemical potential of rods then becomes

$$\mu^{o}_{body} + \frac{1}{s}[\delta + \chi + \sigma + \log\frac{X_s}{s}] + \chi_o\ . \tag{7}$$

This new term σ "fights" with the excluded volume term χ as the excluded volume of a pair of aligned rods is smaller than that of randomly oriented ones. The calculations show indeed the existence of two minima, one corresponding to an isotropic phase of finite rods and the other to a perfectly aligned phase of infinite cylinders. The first one is the lowest at low concentration, the second is the lowest at high concentration. Therefore the system should experience a transition from an isotropic micellar phase of finite rods to an ordered phase of the hexagonal type. In this model there is *no place for a nematic phase* with a partial orientational order of finite rods in contrary to the Onsager's prediction. It must be clear that this discrepancy lies in the very particular nature of our rods which are labile aggregates of molecules whose length can vary whereas the rods considered by Onsager are rigid. Indeed, the competition between the excluded volume and orientational entropies is the origin of a very effective *size/anisotropy coupling* which makes the rods "explode" as they become oriented, because the longer the rods the smaller is the number of pairs.

CONFRONTATION WITH PHASE DIAGRAMS

Following the conclusions drawn from the above models we should expect to meet three situations as the concentration of amphiphilic molecules increases: the micelles do not grow, they grow as rods which become infinite cylinders ordered in a hexagonal phase, they can not grow as disks but vesicles or infinite lamellae in a lamellar phase are formed.

Indeed, up to a recent date they were the reported situations. We give a few examples. In the dodecyltrimethylammonium/water system the micelles do not grow and the first ordered phase observed is a cubic phase where small finite aggregates are organized in a 3-D lattice of cubic symmetry[6]. In the potassium laurate/water system the micelles grow as rods and a hexagonal phase is observed at high concentration[7]. Eventually the same amphiphilic ion, for instance cetyl—pyridinium, may experience the two above situations as the counter ion is changed from Br to Cl [8]. Finally no micelles are observed, but vesicles and a lamellar phase, in the dipalmitoyl phosphatidylcholine/water system[9].

However, recent studies have shown the existence of *nematic phases of discoidal aggregates* which are in contradiction with the above predictions. For instance, in the sodium decyl sulfate/decanol/ water system, nematic phases of small disks and rods are observed in between the domains of the isotropic micellar phase and of the ordered hexagonal, rectangular and lamellar phases[10,11]. Therefore the basic assumptions of the models have to be reconsidered. These are the independence of the energy of the paraffinic medium with respect to the environment of the molecule – i.e. the chains have no preference for lamellar, cylindrical or spherical structures in the aggregate – and the homogeneity of the distribution of the molecules within the aggregate.

ROLE OF THE PARAFFINIC CHAINS[14]

A recent modelling of the behaviour of the chains in aggregates of different shapes[12] and the analysis of NMR data[13] strongly suggest that the free energy of the chains–g–increases with the interfacial curvature. The chains should not be passive. For instance, a "pie" shaped molecule ($a_0 = 2\ v/l$), which would have built only rods with cylindrical interface, could now build disks as its chains would prefer a flat interface along which their energy g is lower. In such a situation the energy of the polar heads in the rim would be minimal as $a = a_0$, but not that of the chains because of the cylindrical curvature; on the other hand the energy of the chains in the lamellar body would be minimum because of the flat interface, but not that of the heads, as $a < a_0$. This might result in an energy difference δ between the two sites smaller than that in the above model, and the two terms of the chemical potential per molecule $s^{-1}[\delta + \log(X_s/s)]$ could compete to make the disks stable. This approach seems also preferable as it permits a minimization of the energy over the whole aggregate whereas this was done in one part of the aggregate only – where $a = a_0$ – in the earlier model. In the absence of any simple analytical expression for the chain energy g as function of the interfacial curvature a phenomenological approach was tried[14,15]. It consists in considering not only the cases $a_0 = i\,v/l$ with $i = 1,2,3$, which correspond to "rod", "pie" and "cone" – shaped molecules, but also the intermediate cases $a_0 = (1+y)\,v/l$ with $0 < y < 2$, which correspond to molecules of "intermediate" shapes. This is a simple way to express the difference between the situation wanted by the chains and by the heads. If this is so the energy $\gamma a + c/a$ could be minimum in no part of the aggregate as $a = a_0/(1+y)$ in the lamellar part, $a = 2a_0/(1+y)$ in the cylindrical part and $a = 3a_0/(1+y)$ in the spherical part. The energies of the different parts of the aggregate would be then on either side of the minimum corresponding to a_0 so that, in certain situations, the energy difference δ may be decreased. The complete calculation shows that this prediction is correct, and that disks and disk–rod coexistence are possible for certain values of the parameter y. For instance, for $y = 0.8$ the micelles stay spherical, for $0.43 < y < 0.8$ the micelles grow as rods, for $y \cong 0.43$ first the micelles grow as disks, then they coexist with rods, and finally only rods are stable, for $0.40 < y < 0.43$ the micelles grow as disks, for $y < 0.4$ infinite lamellae only are stable. It is quite noticeable that this sequence of structures calculated in the diluted range can be put in close correspondence with that observed in the concentrated liquid crystalline region of the phase diagram of the sodium decyl sulfate /decanol/ water system, as the decanol content increases[10]: a nematic phase of rods is followed by a biaxial nematic phase, which might be thought of as being a coexistence zone of rods and disks, then a nematic phase of disks, and finally a lamellar phase of infinite lamella.

Therefore more realistic models, where the chains play an active role, give account of the existence of finite oblate aggregates hitherto excluded. However, there is still a question left as the new model[14] predicts a growth of the aggregates with the concentration which has not been observed, the aggregates in the concentrated nematic phases being small enough for the nematic phase to exist, with a low aspect ratio between 2 and 3. We can find an argument for such a slowing down of the growth examining the last point.

DISTRIBUTION OF MOLECULES IN AN AGGREGATE

The above models assume a homogeneous distribution of the amphiphilic molecules in an aggregate, here soap and fatty alcohol. In fact a recent neutron scattering study shows that it is not so[16]. The probability to see the soap molecules in the rim of a disk is slightly higher than in the lamellar body. It is therefore reasonable to think that the soap/alcohol ratio may act as a factor limiting the growth of the aggregate enabling the existence of nematic phases. This was formalized in a phenomenological way by making the terms δ in the chemical potential decrease with s following $\delta = \delta_0 + \delta_1/s$ [5].

CONCLUSION

We discussed thermodynamical approaches of the process of aggregation of amphiphilic molecules in water in the light of recent studies of phase diagrams where nematic phases are present. We showed that the structural studies of these ordered nematic phases, which are relatively easy because of their anisotropy, provide valuable information about the growth of anisotropic aggregates, an information difficult to obtain in the disordered micellar phases because of their isotropy. The models developed up to now may be thought satisfying in the sense that they help to have a coherent view of the rather complex phase diagrams of ternary mixtures of two amphiphiles in water. However the scheme developed above is not quite general as its last step, that of the distribution of the molecules in the aggregates, cannot be invoked to explain a few cases of nematic phases in binary mixtures with only one type of amphiphilic molecules in water[17–19].

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