EUROPHYSICS LETTERS 10 October 1993

Europhys. Lett., 24 (2), pp. 105-108 (1993)

Continuous Membrane-Micelle Phase Transition.

V. I. MARCHENKO (*)

GDPC Case courrier 026, Université Montpellier II
Pl. Bataillon, 34095 Montpellier Cedex 5, France

(received 19 April 1993; accepted 6 September 1993)

PACS. 64.00 – Equations of state, phase equilibria, and phase transitions.
PACS. 68.00 – Surfaces and interfaces: thin films and whiskers.

Abstract. – We show the possibility of second-order phase transition from the smectic lamellar phase to the isotropic micelle phase in a dilute surfactant-water solution. A simple picture of the transition is proposed.

There are two classes of amphiphilic-molecule structures, membrane and micelle, in a dilute surfactant solution [1]. The most simple example of the first class is the lamellar phase (smectic order), which consists of parallel bilayers with a period d increasing upon dilution (see fig. 1). The second class is exemplified by an isotropic solution of spherical micelles, each consisting of $N \sim 10^2$ molecules (see fig. 2).

Experimentally, first-order phase transitions are observed between two different membrane phases (the lamellar and a less trivial sponge phase [2]) and between a membrane and isotropic micelle phases. It will be shown below that, at high dilution, there arises the possibility of a continuous membrane-micelle phase transition.

Consider the most simple case of the transition between the lamellar phase and a solution of spherical micelles. At a very high dilution, one can disregard membrane-membrane and micelle-micelle interactions when considering the thermodynamics of the phases. Let α be the difference of the free energy per molecule in a micelle and a membrane. If one neglects thermal fluctuations at all, then α (which is a function of temperature, pressure, salinity ...) will be the driving parameter of the transition from the lamellar phase ($\alpha < 0$) to the micellar phase ($\alpha > 0$). But, due to the logarithmic behaviour of the free energy of a dilute solution [3], the transition must occur at a finite and positive α.

In the lamellar phase, the thermally activated concentration of micelles in a layer of water between membranes will be given by

$$c_0 = n \exp[-\alpha N/T], \tag{1}$$

where the prefactor n is of the order of the molecular density of water, T is the temperature.

(*) Permanent address: Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow region, Russia.

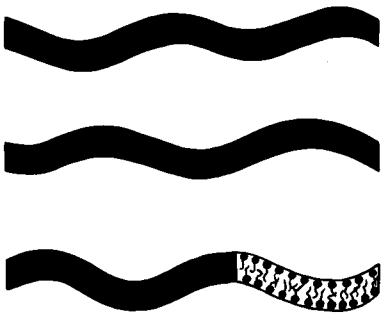

Fig. 1.

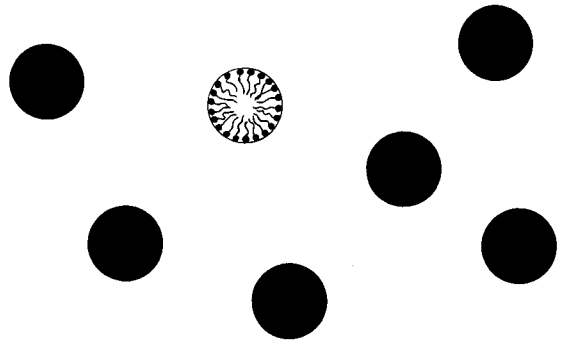

Fig. 2.

Due to this fact, the period d of the considered structure (see fig. 3) must be larger than that without the gas of the micelles. If ν is the two-dimensional density of molecules in a membrane, the total concentration c of the molecules in the structure (the membranes and the water solution in between) equals

$$c = \frac{\nu}{d} + c_0 \,. \tag{2}$$

Hence, the period of the structure is

$$d = \frac{\nu}{c - c_0} = \nu(c - n\exp[-\alpha N/T])^{-1} \,. \tag{3}$$

This result shows that, at small concentrations, $c \ll n$, there is the possibility of a specific critical phenomenon, since the period of the structure tends to become infinite:

$$d = \frac{A}{c\tau} \,, \tag{4}$$

here $\tau = T_c - T$ and

$$A = \nu \Big/ \left(\frac{\partial n}{\partial T} - \frac{\partial(\alpha N/T)}{\partial T} \right) \Bigg|_{T = T_c} , \tag{5}$$

at the temperature T_c

$$T_c = \alpha N / \ln \frac{n}{c} \,. \tag{6}$$

If $A > 0$, then the lamellar phase exists at $T < T_c$, if $A < 0$, at $T > T_c$. For small concentrations, one can neglect the temperature dependence of n, α, N in (5) and obtain for A

$$A = \frac{\nu T_c^2}{\alpha N} = \nu\alpha N / \ln^2 \frac{n}{c} > 0 \,. \tag{7}$$

It is useful to consider the transition on the chemical potential-temperature diagram (see fig. 4). Here the dashed lines are the chemical potential of surfactant molecules in the micelle

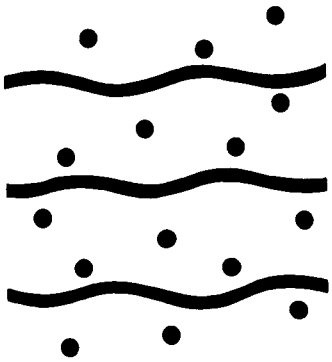

Fig. 3.

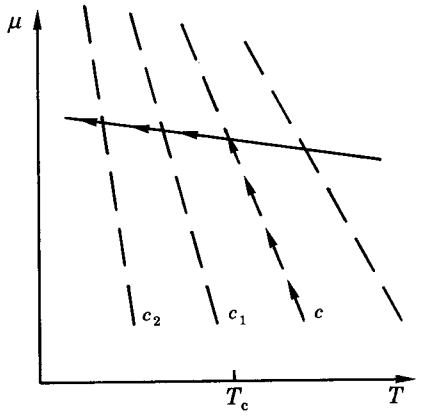

Fig. 4.

gas, each corresponding to the definite concentrations ($c_2 < c_1 < c$), the continuous curve is the potential in the membranes. As the temperature decreases, the system with constant concentration c moves along the broken curve with arrows.

The proposed simple picture will be incorrect if the membrane fluctuations are too big. Quantitatively, one should insist that the fluctuational correction to the elastic constant K, which defines the bending energy of membranes (see [1]) should be small compared with K at the transition temperature:

$$K \gg \frac{3T}{4\pi} \ln \frac{\xi}{a} \tag{8}$$

(see [4]); here a is of the order of molecular size and ξ is the characteristic wavelength of the fluctuations. In the lamellar phase

$$\xi \propto (K/T)^{1/2} d \tag{9}$$

(see [5]); so, from (8) and (9), one can write

$$d \ll a(T_c/K)^{1/2} \exp[4\pi K/3T_c]. \tag{10}$$

With the aid of relations (4) and (6), one can rewrite inequality (10) in the following way:

$$\tau \gg T_c \frac{AK^{1/2}}{an(\alpha N)^{3/2}} \left(\frac{c}{n}\right)^{4\pi K/3\alpha N - 1} \ln^{3/2}\left(\frac{n}{c}\right). \tag{11}$$

So, for $c \ll n$, one can neglect fluctuational effects and the proposed picture of the transition with the simple law (4) will be valid in a close (but not so much) temperature region near the transition, if

$$\frac{4\pi K}{3\alpha N} > 1. \tag{12}$$

In the opposite case there should be a critical behaviour with the strong fluctuations. Inequality (12) plays the role of Ginzburg-Levanyuk criterion for the transition. It should be

mentioned that, since an exact numerical prefactor has no real sense in inequality (8), instead of (12) one has only the following criterion:

$$K > b\alpha N , \tag{13}$$

with some unknown numerical multiple b, which is of the order of unity. In principle, there is the possibility of observing a threshold point on the line of the second-order phase transition when inequality (13) is violated.

From a general point of view, the proposed phase transition is an example of a second-order isotropic-crystalline phase transition, but it is significantly different from the continuous crystallization [6] considered in the frame of the Landau theory of the second-order phase transitions.

There is a similarity between the considered phenomenon and the commensurate-incommensurate phase transition (and the behaviour of ferromagnetic domain structures in high magnetic fields, behaviour of strictional domains on the surface of the crystals). In all cases, there is the possibility of observing an increase in the distances between the incommensurabilities (domain, domain boundaries) at some critical temperature (magnetic field, adatom concentrations). However, the proposed phase transition differs radically from the above examples, since it arises without any direct interaction between elements of the structure (membranes and micelles). More rigorously, one must keep in mind that an interaction between membranes (small, but repulsive) is indispensable for the stabilization of the lamellar structure. Nonetheless, it need not be taken into account in the description of the transition.

At not too small concentrations of the surfactants, one has to consider membrane-membrane, membrane-micelle and micelle-micelle interactions, but it is natural to believe that the picture given above will not change qualitatively up to the moment when a non-monotonic behaviour of the interactions with distances leads to the usual first-order phase transition.

In conclusion, we have shown the possibility of a new type of continuous phase transition from crystalline order to an isotropic phase in a diluted surfactant-water solution. The crystalline (lamellar) phase consists of a regular stack of parallel membranes with a water solution of micelles in between. The period of the structure goes to infinity at the transition temperature. The Ginzburg-Levanyuk criterion is determined for the transition.

* * *

The idea of the proposed transition has originated from discussions with G. PORTE on the possible properties of highly diluted surfactant solutions.

REFERENCES

[1] PORTE G., *J. Phys. Condens. Matter*, **4** (1992) 8649.
[2] PORTE G., MARIGNAN J., BASEREAU P. and MAY R., *J. Phys. (Paris)*, **49** (1988) 511.
[3] LANDAU L. D. and LIFSHITS E. M., *Statistical Physics*, Part 1 (Pergamon Press) 1980.
[4] HELFRICH W., *J. Phys. (Paris)*, **46** (1985) 1263; PELITI L. and LEIBLER S., *Phys. Rev. Lett.*, **54** (1985) 1690; FOERSTER D., *Phys. Lett. A*, **114** (1986) 115.
[5] HELFRICH W., *Naturforsch. A*, **33** (1978) 305.
[6] MARCHENKO V. I., *Sov. Phys. JETP*, **73** (1991) 759.