

Nanostructural Models of Micelles and Primicellar Aggregates

A. I. Rusanov, A. P. Grinin, F. M. Kuni, and A. K. Shchekin

St. Petersburg State University, St. Petersburg, Russia

Received October 15, 2001

Abstract—For the case of direct spherical micelles, two nanostructural models of molecular aggregates have been discussed: the classical drop model implying flexibility of hydrocarbon chains of molecules and their full immersion into the hydrocarbon core of an aggregate, and a quasi-drop model allowing partial outcropping of the chains in the strainless state from the core. For the sake of simplicity, a solution is assumed to contain only a single surfactant whose molecules possess only one, unbranched hydrocarbon radical. Within the frames of the models, the behavior of the chemical potential of surfactant molecules in a primicellar and micellar molecular aggregate has been analyzed, as well as the work of formation of the molecular aggregate as a function of the aggregation number and the solution concentration.

INTRODUCTION

The rigorous theory of micellar systems, as well as the theory of molecular aggregative systems at all, is formulated on the basement of the mass action law. The mass action law constant is known to include the Gibbs energy of a single micelle, so that the calculation of this quantity proves to be necessary in the theoretical description of micelles. The general theoretical formalism for the description of a single micelle has been already developed [1, 2], but models are needed for particular estimations. The data on the structure and properties of quite ready stable micelles are accessible from experiment, but the knowledge of the properties of primicellar (molecular or ionic) aggregates is also needed for the creation of the kinetic theory of micellization. What is especially important for the kinetic theory is the behavior of critical (unstable) micelle embryos whose properties are practically unknown up to the present time. The use of as-plausible-as-possible speculative models of embryos remains the only approach to carrying out necessary calculations.

In this presentation, we will confine ourselves with the case of direct spherical micelles. We will consider two nanostructural models for primicellar and micellar molecular aggregates: the classical drop model implying flexibility of hydrocarbon chains of molecules and their full immersion into the hydrocarbon core of an aggregate, and a quasi-drop model allowing partial outcropping of the chains in the strainless state from the core. For the sake of simplicity, a solution is assumed to contain only a single surfactant whose molecules possess only one hydro-

carbon radical, the hydrocarbon chain having no branches.

1. DROP MODEL OF MOLECULAR AGGREGATE

1.1. Parameters of Hydrocarbon Chain

We will use for calculations the following formulas for the length l_C and the volume v_C of a hydrocarbon chain including n_C carbon atoms [3]

$$l_C = (1.5 + 1.265n_C) \text{ \AA}, \quad (1.1.1)$$

$$v_C = (27.4 + 26.9n_C) \text{ \AA}^3. \quad (1.1.2)$$

From here the length of a single segment in the middle of the hydrocarbon chain is $l_1 = 1.265 \text{ \AA}$ and its volume is $v_1 = 26.9 \text{ \AA}^3$. Then the cross-section area in the middle of the hydrocarbon chain is

$$a_1 = v_1/l_1 = 21.265 \text{ \AA}^2 \quad (1.1.3)$$

(if the cross-section is round, its diameter is 5.203 \AA). On the other side, the average cross-section area for the whole chain a_C is

$$a_C = v_C/l_C. \quad (1.1.4)$$

Accounting for (1.1.1) and (1.1.2), it is easy to see that always $a_C < a_1$ (for example, we have $a_C = 19.638 \text{ \AA}^2$ at $n_C = 1$ and $a_C = 20.995 \text{ \AA}^2$ at $n_C = 12$). This gives evidence for the existence of a coning at the chain end.

If one simulates the middle part of the chain with a round cylinder, its end can be represented as a

truncate cone. Let us find its geometrical parameters. The radius of the lateral cylindrical surface of the chain

$$r_1 = \sqrt{a_1/\pi} = 2.602 \text{ \AA} \quad (1.1.5)$$

simultaneously is the radius of the larger base of the truncate cone with the area $a_1 = 21.265 \text{ \AA}^2$. According to (1.1.1) and (1.1.2) (at $n_C = 0$), the cone height is $h = 1.5 \text{ \AA}$ and its volume is $V = 27.4 \text{ \AA}^3$. Using now the geometrical relationship

$$r_1^2 + r_2^2 + r_1 r_2 = 3V/\pi h, \quad (1.1.6)$$

we obtain the radius of the smaller base of the truncate cone $r_2 = 2.2155 \text{ \AA}$. Correspondingly, the smaller base area (the end face area of the hydrocarbon chain) is

$$a_2 = \pi r_2^2 = 15.42 \text{ \AA}^2, \quad (1.1.7)$$

which makes 72.5% of the cross-section area of the uniform part of the chain. With known the radii of both of the bases, the slope angle of the cone generator is readily estimated at 75.55° (the angle at the full cone vertex is about 29°).

We now have the total set of the geometrical parameters of the chain model. It is also of interest to estimate specific surface free energy σ for the same model at contact with water. For this purpose, we use the Dupre rule

$$w_1 = a'_1 \Delta\sigma = a'_1 \sigma, \quad (1.1.8)$$

where w_1 is the work of transfer of one chain segment from a hydrocarbon phase to water (constituent of the experimental total work of transfer of the hydrocarbon chain w_C), $\Delta\sigma$ is the change of σ at the transfer (it is assumed that $\sigma = 0$ in the hydrocarbon phase), and a'_1 is the lateral surface area of a single segment:

$$a'_1 = 2\pi r_1 l_1 = 20.68 \text{ \AA}^2. \quad (1.1.9)$$

According to available experimental data, $w_1 = 1.39kT$ at 25°C [1] (k is Boltzmann's constant and T is the absolute temperature). Then, from (1.1.8) and (1.1.9), we obtain

$$\sigma = w_1/a'_1 = 0.0672 \times 10^{16} \text{ kT} = 27.64 \text{ mJ/m}^2. \quad (1.1.10)$$

This result predicts the free surface energy at the strongly curved surface of a hydrocarbon chain to be approximately half that for a flat interface (50 mJ/m^2).

1.2. Packing of Chains into the Hydrocarbon Core

If chains are compactly (without cavities) packed into a spherical core of radius r , the condition holds

$$4\pi r^3/3 = nv_C, \quad (1.2.1)$$

where n is the aggregation number. From (1.2.1)

$$r = (3nv_C/4\pi)^{1/3} = \lambda n^{1/3}, \quad (1.2.2)$$

where $\lambda = (3v_C/4\pi)^{1/3}$ is the radius of a sphere which is equivalent, by volume, to a single hydrocarbon chain [according to (1.1.2), $\lambda = 4.37 \text{ \AA}$ at $n_C = 12$]. The core surface area is given by the expression

$$A = 3nv_C/r = 4\pi r^2. \quad (1.2.3)$$

One more important characteristic of packing is the core surface area per one chain

$$a = 3v_C/r = 4\pi r^2/n. \quad (1.2.4)$$

Comparing (1.1.4) and (1.2.4), we arrive at the relationship

$$a/a_C = 3l_C/r, \quad (1.2.5)$$

that shows that the core surface area per one chain decreases with increasing core radius and attains the value $3a_C$ at $r = l_C$. This value of the hydrocarbon core radius is regarded as a maximum one for direct micelles. So we see that, even at a maximum size of a spherical micelle, the hydrocarbon core surface area per one chain still treble exceeds the chain cross-section area. The ratio is lower for micelles of other shapes.

The chains are assumed to be ideally flexible in this (drop) model. In reality, chain flexibility is restricted (it is well known that rotation around C–C bonds in hydrocarbon chains is hindered). Therefore, the model works the better the longer are hydrocarbon chains and the higher is the aggregation number.

1.3. Elements of the Gibbs Energy of Molecular Aggregate

It is assumed in the drop model of a molecular aggregate that the mechanical (γ) and thermodynamic (σ) definitions of surface tension coincide, as it should be for fluids. The possibility for micelles to possess solid-like properties was taken into account in [1] and, correspondingly, the difference in the above quantities was taken into account (the theory was formulated in terms of σ in [1]). A surfactant micelle has a multi-

layer (onion-like) structure, so one may ascribe an individual tension γ_k to each layer. It is convenient that the Gibbs energy of a molecular aggregate G_M is additive with respect to the contributions of individual layers and, therefore, the contribution of each layer may be calculated separately. This is seen from the equation [2]

$$G_M = \sum_k \gamma_k A_k / 3 + \mu^\alpha n, \quad (1.3.1)$$

where A_k is the area of the surface of tension for the k th layer, μ^α is the chemical potential of a molecule in a micelle (α symbolizes the hydrocarbon phase of the micelle core). Two terms in the right-hand side of Eq. (1.3.1) are related by the relationship

$$nd\mu^\alpha = -\sum_k d(\gamma_k A_k / 3) \quad (T, p^\beta, \mu_i - \text{const}), \quad (1.3.2)$$

where p^β is the pressure in the solution surrounding a micelle (β is the symbol of this phase) and μ_i are the chemical potentials of the solvent components. In contrast with μ^α , the chemical potential μ^α refers to a higher pressure $p^\alpha > p^\beta$. However, if p^β is reduced to its value $\mu^\alpha(p^\beta) \equiv \mu^{\alpha(\beta)}$ for the pressure p^β , Eq. (1.3.1) is simplified to the expression [2]

$$G_M = \sum_k \gamma_k A_k + \mu^{\alpha(\beta)} n. \quad (1.3.3)$$

In a direct micelle or a corresponding molecular aggregate of a surfactant, two tensile surfaces can be distinguished: the boundary between the hydrocarbon core and a polar solvent, and the surface of tension (of negative tension because of repulsion) for polar groups. In the former case, neglecting the curvature dependence of surface tension, we may set the surface tension γ_0 equal to its macroscopic value ($\gamma_0 = 50$ mH/m for the boundary between the hydrocarbon phase and water). Then the contribution of this surface is explicitly present in Eqs. (1.3.1) and (1.3.2). The contribution of polar groups is more complex. Polar groups, both dipole and ionic, form the electrical double layer. So, strictly speaking, we deal with two surfaces (plates of the double layer), but it is more reasonable to consider them conjointly.

Turning to spherical molecular aggregates of sufficiently large dimensions, we may estimate the electrostatic contribution with the aid of the spherical capacitor model. The expression for its energy (the work of charging) is well known. The charging at a fixed state of the surrounding medium just yields the electrical contribution G_M^{el} to the Gibbs energy of a molecular aggregate:

$$G_M^{\text{el}} = \frac{(ezn)^2}{8\pi\epsilon_0\epsilon} \left(\frac{1}{r + \Delta r} + \frac{1}{r + \Delta r + \delta} \right) = \frac{(ezn)^2\delta}{8\pi\epsilon_0\epsilon(r + \Delta r)(r + \Delta r + \delta)}, \quad (1.3.4)$$

where ezn is the charge of the primary (internal) capacitor plate (e is the elementary charge and z is the charge ratio), ϵ_0 is the electric constant, ϵ is the dielectric permittivity, Δr is the distance between the internal capacitor plate and the hydrocarbon core surface ($r + \Delta r$ is the radius of the internal capacitor plate), and δ is the distance between the capacitor plates. We assume the parameters Δr and δ to be independent of the core radius and the aggregation number. Then substitution of (1.2.2) in (1.3.4) gives an explicit dependence of G_M^{el} on the aggregation number:

$$G_M^{\text{el}} = \frac{(ez)^2\delta}{8\pi\epsilon_0\epsilon\lambda^2} \frac{n^2}{(n^{1/3} + k_1)(n^{1/3} + k_2)}. \quad (1.3.5)$$

For the sake of brevity, the notations $k_1 \equiv \Delta r/\lambda$ and $k_2 \equiv (\Delta r + \delta)/\lambda$ have been introduced in Eq. (1.3.5), so that $k_2 - k_1 = \delta/\lambda$.

Using the definition of chemical potential [2]

$$\mu^\alpha = \left(\frac{\partial G_M}{\partial n} \right)_{T, p^\beta, \mu_i} \quad (1.3.6)$$

and Eq. (1.3.5), we also can calculate the electrostatic contribution μ_{el}^α to the chemical potential μ^α :

$$\mu_{\text{el}}^\alpha = \left(\frac{\partial G_M^{\text{el}}}{\partial n} \right)_{T, p^\beta, \mu_i} = \frac{(ez)^2\delta}{24\pi\epsilon_0\epsilon\lambda^2} \cdot \frac{4n^{5/3} + 5(k_1 + k_2)n^{4/3} + 6k_1k_2n}{[n^{2/3} + (k_1 + k_2)n^{1/3} + k_1k_2]^2}. \quad (1.3.7)$$

To discuss the role of this contribution, let us consider the detailed expression for the chemical potential of a molecular aggregate as a function of the aggregation number.

1.4. Chemical Potential of Surfactant Molecule in Molecular Aggregate (Phase Approach)

The concentration of molecular aggregates is not taken into account in the phase approach: each molecular aggregate is considered as if it would be alone and would be a phase. It is known, however, that such a "phase" chemical potential coincides with the real chemical potential in an aggregative system at the extreme points in the curve of the distribution of

aggregates in the aggregation numbers [4, 5]. Just these points are of the most interest for us.

In any phase α , the molecular chemical potential μ^α is given by the standard expression of statistical mechanics

$$\mu^\alpha = \mu^0 + w^\alpha + kT \ln(c^\alpha \Lambda^3), \quad (1.4.1)$$

where μ^0 is the chemical potential of an isolated molecule with resting center of mass in a vacuum, w^α is the work of transfer of the molecule from a fixed position in a vacuum to a fixed position in phase α with the molecular concentration c^α , $L \equiv h(2\pi mkT)^{-1/2}$ is the mean de Broglie wavelength (h is Planck's constant, m is the molecular mass). We will apply Eq. (1.4.1) to a surfactant molecule located inside a molecular aggregate in a surface solution.

Regarding the solution surrounding an aggregate as phase β (this is a real phase without any ifs), we can write a similar expression for the surfactant chemical potential in phase β and subtract it from Eq. (1.4.1) to obtain the expression

$$\mu^\alpha = \mu^\beta + w^\alpha - w^\beta + kT \ln(c^\alpha/c_1^\beta), \quad (1.4.2)$$

where c_1^β is the concentration of surfactant monomers in solution. Obviously, the difference $w^\alpha - w^\beta$ is the work of transfer of a surfactant molecule from the aqueous phase to the aggregate. In such transfer, only the hydrophobic part of the surfactant molecule changes its surrounding medium and passes from the solution into the hydrocarbon core of the molecular aggregate. If the hydrocarbon core surface were flat, the work of transfer of a single hydrocarbon chain from water into the depth of the hydrocarbon phase would be $-w_C$ (as already stated above, this quantity is known from experiment). However, since the hydrocarbon core surface is curved and possesses tension γ_0 , the work of transfer is complemented by the term w_L giving the work necessary for overcoming the Laplace pressure difference at the surface under consideration (we will account for the surface of polar groups separately). In the case of a spherical surface of radius r , this term (the contribution to molecular chemical potential) is

$$w_L = v_C(2\gamma_0/r) \quad (1.4.3)$$

and plays the role of a correction to $-w_C$ (as estimated per a chain segment, this term contributes $2v_1\gamma_0/r$, which, at $v_1 = 26.9 \text{ \AA}^3$ and $\gamma_0 = 50 \text{ mH/m}$, makes $0.654kT$, i.e. 47% of the above quantity w_1 ; the con-

tribution of w_L will become still smaller at increasing r). Using (1.2.2), Eq. (1.4.3) can be transformed to the form

$$w_L = b_L n^{-1/3}, \quad b_L \equiv (32\pi/3)^{1/3} \gamma_0 v_C^{2/3}. \quad (1.4.4)$$

In addition, we have to take into account that a surfactant molecule is not transferred into the depth of the hydrocarbon phase as a whole, but remains in a position when it intersects the dividing surface (to which surface tension refers) inside the aggregate. Therefore, the work of transfer also contains the surface contribution $-\gamma_0 a_0$, where a_0 is the effective area occupied by a surfactant molecule on the dividing surface (usually, this is the parking area of a polar group). We note at once that such an additive is constant and, hence, does not influence the following calculations.

As for polar groups, they remain in the solvent medium in the course of transfer of a surfactant molecule in a molecular aggregate but come closer to each other and form an electrical double layer, which requires (as estimated per one molecule) the work w_{el} (the subscript *el* indicates an electrical nature of the work). Above, we have already estimated this contribution to the chemical potential as μ_{el}^α in Eq. (1.3.7), and we now write it in the form

$$w_{el} = b_{el} \frac{n^{5/3} + \frac{5}{4} kn^{4/3} + \frac{3}{2} k'n}{(n^{2/3} + kn^{1/3} + k')^2}, \quad (1.4.5)$$

$$b_{el} = \frac{(ez)^2 \delta}{6\pi\epsilon_0 \epsilon \lambda^2},$$

where

$$k \equiv k_1 + k_2 \equiv (2\Delta r + \delta)/\lambda,$$

$$k' \equiv k_1 k_2 \equiv \Delta r(\Delta r + \delta)/\lambda^2. \quad (1.4.6)$$

It is easy to see that w_{el} is a monotone increasing function of the aggregation number n .

Neglecting other interactions (in particular, we consider the polar groups not to be in direct contact and interacting only electrostatically), we now can write Eq. (1.4.2) in the form

$$\mu^\alpha = \mu - w_C + w_L - \gamma_0 a_0 + w_{el} + kT \ln(c^\alpha/c_1), \quad (1.4.7)$$

where all the quantities w are positive and the superscript β is omitted (at equilibrium, μ^β is just the real chemical potential μ in the whole aggregative system). By referring w_C to the macroscopic phase, we imply the matter density in the macroscopic phase and inside

the micelle hydrocarbon core to be the same. At a constant density of hydrocarbon chains, one may also consider the molecular concentration c^α as approximately constant, not to speak that c^α stands in the logarithmic form in (1.4.6). The quantities μ and c_1 are also constants at a given state of solution, so that the whole dependence of μ^α on the aggregation number n is realized via w_L and w_{el} . Hence,

$$\frac{d\mu^\alpha}{dn} = \frac{dw_L}{dn} + \frac{dw_{el}}{dn}. \tag{1.4.8}$$

To avoid dealing with fractional exponents, it is more convenient to perform differentiation with respect to the variable $n^{1/3} \equiv x$. Using (1.4.4) and (1.4.5), we obtain

$$\frac{d\mu^\alpha}{dx} = \frac{dw_L}{dx} + \frac{dw_{el}}{dx} = -\frac{b_L}{x^2} + b_{el} \frac{x^6 + 3kx^5 + (2.5k^2 + 3.5k')x^4 + 6.5kk'x^3 + 4.5k'^2x^2}{(x^2 + kx + k')^3}. \tag{1.4.9}$$

The second differentiation yields

$$\frac{d^2\mu^\alpha}{dx^2} = \frac{2b_L}{x^3} + b_{el} \frac{(k^2 - k')x^5 + (2.5k^3 - kk')x^4 + (10k^2k' - 4k'^2)x^3 + 15kk'^2x^2 + 9k'^3x}{(x^2 + kx + k')^4} > 0, \tag{1.4.10}$$

showing that the curve of the dependence of μ^α on x is concave in its whole length [there are differences in the numerator of (1.4.10), but all of them are positive, as it is easy to see with using (1.4.6)]. Let us examine the dependence with respect to the presence of stationary points. By equating (1.4.9) to zero, we arrive at the algebraic equation of the eighth degree

$$x^8 + 3kx^7 + (2.5k^2 + 3.5k')x^6 + 6.5kk'x^5 + 4.5k'^2x^4 - b(x^2 + kx + k')^3 = 0, \tag{1.4.11}$$

where the notation $b \equiv b_L/b_{el}$ is introduced for the sake of convenience. In Eq. (1.4.11), the terms of order x^8 and x^7 are positive, and the terms of order x^3 and lower are negative, whereas three middle terms can be of any sign depending on the value of b . We write these terms in the form

$$(a_6 - b)x^6 + 3k(a_5 - b)x^5 + 3(k^2 + k')(a_4 - b)x^4, \tag{1.4.12}$$

where

$$a_6 \equiv 2.5k^2 + 3.5k' > a_5 \equiv 13k'/6 > a_4 \equiv 1.5k^2/(k^2 + k'). \tag{1.4.13}$$

At the above proportion of positive quantities a_4 , a_5 , and a_6 , there is only one sign change in the sequence of coefficients of Eq. (1.4.11), irrespective of the b value. Then, in accordance with the Descartes sign rule, Eq. (1.4.11) has a unique positive root.

Thus, a stationary point has been found as a unique point, and the condition expressed in Eq. (1.4.10) gives evidence that this is a minimum.

The conclusion on the existence of a unique minimum evidently remains true also for the dependence of μ^α on n . We designate the minimum value of μ^α as μ_{min}^α and the aggregation number n at the minimum point as n_0 . As was already noted, the condition

$$\mu = \mu^\alpha \tag{1.4.14}$$

corresponds to extremes in the curve of aggregate distribution in size. The μ value is given by the concentration of the surfactant solution. If $\mu < \mu_{min}^\alpha$, the existence of extremes and, therefore, micelle formation (a maximum in the distribution curve corresponds to micelles) is impossible. This is the primicellar concentration range. There are two extremes (a minimum and a maximum) at $\mu > \mu_{min}^\alpha$. If $\mu = \mu_{min}^\alpha$, both the extremes merge and degenerate into an inflection point, the precursor of micellization, whose coordinate n_0 is an important parameter of the theory.

The positive root of Eq. (1.4.11) gives $n_0^{1/3}$ and can be expressed analytically only when kx^{-1} and $k'x^{-2}$ are small as compared with unity (when n_0 lies in the range of values, where $n^{1/3} \gg (\Delta r + \delta)/\lambda$). At $kx^{-1} \ll 1$ and $k'x^{-2} \ll 1$, we immediately obtain from (1.4.11)

$$x \approx b^{1/2}, \quad n_0 \approx (b_L/b_{el})^{3/2}. \tag{1.4.15}$$

If the internal capacitor plate is located close to the hydrocarbon core ($k' \approx 0$, $k \neq 0$), the degree of the algebraic equation (1.4.11) is reduced to five, but, nevertheless, Eq. (1.4.11) is only solved numerically. As an example with $k' = 0$, we consider the packing into a spherical micelle, of molecules of a nonionic surfactant containing one polar (dipole) group and dodecyl as a hydrocarbon radical. In accordance with published data, we set $n_C = 12$, $\lambda = 4.37 \text{ \AA}$, $v_C = 350 \text{ \AA}^3$, $\gamma = 50 \text{ mH/m}$, $z = 1$, $\varepsilon = 40$, and, for the beginning, $k = 1$ (i.e. $\delta = \lambda = 4.37 \text{ \AA}$). Computation via Eqs. (1.4.4) and (1.4.5) yields $b = 9.111$ and, correspondingly, Eqs. (1.4.11) and (1.4.15) lead to the values $n_0 \approx 27.5$ and $n_0 \approx 29.1$. If we set $k = 0.5$ ($\delta = 2.185 \text{ \AA}$), Eqs. (1.4.11) and (1.4.15) give close values $n_0 \approx 78.5$ and $n_0 \approx 77.8$. If, however, $k = 2$ ($\delta = 8.74 \text{ \AA}$) is taken, Eq. (1.4.15) yields $n_0 \approx 9.7$, while the exact Eq. (1.4.11) yields $n_0 \approx 12.6$ (such discrepancy is of no wonder, since the condition $n^{1/3} \gg k$ is here not fulfilled any more). In accordance with (1.1.1) and (1.1.2), the limiting value of the aggregation number is 55.5 in the model under consideration. We see that there is a certain range of δ -values where the realization of a minimum of the chemical potential of surfactant molecules in a micelle is secured by electrostatic repulsion forces in the absence of more powerful short-range repulsion forces.

1.5. Transition to Ionic Surfactants

In the case of an ionic surfactant, the electrical double layer of a molecular aggregate possesses a more complex structure, on account of the spatial distribution of counterions. One can distinguish between the layer of bound counterions (Stern layer) adjacent direct to the surface of the primary charge of the molecular aggregate (one cannot exclude partial penetration of counterions into the primary charge layer) and the diffuse part of the double layer. Still operating with the image of a spherical capacitor, one can say the outer plate has become more distant from the inner one as compared with the case of a dipole double layer, and, therefore, the capacitor energy has become higher. Herewith, the coefficient b_{el} in Eq. (1.4.5) increases, the coefficient b in Eq. (1.4.11) decreases, and, as a consequence, the aggregation number n_0 decreases. To be more exact, one can say the outer plate has segregated into to plates. The first of them coincides in position with the surface of bound counterions which bring, with themselves, bound water of a reduced dielectric permittivity ε_1 and are located, although not so close as in the dipole case, at a small distance δ_1 from the inner plate. As for the second plate simulating the diffuse part of the double layer, it is located at a sufficiently long distance δ_2

from the inner plate. If the degree of counterion binding β is high enough in a molecular aggregate and the concentration of monomeric ions in solution is still low enough, the Debye length δ_D , the principal parameter of the theory of electrolyte solutions, plays the role of δ_2 . Under ordinary conditions (at 293 K), the dependence of the Debye length on the monomer concentration c_1 (M) can be approximated by the formula

$$\delta_D \approx 3/(z\sqrt{c_1}) \text{ \AA}, \quad (1.5.1)$$

where z is the ion valency. The critical micelle concentration of ionic surfactants typically ranges within 10^{-3} – 10^{-2} M, so δ_D takes values 30 \AA and more at $z = 1$. For such long distances between plates, one should already use the macroscopic value ε of dielectric permittivity (80 for water). To complete the picture, we should account for a small probability of penetration of counterions into inner capacitor plate. This lead to the change of its charge by $1 - \beta_1$ times if β_1 is the degree of counterion binding in the inner plate.

In such a model, the capacitor energy is given by the expression {see [1], Eq. (33.1)}

$$G_M^{el} = \frac{(ezn)^2}{8\pi\varepsilon_0} \left[\frac{(1 - \beta_1)^2}{\varepsilon_1} \left(\frac{1}{r + \Delta r} - \frac{1}{r + \Delta r + \delta_1} \right) + \frac{(1 - \beta)^2}{\varepsilon} \left(\frac{1}{r + \Delta r + \delta_1} - \frac{1}{r + \Delta r + \delta_1 + \delta_2} \right) \right]. \quad (1.5.2)$$

Equation (1.5.2) changes to Eq. (1.3.4) (we now designate this value as G_M^{el}) at $\beta_1 = 0$ and $\delta_2 = 0$. For comparison of these equations, it is convenient to write Eq. (1.5.2) as

$$G_M^{el} = (G_M^{el})_0 \left[(1 - \beta_1)^2 + \frac{\delta_2 \varepsilon_1 (1 - \beta)^2 (r + \Delta r)}{\delta_1 \varepsilon (r + \Delta r + \delta_1 + \delta_2)} \right]. \quad (1.5.3)$$

Water has $\varepsilon_1/\varepsilon = 0.5$, and the factor $\varepsilon_1(1 - \beta)^2/\varepsilon$ in Eq. (1.5.3) amounts to 0.02–0.08 at $\beta = 0.6$ – 0.8 . The ratio $\delta_2/(r + \Delta r + \delta_1 + \delta_2)$ is always smaller than unity, and, therefore, a significant value of the second term in brackets in Eq. (1.5.3) might be only caused by a small value of δ_1 . However, in the case under consideration, the value of δ_1 is not so small as for dipoles, for we now speak about the contact of two hydrated ions (one has to add two diameters of water molecules to the own radii of the two ions). If δ_1 is of order 10 \AA , the ratio $(r + \Delta r)/\delta_1$ is of order 2, so that the value of the whole second term in brackets in Eq. (1.5.3) is smaller than 0.04–0.16 and plays the role of

a small correction at not large β_1 values (this correction, however, stands in the exponent if speaking about the size distribution of aggregates). Thus we see that Eq. (1.3.4) proves to be a good approximation also for ionic surfactants in many cases. This allows us to apply also other results of the preceding section (the existence of a unique minimum of the chemical potential of molecules in a molecular aggregate as a function of the aggregation number and the existence of two extremes in the curve of the size distribution of molecular aggregates) to ionic surfactants.

1.6. Condition of Phase Equilibrium

At phase equilibrium, $\mu^\alpha = \mu$ (using this, we address to stationary points in the curve of the size distribution of aggregates), and Eq. (1.4.7) changes to

$$-w_C + w_L - \gamma_0 a_0 + w_{el} + kT \ln(c^\alpha/c_1) = 0. \quad (1.6.1)$$

Putting (1.4.4) and (1.4.5) in (1.6.1) and accounting for $b \equiv b_L/b_{el}$, we write (1.6.1) in the form

$$\frac{b}{n^{1/3}} + \frac{n^{1/5} + \frac{5}{4}kn^{4/3} + \frac{3}{2}k'n}{(n^{2/3} + kn^{1/3} + k')^2} = B, \\ B \equiv \frac{w_C + \gamma_0 a_0 - kT \ln(c^\alpha/c_1)}{b_{el}}. \quad (1.6.2)$$

As was already stated above, the concentration c^α may be regarded as a constant in the model under consideration. Then Eq. (1.6.2) allows us to calculate the aggregation numbers for stationary points at a given c_1 .

Again introducing the notation $n^{1/3} \equiv x$, we rewrite Eq. (1.6.2) as

$$x^6 + (a_5 - B)x^5 + 2k(a_4 - B)x^4 + (k^2 + 2k')(a_3 - B)x^3 + 2kk'(a_2 - B)x^2 + k^2(a_1 - B)x + bk^2 = 0, \quad (1.6.3)$$

where the set of positive quantities a_i ($i = 1, 2, 3, 4, 5$) has been given:

$$a_1 \equiv 2bk/k' > a_2 \equiv b(k^2 + 2k')/2kk' > a_3 \equiv 2bk/(k^2 + 2k'), \\ a_4 \equiv (b + 1.5k)/2k, \quad a_5 \equiv 1.25k. \quad (1.6.4)$$

The quantity B increases with the surfactant concentration in solution. If the concentration is very low, $B < 0$, all the coefficients in Eq. (1.6.3) are positive, and, hence, Eq. (1.6.2) has no solution. However, the condition

$$B > 0, \quad (w_C + \gamma_0 a_0)/kT > \ln(c^\alpha/c_1) \quad (1.6.5)$$

is fulfilled in practice long before the critical micelle concentration (for dodecyl, for instance, $w_C/kT \approx 16.7$ at 293 K, $c^\alpha \sim 1/v_C \sim 10^{21} \text{ cm}^{-3} \sim 5 \text{ M}$ and, even at $a_0 = 0$, extremely low surfactant concentrations ($c_1 < 3 \times 10^{-7} \text{ M}$) are needed in solution to disturb Eq. (1.6.5)). Further increase in the concentration leads to a situation, when B becomes larger than the smallest of the quantities a_i . Then two changes of sign appear in the sequence of coefficients of Eq. (1.6.2). Such a situation is maintained at any still larger values of B , if a_4 proves to be the smallest or a_4 is intermediate between a_3 and a_5 . If, however, a_4 is larger than a_3 and a_5 , four sign changes may arise at further increase of B . In this case, the Descartes sign rule is not so categorical as at a single sign change, and predicts the number of positive roots either equal to the number of sign changes or smaller than the number of sign changes by an even. In the preceding section, however, we proved that, at $c_1 > c_{10}$ (if c_{10} is the concentration corresponding to a minimum value of the chemical potential μ^α), Eq. (1.6.2) has two roots evidently corresponding to a minimum and a maximum in the curve of size distribution of aggregates.

1.7. Work of Formation of Molecular Aggregate as a Function of the Aggregation Number

If the process of formation of a molecular aggregate occurs at constant temperature, external pressure, and the state of solution, the work of the process W is given by a change in the Gibbs energy of the molecular aggregate cell. Using (1.3.3), we can write

$$W = G_M - \mu n = \sum_k \gamma_k A_k + (\mu^{\alpha(\beta)} - \mu)n. \quad (1.7.1)$$

The expression of this form has already been analyzed in [1], but in terms of another model of molecular aggregate, with resting center of mass. Such a molecular aggregate never is in equilibrium with solution, and, when differentiating between phases α and β , the latter is understood as the region between the hydrocarbon core surface and the outer boundary of the molecular aggregate, where polar groups of surfactant molecules are located. For this reason, the electrostatic repulsion of polar groups was not related to the surface and was ascribed to the chemical potential $\mu^{\alpha(\beta)}$. We now consider a mobile molecular aggregate that can be in equilibrium with a real solution forming phase β . The electrostatic repulsion of polar groups simulated with a spherical capacitor is expressed in Eq. (1.7.1) as an interface with a negative surface tension and, in addition, as a certain contribution to the chemical potential $\mu^{\alpha(\beta)}$. It is no need to compute these quantities separately, because

we already know their joint contribution G_M^{el} given by Eq. (1.3.4). This means that, if we add G_M^{el} to Eq. (1.7.1), we simultaneously exclude the electrostatic contribution both from the sum standing in Eq. (1.7.1) and from $\mu^{\alpha(\beta)}$:

$$W = G_M^{\text{el}} + \gamma_0 A + (\mu_0^{\alpha(\beta)} - \mu)n. \quad (1.7.2)$$

Instead of the sum, we now have the only term related to the hydrocarbon core surface, and should be understood as $\mu_0^{\alpha(\beta)}$ after subtracting both the Laplace (we remind that $\mu^{\alpha(\beta)}$ has been reduced to pressure p^β) and electrostatic contributions. Turning to Eq. (1.4.7), we can now write an explicit expression for the chemical potential difference in Eq. (1.7.2):

$$\mu_0^{\alpha(\beta)} - \mu = -w_C - \gamma_0 a_0 + kT \ln(c^\alpha/c_1), \quad (1.7.3)$$

which is practically independent of the aggregation number. The surface A in Eq. (1.7.2) coincides with the hydrocarbon core area and is estimated, according to (1.2.3) and (1.2.2), as

$$A = 4\pi\lambda^2 n^{2/3}. \quad (1.7.4)$$

Neglecting all other effects and putting now (1.3.5) and (1.7.4) in Eq. (1.7.2), we arrive at the expression

$$W = \frac{b_1 n^2}{(n^{1/3} + k_1)(n^{1/3} + k_2)} - b_2 n + b_3 n^{2/3} + \dots, \quad (1.7.5)$$

where

$$b_1 \equiv \frac{(ez)^2 \delta}{8\pi\epsilon_0 \epsilon \lambda^2} = \frac{3}{4} b_{\text{el}}, \quad (1.7.6)$$

$$b_2 \equiv \mu - \mu_0^{\alpha(\beta)} + \gamma_0 a_0 = w_C + \gamma_0 a_0 + kT \ln(c_1/c^\alpha), \quad (1.7.7)$$

$$b_3 = 4\pi\lambda^2 \gamma_0 = \frac{3}{2} b_L. \quad (1.7.8)$$

At a sufficiently large aggregation number, when $n^{1/3} \gg k_1, k_2$, Eq. (1.7.5) is approximated by the expression

$$W = b_1 n^{4/3} - b_2 n + b_3 n^{2/3} + \dots, \quad (1.7.9)$$

which (with slightly different coefficients) was just analyzed in [1].

To the results obtained in [1], it is useful to add the following. If c_{10} is the monomer concentration in solution at $\mu = \mu_{\text{min}}^\alpha$ [when there is a stationary inflection point in the curve of the size dependence of aggregates and, therefore, also in the curve of the function $W(n)$], the curve of the dependence of W on n exhibits, at $c_1 > c_{10}$, the existence of two extremes and,

naturally, of an (already nonstationary) inflection point between them. The location of the inflection point on the aggregation number axis, n_0 , is found by equating the second derivative of the function $W(n)$ to zero:

$$n_0 = (b_3/2b_1)^{3/2} \quad (1.7.10)$$

[taking into account Eqs. (1.7.6) and (1.7.8), it is seen that Eq. (1.7.10) is equivalent to the second of Eqs. (1.4.15)]. Since, herewith, the coefficient b_2 , the only concentration-dependent coefficient, is absent, we come to the important conclusion that the location of the inflection point in the curve of the dependence of W on n and, therefore, in the curve of the equilibrium size distribution of molecular aggregates, does not depend on the concentration of solution. It is of note that this result is of general character and is unnecessarily related to the approximation expressed in Eq. (1.7.9).

The relation between the coefficients at the inflection point (established in [1])

$$b_2 = \frac{4}{3} (2b_1 b_3)^{1/2} \quad (1.7.11)$$

can be extended to any concentrations if b_2 is replaced by

$$\tilde{b}_2 \equiv b_2 - kT \ln(c_1/c_{10}). \quad (1.7.12)$$

Thus, the relationships are generally fulfilled

$$\tilde{b}_2 = \frac{4}{3} (2b_1 b_3)^{1/2}, \quad b_2 \geq \frac{4}{3} (2b_1 b_3)^{1/2}. \quad (1.7.13)$$

1.8. Work of Deformation of Hydrocarbon Chain. Proceeding to the Model of Rigid Chains

The hydrophobic part of a surfactant molecule undergoes a certain deformation at packing into the spherical hydrocarbon core of a molecular aggregate. So, on the average, the chain conformation will be different from that in a hydrocarbon phase. The conformational difference produces a positive contribution w_d to the chemical potential μ^α . Nagarajan [6] gives the expression for the deformation work obtained from Semenov's formula [7] by means of integration over the whole aggregate volume (i.e. this is the work per the whole aggregate $W_d = n w_d$):

$$\frac{W_d}{kT} = \frac{3\pi^2}{80} \frac{r^2}{n_s L_s^2} = \frac{3\pi^2 r^2}{80 l_C L_s}, \quad (1.8.1)$$

where n_s is the number of rigid segments per chain, L_s is the length of a rigid segment (4.6 Å), and $l_C = n_s L_s$ is the chain length. Using (1.2.2), we can

represent Eq. (1.8.1) as

$$\frac{W_d}{kT} = b_d n^{2/3}, \quad b_d \equiv \frac{3\pi^2 \lambda^2}{80l_C L_s} \approx 0.37 \frac{\lambda^2}{l_C L_s}. \quad (1.8.2)$$

For dodecyl $b_d \approx 0.092$, and we obtain $W_d/kT \approx 1.34$ even for the maximum value 55.5 of the aggregation number. Concerning the deformation work as a whole given by Eqs. (1.8.1) and (1.8.2), one can say it contributes to the total work with the same dimensionality with respect to n as the surface energy of the hydrocarbon core. The improved value of the coefficient b_3 in Eq. (1.7.5) should be written as

$$b_3 \equiv 4\pi\lambda^2\gamma_0 + b_d = 4\pi\lambda^2\gamma_0 \left(1 + \frac{3\pi kT}{320l_C L_s \gamma_0} \right). \quad (1.8.3)$$

The estimation for dodecyl at $T = 293$ K and $\gamma_0 = 50$ mH/m

$$\frac{3\pi kT}{320l_C L_s \gamma_0} = 3.16 \times 10^{-3}$$

clearly demonstrates that the correction under discussion to b_3 is small (the uncertainty of the choice of γ_0 yields a more significant error) and may be neglected.

Another model, where the work of deformation of chains is strictly zero, is the model of rigid chains (rods) which cluster round a certain element, a gas molecule dissolved or an admixture. It is most natural to take for such an element an end CH_3 group of a hydrocarbon chain. According to (1.1.2), the volume of the CH_3 group is 54.3 \AA^3 . Then its minimum surface area (corresponding to a spherical shape with radius 2.349 \AA) is 69.345 \AA^2 . In accordance with Eq. (1.1.7), this area can be easily covered by the ends of four chains, one of which (to whom the CH_3 group belongs) already exists. Four rods make a seed tetrahedron whose interspaces are filled with new chains. In this way, a hedgehog-like aggregate is formed. The rod ends can be located at different levels, and filling in is completed when all the interspaces between the chains up to polar groups of the four first molecules has been filled. Such a model of a molecular aggregate feature a more complex charge distribution which cannot already be approximated by a spherical capacitor. If, however, the condition is required that the charges of each sign are located at the same distance from the micelle center, one has either to allow existence of a cavity at the center of a molecular aggregate (the cavity regularly grows with the aggregate size), or to consider the chains to be partly (far from the polar groups) flexible and also capable to coiling into a internal

hydrocarbon phase, although of a smaller size than in the drop model. The first variant has already been analyzed in [8]. The second one (we call it a quasi-drop model) is considered below. It is of note that a realistic feature of this model will be accounting for the partial penetration of water into the hydrocarbon core of a direct micelle, which is known from experiment and was regarded as probable in [9].

2. QUASI-DROP MODEL OF MOLECULAR AGGREGATE

2.1. Geometrical Parameters of Surfactant Molecular Aggregate in the Quasi-Drop Model

Formation of micelles in a surfactant solution involves initial formation of aggregates of two, three, etc. molecules. Herewith, part of the volume of a future micelle is filled with water. As new surfactant molecules join an aggregate, water is extruded from the interspaces between molecules. Nevertheless, water can penetrate sufficiently deep into a molecular aggregate at small aggregation numbers. The maximum possible penetration of water in a molecular aggregate is assumed in the consideration given below.

In the quasi-drop model, the hydrophobic part of each molecule in an aggregate is regarded to be composed of two fragments. The first (reckoning from the hydrophilic part) is still surrounded by water molecules. The second fragment is located in the inner region of the molecular aggregate, where water molecules cannot penetrate. This region is similar to the hydrocarbon core in the drop model of a molecular aggregate, which explains the term "quasi-drop model." Due to the mutual repulsion of the hydrophilic parts, the first fragments of the hydrophobic parts of surfactant molecules forming the aggregate are located, on the average, along the radii outspreading from the aggregate center and angularly uniformly distributed in space. The plane angle φ between two such radii corresponding to neighboring aggregate molecules is determined by the aggregation number n and, for not too small aggregates, is given by the simple formula

$$\varphi = (4\pi/n)^{1/2} \quad (n \gg 1). \quad (2.1.1)$$

In particular, we understand as "not too small" such values of n as to justify the inequality $\varphi/2 \ll 1$, which, for example, allows us to replace the function $\sin(\varphi/2)$ with its argument. In this sense, the value $n = 10$ already acts as "not too small."

The possibility of accommodation of a water molecule with a typical diameter $d_{\text{H}_2\text{O}}$ between the hydrophobic parts of neighboring surfactant molecules

with a typical cross-section diameter $d = 2r_1$ is determined by the radius r_α of the inner region at the molecular aggregate center, free from water molecules and filled by the above second fragments of the hydrophobic parts of the aggregate molecules coming out of the aqueous medium. Accounting for Eq. (2.1.1), we estimate the radius r_α as

$$r_\alpha = \frac{d + d_{\text{H}_2\text{O}}}{2\pi^{1/2}} n^{1/2}, \quad (2.1.2)$$

where the approximation $\sin(\varphi/2) \approx \varphi/2$ has been used. As in the drop model, we assume the hydrophobic part fragments filling the inner region of a molecular aggregate, to interact mutually so as if they formed a hydrocarbon phase. We will term "molecular aggregate core" the inner part of the molecular aggregate defined as was said above. When carrying out numerical estimations, we shall use, in addition to the data from Section 1.1, the value $d = 5.2 \text{ \AA}$ following from the above definition of d , and also the value $d_{\text{H}_2\text{O}} = 3.1 \text{ \AA}$.

Let us find the number of hydrocarbon groups Δn_{C} of the hydrophobic part of each aggregate molecule entered the aggregate core. This number is evident to equal the number of hydrocarbon groups in the second fragments of the hydrophobic parts of the molecules. The volume Δv_{C} of each such fragment is represented, with the aid of Eq. (1.1.2), in the form

$$\Delta v_{\text{C}} = v_1(\Delta n_{\text{C}} + 1), \quad (2.1.3)$$

where the unity in parentheses is the approximate value of the ratio $27.4/26.7$ [see Eq. (1.1.2)]. According to the rule of packing, we have

$$\frac{4}{3} \pi r_\alpha^3 = n \Delta v_{\text{C}}. \quad (2.1.4)$$

From (2.1.4) and (2.1.3) it follows

$$\Delta n_{\text{C}} = \frac{4}{3} \pi \frac{r_\alpha^3}{nv_1} - 1. \quad (2.1.5)$$

Using (2.1.2), we transform Eq. (2.1.5) to

$$\Delta n_{\text{C}} = \frac{(d + d_{\text{H}_2\text{O}})^3 n^{1/2}}{6\pi^{1/2} v_1} - 1. \quad (2.1.6)$$

The determination of Δn_{C} from Eq. (2.1.4) as a continuous variable implies that this number itself is not smaller than three to four units:

$$\Delta n_{\text{C}} > 3 \text{ to } 4. \quad (2.1.7)$$

The same restriction for Δn_{C} will be needed below

for deriving the chemical potential of a surfactant molecule in a molecular aggregate. Because of Eq. (2.1.6), the aforesaid implies existence of a lower limit n_1 :

$$n > n_1, \quad (2.1.8)$$

for aggregation number values securing the validity of the results obtained with using the model under consideration. From Eqs. (2.1.6) and (2.1.7), we obtain for the n_1 value

$$n_1^{1/2} = (5-6) \frac{6\pi^{1/2} v_1}{(d + d_{\text{H}_2\text{O}})^3}. \quad (2.1.9)$$

By contrast, the condition

$$\Delta n_{\text{C}} < n_{\text{C}}, \quad (2.1.10)$$

introduces an upper limit n_2

$$n < n_2, \quad (2.1.11)$$

for the aggregation numbers n compatible with the validity of the model. Accounting for Eqs. (2.1.6) and (2.1.10), the n_2 value is determined from the relationship

$$n_2^{1/2} = (n_{\text{C}} + 1) \frac{6\pi^{1/2} v_1}{(d + d_{\text{H}_2\text{O}})^3}. \quad (2.1.12)$$

Using typical values of d , $d_{\text{H}_2\text{O}}$, and v_{C} quantities, we obtain the estimate

$$\frac{6\pi^{1/2} v_1}{(d + d_{\text{H}_2\text{O}})^3} \approx \frac{1}{2}. \quad (2.1.13)$$

We combine the inequalities (2.1.8) and (2.1.11). From (2.1.9) and (2.1.12) with account for the estimate (2.1.13), it follows that, for the validity of the model, the aggregation numbers should lie within the interval

$$(5 - 6)^2/4 < n < (n_{\text{C}} + 1)^2/4. \quad (2.1.14)$$

As determined by (2.1.14), the range of the aggregation number n is already representative enough at $n_{\text{C}} \geq 12$. It is of note that the restriction on n from below in (2.1.14) is compatible with the restriction introduced in the comment to Eq. (2.1.1).

Of the first (surrounded by water molecules) fragments of the hydrophobic parts of surfactant molecules in the aggregate, each contains, evidently, $n_{\text{C}} - \Delta n_{\text{C}}$ hydrocarbon groups and has the length $(n_{\text{C}} - \Delta n_{\text{C}})l_1$. By adding this length to the radius r_α , we

obtain the radius r of the sphere (with its center at the center of the molecular aggregate) holding the whole hydrophobic parts of surfactant molecules in the aggregate:

$$r = l_1(n_C + 1) + \left[\frac{d + d_{H_2O}}{2\pi^{1/2}} - \frac{(d + d_{H_2O})^3 l_1}{6\pi^{1/2} v_1} \right] n^{1/2}, \quad (2.1.15)$$

where Eqs. (2.1.2) and (2.1.6) have been taken into account. In accordance with (2.1.10), $r - r_\alpha \geq 0$. Introducing the designation

$$\alpha = \left[\frac{d + d_{H_2O}}{2\pi^{1/2}} - \frac{(d + d_{H_2O})^3 l_1}{6\pi^{1/2} v_1} \right] [l_1(n_C + 1)]^{-1}, \quad (2.1.16)$$

we represent Eq. (2.1.15) in the form convenient for further use

$$r = l_1(n_C + 1)(1 + \alpha n^{1/2}). \quad (2.1.17)$$

Putting numerical values for the quantities in Eq. (2.1.16), we arrive at the estimate

$$\alpha \approx -\frac{0.15}{n_C + 1}. \quad (2.1.18)$$

With account for the restriction expressed in (2.1.14), the estimate given in (2.1.18) shows that, in the model under consideration, the term $\alpha n^{1/2}$ in the second parentheses on the right-hand side of Eq. (2.1.17) cannot exceed the value

$$|\alpha n^{1/2}| \lesssim 0.08 \quad (2.1.19)$$

that is small as compared with unity. The numerical value of the parameter α given by (2.1.18) and the corresponding restriction expressed in (2.1.19) can change at using other numerical values of the quantities in calculations. However, in any case, this parameter is expected to be small in its absolute value, as well as the number on the right-hand side of (2.1.19) will be small as compared with unity.

Eqs. (2.1.1), (2.1.2), and (2.1.17) determine the geometrical parameters of a molecular aggregate in the model under discussion. We assume that, at these parameters, a molecular aggregate is in mechanical equilibrium. In any case, if mechanical equilibrium is established at r_α and r values different from those given by Eqs. (2.1.2) and (2.1.17), respectively, the difference is assumed to be relatively small.

2.2. Chemical Potential of Surfactant Molecules in Molecular Aggregate

Searching for thermodynamic quantities to characterize a molecular aggregate in the quasi-drop model, we

shall basically follow the reasoning in Section 1. As possible, we will also use the notation in Section 1 for quantities of same meaning, additionally marking such quantities in the quasi-drop model with a bar. For example, the chemical potential of surfactant molecules in a molecular aggregate is designated as $\bar{\mu}^\alpha$. Strictly speaking, α should also be barred, since the hydrocarbon core of a molecular aggregate as a hypothetical condensed phase α now consists not of whole hydrocarbon chains of surfactant molecules, but of the second (as defined in Section 2.1) fragments of the chains. All phase characteristics change with the length of the fragments.

By analogy with Eq. (1.4.7), we have the expression for $\bar{\mu}^\alpha$

$$\bar{\mu}^\alpha = \mu - \bar{w}_C + \bar{w}_L - \gamma_0 \bar{a}_0 + \bar{w}_{el} + \bar{w}_{conc}, \quad (2.2.1)$$

where \bar{a}_0 can now be understood as the cross-section area of a hydrocarbon chain (the quantity a_1 defined in (1.1.3)). The quantity $-\bar{w}_C$ on the right-hand side of Eq. (2.2.1) is the work of transfer of the second fragment of the hydrocarbon chain of a surfactant molecule from solution to the hydrocarbon core of a molecular aggregate under the assumption that the core surface is flat. This $\bar{\mu}^\alpha$ quantity is related to its analog $-w_C$ from Eq. (1.4.7) by the equation

$$\bar{w}_C \approx \frac{w_C}{n_C} \left(\Delta n_C + n \frac{d\Delta n_C}{dn} \right). \quad (2.2.2)$$

Due to Eqs. (2.2.2) and (2.1.6), the quantity \bar{w}_C (in contrast with w_C) is a function of the aggregation number n . It is of note that the second term in the parentheses on the right-hand side of Eq. (2.2.2) accounts for the change of the length of the second chain fragments as another surfactant molecule joins the aggregate. Using the notation w_1 introduced for the ratio w_C/n_C in Section 1 and accounting for Eq. (2.1.6), we represent Eq. (2.2.2) in the form

$$\bar{w}_C = \frac{3}{2} a n^{1/2} - w_1, \quad (2.2.3)$$

$$a = w_1 \frac{(d + d_{H_2O})^3}{6\pi^{1/2} v_1}. \quad (2.2.4)$$

The curvature of the hydrocarbon core surface in the quasi-drop model and the existence of surface tension γ_0 at this surface are taken into account, on the right-hand side of Eq. (2.2.1), by the contribution \bar{w}_L giving the work needed for overcoming the Laplace pressure difference at adding a molecule to the aggregate. Writing for \bar{w}_L a relationship similar to Eq. (2.2.2) and taking into account that the quantity

Δv_C (molecular fragment volume in phase α) is dependent on n but practically independent of the phase pressure, we have

$$\bar{w}_L \approx \frac{2\gamma_0}{r_\alpha} \left(\Delta v_C + n \frac{d\Delta v_C}{dn} \right). \quad (2.2.5)$$

Using (2.2.5) with accounting for (2.1.2), (2.1.3), and (2.1.6), we obtain

$$\bar{w}_L = \gamma_0(d + d_{H_2O})^2. \quad (2.2.6)$$

As follows from Eq. (2.2.6), the contribution \bar{w}_{el} to the molecular chemical potential $\bar{\mu}^\alpha$ does not depend on the aggregation number. This circumstance is a particular feature of the quasi-drop model.

The electrostatic contribution \bar{w}_{el} on the right-hand side of Eq. (2.2.1) is estimated using the spherical capacitor model. We apply general equations (1.3.4) and (1.3.6) and Eq. (2.1.17) for the radius of the surface bounding the hydrocarbon parts of surfactant molecules in the quasi-drop model of a molecular aggregate. Repeating the reasoning leading to Eq. (1.4.5), we obtain

$$\bar{w}_{el} = \frac{2n(1 + \bar{k}_1)(1 + \bar{k}_2) + 3\alpha n^{3/2} \left[1 + \frac{1}{2}(\bar{k}_1 + \bar{k}_2) + \alpha^2 n^2 \right]}{[(1 + \bar{k}_1)(1 + \bar{k}_2) + \alpha n^{1/2}(2 + \bar{k}_1 + \bar{k}_2) + \alpha^2 n]^2}, \quad (2.2.7)$$

where

$$\bar{b}_{el} \equiv \frac{(ez)^2 \delta}{8\pi\epsilon_0 \epsilon l_C^2}, \quad \bar{l}_C = l_1(nc + 1), \quad (2.2.8)$$

$$\bar{k}_1 = \Delta r / \bar{l}_C, \quad \bar{k}_2 = (\Delta r + \delta) / \bar{l}_C. \quad (2.2.9)$$

From Eq. (2.2.7) with accounting for (2.1.19), the contribution \bar{w}_{el} is seen to be an increasing function of the aggregation number n in the range of applicability of the quasi-drop model [within the limits where the inequality (2.1.19) holds].

According to Eq. (2.1.3), the concentration c^α an analog of the molecular concentration \bar{c}^α of the hydrocarbon phase in the drop model, is derived from the relationship $\bar{c}^\alpha = [v_1(\Delta n_C + 1)]^{-1}$ and depends on the aggregation number n , as it follows from Eq. (2.1.6):

$$\bar{c}^\alpha = gn^{-1/2}, \quad (2.2.10)$$

where

$$g = \frac{6\pi^{1/2}}{(d + d_{H_2O})^3}. \quad (2.2.11)$$

The dependence of the concentration \bar{c}^α on n influences the contribution \bar{w}_{conc} related to the concentration \bar{c}^α on the right-hand side of Eq. (2.2.1). The analogous contribution in the drop model is given by the last term on the right-hand side of Eq. (1.4.7). This term is of the form $kT \ln(c^\alpha/c_1)$. Taking this into consideration and also accounting for Eq. (2.2.10), we write, for the contribution \bar{w}_{conc} , the relationship similar to Eqs. (2.2.2) and (2.2.5):

$$\begin{aligned} \bar{w}_{conc} &= kT[\ln(\bar{c}^\alpha/c_1) + nd \ln(\bar{c}^\alpha/c_1)/dn] \\ &= kT[\ln(\bar{c}^\alpha/c_1) - 1/2]. \end{aligned} \quad (2.2.12)$$

At a given state of solution (the quantities μ and c_1 are constant), the dependence of $\bar{\mu}^\alpha$ on the aggregation number n is executed via \bar{w}_C , \bar{w}_{el} , and the concentration \bar{c}^α . Hence

$$\frac{d\bar{\mu}^\alpha}{dn} = -\frac{d\bar{w}_C}{dn} + \frac{d\bar{w}_{el}}{dn} + \frac{d\bar{w}_{conc}}{dn}. \quad (2.2.13)$$

Not to deal with fractional exponents in the analysis of the dependence of $\bar{\mu}^\alpha$ on the aggregation number n in the quasi-drop model, it is convenient to proceed from derivatives with respect to the aggregation number to derivatives with respect to the variable $y \equiv n^{1/2}$. Accounting for Eqs. (2.2.3), (2.2.7), (2.2.10), and (2.2.12), we replace (2.2.13) with the equation

$$\begin{aligned} \frac{d\bar{\mu}^\alpha}{dy} &= -\frac{3}{2}a - \frac{kT}{y} \\ &+ \bar{b}_{el} y \frac{4m_2^2 + 9m_2m_1\alpha y + 6m_1^2\alpha^2 y^2 + m_1\alpha^3 y^3}{[m_2 + 2m_1\alpha y + \alpha^2 y^2]^3}, \end{aligned} \quad (2.2.14)$$

where, for the sake of brevity, we introduced the notations

$$m_1 = 1 + \frac{1}{2}(\bar{k}_1 + \bar{k}_2), \quad m_2 = (1 + \bar{k}_1)(1 + \bar{k}_2). \quad (2.2.15)$$

After the second differentiation, we obtain

$$\begin{aligned} \frac{d^2\bar{\mu}^\alpha}{dy^2} &= \frac{kT}{y^2} + \frac{2\bar{b}_{el}}{[m_2 + 2m_1\alpha y + \alpha^2 y^2]^4} [2m_2^3 + m_1m_2^2\alpha y \\ &- 10m_2^2\alpha^2 y^2 - 16m_1m_2\alpha^3 y^3 - 8m_1^2\alpha^4 y^4 - m_1\alpha^5 y^5]. \end{aligned} \quad (2.2.16)$$

It follows from Eqs. (2.2.16) and (2.2.15) that the curve for the dependence of $\bar{\mu}^\alpha$ on y is concave within the range of applicability of the model under consi-

deration [when (2.1.19) is fulfilled]. Let us investigate the existence of stationary points in the dependence of $\bar{\mu}^\alpha$ on y . Equating the right-hand side of Eq. (2.2.14) to zero, we arrive at an algebraic equation of the seventh degree

$$\sum_{i=0}^7 q_i y^i = 0 \quad (2.2.17)$$

with the coefficients q_i including

$$\begin{aligned} q_0 &= 2kTm_2^3, & q_1 &= 3am_2^3 + 12kT\alpha m_2^2 m_1, \\ q_2 &= -8\bar{b}_{el} m_2^2 + 18\alpha\alpha m_2^2 m_1 + 6kT\alpha^2 m_2(4m_1^2 + m_2), \\ q_3 &= 9\alpha\alpha^2 m_2(4m_1^2 + m_2) + 8kT\alpha^3 m_1(2m_1^2 + 3m_2) \\ &\quad - 18\bar{b}_{el}\alpha m_1 m_2, \\ q_4 &= 12\alpha\alpha^3 m_1(2m_1^2 + 3m_2) + 6kT\alpha^4(4m_1^2 + m_2) \\ &\quad - 12\bar{b}_{el}\alpha^2 m_1^2, \\ q_5 &= 9\alpha\alpha^4(4m_1^2 + m_2) + 12kT\alpha^5 m_1 - 2\bar{b}_{el}\alpha^3 m_1, \\ q_6 &= 18\alpha\alpha^5 m_1 + 2kT\alpha^6, & q_7 &= 3\alpha\alpha^6. \end{aligned} \quad (2.2.18)$$

Generally, the coefficients q_i do not possess the property of predicting a unique solution of an algebraic equation, as it was with the coefficients of Eq. (1.4.11). Nevertheless, a unique physically significant root of Eq. (2.2.17) can exist in the range of applicability of the quasi-drop model. In terms of the variable y , this range is restricted by the condition $|\alpha y| \lesssim 0.08$ according to (2.1.19). In accordance with the aforesaid, the root of Eq. (2.2.17) corresponds to a minimum of the chemical potential $\bar{\mu}^\alpha$. To prove this statement, we have, first of all, to estimate the coefficients a and b_{el} in Eqs. (2.2.7) and (2.2.4), respectively. From Eqs. (2.2.4) and (2.1.13) at the above work value $w_1 = 1.39kT$, we obtain for the coefficient a

$$a \approx 2.78kT. \quad (2.2.19)$$

Putting the values of known constants in the definition of the coefficient \bar{b}_{el} , Eq. (2.2.8) and taking $l_1 = 1.265 \text{ \AA}$, we write

$$b_{el} = 220 \frac{\delta}{\varepsilon l_1 (n_C + 1)^2} kT. \quad (2.2.20)$$

Using Eq. (2.2.20) with $\varepsilon = 40$, $n_C = 12$ and three values of the δ parameter 4.37 \AA , 2.185 \AA , and 8.74 \AA used as examples at the end of Section 1.4, we obtain, for the coefficient \bar{b}_{el} , three corresponding values $0.084kT$, $0.042kT$, and $0.169kT$ as a representative set of values. Neglecting Δr as compared with $\bar{l}_C(\bar{k}_1 = 0)$, the quantities m_1 and m_2 amount, according to (2.2.15) and (2.2.9), $m_1 \approx 1.25$ and $m_2 \approx 1.5$ even for

the largest of the above values of the δ parameter. Thus, the quantities m_1 and m_2 are somewhat larger than unity. The δ parameter is about 0.01 in its absolute value at $n_C = 12$. It is of note that both the coefficient \bar{b}_{el} and the square of the α parameter equally steeply decrease with increasing n_C .

Let us consider Eqs. (2.2.18) with using the above estimates. It is seen that the order of magnitude of the right-hand side of each of Eqs. (2.2.18) is determined by the first terms (they also are the only terms for q_0 and q_7). The first terms for q_i with $i \geq 3$ include the multipliers α^{i+1} . Therefore, one can assert that the terms with $i \geq 3$ on the left-hand side of Eq. (2.2.17) steeply decrease with increasing their ordinal number in the range $|\alpha y| \lesssim 0.08$. The term with $i = 3$ is already small as compared with the term with $i = 2$. Hence, retaining only the first three terms on the left-hand side of Eq. (2.2.17), we obtain the equation of the second degree as a good approximation of the exact equation. A positive root of the equation is of physical meaning. We retain the main terms in the expressions for the coefficients q_1 and q_2 . Designating the corresponding (to the above root) aggregation number as \bar{n}_0 , we obtain

$$\bar{n}_0 \approx \left[\frac{3am_2}{16\bar{b}_{el}} + \sqrt{\left(\frac{3am_2}{16\bar{b}_{el}} \right)^2 + \frac{kTm_2}{8\bar{b}_{el}}} \right]. \quad (2.2.21)$$

Using the numerical estimates of the coefficients a and \bar{b}_{el} , as well as of the quantity m_2 , we affirm that the second term in the square root on the right-hand side of Eq. (2.2.21) is numerically small as compared with the first one and can be neglected. As a result, we have for the aggregation number \bar{n}_0 corresponding to a minimum of the chemical potential $\bar{\mu}^\alpha$ and approximately estimating the aggregation number of micelles.

$$\bar{n}_0 \approx \left(\frac{3am_2}{8\bar{b}_{el}} \right)^2. \quad (2.2.22)$$

Accounting for Eqs. (2.2.22), (2.2.19), (2.2.20), and (2.2.15), the condition that the minimum of $\bar{\mu}^\alpha$ is located in the range of applicability of the quasi-drop model is

$$|\alpha \bar{n}_0^{1/2}| \lesssim 0.08 \quad (2.2.23)$$

Equation (2.2.23) is a necessary condition imposed on the physical parameters of surfactant molecules to make possible the application of the quasi-drop model. For the above numerical value for the coefficient a , the three above values for the coefficient \bar{b}_{el} , and three corresponding values for the quantity m_2 , the left-

hand side of the inequality (2.2.23) is 0.121, 0.216, and 0.093, respectively. Thus, with such parameters, the necessary condition expressed in (2.2.23) is strictly fulfilled in no one of the examples given. In accordance with Eq. (2.2.22), $\bar{n}_0 \approx 86$ in the third example which is the closest to satisfy (2.2.23). This n_0 value is larger than the corresponding value obtained in Section 1 for the drop model. The cause of the discrepancy is that, in the quasi-drop model, the hydrophilic parts of surfactant molecules in a molecular aggregate are more distant from the aggregate center. As a consequence, the effect mutual repulsion of hydrophilic groups is reduced. Returning to the initial equation (2.2.17), we note that an exact physically significant numerical solution of Eq. (2.2.17) is determined as a smallest positive root of the equation. The \bar{n}_0 value corresponding to this root, will be the closer to that found from (2.2.22), the smaller are the absolute value of parameter α and the value of m_1 .

2.3. Stationary Points in the Curve of Size Distribution of Molecular Aggregates. Work of Formation of Molecular Aggregate in the Quasi-Drop Model

We designate the minimum value of $\bar{\mu}^\alpha$ as $\bar{\mu}_{\min}^\alpha$. As was already stated, the phase equilibrium condition

$$\mu = \bar{\mu}^\alpha \quad (2.3.1)$$

corresponds to stationary points (extremes) in the curve of the size distribution of aggregates. Putting the expression for the chemical potential $\bar{\mu}^\alpha$, Eq. (2.2.1), in Eq. (2.3.1) changes Eq. (2.3.1) to an equation for finding the coordinates of stationary points

$$-\bar{w}_C + \bar{w}_L - \gamma_0 \bar{a}_0 + \bar{w}_{el} + \bar{w}_{conc} = 0. \quad (2.3.2)$$

Accounting for Eqs. (2.2.3), (2.2.7), (2.2.10), (2.2.12), and (2.2.15), Eq. (2.3.2) becomes

$$\begin{aligned} \frac{3}{2} an^{1/2} + \frac{kT}{2} \ln n - \bar{b}_{el} \frac{2m_2n + 3\alpha m_1 n^{3/2} + \alpha^2 n^2}{[m_2 + 2\alpha m_1 n^{1/2} + \alpha^2 n^2]^2} \\ = w_1 + \bar{w}_L - \gamma_0 \bar{a}_0 + kT \left[\ln(g/c_1) - \frac{1}{2} \right]. \end{aligned} \quad (2.3.3)$$

The value of μ is determined by the concentration of a surfactant solution. If $\mu < \bar{\mu}_{\min}^\alpha$ (primicellar concentration range), the existence of extremes and, hence, the appearance of micelles is impossible. Equation (2.3.3) has no solution in the primicellar concentration range. At the solution concentration securing the equality $\mu = \bar{\mu}_{\min}^\alpha$ (we designate this concentration as \bar{c}_{10}), n_0 is evident to be a root of

Eq. (2.3.3). If \bar{n}_0 satisfies the condition expressed in Eq. (2.2.23), when already the inequality $\mu > \bar{\mu}_{\min}^\alpha$ holds, Eq. (2.3.3) will have two roots because of the concave shape of the dependence of $\bar{\mu}^\alpha$ on n . Here-with, the condition that the larger root of the equation satisfies the inequality (2.1.19), acts as the sufficient condition for applicability of the quasi-drop model. In the general case, the roots of Eq. (2.3.3) at $c_1 > \bar{c}_{10}$ are found numerically.

The basic principles of deriving the work of formation of a surfactant molecular aggregate, formulated in Section 1.7, also remain valid in the case of the quasi-drop model under consideration. The analog of Eq. (1.7.2) for the sought-for work $\bar{W} = \bar{G}_M - \mu n$ is

$$\bar{W} = \bar{G}_M^{el} + \gamma_0 \bar{A} + (\bar{\mu}_0^{\alpha(\beta)} - \mu)n. \quad (2.3.4)$$

The electrostatic contribution \bar{G}_M^{el} on the right-hand side of Eq. (2.3.4) is given by Eq. (1.3.4), where Eq. (2.1.17) is now used for the radius r . Accounting for Eq. (2.1.1), the surface area of the hydrocarbon core \bar{A} is estimated as

$$\bar{A} = 4\pi r_\alpha^2 = a_\alpha n, \quad (2.3.5)$$

where

$$a_\alpha = (d + d_{H_2O})^2. \quad (2.3.6)$$

The quantity $\bar{\mu}_0^{\alpha(\beta)}$ on the right-hand side of Eq. (2.3.4) is understood as the chemical potential (without the Laplace and electrical contributions and reduced to the outer pressure) of a surfactant molecule in the aggregate under the condition that hydrocarbon chains only partly enter the hydrocarbon core. The difference $\bar{\mu}_0^{\alpha(\beta)} - \mu$ is given by the relationship

$$\bar{\mu}_0^{\alpha(\beta)} - \mu = -w_C \Delta n_C / n_C - \gamma_0 \bar{a}_0 + kT \ln(\bar{c}^\alpha / c_1), \quad (2.3.7)$$

that almost coincides with Eq. (1.7.3). However, this difference now depends on the aggregation number n , as is seen from Eqs. (2.1.6) and (2.2.10).

Summing up the aforesaid with taking into account (1.3.4), (2.1.17), (2.2.8)–(2.2.10), (2.3.5), (2.3.7), (2.1.6), and (2.2.4), we represent Eq. (2.3.4) in the form

$$\begin{aligned} W = \bar{b}_{el} \frac{n^2}{(1 + \bar{k}_1 + \alpha n^{1/2}(1 + \bar{k}_2 + \alpha n^{1/2}))} \\ - an^{3/2} - \bar{b}_2 n + \frac{1}{2} kT n \ln n, \end{aligned} \quad (2.3.8)$$

where

$$\bar{b}_2 = w_1 + kT \ln(c_1/g) - \gamma_0(a_\alpha - \bar{a}_0). \quad (2.3.9)$$

In the zero-limit for \bar{k}_1 , \bar{k}_2 , and α , Eq. (2.3.8) coincides in form with that obtained in [8]. The presence of additional numerical coefficients in the respective equation in [8] is related to the neglect of variability of the length of second fragments of the surfactant hydrocarbon chains at adding a molecule to the aggregate.

Comparison of the forms of Eq. (2.3.8) and Eq. (1.7.5) for the work of formation a molecular aggregate in the drop model leads to the following conclusion. According to Eq. (1.7.5), the dependence of the work of formation of a molecular aggregate on the aggregation number is expressed by means of the cubic root of the aggregation number (this is seen more explicitly from approximate Eq. (1.7.9)). By contrast, this dependence is realized through the square root of the aggregation number according to Eq. (2.3.8). The square-root dependence may be considered as reflecting the quasi-two-dimensional structure of surfactant molecular aggregates.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 01-03-32334).

REFERENCES

1. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
2. Rusanov, A.I., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 4, p. 532.
3. Tanford, C., *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Toronto: Wiley, 1980, 2nd ed.
4. Rusanov, A.I., Kuni, F.M., and Shchekin, A.K., *Mendeleev Commun.*, 1995, no. 3, p. 93.
5. Rusanov, A.I., Kuni, F.M., and Shchekin, A.K., *Colloids Surf.*, 1997, vol. 128, nos. 1–3, p. 13.
6. Nagarajan, R. *Structure–Performance Relationships in Surfactants*, Esumi, K. and Ueno, M., Eds., New York: Dekker, 1997, p. 1.
7. Semenov, A.N., *Zh. Exp. Teor. Fiz.*, 1985, vol. 88, no. 4, p. 1242.
8. Grinin, A.P., *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Fiz., Khim.*, 1996, issue 1, no. 4, p. 3.
9. Tanford, C., *J. Phys. Chem.*, 1974, vol. 78, no. 21, p. 2469.