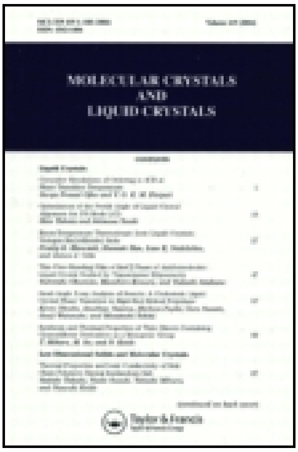

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A Novel Mesoscopic Model for Micellization and Formation of Liquid Crystalline Phases in Surfactant Solutions

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A new universal approach to the description of the formation of the supramolecular structures in surfactant solutions based on the Landau theory of phase transitions with coupled order parameters has been proposed. It has been shown that the specific interaction of amphiphiles with random inhomogeneities of the solvent may lead to a particular type of phase transition: spontaneous aggregation process as well as following formation of lyotropic liquid crystalline phases.

1. INTRODUCTION

It is well known that surfactant solutions display a great variety of exotic both liquid crystalline and isotropic phases having considerable scientific and practical interest.[1–3] However, in spite of never ceasing flow of theoretical and experimental works on this subject, a universal approach, being able to explain entire succession of phase transitions in such a system, is still lacking.

The clue for understanding of the supramolecular structure formation mechanism in surfactant solutions is hidden in the first stage of this process: appearance of micelles. Micellization in surfactant solutions draws attention of the specialists in phase-transition physics by its resemblance to a second-order transition.[4–6] The process has a threshold character, takes place in the whole volume of the solution and in a relatively narrow range of surfactant concentrations. Micellar phase is macroscopically homogeneous, its properties in the vicinity of the critical micelle concentration (CMC) differing vanishingly small from those of a monomer phase. On the other hand, on the scale larger than the molecular scale of the solvent, but comparable with the molecular size of the solute, the transition is more likely of a first order: physical properties change abruptly on the micelle-solvent "interface." Phenomenological description of micellization shows that the range of smearing of the transition is getting smaller with increasing aggregation number M of a micelle. In the limit $M \rightarrow \infty$ the transition is not smeared at all.

Unfortunately phenomenological description of the micellization does not give an answer to the main question: whether it is possible to create a universal description of all varieties of phase transitions in amphiphilic solutions, where micellization will be regarded as a first and necessary step. Achievements of the modern phase-transition theory, successfully describing both the simplest systems as the liquid-vapour critical point and such complicated transitions as those between different liquid crystalline phases, stimulate the work in this direction.[7]

We propose a new semiphenomenological approach, which, as it seems, will allow us to explain a variety of phase transitions in surfactant solutions, including microemulgation and formation of lyotropic liquid crystalline phases.

A transition to a microheterogeneous state we shall consider as an appearance of an "interface" stabilized by surfactant inside the solution volume. A detailed description of such an interface is an extremely complicated problem. We shall consider two alternative limits. The first approach is valid in the case of a sufficiently large, relative to molecular sizes, thickness of the transition layer, where one can use the Landau-like expansion of the free energy on the density gradients (so-called "gradient approximation"). The second approach deals with the case of a relatively sharp surface (border), when one can neglect the width of the interfacial region ("sharp border" approximation).

2. STABILIZATION OF LOCAL INHOMOGENEITIES IN SURFACTANT SOLUTIONS: "GRADIENT APPROACH"

Let us determine the main difference of surfactant molecules from both, roughly-speaking, "ball-like" molecules, which form usually isotropic liquids, and "rod-like" molecules, constituting thermotropic liquid crystalline phases. The presence of a small parameter $a/\xi << 1$ (where a is a diameter of an amphiphilic molecule, ξ is its length) relates these molecules to "rod-like" molecules and differs from "ball-like" molecules. Nevertheless, in contrast to rod-like molecules in thermotropic liquid crystals, the hydrophobic and the hydrophillic tails of the surfactant molecule are not equivalent with respect to the solvent. This leads to the specific (only for such systems) interaction of such molecules with density or concentration inhomogeneities, either of a spontaneous fluctuation character, or with interfaces already existing in solution (e.g., "water-air" or "water-oil" surface).

In the framework of the Landau phase-transition theory [7,8], the energy needed for the creation of such inhomogeneities may be written in the following form:

$$A_1 = \int [\chi^{-1}\rho^2 + b(\nabla\rho)^2 + \ldots] \, dV$$

where $\rho(\vec{r}) = (\rho(\vec{r}) - \langle\rho\rangle)/\langle\rho\rangle$ is the dimensionless local deviation of the solvent density from its mean value $\langle\rho\rangle$, χ^{-1} is the inverse susceptibility (compressibility) of the solvent ($\chi^{-1} \propto (\partial P/\partial\rho)_T$, P is pressure, V is volume).

In the absence of surfactant the coefficient b is a positive constant, which means that the creation of inhomogeneities, for example fluctuatively, is always thermodynamically unfavorable.

In the presence of surfactant the amphiphilic nature of its molecules can be accounted for by introducing the following interaction term in addition to A_1:

$$A_2 = -\int \lambda c(\vec{r})(\nabla\rho)^2 \, dV$$

Here $c(\vec{r})$ is the local surfactant concentration, λ is the coupling constant ($\lambda > 0$). Such coupling leads to an increase of concentration $c(\vec{r})$ in the vicinity of inhomogeneities. Thus an increase of the thermodynamical potential due to solvent density fluctuations (or concentration fluctuations in oil-water system), can be compensated by the redistribution of surfactant molecules. This leads to the stabilization of these fluctuations and formation of micelles or microemulsion droplets.

For the sake of illustration of the stabilization of fluctuations in details, we shall describe this process within the framework of the Landau theory of phase transitions.[7] This description enables us to explain the physical mechanism of the appearance of inhomogeneities in isotropic and homogeneous solvent and, in principle, describe the structure of the interface.

The change of the thermodynamic potential of the system accounting for the appearance of inhomogeneities of the solvent density has the form

$$\Delta\Phi = \Delta\Phi_1 + \Delta\Phi_2 + \Delta\Phi_{\text{int}} \tag{1}$$

The expressions for $\Delta\Phi_1$, $\Delta\Phi_2$, and $\Delta\Phi_{\text{int}}$ may be written as

$$\Delta\Phi_1 = (T/a^3) \int [\chi^{-1}\rho^2 + b_1 a^2(\nabla\rho)^2 + b_2 a^4(\Delta\rho)^2 + b_3 a^4(\nabla\rho)^4] \, dV \tag{2}$$

$$\Delta\Phi_2 = (1/v_s) \int \{\varphi[c(\vec{r})] - \varphi(c_0) - [\partial\varphi(c_0)/\partial c_0][c(\vec{r}) - c_0]\} \, dV \tag{3}$$

$$\Delta\Phi_{\text{int}} = (T/v_s) \int c(\vec{r})[-\lambda_1\xi^2(\nabla\rho)^2 + \lambda_2\xi^4(\Delta\rho)^2 + \lambda_3\xi^4(\nabla\rho)^4] \, dV \tag{4}$$

where $\rho(\vec{r})$ and χ are introduced above, $\Delta\Phi_1$ is related to inhomogeneities of the solvent, $\Delta\Phi_2$ is related to deviations of the surfactant local concentration from its mean value c_0, $\Delta\Phi_{\text{int}}$ is the part of the thermodynamic potential connected with the interaction of the surfactants with inhomogeneities of the solvent, a and ξ are linear sizes of solvent and surfactant molecules respectively, a^3 and $v_s \approx a^2\xi$ are their molecular volumes. We emphasize that inverse susceptibility of the solvent, as well as b_i and λ_i are essentially positive.

In regular solution approximation the density of the thermodynamic potential $\varphi(c)$ has the form:

$$\varphi(c) = c(\mu_1^{(0)} + T\ln c/e) + (1 - c)(\mu_w^{(0)} + T\ln(1 - c)/e) + \alpha Tc(1 - c) \tag{5}$$

where $\mu_1^{(0)}$, $\mu_w^{(0)}$ are standard chemical potentials of surfactant and solvent, α is intermolecular interaction constant, e is the base of natural log. Equilibrium distribution $\rho(\vec{r})$ and $c(\vec{r})$ are found from the minimization conditions for the thermodynamic potential $\Delta\Phi$:

$$\delta\Delta\Phi/\delta c(\vec{r}) = 0 \tag{6}$$

$$\delta\Delta\Phi/\delta\rho(\vec{r}) = 0 \tag{6a}$$

The first of the above equations may be written in the form

$$\ln\{c(\vec{r})(1 - c_0)/[c_0(1 - c(\vec{r}))]\} = 2\alpha(c(\vec{r}) - c_0) + \lambda_1\xi^2(\nabla\rho)^2 - \lambda_2\xi^4(\Delta\rho)^2 - \lambda_3\xi^4(\nabla\rho)^4 \tag{7}$$

Equation (7) defines an implicit dependence of c on ρ and c_0:

$$c(\vec{r}) = c_0[c_0 + (1 - c_0)\kappa]^{-1} \tag{8}$$

where $\kappa = \exp(-E(c,\rho)\}$. Here by function $E(c,\rho)$ we denote the right hand side of Equation (7).

It should be noted that when $\alpha = 0$, κ in Equation (8) ceases to depend on ρ. Thus we obtain for $C(c_0)$ the solution which is reminiscent of the well-known Langmuir-Gibbs isotherm for adsorbtion on a surface.

In fact, expression (8) really describes the adsorbtion isotherm when $(\nabla\rho)^2$ in the function $E(\nabla\rho)$, is related to macroscopic interface.

When $\alpha \neq 0$, the intermolecular interaction of the solvent and solute is taken into account, and the adsorption isotherm may take the form analogous to Van der Waals loops, which corresponds to a phase transition on the interface (Figure 1). In this case two values of equilibrium surface concentrations correspond to one value of chemical potential (μ_1, $\propto \ln c_0$). Recent experimental data[9] confirm the possibility of the existence of such a surface phase transition.

Substituting the calculated value of $c(\vec{r})$ into Equation (1), we find the functional, which defines the density dependence of the thermodynamic potential:

$$\Delta\Phi = \Delta\Phi_1 + (T/v_s)\int\{\ln[(1 - c(\vec{r}))/(1 - c_0)] + \alpha(c^2(\vec{r}) - c_0^2)\}\,dV \tag{9}$$

Strictly speaking, equilibrium density distribution is defined by the condition (6a) together with Equations (8) and (9). Unfortunately the analytical solution of corresponding equation is not available because of strong nonlinearity. For qualitative estimates we shall adopt some simplifications: first, we put $\alpha = 0$, second, we omit the square Laplacian terms as well as the term $b_3a^4(\nabla\rho)^4$ in Equation (2) and, third, we omit the term $\chi^{-1}\rho^2$ (the parameter $\xi^2/r_c^2 = (\xi/a)^2\chi^{-1}$ is small). These assumptions do not change qualitative results, but make it possible to obtain analytical expressions. Then the thermodynamical potential $\Delta\Phi$ depends only on $\eta \equiv (\nabla\rho)^2$ and the minimization condition (6a) may be rewritten in the form

$$\delta(\Delta\Phi)/\delta\eta = 0$$

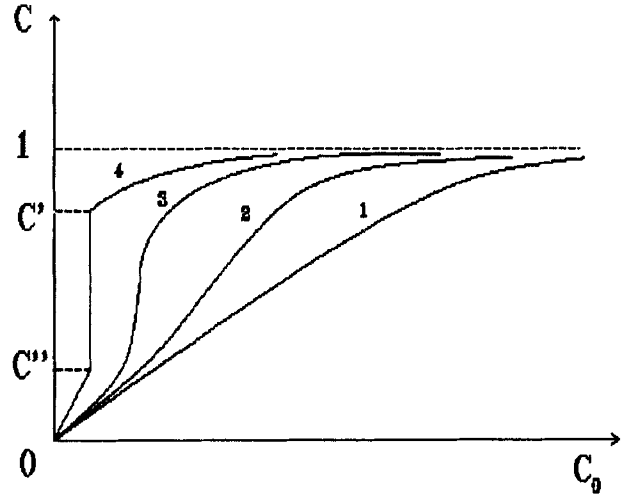

FIGURE 1 Surface surfactant concentration c as a function of mean concentration in solution volume c_0 for different values of α—the solvent-solute interaction parameter (see text). (1) is the usual Gibbs-Langmuir adsorbtion isotherm ($\alpha = 0$); (2), (3) and (4) are quasi Van der Waals curves for increasing values of α.

Now, for the characteristic value of $(\nabla\rho)^2$ providing the minimum of $\Delta\Phi$ we get:

$$(\nabla\rho)^2 \simeq \{\lambda_1 - b_1 v_s/(a\xi^2)[1 + c_0^{-1}\exp(-\lambda_1^2/(4\lambda_3))]\}/(2\lambda_3\xi^2) \tag{10}$$

From Equations (9) and (10) it is obvious that at a small mean concentrations $0 \leq c_0 \leq c_0^* = b_1 v_s(a\xi^2)\exp[-\lambda_1^2/(4\lambda_3)]$ thermodynamical potential $\Delta\Phi$ as a function of $(\nabla\rho)^2$ has only one minimum at $(\nabla\rho)^2 = 0$. When $c_0 > c_0^*$ a new minimum appears on the curve $\Delta\Phi\{(\nabla\rho)^2\}$. This second minimum initially lies higher than the first one (at $(\nabla\rho)^2 = 0$), but with the increase of mean concentration c_0 it moves to the right and downwards closer to $(\nabla\rho)^2$ axis (see Figure 2). When the value of $\Delta\Phi$ at the second minimum goes down to zero, the non-zero equilibrium value of $(\nabla\rho)_c^2$ appears spontaneously in the system. This corresponds to a formation of "surface" inside the solution volume, what we interpret as the beginning of micellization.

The critical micelle concentration (CMC) $c_0^{(\mathrm{cmc})}$ and characteristic value of $(\nabla\rho)_c^2$ may be calculated from the condition $\delta(\Delta\Phi)/\delta\eta = 0$ together with the condition of the equality of the values $\Delta\Phi$ in minima:

$$\Delta\Phi[(\nabla\rho)^2 = 0] = \Delta\Phi[(\nabla\rho)^2 = (\nabla\rho)_c^2].$$

We get approximately

$$c_0^{(\mathrm{cmc})} \simeq b_1(\lambda_1/\lambda_3)(a/\xi)\exp(-\lambda_1^2/(4\lambda_3)) \simeq (\lambda_1^2/\lambda_3)c_0^*;\ (\nabla\rho)_c^2 \simeq \lambda_1/(2\lambda_3\xi^2)$$

Thus the transition to micellar phase may be interpreted as a spontaneous ap-

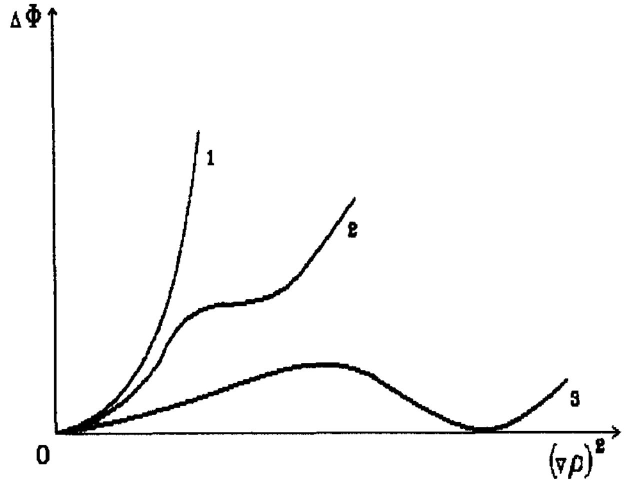

FIGURE 2 The dependence of the excess thermodynamic potential $\Delta\Phi$ on the square gradient of solute density for different values of mean surfactant concentrations c_0. (1)—$c_0 << c_0^*$, (2)—$c_0 \approx c_0^*$, (3)—$c_0 = c_0^{(\mathrm{cmc})}$. Here c_0^* corresponds to appearance of the inflection point on the $\Delta\Phi[(\nabla\rho)^2]$ curve, while $c_0^{(\mathrm{cmc})}$ is the critical micelle concentration. In this case the competing minimum of $\Delta\Phi$ touches the $(\nabla\rho)^2$-axis at non-zero value of the square gradient $(\nabla\rho)_c^2$.

pearance of equilibrium denisty gradient in the system or a formation of surface inside the solution volume.

Such an interpretation enables us to propose the simple and, at the same time, more realistic approach to the problem of lyotropic liquid crystalline phases in general as well as the micellization process in particular. For this purpose we pass to an alternative limiting case: "sharp border approximation." This approximation has the advantage of establishing the bridge between different existing theories of micellization. It makes also possible to formulate the unified approach to the description of lyotropic liquid crystalline phases.

3. "SHARP BORDER" APPROXIMATION

For definitiveness we shall consider below the water solution of surfactant molecules. Passing to mathematical formulation of our model, we note that to account for the non-equivalence of the surfactant molecule's ends, one can introduce a unit vector $\vec{p}_i$ corresponding to a molecule, which defines its orientation in space. Let us consider this vector as being directed from hydrophobic tail to polar head of the molecule. Taking a volume, which is small, as compared to the volume of the system, but containing considerable value of molecules ΔN, we define the mean value of $\vec{p}_i$ by the following relation:

$$\vec{p} \equiv \langle \vec{p}_i \rangle = (1/\Delta N) \sum_i \vec{p}_i$$

Thus, besides usual thermodynamic variables like temperature, pressure and concentration, the solution is characterized by vector $\vec{p}$.

The existence of such vector allows us to define in a natural way the interaction of surfactant molecules with a surface. Corresponding term has the form: $c(\vec{r})\vec{p}\vec{n}$ ($\vec{n}$ is the unit vector normal to a surface).

By "surface" we mean a compact distribution of surfactant molecules when their hydrophobic tales are mostly "screened" from water by polar heads. In other words it could be micelles of any kind, flattening out to bilayers in the limit of $M \to \infty$ (M is an aggregation number). As, in any case, the characteristic size of inhomogeneities in the direction normal to surface, is of the order of amphiphile molecule length, and their concentration in the region of inhomogeneity is close to unity, the main contribution to the energy of the system comes from the surface terms. Other terms happen to be relatively small. Let us assume that the surface equation is given by a function $W(\vec{r})$ which goes to zero when $\vec{r}$ denotes points lying on the surface. It means that on the surface $W(\vec{r}) = 0$ and $\nabla W/|\nabla W| = \vec{n}$ is the unit vector normal to the surface.

Thermodynamic potential of the solution Φ consists of the sum of the background term Φ_1 and the potential of the surface distributed in volume. When the surface equation in volume is known, the corresponding thermodynamic potential $\Phi_s(W)$ consists of the following terms:

1. The energy needed to redistribute surfactant molecules in solution ($\Delta\Phi_2$);
2. The surface energy, characterized by a certain bare surface tension σ_0 (in the absence of surfactant), ($\Delta\Phi_3$);
3. The energy of interaction between surfactant molecules and a surface ($\Delta\Phi_4$);
4. The energy of interaction of different parts of the surface with each other ($\Delta\Phi_{\text{int}}$)

$$\Phi = \Phi_1 + \Phi_s(W) = \Phi_1 + \Delta\Phi_2 + \Delta\Phi_3 + \Delta\Phi_4 + \Delta\Phi_{\text{int}} \tag{11}$$

It is not difficult to write down each of the terms introduced above:

$$\Phi_1 = N[c_b(\mu_1^{(0)} + T\ln(c_b/e)) + (1 - c_0)(\mu_w^{(0)} + T\ln((1 - c_0)/e))] \tag{12}$$

$$\Delta\Phi_2 = \int \{\varphi[c(\vec{r})] - \varphi(c_0) - [\partial\varphi(c_0)/\partial c_0][c(\vec{r}) - c_0]\}\delta(W)|\nabla W|\, dV \tag{13}$$

$$\Delta\Phi_3 = \sigma_0 \int \delta(W)|\nabla W|\, dV \tag{14}$$

$$\Delta\Phi_4 = \int c(\vec{r})\}\chi_p^{-1}\vec{p}^2 - \lambda\vec{p}(\nabla W/|\nabla W|) - \beta\nabla_i[(\nabla_i W)/|\nabla W|] + \gamma[\nabla_i((\nabla_i W)/|\nabla W|)]^2\}\delta(W)|\nabla W|\, dV \tag{15}$$

$$\Delta\Phi_{\text{int}} = \int d\vec{r}\, d\vec{r}^1\, c(\vec{r})\delta[W(\vec{r})]|\nabla W(\vec{r})|[\nabla_\alpha W(\vec{r})\nabla_\beta W(\vec{r})]/|\nabla W(\vec{r})|^2 \times U_{\alpha\beta}^{\gamma\delta}\,(\vec{r} - \vec{r}^1)\cdot[\nabla_\gamma W(\vec{r}^1)\nabla_\delta W(\vec{r}^1)]/|\nabla W(\vec{r}^1)|^2 \times \delta[W(\vec{r}^1)]|\nabla W(\vec{r}^1)|c(\vec{r}^1) \tag{16}$$

where c_0, c_b, $c(\vec{r})$ are, respectively, mean concentration, background concentration and local concentration in the region of inhomogeneity (on the spontaneously formed surface); $\varphi(c)$ is the thermodynamic-potential surface density of the solution; σ_0 is the bare surface tension in the absence of surfactant molecules equal to water-air or water-oil surface tension; $\delta(w)$ is the δ-function.

The coefficient χ_p characterizes susceptibility with respect to $\vec{p}$-ordering, (the case $\chi_p^{-1} = 0$ corresponds to the spontaneous ordering of $\vec{p}_i$), λ is the coupling constant of the vector $\vec{p}$ with the surface, β is defined by spontaneous curvature, γ is related to elasticity of the surface with respect to deformations. It should be noted that interaction of $\vec{p}$ with the surface, as well as spontaneous curvature decrease the thermodynamic potential.

In expression (16) defining the interaction of different parts of the surface with each other we have taken into account that interaction energy depends only on relative orientation of the main axis of the interactig surfaces, and not on its directions. The explicit form of the function $U^{\gamma\delta}_{\alpha\beta}(\vec{r} - \vec{r}')$, is unknown and should be obtained from model considerations.

Separating the interaction energy $U^{\gamma\delta}_{\alpha\beta}(\vec{r} - \vec{r}')$ into isotropic and anisotropic parts:

$$U^{\gamma\delta}_{\alpha\beta}(\vec{r} - \vec{r}') = U_1(\vec{r} - \vec{r}')\delta_{\alpha\beta}\delta_{\gamma\delta} + (1/2)U_2(\vec{r} - \vec{r}')(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) \tag{17}$$

we get

$$\begin{aligned}\Delta\Phi_{\text{int}} = \int d\vec{r}\, d\vec{r}' c(\vec{r})\delta[W(\vec{r})]|\nabla W(\vec{r})|\{U_1(\vec{r} - \vec{r}') + (1/3)U_2(\vec{r} - \vec{r}')\\ + [(\nabla_\alpha W(\vec{r})\nabla_\beta W(\vec{r}))/|\nabla W(\vec{r})|^2 - (1/3)\delta_{\alpha\beta}] \times U_2(\vec{r} - \vec{r}')\\ \cdot [(\nabla_\alpha W(\vec{r}')\nabla_\beta W(\vec{r}'))/|\nabla \vec{W}(\vec{r}')|^2 - (1/3)\delta_{\alpha\beta}]\} \times \delta[W(\vec{r}')]|\nabla W(\vec{r}')|c(\vec{r}')\end{aligned} \tag{18}$$

Assuming that surface consists of a set of $\tilde{N}$ identical aggregates (e.g., spheres or ellipsoids with the centers at points $\vec{r}_1, \ldots, \vec{r}_{\tilde{N}}$), we get

$$W(\vec{r}) = \prod_{i=1}^{\tilde{N}} W(\vec{r}_i, \vec{r})$$

In the specific case of spherical micelles with radius R

$$W(\vec{r}) = \prod_{i=1}^{\tilde{N}} W(\vec{r}_i, \vec{r}) = \prod_{i=1}^{\tilde{N}} [(\vec{r} - \vec{r}_i)^2 - R^2] \tag{19}$$

It is obvious, that in order to get full thermodynamic potential one should average over all possible distributions of surface in volume:

$$\tilde{\Phi}_s = -T \ln \int e^{-\Phi_s(W)/T} d\Gamma \tag{20}$$

where Γ is the phase space. If we limit ourselves to the case of spherical micelles, defined above, the integration over the phase space reduces to integration over the coordinates of centers of spheres and over their radius

$$d\Gamma = (1/\tilde{N}!)\, dr_1, \ldots, dr_{\tilde{N}}\, dR$$

In the more general case of ellipsoids an extra integration over eccentricity and orientational angles is needed.

Expression (20) with the account of (13)–(16) contains all that is needed for the construction of the phase diagram of the solution.

Let us consider, first of all, the process of micellar phase formation, i.e., the region of very small average concentrations c_0. We neglect in this case the surface-surface interaction term and introduce explicitly the local density of thermodynamic potential, related with inhomogeneous distribution of amphiphiles in solution:

$$\begin{aligned}\varphi\{c(\vec{r})\} = (1/s_0)[c(\vec{r})(\tilde{\mu}_1^{(0)} + T\ln(c(\vec{r})/e)) \\ + (1 - c(\vec{r}))(\tilde{\mu}_w^{(0)} + T\ln((1 - c(\vec{r}))/e)] \qquad (21)\end{aligned}$$

(here s_0 is surface per molecule).

It should be noted, that quantities $\mu_1^{(0)}$ and $\tilde{\mu}_1^{(0)}$ in expressions (12) and (21) are not identical: $\mu_1^{(0)}$ in expression (12) represents the energy of interaction of the amphiphile with the solvent in dilute solution, the value $\tilde{\mu}_1^{(0)}$ is the same energy, but in the region of inhomogeneity, i.e., in the region, where $c(\vec{r})$ is close to unity. Analogous changes in standard chemical potentials of water molecules in dilute solutions $\mu_w^{(0)}$ and in the inhomogeneity region $\tilde{\mu}_w^{(0)}$ will be neglected.

Minimizing

$$\Phi_s(w) = \Delta\Phi_2(w) + \Delta\Phi_3(w) + \Delta\Phi_4(w) \qquad (22)$$

over $\vec{p}$ and $c(\vec{r})$, we get the concentration distribution in solution:

$$\begin{aligned}c(\vec{r}) = c_0\{c_0 + (1 - c_0)\exp[(s_0/T)(-\lambda^2/4\chi_p^{-1} + (\tilde{\mu}_1^{(0)} - \mu_1^{(0)})/s_0 \\ - \beta\nabla_i((\nabla_i W)/|\nabla W|) + \gamma(\nabla_i((\nabla_i W)/|\nabla W|))^2)]\}^{-1} \qquad (23)\end{aligned}$$

From expression (23) it could be seen that when the argument of the exp-function is large enough and negative, the value of $c(\vec{r})$ may become very close to unity.

Substituting the expression (23) into Equation (22), we get

$$\Phi_s(w) = \int [\sigma_0 + (T/s_0)\ln((1 - c(\vec{r}))/(1 - c_0))]\delta(W)|\nabla W|\, dV \qquad (24)$$

It should be noted, that in the process of derivation of Equation (24), the explicit form of the surface appearing inside the solution volume (i.e., explicit form of $W(\vec{r})$-function) should be determined from the minimization of functional (24).

However, we shall use a direct variational method. Let us choose the trial function $W(\vec{r})$ in the form of Equation (19). Here, the radius of aggregates (R) as well as their number ($\tilde{N}$) are adjustable parameters and must be determined from minimization of corresponding functional.

Substituting (19) into (24) we get:

$$\Phi_s(W) = \tilde{N}\{\sigma_0 + (T/s_0)\ln[(1 - c(R))/(1 - c_0)]\}4\pi R^2 \tag{25}$$

where

$$c(R) = c_0\{c_0 + (1 - c_0)\exp[(s_0/T)(-\lambda^2/4\chi_p^{-1} + (\tilde{\mu}_1^{(0)} - \mu_1^{(0)})/s_0 - \beta/R + \gamma/R^2)]\}^{-1}$$

Carrying out final averaging (20), we obtain

$$\Phi = \Phi_1 + \Phi_s \approx N\mu_w^{(0)} + Nc_b[\mu_1^{(0)} + T\ln(c_b/e)] + MN\tilde{c}[\mu_m + (T/M)\ln(\tilde{c}/e)] \tag{26}$$

where we use notations common to the thermodynamic theory of micellization: $\tilde{c} = \tilde{N}/N$ is the concentration of micelles; $\mu_m = [\sigma_0 + (T/s_0)\ln((1 - c(R))/(1 - c_0))]s_0/c(R)$ is the chemical potential of the amphiphile molecule in a micelle; and $M = 4\pi R^2 c(R)/s_0$ is the aggregation number.

The quantity $[\sigma_0 + (T/s_0)\ln((1 - c(R))/(1 - c_0))]$ plays the role of an effective surface tension, $s_0/c(R)$ is the surface per one surfactant molecule in micelle.

In derivation of the expression (26) the integral over R was obtained by the steepest descent method, which gives an additional condition

$$\partial\{4\pi R^2[\sigma_0 + (T/s_0)\ln((1 - c(R))/(1 - c_0))]\}/\partial R = 0 \tag{27}$$

Minimizing (26) over $\tilde{N}$ or equally over $\tilde{c}$ with an extra condition: $c_0 = c_b + M\tilde{c} = \text{const}$, it is not difficult to obtain an equation for $\tilde{c}$, the solution of which in the limit $M >> 1$ has the form

$$\tilde{c} = (c_0/M)[(\mu_1^{(0)} - \mu_m)/T + \ln c_0] \tag{28}$$

The solution of Equation (28) may be obtained when the following condition is satisfied:

$$(\mu_1^{(0)} - \mu_m)/T + \ln c_0 \leq 0$$

So for critical micelle concentration ($c_0^{(\mathrm{cmc})}$) we get

$$\ln c_0^{(\mathrm{cmc})} = (1/T)\{(\sigma_0 + (T/s_0)\ln[(1 - c(R))/(1 - c_0^{(\mathrm{cmc})})]) \times (s_0/c(R)) - \mu_1^{(0)}\} \quad (29)$$

In fact, expression (29) is nothing but equation for $c_0^{(\mathrm{cmc})}$, as quantity $c(R)$ depends itself on $c_0^{(\mathrm{cmc})}$. At $1 - c(R) << 1$ (which always holds) the solution of this equation is fairly trivial:

$$\ln c_0^{(\mathrm{cmc})} \simeq (1/2T)\{\tilde{\mu}_1^{(0)} - \mu_1^{(0)} + (\sigma_0 - (\lambda^2/4)\chi_p - \beta^2/4\gamma)s_0\} \quad (30)$$

When $c_0 > c_0^{(\mathrm{cmc})}$, micelle concentration depends on c_0

$$\tilde{c} = (1/M)[c_0 - c_0^{(\mathrm{cmc})}] \quad (31)$$

The appearance of micelles is equivalent to the appearance of a surface distributed in solvent volume, the density of which $\tilde{S}$ is $\tilde{S} = \langle\delta(W)|\nabla W|\rangle$.

The quantity $\tilde{S}$ in the vicinity of CMC may be easily defined from the micelle concentration $\tilde{c}$: $\tilde{S} = (4\pi R^2/a^3)\cdot\tilde{c}$ (here a^3 is a volume per solvent molecule).

4. FORMATION OF LYOTROPIC LIQUID CRYSTALLINE PHASES

Up to now we had no reasons to assume for a micelle any other form than spherical. However, with the increase of surface concentration $c(R)$ in the case where spontaneous ordering of vectors $\vec{P}_i$ with direction different from normal to the surface, is possible, the micelles will take the form of ellipsoids. It defines, in fact, a certain anisotropy of inverse susceptibility χ_p^{-1} (see Equation (15)).

When such anisotropy is present, the term $\chi_p^{-1}c(\vec{r})\vec{P}^2$ in Equation (15) must be substituted by expression $c(\vec{r})(\chi_n^{-1}\vec{p}_n^2 + \chi_\tau^{-1}\vec{P}_\tau^2)$, where indices n and τ denote normal and tangent components respectively. When $\vec{P}_\tau = 0$ micelle is spherical. If $\chi_\tau^{-1} = 0$, a solution with $\vec{P}_\tau = 0$ appears and micelle changes its shape from spherical to ellipsoidal.

With the increase of mean concentration c_0, the micelle concentration increases proportional to $(c_0 - c^{\mathrm{cmc}})$ and it becomes necessary to take the interaction of micelles (or surface-surface interaction) into account.

It should be noted that micellar system (or micellar phase) in this case becomes analogous, to some extent, to a simple molecular system.

It is thus clear that when the anisotropic part of interaction enegy is small (U_2

$\ll U_1$, see Equation (17)), we should observe the following succession of phases in the system: surfactant molecular solution ($\tilde{S} = 0$) → micellar solution ($\tilde{S} > 0$)→ phase separation in micellar system into micellar "gas" and micellar "liquid" ($\tilde{S}_j = \tilde{S}_c - \delta\tilde{S}$; $\tilde{S}_L = \tilde{S}_c + \delta\tilde{S}$; where $\tilde{S}_c$ is the surface density in the critical consolute point) → micellar liquid crystalline phases ($\tilde{S}(\vec{r}) = \tilde{S}_0 + {}_j\Delta\tilde{S}_0\Sigma e^{i\vec{k}j\vec{r}}$ see Figure 3).

All combinations of liquid crystalline phases ($Q_{\alpha\beta} \equiv \langle\delta(W)\rangle|\nabla W|[(\nabla_\alpha W\nabla_\beta W)/|\nabla W|^2 - (1/3)\delta_{\alpha,\beta}]\rangle \neq 0$) may appear first of all in the case when $P_\tau \neq 0$ and the micelle shape is nonspherical (see above).

To obtain "condensed" micellar phases (liquid or liquid crystalline) it is sufficient to use any traditional approach including the interaction into account (e.g., virial expansion up to the second term at least).

It should be also noted that micellar systems have one more specific feature, which differs them from molecular solutions. The fact is that both micelles and intermicellar interaction energy are of macroscopic nature. This means that micellar structure may be transformed during the phase transition processes. So, for example, even in the case of spherical micelles but when anisotropic energy $U_2(\vec{r} - \vec{r}')$ is noticeable, a simultaneous transition to nematic phase may take place on the scale of the whole system while on the scale of a single micelle there will be a structural transition from sphere to ellipsoid or cylinder. Here, a certain increase of surface energy will be compensated by considerable decrease of energy related with the transition to nematic phase. Besides, when the density of surface increases the properties of solvent itself may change too. For example, the close crystalline ordering may appear in water, confined between two interacting surfaces. It leads to a change in interaction energy $U_2(\vec{r} - \vec{r}')$ (see Equation (16)) and its substitution by some effective interaction.[2] This effect may be of a great significance when one deals with lamellar phases.

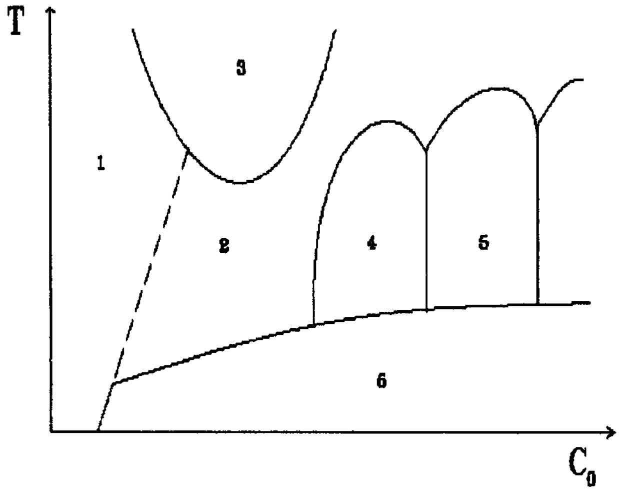

FIGURE 3 Schematic phase diagram of surfactant-water solution. (1) is isotropic monomer solution; (2) is micellar phase; (3) is two-phase region; (4) is hexagonal phase; (5) is lamellar phase; (6) is solid crystalline phase. Dashed line corresponds to CMC values.

5. CONCLUSION

We see that specific interaction of amphiphiles with random inhomogeneities of the solvent leads to a particular type of phase transition—supramolecular structure formation, the process, which can be interpreted as the appearance of extra surface inside the solution volume. The order parameter here may be connected with surface density. Specific feature of this transition is characterized by the fact that aggregation number is proportional to surface area (all molecules are located at the surface). While for usual phases the number of molecules is always proportional to volume. One could say that we are dealing with the transition to a "two-dimensional" phase (surface) for which thermal fluctuations may play much more prominent role than for volume phases.

The order parameter introduced above, is of a tensor nature. Only its scalar part represents the surface density. While surfactant concentration increases the surface density also grows and the anisotropic part of order parameter becomes important. It is related to complicated interactions of different aggregates or differrent parts of the surface with each other. Such interactions may be isotropic and lead to isotropic phases or it may be anisotropic, then liquid crystalline structures will be formed.

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