

# Thermodynamic Characteristics of a Spherical Molecular Surfactant Aggregate in a Quasi-Droplet Model

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**Abstract**—The model of spherical molecular aggregate of nonionic surfactant is proposed. This model allows for the maximal (in accordance with packing rules) penetration of water molecules into an aggregate and is an alternative to the droplet model of molecular aggregate. Necessary conditions for the applicability of a model named quasi-droplet model are formulated. Based on this model, the dependence of the work of molecular aggregate formation on the aggregation number and surfactant monomer concentration in solution that plays the key role for the theory of micellization is studied. The equation is derived for the coordinates of maximum and minimum of aggregate formation work on the aggregation number axis arising with an increase in the concentration of micellar solution. Model calculations of the thermodynamic characteristics of the kinetics of micellization are performed. The approximation of the work of molecular aggregate formation allowing for the analytical study is constructed.

## INTRODUCTION

One of the widely recognized and, until present, the only productive model of a spherical aggregate composed of surfactant molecules is the droplet model of an aggregate with a liquidlike core formed by the hydrophobic fragments of surfactant molecules proposed by Tanford [1] and elaborated later in [2–8]. Based on this model, the dependence of the work of molecular aggregate formation on the aggregation number and surfactant monomer concentration in solution that has the key role for the theory of micellization was studied, and the model calculations of all thermodynamic characteristics of the kinetics of micellization were performed within a wide range of solution concentrations including the critical micellization concentration (CMC) [9].

At the same time, it is known from experiments and was admitted in [1] that water molecules can partly penetrate into the interior of a micelle. In this sense, the limiting variant of the structure of molecular aggregate is realized in the droplet model that completely excludes water penetration into the hydrocarbon core. It was of interest (and turned out to be possible) to construct the model of surfactant spherical molecular aggregate allowing for the maximal (in accordance with packing rules) penetration of water molecules into the aggregate and, hence, realizing another limiting variant of the structure of hydrocarbon core. This model will be named the quasi-droplet model of surfactant spherical molecular aggregate.

Special importance of quantitative data on molecular aggregates in the pre-micellar region of their sizes obtained in model calculations should be particularly emphasized. It is these aggregates, whose formation

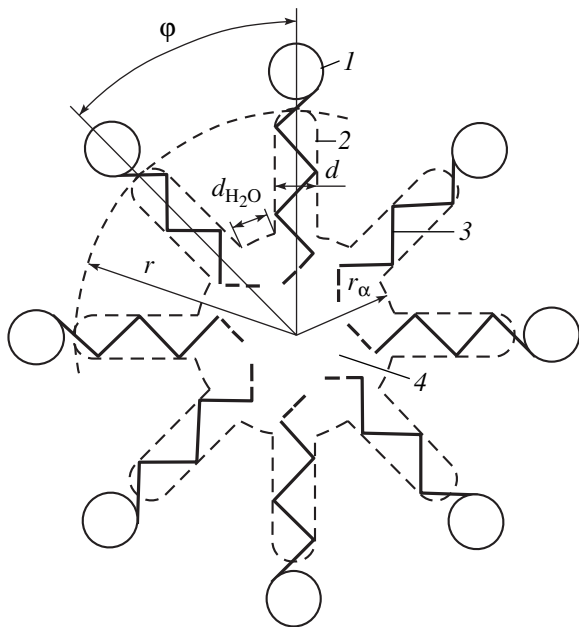
work is the largest and, conversely, the concentration is the lowest, that play, as was disclosed in [10], the key role in the relaxation processes of micellization.

## 1. GEOMETRIC PARAMETERS OF SURFACTANT SPHERICAL MOLECULAR AGGREGATE IN A QUASI-DROPLET MODEL

Let us consider aqueous nonionic surfactant solution. The formation of micelles from surfactant molecules begins with the appearance of molecular aggregates of two, three, etc. molecules. In this case, the part of would-be micelle is occupied by water. As new surfactant molecules are added to the aggregate, water is displaced from the space between molecules; however, at small aggregation numbers, water can rather deeply penetrate inside the molecular aggregate.

Let us denote the number of carbon atoms in a hydrocarbon chain of surfactant molecule by  $n_C$ . The terminal methyl group has the characteristic volume  $v_0$  and methylene group,  $v_1$ . The length of methylene group is denoted by  $l_1$ . According to data reported in [7], at absolute solution temperature  $T_0 = 298$  K we have  $v_0 = 54.3 \text{ \AA}^3$ ,  $v_1 = 26.9 \text{ \AA}^3$ , and  $l_1 = 1.265 \text{ \AA}$ . Hereafter, we assume that  $v_0/v_1 \approx 2$ . The aggregation number is denoted by  $n$ .

In the proposed quasi-droplet model of molecular aggregate shown schematically in Fig. 1, the hydrophobic moiety of each molecule constituting aggregate is represented in the form of two fragments. The first fragment counted from the hydrophilic moiety is still surrounded by water molecules. The second fragment is in the internal region of molecular aggregate into which water molecules cannot penetrate. This region is similar



**Fig. 1.** Quasi-droplet model of molecular aggregate: (1) the hydrophilic portion of surfactant molecule, (2) the boundary of water penetration into aggregate, (3) the hydrophobic portion of surfactant molecule, and (4) the hydrocarbon core of molecular aggregate. Other designations are explained in the text.

to the hydrocarbon core in the droplet model of molecular aggregate, that explains the name quasi-droplet model in the title of this paper. Due to mutual repulsion of hydrophilic portions, the first fragments of hydrophobic portions constituting surfactant molecular aggregate are located, on the average, on the radii coming out from the aggregate center and uniformly distributed over the angles in a space. Plane angle  $\varphi$  formed by two such radii corresponding to adjacent aggregate molecules is determined by the aggregation number  $n$  and, at fairly large values of  $n$  considered in this work, is given by a simple formula

$$\varphi = (4\pi/n)^{1/2} \quad (n \gg 1). \quad (1.1)$$

By fairly large values are meant, in particular, such  $n$  values which can provide inequality  $\varphi/2 \ll 1$  that allows, for example, to replace function  $\sin(\varphi/2)$  by its argument. In this sense, value  $n = 10$  is no longer too small.

The  $r_\alpha$  radius of the internal (free of water molecules) region in the center of molecular aggregate is determined by the possibility of the arrangement of water molecule with characteristic diameter  $d_{\text{H}_2\text{O}}$  between the hydrophobic portions of neighbor surfactant molecules with characteristic cross-section diameter  $d$ . This internal region is filled with the second (in the aforementioned meaning) fragments of the hydrophobic portions of molecules constituting aggregate that came out from aqueous medium. With allowance for relation (1.1) for radius  $r_\alpha$ , we obtain

$$r_\alpha = \frac{d + d_{\text{H}_2\text{O}}}{2\pi^{1/2}} n^{1/2}, \quad (1.2)$$

where the approximate equality  $\sin(\varphi/2) \approx \varphi/2$  is used. As in the droplet model, we assume that the fragments of hydrophobic portions occupied the internal region of molecular aggregate interact with each other so that they seemingly constitute the hydrocarbon phase. The internal region of molecular aggregate determined as described above is called its core. We use values  $d = 5.2 \text{ \AA}$  [7] and  $d_{\text{H}_2\text{O}} = 3.1 \text{ \AA}$ , provided that numerical estimates are true.

Let us find the  $\Delta n_C$  number of hydrocarbon groups (constituting the aggregate core) of the hydrophobic portion of each molecule constituting aggregate. Evidently, this number is equal to the number of hydrocarbon groups in the second fragments of the hydrophobic portions of molecules. The volume  $\Delta v_C$  of each fragment is represented in the form

$$\Delta v_C = v_1(\Delta n_C + 1), \quad (1.3)$$

where the fact that terminal methyl group has characteristic volume  $v_0$  that is approximately twice as large as volume  $v_1$  is taken into account. According to packing rule, we have

$$\frac{4}{3}\pi r_\alpha^3 = n\Delta v_C. \quad (1.4)$$

From Eqs. (1.4) and (1.3), we have

$$\Delta n_C = \frac{4}{3}\pi \frac{r_\alpha^3}{n v_1} - 1. \quad (1.5)$$

Using Eq. (1.2), we transform Eq. (1.5) into the following form

$$\Delta n_C = \frac{(d + d_{\text{H}_2\text{O}})^3 n^{1/2}}{6\pi^{1/2} v_1} - 1. \quad (1.6)$$

The determination of  $\Delta n_C$  number from relation (1.6) as a continuous quantity suggests that this number is already fairly large. Let us assume that this condition is fulfilled, if

$$\Delta n_C > 4-5. \quad (1.7)$$

The constraint of such type imposed on  $\Delta n_C$  will be needed hereafter for determining chemical potential of a surfactant molecule in the molecular aggregate. In view of relation (1.6), all what have been said above implies the existence of lower bound ( $n_1$ )

$$n > n_1 \quad (1.8)$$

for the aggregation numbers satisfying the results obtained with the use of proposed model. From Eqs. (1.6) and (1.7), we obtain for the  $n_1$  value

$$n_1^{1/2} = (5-6) \frac{6\pi^{1/2} v_1}{(d + d_{H_2O})^3}. \quad (1.9)$$

On the contrary, condition

$$\Delta n_C < n_C \quad (1.10)$$

introduces the upper bound ( $n_2$ )

$$n < n_2 \quad (1.11)$$

of aggregation number  $n$  permissible for the applicability of the proposed model. Using Eqs. (1.6) and (1.10), the  $n_2$  value is determined from relation

$$n_2^{1/2} = (n_C + 1) \frac{6\pi^{1/2} v_1}{(d + d_{H_2O})^3}. \quad (1.12)$$

At the characteristic values of  $d$ ,  $d_{H_2O}$ , and  $v_1$ , we have an estimate

$$\frac{6\pi^{1/2} v_1}{(d + d_{H_2O})^3} \approx \frac{1}{2}. \quad (1.13)$$

Let us combine inequalities (1.8) and (1.11). It follows from Eqs. (1.9) and (1.12) with allowance for estimate (1.13) that the values of aggregation number  $n$  permissible for the applicability of the proposed model should fit the range

$$(5-6)^2/4 < n < (n_C + 1)^2/4. \quad (1.14)$$

At  $n_C \geq 12$ , the range of aggregation number  $n$  determined by inequality (1.14) is already fairly representative. Note that the lower bound of  $n$  in (1.14) agrees with the constraint introduced in the note to formula (1.1).

Evidently, the first (surrounded by water molecules) fragments of hydrophobic portions of surfactant molecules constituting aggregate contain  $(n_C - \Delta n_C)$  hydrocarbon groups each and have the length  $(n_C - \Delta n_C)l_1$ . Adding this length to radius  $r_\alpha$ , we find radius  $r$  of a sphere with the center in the middle of molecular aggregate; this sphere includes totally the hydrophobic portions of surfactant molecules formed aggregate

$$r = l_1(n_C + 1) + \left[ \frac{d + d_{H_2O}}{2\pi^{1/2}} - \frac{(d + d_{H_2O})^3 l_1}{6\pi^{1/2} v_1} \right] n^{1/2}. \quad (1.15)$$

Equations (1.2) and (1.6) are accounted for in this relation. According to inequality (1.10),  $r - r_\alpha \geq 0$ . Introducing designation

$$\alpha = \left[ \frac{d + d_{H_2O}}{2\pi^{1/2}} - \frac{(d + d_{H_2O})^3 l_1}{6\pi^{1/2} v_1} \right] [l_1(n_C + 1)]^{-1}, \quad (1.16)$$

we represent Eq. (1.15) in the form more convenient for further treatment

$$r = l_1(n_C + 1)(1 + \alpha n^{1/2}). \quad (1.17)$$

Substituting the numerical values of corresponding parameters into Eq. (1.16), we arrive at the estimate

$$\alpha \approx -\frac{0.15}{n_C + 1}. \quad (1.18)$$

With allowance for constraint (1.14), this estimate demonstrates that, in the considered model of molecular aggregate, term  $\alpha n^{1/2}$  in the second round brackets in the right-hand side of Eq. (1.17) cannot exceed (by the absolute value) a value small as compared to unity

$$|\alpha n^{1/2}| \leq 0.08. \quad (1.19)$$

Numerical value of parameter  $\alpha$  given by estimate (1.18) and relevant constraint (1.19) can be changed when somewhat other numerical values of parameters are used in calculations. However, it should be expected that, in all the cases, the absolute value of this parameter is small and the parameter in the right-hand side of relation (1.19) will also be small as compared to unity. Note also that, according to relations (1.15) or (1.17), the  $r$  radius decreases with and increase in aggregation number  $n$  due to the negativity of parameter  $\alpha$ . Nevertheless, at each  $n$  value satisfying constraint (1.11), radius  $r$  is larger than the radius of hydrocarbon core in the droplet model of surfactant molecular aggregate.

Relations (1.1), (1.2), and (1.17) determine the geometric parameters of molecular aggregate in the model in question. Let us assume that, at these parameters, the molecular aggregate is at mechanical equilibrium.

## 2. CHEMICAL POTENTIAL OF SURFACTANT MOLECULES IN A MOLECULAR AGGREGATE

We consider molecular aggregate as a phase particle. Chemical potential of surfactant molecules in molecular aggregate is denoted by  $\bar{\mu}^\alpha$ . The meaning of a bar over symbol  $\bar{\mu}^\alpha$  will be clear later. Chemical potential  $\bar{\mu}^\alpha$  is understood as the change in the Gibbs energy of molecular aggregate on adding new molecule to the aggregate.

In view of a small number of molecules in molecular aggregates that are of interest to us, their geometric and thermodynamic characteristics undergo noticeable changes on adding new molecule to the aggregate. In particular, the hypothetical condensed phase for the substance constituting the hydrocarbon core of molecular aggregate consists only of the second (in the meaning indicated in Section 1) fragments of hydrocarbon chains of surfactant molecules rather than of the whole chains. The characteristics of such a phase are changed as the length of these fragments varied with aggregation numbers. This will be taken into account when finding chemical potential  $\bar{\mu}^\alpha$ . At the same time, at the first

stage of  $\bar{\mu}^\alpha$  finding, the molecular aggregate is considered as a unit that does not change its characteristics on adding a new molecule.

In any  $\alpha$  phase, molecular chemical potential  $\mu^\alpha$  is given by the standard expression of statistical mechanics

$$\mu^\alpha = \mu^0 + w^\alpha + kT \ln(c^\alpha \Lambda^3), \quad (2.1)$$

where  $\mu^0$  is the chemical potential of isolated molecule with the quiescent center of inertia in vacuum;  $w^\alpha$  is the work of molecule transfer from the fixed position in vacuum to the fixed position in the phase with concentration  $c^\alpha$  (the number of molecules per unit volume); and  $\Lambda \equiv h(2\pi mkT)^{-1/2}$  is the mean de Broglie wavelength ( $h$  is Planck's constant and  $m$  is the molecule mass). We will apply expression (2.1) to the surfactant molecule inside the molecular aggregate in surfactant solution.

Considering solution surrounding aggregate as  $\beta$  phase, we can write similar expression for the chemical potential  $\mu^\beta$  of the surfactant monomers in the  $\beta$  phase and, subtracting this expression from Eq. (2.1), we arrive at the relation

$$\mu^\alpha = \mu^\beta + w^\alpha - w^\beta + kT \ln(c^\alpha/c_1), \quad (2.2)$$

where  $c_1$  is the surfactant monomer concentration in the solution. It is evident that  $(w^\alpha - w^\beta)$  difference represents the work of surfactant molecule transfer from the aqueous phase to the molecular aggregate. However, during this process, only the second fragment of the hydrophobic portion of a molecule is transferred from solution to the hydrocarbon core of molecular aggregate.

If the surface of hydrocarbon core had been flat and the hydrophobic portion of surfactant molecule had been completely transferred to the core, the work of transfer of only one hydrophobic portion from water to the depth of hydrocarbon phase would be equal to the value known from experiments. This value is a linear function of the number of carbon atoms constituting hydrocarbon fragment with the coefficient of linear dependence  $-w_1$ , which at temperature  $T = T_0 = 298$  K is approximately equal to [7]

$$-w_1 = -1.39kT_0. \quad (2.3)$$

Since, in the model under consideration, only the second fragment of the hydrophobic portion of surfactant molecule enters into the hydrocarbon core composed of  $\Delta n_C$  hydrocarbon groups and, hence, containing  $\Delta n_C$  carbon atoms, relevant transfer work  $-w_C$  can be evidently represented as

$$-w_C = -w_1 \Delta n_C. \quad (2.4)$$

With allowance for Eq. (1.6), we can write Eq. (2.4) also in the following form:

$$-w_C = -an^{1/2} + w_1, \quad (2.5)$$

where

$$a = w_1 \frac{(d + d_{\text{H}_2\text{O}})^3}{6\pi^{1/2} v_1}. \quad (2.6)$$

The surface of hydrocarbon core is curved and is characterized by tension  $\gamma_0$ ; therefore, the work of surfactant molecule transfer from solution to the molecular aggregate contains contribution (to the chemical potential)  $w_L$  expressing the work spent to overcome the Laplace pressure difference on this surface (the surface of polar groups will be accounted for separately). For the spherical (with radius  $r_\alpha$ ) surface of hydrocarbon core composed of molecular fragments with volume  $\Delta v_C$ , this contribution is

$$w_L = \frac{2\gamma_0}{r_\alpha} \Delta v_C. \quad (2.7)$$

Substitution of expressions (1.2) and (1.3) for the  $r_\alpha$  and  $\Delta v_C$  values into Eq. (2.7) with allowance for Eq. (1.6) yields:

$$w_L = \frac{2}{3} \gamma_0 (d + d_{\text{H}_2\text{O}})^2. \quad (2.8)$$

In addition, one should take into account that the surfactant molecule is not transferred as a whole into the depth of hydrocarbon phase but remains in a position when it intersects the dividing surface (to which the surface tension is referred) inside the aggregate. Therefore, the work of transfer contains also, according to [11], the surface contribution  $-\gamma_0 a_0$ , where  $a_0 = \pi d^2/4$  is the effective area occupied by one surfactant molecule on the dividing surface (cross-section area of molecule hydrophobic portion).

During the transfer of surfactant molecule to the molecular aggregate, polar groups remain in the solvent medium; however, they approach each other and from the electrical double layer spending (per one molecule) work  $w_{\text{el}}$  (index "el" indicates the electrostatic nature of this component). The electrostatic contribution  $w_{\text{el}}$  is estimated, as in [9], with the aid of the model of spherical capacitor. We take advantage of the known formula for electrostatic contribution  $G^{\text{el}}$  to the Gibbs energy of molecular aggregate

$$\begin{aligned} G^{\text{el}} &= \frac{(ezn)^2}{8\pi\epsilon_0\epsilon} \left( \frac{1}{r + \Delta r} - \frac{1}{r + \Delta r + \delta} \right) \\ &= \frac{(ezn)^2 \delta}{8\pi\epsilon_0\epsilon(r + \Delta r)(r + \Delta r + \delta)}, \end{aligned} \quad (2.9)$$

where  $ezn$  is the charge of primary (internal) capacitor plate ( $e$  is the elementary charge and  $z$  is the charge multiplicity),  $\epsilon_0$  is the electric constant,  $\epsilon$  is the permittivity,  $\Delta r$  is the distance from the capacitor internal plate to the sphere of radius  $r$  ( $r + \Delta r$  is the radius of capacitor internal plate), and  $\delta$  is the distance between the plates. Let us assume that parameters  $\Delta r$  and  $\delta$  are independent of  $r$  and aggregation number  $n$ . From the definition of chemical potential [11], we can calculate

the electrostatic contribution  $w_{el}$  to the chemical potential differentiating expression (2.9) for the electrostatic contribution  $G^{el}$  with respect to aggregation number  $n$ , provided that other conditions are fixed. When writing the result, we ignore the second-order terms due to small (because of constraint (1.19))  $\alpha n^{1/2}$  value. With allowance for formula (1.17) for the radius  $r$  of the surface confining the hydrocarbon portions of surfactant molecules in the quasi-droplet model of molecular aggregate, we find

$$w_{el} = b_{el} \frac{2n}{m_2} \left( 1 - \alpha n^{1/2} \frac{5m_1}{2m_2} \right), \quad (2.10)$$

where

$$b_{el} \equiv \frac{(ez)^2 \delta}{8\pi\epsilon_0 \epsilon l_C^2}, \quad l_C = l_1(n_C + 1), \quad (2.11)$$

$$m_1 = 1 + \frac{2\Delta r + \delta}{2l_C}, \quad (2.12)$$

$$m_2 = \frac{(l_C + \Delta r)(l_C + \Delta r + \delta)}{l_C^2}.$$

From Eq. (2.10) with account of relation (1.19) it is seen that, within the domain of applicability of quasi-droplet model (for which inequality (1.19) is fulfilled), contribution  $w_{el}$  is an increasing function of aggregation number  $n$ . In this case, contribution  $w_{el}$  increases more rapidly than for the analogous contribution in the droplet model [9] due to the negative value of parameter  $\alpha$  in Eq. (2.10).

By the derivation procedure, contribution  $w_{el}$  accounts for the change in the characteristics of molecular aggregate (more specific, its radius  $r$ ) on the attachment of new molecule to the aggregate. Let us take into account contributions  $-w_C$  and  $w_L$ , as well as  $c^\alpha$ -dependent concentration contribution given by the last term in the right-hand side of Eq. (2.2). The last contribution is denoted by  $w_{conc}$ . According to Eq. (2.2)

$$w_{conc} = kT \ln(c^\alpha/c_1). \quad (2.13)$$

Chemical potentials of surfactant molecular aggregate and relevant contributions refined to the change in characteristics of molecular aggregate are denoted by the bar above the corresponding symbol.

It follows from above that

$$\bar{w}_{el} = w_{el}. \quad (2.14)$$

As is seen from Eq. (1.6), when the next molecule is attached, the number  $\Delta n_C$  of hydrocarbon groups (entering into the aggregate core) of the hydrophobic portion of each molecule constituting aggregate increases. According to Eq. (1.3), the  $\Delta v_C$  volume of the fragments of the hydrophobic portions of surfactant molecules forming the hydrocarbon core also increases. As increase in number  $\Delta n_C$  gives rise to the energy gain from the transfer of the corresponding frag-

ment of the hydrophobic portion of surfactant molecules to the aggregate hydrocarbon core. Extending formula (2.4), we can write

$$-\bar{w}_C = -w_1 \left( \Delta n_C + n \frac{\partial \Delta n_C}{\partial n} \right). \quad (2.15)$$

Factor  $n$  in front of derivative with respect to  $n$  suggests that all  $n$  molecules in the molecular aggregate participate in the formation of chemical potential in this aggregate. From Eq. (2.15) with allowance for Eqs. (1.6) and (2.5), we obtain

$$-\bar{w}_C = -\frac{3}{2} a n^{1/2} + w_1. \quad (2.16)$$

The contribution similar to  $\bar{w}_C$  is independent of aggregation number in the droplet model of molecular aggregate; however, in the quasi-droplet model, the contribution  $\bar{w}_C$  increases with  $n$  according to Eq. (2.16). In this case, it can be shown that contribution  $\bar{w}_C$  in the lower part of the range of permissible values of aggregation numbers determined by inequalities (1.14) is smaller than similar contribution for the droplet model [9]; on the contrary, it is larger in the upper part.

During the attachment of a new molecule to the aggregate, an increase in volume  $\Delta v_C$  of all second fragments of the hydrophobic portions of molecules constituting the aggregate hydrocarbon core tends to increase the work consumed for overcoming the Laplace pressure difference on the surface of hydrocarbon core. Contribution  $\bar{w}_L$  that takes into account this effect we determine by the formula generalizing Eq. (2.7)

$$\bar{w}_L = \frac{2\gamma_0}{r_\alpha} \left( \Delta v_C + n \frac{\partial \Delta v_C}{\partial n} \right). \quad (2.17)$$

Hence, combining Eqs. (1.2), (1.3), and (1.6), we arrive at

$$\bar{w}_L = \gamma_0 (d + d_{H_2O})^2. \quad (2.18)$$

The values of accounted changes in the characteristics of molecular aggregate occurring during the attachment of the new molecule to the aggregate can be estimated comparing Eqs. (2.5), (2.16) and (2.8), (2.18), respectively. As follows from Eq. (2.18), contribution  $\bar{w}_L$  to the molecular chemical potential  $\bar{\mu}^\alpha$  is independent of aggregation number. This circumstance distinguishes the quasi-droplet model from the droplet model [9] where similar contribution is inversely proportional to the square root of  $n$ .

Molecular concentration  $c^\alpha$  in the standard expression (2.1) in the case of discussed model is estimated as the concentration of the second fragments of the hydrophobic portions of surfactant molecules constituting hydrocarbon core of molecular aggregate. According to Eq. (1.3), at suggested dense core packing, concentration  $c^\alpha$  is then estimated by relation

$$c^\alpha = [v_1(\Delta n_C + 1)]^{-1} \quad (2.19)$$

and, as follows from Eq. (1.6), depends on the aggregation number  $n$ :

$$c^\alpha = gn^{-1/2}, \quad (2.20)$$

where

$$g = \frac{6\pi^{1/2}}{(d + d_{H_2O})^3}. \quad (2.21)$$

The dependence of concentration  $c^\alpha$  on the aggregation number  $n$  (that was absent in the droplet model) necessitates the refinement of contribution (2.13) related to concentration  $c^\alpha$ . Performing this refinement, accounting for Eq. (2.20), and acting by analogy with Eqs. (2.15) and (2.17), we obtain

$$\begin{aligned} \bar{w}_{\text{conc}} &= kT \left[ \ln(c^\alpha/c_1) + n \frac{\partial \ln(c^\alpha/c_1)}{\partial n} \right] \\ &= kT [\ln(g/n^{1/2}c_1) - 1/2]. \end{aligned} \quad (2.22)$$

For the dilute solutions,  $c^\alpha/c_1$  ratio is fairly large (about  $10^5$ ); Although expressions (2.19) and (2.20) for  $c^\alpha$  are rough estimates, these values lead to virtually exact expressions for  $\ln(c^\alpha/c_1)$ , which have been actually used in Eq. (2.22).

Using general relation (2.2), we represent now the desired chemical potential  $\bar{\mu}^\alpha$  of surfactant molecules in the molecular aggregate in the following form:

$$\bar{\mu}^\alpha = \mu^\beta - \bar{w}_C + \bar{w}_L - \gamma_0 a_0 + \bar{w}_{\text{el}} + \bar{w}_{\text{conc}}. \quad (2.23)$$

With allowance for Eqs. (2.10), (2.14), (2.16), (2.18), and (2.22), formula (2.23) determines chemical potential  $\bar{\mu}^\alpha$  as the explicit function of aggregation number  $n$  and the main parameters of surfactant molecules and solution.

### 3. STATIONARY POINTS ON THE MOLECULAR AGGREGATE SIZE DISTRIBUTION CURVE. THE WORK OF MOLECULAR AGGREGATE FORMATION

At a given solution state ( $\mu^\beta$  and  $c_1$  values are constant), the dependence of  $\bar{\mu}^\alpha$  on the aggregation number  $n$  is realized according to Eq. (2.23) via  $\bar{w}_C$ ,  $\bar{w}_{\text{el}}$ , and  $\bar{w}_{\text{conc}}$  values ( $\bar{w}_L$  and  $\gamma_0 a_0$  are independent of  $n$ ). Then, from Eq. (2.23) we obtain

$$\frac{\partial \bar{\mu}^\alpha}{\partial n} = -\frac{\partial \bar{\mu}_C}{\partial n} + \frac{\partial \bar{\mu}_{\text{el}}}{\partial n} + \frac{\partial \bar{\mu}_{\text{conc}}}{\partial n}. \quad (3.1)$$

In order not to deal with the fractional powers during the analysis of the dependence of  $\bar{\mu}^\alpha$  on the aggregation number  $n$ , in the quasi-droplet model it seems con-

venient to pass from the derivatives with respect to aggregation number  $n$  to the derivatives with respect to variable  $y \equiv n^{1/2}$ . Taking into account Eqs. (2.10), (2.14), (2.16), and (2.22), instead of Eq. (3.1) we write

$$\frac{\partial \bar{\mu}^\alpha}{\partial y} = -\frac{3}{2}a - \frac{kT}{y} + \frac{4b_{\text{el}}}{m_2} y \left( 1 - \alpha y \frac{15m_1}{4m_2} \right). \quad (3.2)$$

After the second differentiation, we obtain

$$\frac{\partial^2 \bar{\mu}^\alpha}{\partial y^2} = \frac{kT}{y^2} + \frac{4b_{\text{el}}}{m_2} \left( 1 - \alpha y \frac{15m_1}{2m_2} \right). \quad (3.3)$$

Because  $\alpha < 0$ , the right-hand side of relation (3.3) is larger than zero in the region of positive  $y$  values. Consequently, the dependence of  $\bar{\mu}^\alpha$  on  $y$  is concave in this region.

Let us consider the problem of the presence of stationary points on this dependence. Equating the right-hand side of Eq. (3.2) to zero, we arrive at the third-degree algebraic equation with respect to  $y$

$$\frac{3}{2}a + \frac{kT}{y} = \frac{4b_{\text{el}}}{m_2} y \left( 1 - \alpha y \frac{15m_1}{4m_2} \right). \quad (3.4)$$

At  $y > 0$ , the left-hand side of Eq. (3.4) decreases monotonically with an increase in  $y$ , whereas the right-hand side (recall that  $\alpha < 0$ ) increases monotonically. Hence, Eq. (3.4) has only one positive root, as it could be on the concavity of the dependence of  $\bar{\mu}^\alpha$  on  $y$ . We denote this root by  $y_0$ . According to what have been said above, the minimum of chemical potential  $\bar{\mu}^\alpha$  corresponds to root  $y_0$  and, hence, to the aggregation number  $n_0 \equiv y_0^2$ . Let us emphasize that, as is seen from Eq. (3.4), the value of root  $n_0 \equiv y_0^2$  is independent of solution concentration  $c_1$ . Equation (3.4) can be solved numerically very easy. Necessary condition of the applicability of quasi-droplet model at the concrete values of parameters of Eq. (3.4) is the fulfillment of double inequality (1.14) at  $n = n_0$ .

Let us denote the minimal  $\bar{\mu}^\alpha$  value by  $\bar{\mu}_{\text{min}}^\alpha$ . Then we have

$$\bar{\mu}_{\text{min}}^\alpha = \bar{\mu}^\alpha|_{n=n_0}. \quad (3.5)$$

The condition of phase equilibrium

$$\mu^\beta = \bar{\mu}^\alpha \quad (3.6)$$

corresponds to the stationary points (extrema) on the size aggregate distribution curve. Using Eqs. (2.10), (2.14), (2.16), and (2.22) in Eq. (2.23), we obtain

$$\begin{aligned} \bar{\mu}^\alpha - \mu^\beta &= -\frac{3a}{2}n^{1/2} + A + \frac{2nb_{\text{el}}}{m_2} \left( 1 - \alpha n^{1/2} \frac{5m_1}{2m_2} \right) \\ &\quad - \frac{kT}{2} \ln n - kT \ln c_1, \end{aligned} \quad (3.7)$$

where the designation

$$A = \bar{w}_L - \gamma_0 a_0 + w_1 + kT(\ln g - 1/2) \quad (3.8)$$

is introduced for the parameter independent of  $n$ ,  $n_C$ , and  $c_1$ . Using Eq. (3.7), we write the condition of phase equilibrium (3.6) in the form

$$\frac{3}{2}an^{1/2} + \frac{kT}{2}\ln n - b_{el}\frac{2n}{m_2}\left(1 - \alpha n^{1/2}\frac{5m_1}{2m_2}\right) = A - kT\ln c_1. \quad (3.9)$$

The  $\mu^\beta$  value is determined by the concentration of surfactant solution. When  $\mu^\beta < \bar{\mu}_{\min}^\alpha$  (premicellar concentration range), the existence of extrema and, hence, the appearance of micelles is impossible. Equation (3.9) has no solutions in a premicellar concentration range. It is evident that, according to Eq. (3.5), at the solution concentration ensuring equality  $\mu^\beta = \bar{\mu}_{\min}^\alpha$  and denoted by  $c_{10}$ , the root of Eq. (3.9) will be equal to  $n_0$ . In turn, substituting the  $n_0$  values into the left-hand side of Eq. (3.9) instead of desired root  $n$  [found from (3.4)], we transform Eq. (3.9) into the formula for determining concentration  $c_{10}$

$$\ln c_{10} = \frac{A}{kT} - \frac{3an_0^{1/2}}{2kT} - \frac{1}{2}\ln n_0 + \frac{b_{el}2n_0}{kT m_2}\left(1 - \alpha n_0^{1/2}\frac{5m_1}{2m_2}\right). \quad (3.10)$$

It is evident that, as  $n_0$  and  $A$ ,  $c_{10}$  is independent of  $c_1$ . By its meaning, concentration  $c_{10}$  is close to the CMC, albeit smaller than this value.

Let us study the dependence of concentration  $c_{10}$  on the main parameters of surfactant molecules using relation (3.10). We estimate preliminarily the characteristic values of the parameters of the theory. When calculating, we assume temperature  $T$  of micellar solution as equal to  $T_0 = 298$  K. From Eqs. (2.6) and (1.13) at the indicated in Section 2 value of work  $w_1 = 1.39kT_0$ , we obtain for coefficient  $a$

$$a \approx 2.78kT_0. \quad (3.11)$$

Substituting the values of known constants into the definition (2.11) of coefficient  $b_{el}$  and taking  $l_1 = 1.265 \text{ \AA}$ , we write

$$b_{el} = 225 \frac{z^2 \delta}{\epsilon l_1 (n_C + 1)^2} kT_0. \quad (3.12)$$

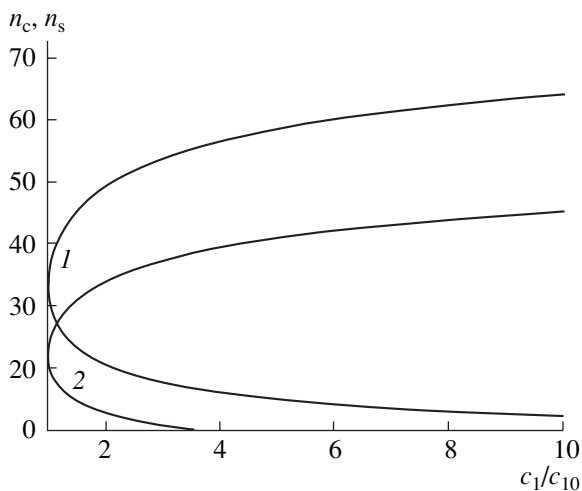
Let us assume  $\epsilon = 40$  [7] and the charge multiplicity  $z$  we take as equal to 2. We perform calculations for the five values of the number of carbon atoms  $n_C$  in the hydrocarbon chain of the hydrophobic portion of surfactant molecule taken from the  $14 \leq n_C \leq 18$  range and for the three values of length  $\delta$  of the dipole of molecule hydrophilic portion (2, 3, and 4  $\text{\AA}$ ). We assume

Values of aggregation numbers  $n_0$  (the upper value in each cell) and  $\ln c_{10} - A/kT_0$  difference (lower value in each cell) at the typical values of number  $n_C$  and length  $\delta$

$n_C \backslash \delta$	2 $\text{\AA}$	3 $\text{\AA}$	4 $\text{\AA}$
14	39.6 -15.3	21.9 -11.3	14.6 -9.1
15	49.3 -17.0	27.2 -12.6	18.0 -10.2
16	60.7 -18.9	33.4 -13.9	22.1 -11.3
17	73.9 -20.8	40.6 -15.3	26.7 -12.4
18	89.0 -22.8	48.8 -16.8	32.3 -13.6

distance  $\Delta r$  in definition (2.12) of parameters  $m_1$  and  $m_2$  as equal to zero.

Table lists the values of aggregation number  $n_0$  (the upper value in each cell) obtained by the numerical solution of Eq. (3.4) with allowance for Eq. (1.8) and the values of  $\ln c_{10} - A/kT_0$  difference (the lower value in each cell) calculated from formula (3.10). The  $n_0$  values are shown for the control of the conditions of applicability of the discussed model. In addition, the  $n_0$  value gives an estimate of the micelle aggregation number. Data of the table demonstrate that all indicated  $n_0$  values satisfy double inequality (1.14). However, if the calculations were performed for  $z = 1$ , all calculated  $n_0$  values would be larger than the limiting aggregation numbers admissible according to Eq. (1.14). As is also seen from the table, the negative  $\ln c_{10} - A/kT_0$  value ( $A$  is independent of  $n_0$  and  $n_C$ ) increases with the length  $\delta$  of the dipole of hydrophilic portion. The law of a decrease of  $\ln c_{10} - A/kT_0$  value with an increase in the  $n_C$  number is close to linear. Hence, the law of a decrease of the logarithm of concentration  $c_{10}$  with an increase in the  $n_C$  number is also close to linear. Moreover, the absolute value of the coefficient of angular dependence decreases with an increase in the dipole length  $\delta$ . At  $\delta = 2 \text{ \AA}$ , it is equal approximately to 1.9 and at  $\delta = 4 \text{ \AA}$ , approximately to 1.1. When recalculated into decimal logarithms, the absolute values of the coefficient of angular dependence are approximately equal to 0.8 and 0.5, respectively. The absolute values of this coefficient observed for the solutions of surfactants with the dipole hydrophilic portions are also fit the indicated range [7]. A decrease in the absolute values of the coefficients of angular dependence with an increase in the dipole length of hydrophilic portion seems to be natural, because in this case the surfactant with the dipole hydrophilic portion becomes similar to the ionic surfactants for which the lower absolute values of angu-



**Fig. 2.** Dependences of the  $n_c$  and  $n_s$  roots on concentration  $c_1$  taken in  $c_{10}$  units. Curve 1 corresponds to  $\delta = 3 \text{ \AA}$ , curve 2, to  $\delta = 4 \text{ \AA}$ .

lar coefficients are observed in the discussed dependence.

The following useful observation can also be made from the performed calculations. At the used values of the main parameters of surfactant molecules, the  $b_{el}/kT_0$  coefficient varies approximately from 0.10 at  $n_C = 18$  and  $\delta = 2 \text{ \AA}$  to 0.32 at  $n_C = 14$  and  $\delta = 4 \text{ \AA}$ ; the absolute value of parameter  $\alpha$  was no larger than 0.01 and the  $m_1$  and  $m_2$  values slightly exceeded unity. Let us take into account estimate (3.11) and the fact that, according to Eq. (1.14) and  $y = n^{1/2}$ , of interest are only the solutions of  $y_0$  of Eq. (3.4) satisfying inequality  $y_0 \geq (n_C + 1)/2$ . Analyzing the characteristic values of the terms of Eq. (3.4), we conclude that the second term in its left-hand side has the form of correction and can be omitted. In this case, Eq. (3.4) is transformed into quadratic equation. The root of Eq. (3.4) (which is of interest to us) is found from relation

$$y_0 \approx \frac{2m_2}{15\alpha m_1} - \left[ \left( \frac{2m_2}{15\alpha m_1} \right)^2 - \frac{am_2^2}{10\alpha b_{el}m_1} \right]^{1/2}. \quad (3.13)$$

The  $n_0$  values calculated with the aid of Eq. (3.13) are well consistent with those listed in the table.

As concentration  $c_1$  exceeds  $c_{10}$  value, when inequality  $\mu^\beta > \bar{\mu}_{\min}^\alpha$  is already fulfilled, Eq. (3.9) will have two roots due to the concavity of the dependences of  $\bar{\mu}^\alpha$  on  $y$  and  $n$  (the latter dependence followed from the former at not so long a distance of aggregation number  $n$  from  $n_0$ ). In this case, the condition that both roots satisfy double inequality (1.14) acts as a necessary condition of the applicability of quasi-droplet model. The larger root is denoted by  $n_s$ . It corresponds to relatively stable molecular aggregates (micelles). The smaller root denoted by  $n_c$  corresponds to the aggregates that

are in unstable equilibrium with the solution. This root has the meaning of the number of molecules of critical nucleus in the theory of nucleation (in this case, critical nucleus of a micelle).

In the general case, at  $c_1 > c_{10}$ , the roots of Eq. (3.9) are calculated numerically. If concentration  $c_1$  is measured in units of  $c_{10}$  concentration, then, in view of Eq. (3.10), Eq. (3.9) for the desired roots acquires more convenient (albeit more cumbersome) form

$$\frac{3}{2}a(n^{1/2} - n_0^{1/2}) + \frac{kT}{2} \ln \frac{n}{n_0} - \frac{2b_{el}}{m_2} \left[ n \left( 1 - \alpha n^{1/2} \frac{5m_1}{2m_2} \right) - n_0 \left( 1 - \alpha n_0^{1/2} \frac{5m_1}{2m_2} \right) \right] = -kT \ln \frac{c_1}{c_{10}}. \quad (3.14)$$

Curves in Fig. 2 illustrate the dependences of the  $n_c$  and  $n_s$  roots on the  $c_{10}$  concentration expressed in  $c_1$  units. The curves were obtained by the numerical calculation of Eq. (3.14) at  $n_C = 16$  and two values of parameter  $\delta$  (3 and 4  $\text{\AA}$ ). The other parameters needed for the calculations are taken the same as for constructing the table. Each of the curves contacts the vertical axis in the corresponding point  $n_0$ , which divides the curve into two branches. The upper branch corresponds to root  $n_s$ , the lower curve, to root  $n_c$ . According to calculations, at  $\delta = 2 \text{ \AA}$ , root  $n_s$  ceases to satisfy the upper of constraints (1.14) at a fairly low excess of concentration  $c_1$  over  $c_{10}$ .

Main principles of the development of the formation work of surfactant molecule aggregate used in [9] remain true also in the case of quasi-droplet model of molecular aggregate under consideration. According to [9], for work  $W_n$  of the aggregate formation from  $n$  molecules we write

$$W_n = \int_1^n (\bar{\mu}^\alpha - \mu^\beta) dn. \quad (3.15)$$

Expressing parameter  $A$  in Eq. (3.7) with the use of Eq. (3.10), substituting the result into Eq. (3.15), and integrating with respect to  $n$  at  $n \gg 1$ , we find for the desired work  $W_n$  the following relation:

$$W_n = -an^{3/2} + \frac{b_{el}n^2}{m_2} \left( 1 - \alpha n^{1/2} \frac{2m_1}{m_2} \right) - \frac{kT}{2} \times n(\ln n - 1) + n \left[ \frac{3}{2}an_0^{1/2} - \frac{2b_{el}n_0}{m_2} \right] \times \left( 1 - \alpha n_0^{1/2} \frac{5m_1}{2m_2} \right) + \frac{kT}{2} \ln n_0 - nkT \ln \frac{c_1}{c_{10}}. \quad (3.16)$$

From Eqs. (3.15), (3.2), (3.4), and at  $y = n^{1/2}$ , we obtain

$$(\partial^2 W_n / \partial n^2)_{n=n_0} = 0, \quad (3.17)$$



so that  $n_0$  is the inflection point of work  $W_n$ . According to the aforementioned remarks, point  $n = n_0$  is independent of solution concentration  $c_1$ .

At  $c_1 < c_{10}$ , work  $W_n$  rises monotonically with  $n$  that means the absence of relatively stable aggregates in the solutions of such surfactant concentration. At  $c_1 = c_{10}$ , the appearance of local maximum and minimum of work  $W_n$  in its inflection point  $n = n_0$  is observed. Taking into account that steady-state conditions  $\partial W_n / \partial n = 0$  of work  $W_n$  in the local maximum and minimum (merged in the point  $n = n_0$ ) are simultaneously fulfilled at  $c_1 = c_{10}$ , we obtain

$$(\partial W_n / \partial n)_{c_1 = c_{10}, n = n_0} = 0. \quad (3.18)$$

At  $c_1 > c_{10}$ , work  $W_n$  is characterized by the local maximum in point  $n_c$  and the local minimum in point  $n_s$  corresponding to micelles. As  $c_1$  increases, the  $n_c$  and  $n_s$  points are withdrawn correspondingly to the left and right of point  $n_0$  that is independent of  $c_1$ . All what have been said above is illustrated by Fig. 3 where work  $W_n$  is represented in units of thermal energy  $kT$  ( $T = T_0$ ). Curves in Fig. 3 are plotted at  $n_c = 16$  and  $\delta = 3 \text{ \AA}$ . The curves refer to the ratio  $c_1/c_{10}$  values equal to 0.5, 1, and 3, respectively. The other parameters needed for the calculations are taken the same as when constructing the table.

According to Eq. (3.16), we have

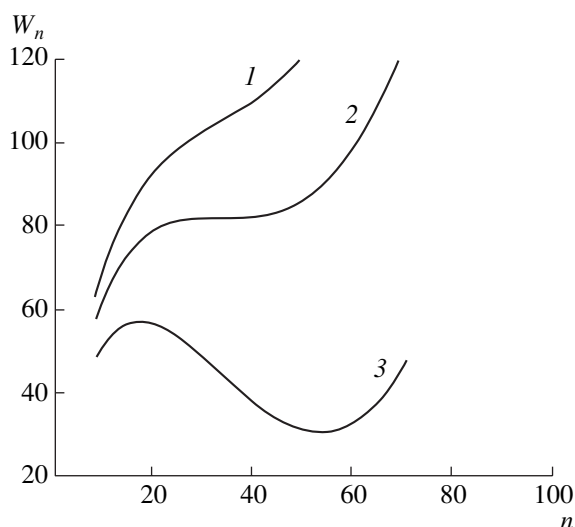
$$\partial W_n / \partial c_1 = -nkT/c_1. \quad (3.19)$$

Recall that  $c_{10}$  is independent of  $c_1$ . Although  $n_c$  and  $n_s$  depend on  $c_1$ , however, due to steady-state conditions  $(\partial W_n / \partial n)_{n = n_c} = 0$  and  $(\partial W_n / \partial n)_{n = n_s} = 0$  of work  $W_n$  in the  $n = n_c$  and  $n = n_s$  points of its local maximum and minimum, conditions  $\partial W_{n_c} / \partial c_1 = (\partial W_n / \partial c_1)_{n = n_c}$  and  $\partial W_{n_s} / \partial c_1 = (\partial W_n / \partial c_1)_{n = n_s}$  are true. Then, it follows from Eq. (3.19)

$$\partial W_{n_c} / \partial c_1 = -n_c kT / c_1, \quad \partial W_{n_s} / \partial c_1 = -n_s kT / c_1. \quad (3.20)$$

Because  $n_c < n_s$ , the local maximum  $W_{n_c}$  of work  $W_n$  decreases slower than the local minimum  $W_{n_s}$  of work  $W_n$  with an increase in concentration  $c_1$ .

Let us consider the approximation of work  $W_{n_c}$  allowing for the analytical study at the construction of which we omit, according to constraint (1.19), the terms proportional to parameter  $\alpha$  and let  $\ln n = \ln n_0$  (in agreement with the suggested not so large distance of aggregation number  $n$  from  $n_0$ ). Then, repeating the derivation of Eq. (3.16) with allowance for aforementioned simplifications, we obtain the equation



**Fig. 3.** Dependences of work  $W_n$  on the aggregation number  $n$  at  $c_1/c_{10}$ : (1) 0.5, (2) 1.0, and (3) 3.0;  $n_c = 16$ ,  $\delta = 3 \text{ \AA}$ . Work  $W_n$  is expressed in  $kT_0$  units.

$$W_n = -an^{3/2} + \frac{b_{el}n^2}{m_2} + n \left( \frac{3a}{2} n_0^{1/2} - \frac{2b_{el}n_0}{m_2} - kT \ln \frac{c_1}{c_{10}} \right). \quad (3.21)$$

This equation, as Eq. (3.16), is consistent with Eq. (3.18). From Eqs. (3.17) and (3.21), follows the relation

$$n_0 = (3am_2/8b_{el})^2, \quad (3.22)$$

that could be derived from Eq. (3.13) at  $\alpha \rightarrow 0$ . Substituting Eq. (3.22) into Eqs. (3.21) and (3.10), we correspondingly obtain

$$W_n = -an^{3/2} + \frac{b_{el}n^2}{m_2} + n \left( \frac{9a^2m_2}{32b_{el}} - kT \ln \frac{c_1}{c_{10}} \right), \quad (3.23)$$

$$\ln c_{10} = \frac{A}{kT} - \frac{9a^2m_2}{32kTb_{el}} - \ln \frac{3am_2}{8b_{el}}. \quad (3.24)$$

For the roots of equation  $\partial W_n / \partial n = 0$  determining the  $n_c$  and  $n_s$  aggregation numbers at which work  $W_n$  is characterized by the local maximum and minimum, using Eq. (3.23), we find

$$n_c = \left[ \frac{3am_2}{8b_{el}} - \left( \frac{kTm_2}{2b_{el}} \ln \frac{c_1}{c_{10}} \right)^{1/2} \right]^2, \quad (3.25)$$

$$n_s = \left[ \frac{3am_2}{8b_{el}} + \left( \frac{kTm_2}{2b_{el}} \ln \frac{c_1}{c_{10}} \right)^{1/2} \right]^2.$$

According to Eq. (3.22), at  $c_1/c_{10} = 1$ , the  $n_c$  and  $n_s$  roots naturally coincide with  $n_0$ . As inequality  $c_1 > c_{10}$  becomes stronger, the  $n_c$  and  $n_s$  roots deviate to the left and right of  $n_0$ . However, when  $c_1$  is not so large as  $c_{10}$ , the  $n_c$  root has the positive value.

Note in conclusion that the dependence of work  $W_n$  on the aggregation number  $n$  obtained in the droplet model of surfactant molecular aggregate also possesses all features typical of the micellization process [9]. Differences of the contributions to the chemical potential of surfactant molecules in the molecular aggregate mentioned in Section 2 for the quasi-droplet and droplet models result in the differences of the behavior of work  $W_n$  as a function of aggregation number. In particular, it turned out that, at the identical values of  $c_1/c_{10}$  ratio and other equal conditions, the local maximum of work  $W_n$  in the quasi-droplet model is achieved at larger values, and local minimum, at smaller values of aggregation number than in the droplet model. Significant formal difference between the approximate relation (3.23) and similar relation in the droplet model [9] is in the fact that the work of molecular aggregate formation is represented in [9] as the expansion in powers of cubic root of aggregation number  $n$ , whereas in Eq. (3.23) the expansion is performed in powers of quadratic root of aggregation number. The latter can be considered as the reflection of almost two-dimensional structure of surfactant molecular aggregate in the quasi-droplet model, the structure similar to rolled surfactant monolayer. Comparison of the predictions of both models and the experimental data should demonstrate which of these models and in which cases more fully accounts for the properties of real micellar solutions.

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