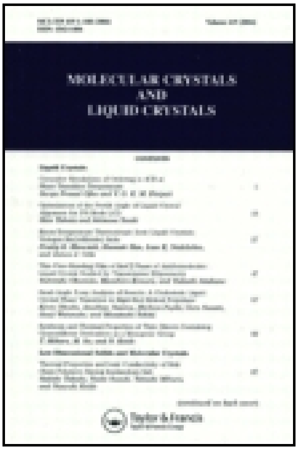

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Micellization as a Phase Transition

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Micellization as a Phase Transition

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A new approach, based on the Landau theory of phase transitions is proposed for the description of the spherical micelle formation. The essence of our approach is that the free energy is expanded in powers of a small parameter (concentration of surfactant molecules aggregated in micelles). This approach describes the smeared second order phase transition from the monomer solution phase to the micellar one.

The relation of the proposed approach with the conventional model of micellization is established.

Keywords: micelles, phase transitions

1. INTRODUCTION

Micellization or the process of aggregation of certain surfactant molecules in dilute aqueous solutions never ceases to bother both theorists and experimentalists due to the variety of still open questions.[1,2] Here we want to consider only one (and not the simplest one as it seems) question: can micellization be treated as a phase transition? The available experimental evidence of rather rapid changes in concentration dependence of surfactant solution physico-chemical properties in the narrow concentration region called the "critical micelle concentration" (CMC) draws an analogy with a somewhat smeared phase transition. This analogy has been widely exploited in the so-called phase-separation model (PSM)[3] where the micellar solution is treated as a two-phase system of the "vapour" or monomers in equilibrium with the "liquid" of micelles. Here the CMC is the concentration where the system enters the two-phase region. The phase transition is clearly a first order one. The drawbacks of the PSM are too obvious to be discussed in details: e.g. may micelle be considered as a separate phase? Still as it seems mostly due to a relatively large micelle aggregation numbers the PSM has not been totally rejected as incorrect from the very beginning. This led to a confused popular version of treatment of the micellization as a certain "arrested form of phase separation"[3]—the first order transition "softened" by the finite size of the micelles formed. We argue that this is not the case. While the smallest finite size micelle strongly reminds of a droplet of liquid in a nucleation process, this analogy is purely "visual". The droplet will grow in size to achieve macroscopical volume and be considered as an equilibrium phase, while micelle being already in equilibrium does not grow at all (at fixed external parameters). Moreover, even an "infinite" micelle for example rod-like, disk-like or lamellar with large aggregation number still cannot be treated as a separate volumic phase according to standard criteria because it is "microscopic" at least in one dimension. One should rather say that in the case of micelles we deal with macroscopic surface formed in solution volume. It is well known that micellar solution is one-phase system from the macroscopic point of view, so the onset of micellization as it was first argued by Hall,[4] can be regarded approximately as the onset of a second order phase transition in a multicomponent system. However this remark has not been explored further so far. It prompts us to examine the possibility of a phenomenological description of micellization using the second order phase transition theory terminology and allows to clarify the meaning of such quantities as order parameter, susceptibility, etc. . . .

2. THERMODYNAMICS

We begin from the usual thermodynamical description of spherical micelles formation in the simplest monodisperse model.[2] This model depicts the main features of the phenomenon since many real systems are characterized by a narrow peak in the micelle size distribution function.[1] The thermodynamic potential per molecule has the form:[5]

$$\Phi(p,T,x) = \mu_0 x_0 + \mu_1 x_1 + \mu_M x_M \tag{1}$$

where

$$\mu_{0,1,M} = \mu_{0,1,M}^{(0)} + k_B T \ln x_{0,1,M}$$

here $\mu_0, x_0, \mu_1, x_M, x_M$ are chemical potentials and concentrations of the solvent, the free surfactant molecules and the micelles with aggregation number M respectively, $\mu_0^{(0)}, \mu_1^{(0)}, \mu_M^{(0)}$ are the standard chemical potentials. Experimental values of M are usually large ($M >> 1$).[1]

The total concentration of surfactant in solution is

$$x = x_1 + \phi \tag{2}$$

where $\phi = Mx_M$ is the concentration of surfactant molecules aggregated in micelles. The equilibrium value of ϕ (or x_1) should be found from the equilibrium condition:

$$\left.\frac{\partial \Phi}{\partial \phi}\right|_{\phi = \phi_{eq}} = 0 \tag{3}$$

and taking into account (2), one can obtain the equation which defines the function $\phi_{eq}(x)$:

$$\mu_1^{(0)} + k_B T \ln (x - \phi_{eq}) = \overline{\mu}_M^{(0)} + \frac{k_B T}{M} \ln \frac{\phi_{eq}}{M} \tag{4}$$

and

$$\phi_{eq} = M[(x - \phi_{eq})f]^M \tag{5}$$

where

$$f = \exp\left(\frac{\mu_1^{(0)} - \overline{\mu}_M^{(0)}}{k_B T}\right); \overline{\mu}_M^{(0)} = \frac{\mu_M^{(0)}}{M}.$$

When $M >> 1$

$$\phi_{eq}(x) \approx x - \frac{1}{f} \tag{6}$$

At CMC ($x = x^*$)

$$x^* \approx \frac{1}{f} \tag{7}$$

In the limit of $M \to \infty$ the concentration dependence of ϕ_{eq} in the micellar phase can be approximated by:

$$\phi_{eq} = x - x^* \tag{8}$$

Having in mind the Landau-like expansion of the free energy we shall consider surfactant concentration x in the CMC region ($x \sim x^*$). In this case relation $\phi << x$ holds and we can expand $\Phi(x,\phi)$ in powers of a small parameter $\frac{\phi}{x} << 1$. From Eq. (1) we obtain

$$\Phi(p,T,x,\phi) = \Phi_0(p,T,x) + A\phi + \\ + B\phi^2 + C\phi^3 + k_BT\frac{\phi}{M}\ln\frac{\phi}{M} + \dots \tag{9}$$

where

$$A = \overline{\mu}_M^{(0)} = k_BT\ln x$$

$$B = \frac{kT}{2x}, \quad C = \frac{kT}{6x^2}$$

$$\Phi_0 = [\mu_0^{(0)} + k_BT\ln(1-x)](1-x) + \mu_1^{(0)}x + xk_BT\ln x$$

The term $k_BT\frac{\phi}{M}\ln\frac{\phi}{M}$ is negligible in the limit $M \to \infty$. As could be seen from Equation (4) this term is responsible for the distortion of the micellization (Figure 1). It is significant only in the immediate vicinity of CMC and it could be omitted in micellar phase. We suppose that A has no singularity at CMC, so it can be expanded in powers of $(x - x^*)$ in the vicinity of x^*. In linear approximation:

$$A = a(x - x^*) \tag{10}$$

where

$$a = -\frac{k_BT}{x^*}$$

If one neglects the term $k_BT\frac{\phi}{M}\ln\frac{\phi}{M}$ the expansion (9) has the simple form:

$$\Phi = \Phi_0 + A\phi + B\phi^2 + C\phi^3 + \dots \tag{11}$$

where

$$\phi \geq 0.$$

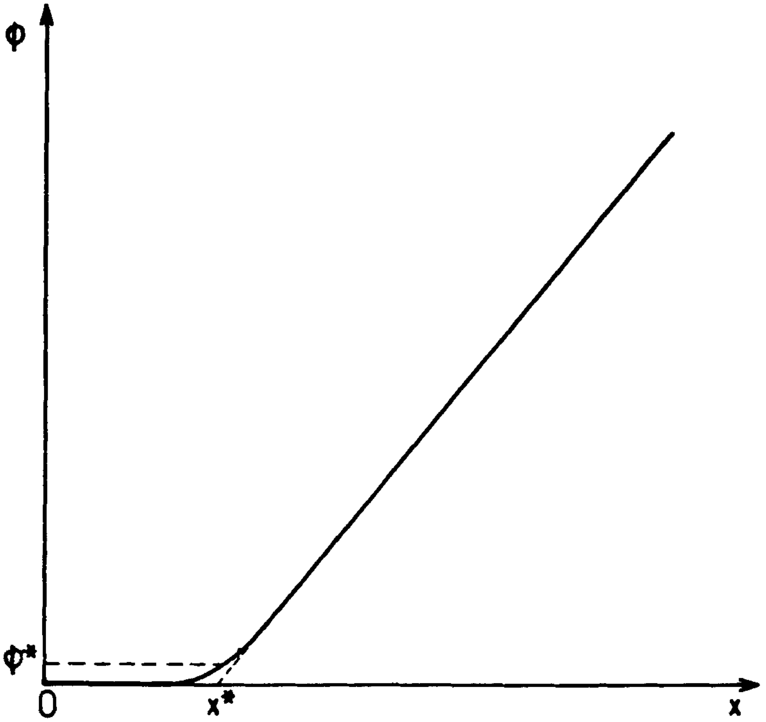

FIGURE 1 Concentration of surfactant molecules aggregated in micelles, $\phi^* \approx \frac{2x^*}{M} \ln M$.

3. SECOND-ORDER TRANSITION ANALOGY

The expansion (11) is analogous to the free energy expansion in powers of an order parameter η in the Landau theory of phase transitions.[5] Having in mind what we said earlier about the expected order of the transition we must insist here that ϕ corresponds to the square of a supposed order parameter: $\sigma \sim \eta^2$. The physical meaning of the order parameter η for the micellization can be cleared out only in a microscopic theory. Nevertheless we shall try to confirm qualitatively our assumption. First of all expression (11) must not be confused with a similar expansion of the free energy in powers of a volumic fraction (or density) of a newly formed phase in the case of a first order transitions. The similarity is again only apparent as we have already mentioned above. Micelles formation is accompanied by the appearance of the surface inside solution volume. The corresponding order parameter should be a vector, normal to the surface

S or $\eta \sim \vec{n} \sim \nabla(\delta\rho)$ where $\delta\rho$ is the solution density variation. The surface term in the free energy expansion in $\delta\rho$ has the form $\delta\Phi_{\text{surf}} \sim [\nabla(\delta\rho)^2]$, thus it is quadratic in order parameter. At the same time we may rewrite $\delta\Phi_{\text{surf}}$ in terms of surface tension γ: $\delta\Phi_{\text{surf}} = \gamma S$ where S is the value of the surface area which in our case of micellar solution is proportional to ϕ:

$$S \sim M x_M = \phi.$$

In sum, the order parameter η for micellization is most probably a vector the square of which must be proportional to the total surface area of micelles formed in a solution. It could be noted that a similar situation occurs in liquid helium-4 in the vicinity of the superfluid transition. Indeed for helium the true order parameter is wave function ψ (non-observable quantity) the free energy is expanded in powers of $|\psi|^2$ (corresponding to the superfluid component concentration). Further one can note that for micellization the value of $x - x$ plays the role of the distance from the critical temperature ($T\text{-}T_c$) in the usual Landau theory. Therefore the critical susceptibility of micellization $\left(\left[\frac{\partial^2\Phi}{\partial\eta^2}\right]^{-1}\right)$ diverges in the vicinity of CMC as $(x - x^*)^{-1}$. However it should be known that observable property of the solution corresponds to micellization susceptibility.

If the coefficients of the expansion (11) satisfy the conditions:

$$\begin{aligned} A(x^*,P,T) &= 0 \\ B(x^*,P,T) &> 0 \end{aligned} \tag{12}$$

a second order phase transition takes place in the system above CMC the parameter $\phi(x)$ increases from zero (Figure 1). Such a behavior of ϕ is supported by experiment.[1] In the vicinity of CMC the parameter ϕ is small, so we can omit the cubic term in (11):

$$\Phi = \Phi_0 + a(x - x^*)\,\phi + B\phi^2 \tag{13}$$

In micellar phase, taking into account the condition (3), we have:

$$\phi = \frac{a}{2B}(x - x^*) \tag{14}$$

and the order parameter:

$$\eta = \left[-\frac{a}{2B}(x - x^*)\right]^{1/2} \tag{15}$$

In the immediate vicinity of CMC the term $\frac{k_B T\phi}{M} \ln \frac{\phi}{M}$ gives a significant contribution to the thermodynamic potential (9). Hence $\phi \neq 0$ at the CMC. One can find the equilibrium values of $\phi = \phi^*$ at $x = x^*$ from the condition (3):

$$\phi = -\frac{k_B T}{2BM} \ln \frac{\phi^*}{M} \tag{16}$$

If $M >> 1$, ϕ^* is small and:

$$\phi^* \simeq \frac{k_B T}{BM} \ln M \tag{17}$$

Thus in the ideal dilute solution:

$$\phi^* \simeq \frac{2x^*}{M} \ln M \tag{18}$$

In the limit $M \to \infty$, $\phi^* \to 0$ and the micellization has no distortion. In the micellar phase the chemical potential of surfactant molecules and its derivative with respect to the total surfactant concentration has the forms:

$$\mu_1 = \frac{\partial \Phi}{\partial x} = \frac{\partial \Phi_0}{\partial x} - \frac{a^2}{2B}(x - x^*) \tag{19}$$

$$\frac{\partial \mu_1}{\partial x} = \frac{\partial^2 \Phi_0}{\partial x^2} - \frac{a^2}{2B} \tag{20}$$

On the other hand in the monomer phase:

$$\mu_1 = \frac{\partial \Phi_0}{\partial x} \tag{21}$$

$$\frac{\partial \mu_1}{\partial X} = \frac{\partial^2 \Phi_0}{\partial X^2} \tag{22}$$

One can see from the comparison of (20) and (22) that the slope of the concentration dependence of the chemical potential changes at CMC and its derivative has a jump equal to:

$$\Delta \frac{\partial \mu_1}{\partial x} = \frac{a^2}{2B} \tag{23}$$

This jump is analogous to the heat capacity jump in the usual Landau theory. At the same time the real heat capacity at constant pressure also has a jump which is related to $\Delta \frac{\partial \mu_1}{\partial x}$ by equation:

$$\Delta\, C_p = \mathrm{T}\left[\Delta \frac{\partial \mu_1}{\partial x}\right]\left[\frac{dx^*}{dT}\right]^2 \tag{24}$$

(here C_p is the heat capacity per solvent molecule). For the dilute solution $\frac{a}{2B} = -1$; $\Delta \frac{\partial \mu_1}{\partial x} = \frac{k_B T}{x^*}$ and:

$$\Delta\, C_p = \frac{k_B T^2}{x^*}\left[\frac{dx^*}{dT}\right]^2 \tag{25}$$

The osmotic pressure is:

$$\Pi(x) = \begin{cases} \dfrac{k_B T}{v_0}\, x & (x < x^*) \\ \dfrac{k_B T}{v_0}\left(x^* + \dfrac{\phi}{M}\right) & (x > x^*) \end{cases} \tag{26}$$

where v_0 is the volume of solution per solvent molecule.

One can also obtain the concentration dependence of the solution density. Let us introduce the notations: N is the number of solvent molecules, m is the molecular mass and v is the molecular volume of the solvent; N_1, m_1 and v_1 are the number of free surfactant molecules, their molecular mass and volume; N_M, m_M and v_M are the number of micelles, mass and volume of a micelle with an aggregation number M.

The density is:

$$\rho = \frac{Nm + N_1 m_1 + N_{\mathrm{M}} m_{\mathrm{M}}}{Nv + N_1 v_1 + N_{\mathrm{M}} v_{\mathrm{M}}} \approx \rho_0 + x_1\left(\rho_1 - \rho_0 \frac{v_1}{v}\right) + M x_m\left(\rho_1 - \rho_0 \frac{\bar{v}}{v}\right) \tag{27}$$

where

$$\rho_0 = \frac{m}{v}\,, \quad \rho_1 = \frac{m_1}{v}\,; \quad \bar{v} = \frac{v_M}{M}$$

Since $x = x_1 + \phi$ we obtain:

$$\rho(x) = \begin{cases} \rho_0 + x\left(\rho_1 - \rho_0\dfrac{v_1}{v}\right) & \text{at} \quad x < x^* \\ \rho_0 + x^*\left(\rho_1 - \rho_0\dfrac{v_1}{v}\right) + \dfrac{\rho_0}{v}(x - x^*)(v_1 - \bar{v}) & \text{at} \quad x > x^* \end{cases} \tag{28}$$

Thus linear dependences of $\Pi(x)$ and $\rho(x)$ with different slopes on both sides of CMC are obtained. Such a behavior is in a qualitative agreement with experiments.[1,6]

4. TRICRITICAL POINT

The coefficient B in the expansion (11) may change its sign, if coupling between ϕ and the solution concentration is concerned. In fact it means the allowance for drastic non-ideality of solution. Let us introduce a parameter $\Delta x = x - x_c$ which can be positive as well as negative. The critical concentration of the liquid-liquid phase equilibrium x_c is larger than x^*.

One can consider Δx to be an additional order parameter. Thus the free energy expansion will have the form:

$$\Phi = \Phi_0 = a(x - x^*)\phi + B\phi^2 + \bar{A}(\Delta x)^2 + \lambda\phi\Delta X \tag{29}$$

The two-parameter potential (29) can be reduced to a one-parameter one.[6] Assuming the critical consolute concentration x_c is far from x^* one can obtain, taking into account the condition $\partial\Phi/\partial(\Delta x) = h_x$, where $h_x \approx \mu_1 - \mu_1(x_c,T)$ is the field thermodynamically conjugate to Δx:

$$\Delta x = \frac{h_x - \lambda\phi}{2\bar{A}} \tag{30}$$

and

$$\begin{aligned} \bar{\Phi}(\phi,h_x) &= \Phi(\phi,\Delta x) - h_x\Delta X = \\ &= \Phi_0 + \left[a(x - x^*) + \frac{h_x\lambda}{\bar{A}}\right]\phi + \left[B - \frac{\lambda^2}{4\bar{A}}\right]\phi^2 + C\phi^3 \end{aligned} \tag{31}$$

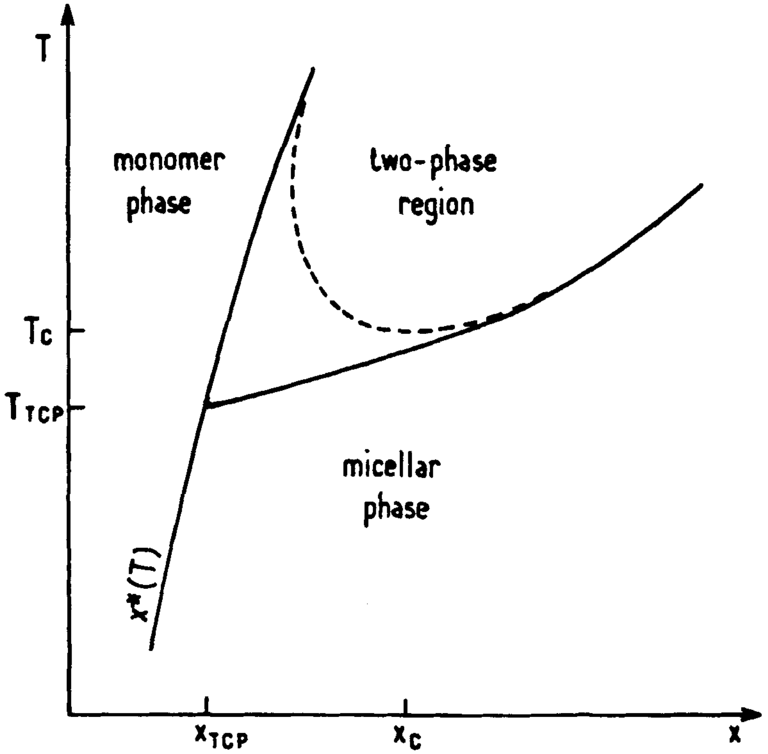

FIGURE 2 Possible phase diagram of a non-ideal dilute surfactant solution. T_{tcp} and x_{tcp} are the coordinates of a tricritical point of micellization, T_c and x_c are the coordinates of a critical consolution point which cannot be realized because it is located in the unstable region.

When $B > \frac{\lambda^2}{4\bar{A}}$ the micellization is a second order transition. When $B < \frac{\lambda^2}{4\bar{A}}$ that is a first order one. If $B = \frac{\lambda^2}{4\bar{A}}$ a tricritical point takes place. Assuming $B \simeq \frac{k_BT}{2x}$; $\lambda \simeq \frac{k_BT}{x}$ one can estimate the value $\bar{A}$ at the tricritical point: $\bar{A} \simeq \frac{k_BT}{2x}$. In the ideal solution $\bar{A}_{\text{id}} \simeq \frac{k_BT}{x}$. One can see that a first order micellization (with consolution phenomena) may result naturally from the nonideality of the dilute solution.

The phase diagram for such a case is shown in Figure 2. It would be interesting to examine phase diagrams of aqueous non-ionic surfactant solutions from this view-point.

5. CONCLUSION

Our model is a mean-field one. For a better description of the micellization phenomenon the fluctuations of the order parameter should be taken into account. Thus critical exponents can be introduced and a scaled equation of state for micellization can be constructed. This problem could be solved if the microscopic nature of the order parameter was discovered.

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