

# Thermodynamic Characteristics of Micellization in the Droplet Model of Surfactant Spherical Molecular Aggregate

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**Abstract**—The dependence of the work of the 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 on the basis of a simple realistic droplet model of spherical aggregate composed of surfactant molecules (the o/w micelle type). Analytical formulas were 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 were performed for premicellar and micellar regions of aggregate sizes within a wide range of solution concentration including the critical micellization concentration.

## INTRODUCTION

Treatment of thermodynamic and kinetic foundations of the theory of micellization in surfactant-containing solution conducted in [1–5] was based on the methods of the theory of nucleation and presupposed the knowledge of the formation work of an aggregate from the surfactant molecules as a function of aggregation number (the number of surfactant molecules in aggregate) and surfactant monomer concentration in solution.

The aggregates composed of surfactant molecules in micellar solution including relatively stable micelles are limited by the number of constituent molecules and have such a structure that they cannot be considered as small parts of macroscopic phase. This fact extremely complicates the study of the thermodynamics of molecular aggregates compared with the theory of nucleation and forces one to apply the model representations of their structure and contributions to the work of their formation. One of the widely recognized model of surfactant molecular aggregate is the droplet model of an aggregate with a liquidlike core formed by the hydrophobic fragments of surfactant molecules proposed by Tanford [6] and developed later in [7–14]. Precisely this model will be used as a basis for finding thermodynamic characteristics of the kinetics of micellization. This model allows us to arrive at a rather simple analytical expression for the work of spherical aggregate formation as a function of aggregation number and solution concentration.

Naturally, one cannot expect immediate quantitative agreement between the experimental data (e.g., for relaxation times) and the predictions of the theory based on model representations. As a rule, there is also

no such an agreement in the applications of the theory of nucleation to much simpler than micellar solution systems. Nevertheless, it is the use of the apparatus of the theory of nucleation that could be productive in the case of micellar solutions. Experimental data on the relaxation of micellar solutions of surfactants of the same type obtained with the wide-range variation of some molecular property, for example, the size of the hydrophobic portion of a molecule, provide a comprehensive information for improving model representations on the structure of molecular aggregates and for reaching better agreement between the theory and experiment.

Let us mention main new data, which are to be presented in this paper with the account of the results of previous studies of micellization. The dependence of the work of aggregate formation on the aggregation number and solution concentration characterized by the three physically clear parameters will be determined within the framework of the droplet model of surfactant spherical molecular aggregate. Analytical formulas for the coordinates (at the aggregation number axis) of the maximum and minimum of the work of aggregate formation arising with an increase in micellar solution concentration will be derived. Using these formulas that allow us to determine the values of work maximum and minimum, as well as the half-widths of potential maximum and potential well of the work at the aggregation number axis, we perform the model calculations of the thermodynamic characteristics of the kinetics of micellization within the wide range of solution concentrations including the critical micellization concentration (CMC). In this case, the CMC determined from the

critical degree of micellization will be expressed via the initial parameters of the droplet model.

Quantitative data on the molecular aggregates in premicellar region of their sizes obtained in model calculations are of prime importance. It is these aggregates, whose formation work is the largest and, vice versa, the concentration is the lowest, that play the key role in the relaxation processes of micellization [15, 16].

Below we confine ourselves only to the consideration of spherical aggregates of the o/w micelle type. It is necessary to impose rather strict constraints on the values of the initial parameters of a model in order for the maximum and minimum of the formation work of aggregate to fit the realistic region of aggregation numbers compatible with the conditions of the applicability of the droplet model of spherical molecular aggregate. These constraints will be controlled throughout the paper.

For definiteness, we deal with a typical case of aqueous solution of the molecules of nonionic or zwitterionic surfactants having the dipole hydrophilic parts and hydrophobic fragments in the form of linear hydrocarbon radicals.

## 1. GEOMETRIC PARAMETERS OF SURFACTANT MOLECULES AND HYDROCARBON CORE

Let us consider aqueous surfactant solution. The number of carbon atoms in a hydrocarbon chain of surfactant molecule is denoted by  $n_C$ . The end methyl group has the characteristic volume  $v_0$  and methylene group,  $v$ . According to published data [6], at the solution absolute temperature  $T = 293$  K, we have  $v_0 \approx 54.3 \text{ \AA}^3$  and  $v \approx 26.9 \text{ \AA}^3$ . Hereafter we assume that  $v_0/v \approx 2$ . The aggregation number is denoted by  $n$ .

In the studied droplet model of spherical molecular aggregate, it is accepted that the total number  $nn_C$  of hydrocarbon segments of all  $n$  surfactant molecules constituting molecular aggregate is packed inside the spherical surface in a compact manner (with no voids). Then, considering volume balance, we have for the radius  $r$  of this surface

$$r = \left[ \frac{3v(n_C + 1)}{4\pi} \right]^{1/3} n^{1/3}, \quad (1.1)$$

where the approximate equality

$$v_0 + v(n_C - 1) \approx v(n_C + 1), \quad (1.2)$$

is taken into account. This equality is valid in view of  $v_0/v_2 \approx 2$ . At  $n_C \gg 1$ , expression (1.1) remains valid also in the case of slight deviation of hydrocarbon chains from their complete insertion inside the sphere of radius  $r$ .

Introducing designation

$$\lambda \equiv \left[ \frac{3v(n_C + 1)}{4\pi} \right]^{1/3}, \quad (1.3)$$

we write Eq. (1.1) as

$$r = \lambda n^{1/3}, \quad (1.4)$$

where parameter  $\lambda$  independent of aggregation number  $n$  is the radius of imagined sphere that is equivalent to the volume of one hydrocarbon chain of surfactant molecule.

The inner contents of a sphere of radius  $r$  occupied completely by hydrocarbon groups of all surfactant molecules  $n$  in a molecular aggregate is taken as a "hydrocarbon core." Let us emphasize that the hydrocarbon core does not contain protruding hydrophilic parts of surfactant molecules.

According to Eq. (1.1), as the aggregation number  $n$  increases, the radius  $r$  increases also. Since the hydrophilic parts of surfactant molecules in an aggregate are located outside the sphere of radius  $r$  and the droplet model does not suggest the existence of cavity inside the molecular aggregate, the hydrocarbon chains of surfactant molecules in aggregate become less curved with an increase in  $n$ . Denoting the length of completely expanded hydrocarbon chain of surfactant molecule by  $l_C$ , for which according to [6, 7] we have

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

we obtain the following condition:

$$r \leq l_C. \quad (1.6)$$

Using Eqs. (1.1) and (1.5) and taking into account the aforementioned equality  $v = 26.9 \text{ \AA}^3$ , we present condition (1.6) in the form of constraint

$$n < 0.3(n_C + 1)^2, \quad (1.7)$$

which gives the upper bound of the aggregation number  $n$  in the droplet model of surfactant spherical molecular aggregate. The stronger the inequality  $n_C \gg 1$ , the weaker constraint (1.7). At a sufficiently large value of  $n_C$ , constraint (1.7) is quite compatible with the constraint  $n \gg 1$ , which is required for the applicability of asymptotic (with respect to  $n$ ) thermodynamic and kinetic theories of micellization.

## 2. CONTRIBUTIONS TO THE WORK OF MOLECULAR AGGREGATE FORMATION

According to [1–5], the formation work of molecular aggregate with aggregation number  $n$  is denoted by  $W_n$ ; the chemical potential of surfactant molecules in aggregate, by  $\mu_{1n}$ . The chemical potential of surfactant monomers in micellar solution is denoted by  $\mu_1$ . All the values having energy dimensionality are expressed in thermal energy units  $kT$ , where  $k$  is Boltzmann's con-

stant and  $T$  is the solution temperature. Significant role is played by thermodynamic relationship [17]

$$\partial W_n / \partial n = \mu_{1n} - \mu_1, \quad (2.1)$$

which is valid at the thermal and mechanical balance between the molecular aggregate and solution.

From evident condition  $W_1 = 0$  (the production of monomers does not require any work, because they are already present in a solution) and Eq. (2.1), we immediately obtain

$$W_n = \int_1^n (\mu_{1n} - \mu_1) dn. \quad (2.2)$$

We also use standard expression for the chemical potential of a molecule in an arbitrary medium

$$\mu = \mu^0 + w + \ln(c\Lambda^3), \quad (2.3)$$

where  $\mu^0$  is the chemical potential of a molecule with a fixed center of mass in vacuum,  $w$  is the work of transfer of a molecule from the fixed position in vacuum to the fixed position in a medium with concentration  $c$  (the number of molecules per unit volume), and  $\Lambda$  is the de Broglie mean wavelength of a molecule. Expression (2.3) is applicable to both  $\mu_{1n}$  and  $\mu_1$ ,  $\mu^0$  and  $\Lambda$ , being identical in both expressions. In the expressions for the chemical potential of a substance in condensed state with pressure  $p$ , term  $v_1 p$ , where  $v_1$  is the partial molar volume of a substance in a given phase, is usually identified. Therefore, for the chemical potential of surfactant in solution (let it be the  $\beta$ -phase) of concentration  $c_1$ , we can write

$$\mu_1 = \mu^0 + w_1 + v_1 p^\beta / kT + \ln(c_1 \Lambda^3), \quad (2.4)$$

where the work of transfer  $w_1$  is referred to zero-valued pressure. In view of the low compressibility of condensed media, the partial molar volume of a substance can be considered as constant and coinciding with the molecular volume. For the dilute solution, the dependence of  $\mu_1$  on  $c_1$  is given by the  $\ln(c_1 \Lambda^3)$  term; as a result, according to Eq. (2.4),  $w_1$  is independent of  $c_1$ .

The situation is more complicated when dealing with the chemical potential of surfactant molecule in molecular aggregate. The structure of molecular aggregate of o/w micelle type is such that the hydrocarbon tails of surfactant molecule are combined into a hydrocarbon core, while polar groups remain outside. Let us consider the inner part of molecular aggregate as the  $\alpha$ -phase. Let the dividing surface be drawn between the  $\alpha$ - and  $\beta$ -phases and use the concepts of thermodynamics of interfacial phenomena. In particular, if both phases are considered to be mechanically uniform up to the dividing surface, we should ascribe a certain surface tension  $\gamma$  to the latter. The position of surfactant mole-

cule in molecular aggregate is such that the dividing surface splits it into two parts with volumes  $v^\alpha$  and  $v^\beta$ :

$$v_1 = v^\alpha + v^\beta, \quad (2.5)$$

moreover, these parts turned out to be at different pressures ( $p^\alpha$  and  $p^\beta$ ). In addition, the molecule intersects the dividing surface (producing cross section  $a$ ) and appeared under the action of surface tension  $\gamma$ . Therefore, for the surfactant molecule in aggregate, we have the following expression:

$$\mu_{1n} = \mu^0 + w_{1n} + (v^\alpha p^\alpha + v^\beta p^\beta - \gamma a) / kT + \ln(c_{1n} \Lambda^3), \quad (2.6)$$

where  $c_{1n}$  is the concentration of surfactant monomers in molecular aggregate, work  $w_{1n}$  of the transfer to the aggregate is referred to zero-valued pressure, and term  $-\gamma a$  is substantiated in the thermodynamics of interfacial phenomena [17, p. 55]. Using Eq. (2.5), formula (2.4) can be rewritten in the form

$$\mu_1 = \mu^0 + w_1 + (v^\alpha p^\beta + v^\beta p^\alpha) / kT + \ln(c_1 \Lambda^3). \quad (2.7)$$

Pressures in the  $\alpha$ - and  $\beta$ -phases are interrelated by the condition of mechanical equilibrium (Laplace's equation)

$$p^\alpha - p^\beta = \frac{2\gamma}{r'}, \quad (2.8)$$

where  $r'$  is the radius of dividing surface. Then, from Eqs. (2.6)–(2.8) we have

$$\mu_{1n} - \mu_1 = w_{1n} - w_1 + 2\gamma v^\alpha / r' kT - \gamma a / kT + \ln(c_{1n} / c_1). \quad (2.9)$$

Substitution of Eq. (2.9) into Eq. (2.2) yields

$$W_n = \int_1^n (w_{1n} - w_1) dn + \int_1^n (2\gamma v^\alpha / r' kT) dn - \int_1^n (\gamma a / kT) dn + \int_1^n \ln(c_{1n} / c_1) dn. \quad (2.10)$$

When directly calculating integrals in Eq. (2.10), it is especially difficult to account for the interactions of polar groups that, in general, result in the  $W_n^p$  contribution to work  $W_n$ . It is more simple to immediately identify this contribution, then calculate it separately, and take all the integrals in Eq. (2.10) as if the interaction of polar groups is nonexistent. Then, surface tension  $\gamma$ , the radius of dividing surface  $r'$ , and limiting area  $a$  can be referred to the surface of hydrocarbon core ( $\gamma = \gamma_0$ ,  $r' = r$ ,  $a = (4\pi)^{1/3} (3v)^{2/3}$ ), and volume  $v^\alpha$  is identified with volume  $v_C$  of hydrocarbon chain constituting the hydro-

carbon core. With such an approach, expression (2.10) is written as

$$W_n = \int_1^n (w_{1n} - w_1) dn + \int_1^n (2\gamma_0 v_C / rkT) dn - \int_1^n (a\gamma_0 / kT) dn + \int_1^n \ln(c_{1n}/c_1) dn + W_n^p. \quad (2.11)$$

Evidently, difference  $w_{1n} - w_1$  is the work of transfer of surfactant molecule from the solution (the  $\beta$ -phase) to the molecular aggregate in the absence of pressure and surface tension. Considering the hydrocarbon core as the  $\alpha$ -phase, we express this work of transfer as  $w^{\beta\alpha}$  (the order of indices indicates the direction of transfer). For the dilute solution, work  $w^{\beta\alpha}$  does not depend on solution concentration. This follows already from the aforementioned absence of the dependence of work  $w_1$  on  $c_1$  for the dilute solution and also from the fact that, in principle, work  $w_{1n}$  is independent of  $c_1$ . If we denote the concentration of hydrocarbon tails in the  $\beta$ - and  $\alpha$ -phases by  $c^\beta$  and  $c^\alpha$ , respectively, then it is evident that  $c^\beta = c_1$ ; however, strictly speaking,  $c^\alpha \neq c_{1n}$  (the concentration of hydrocarbon chains in hydrocarbon core is not equal to that of molecules in aggregate). However, according to Eq. (1.1), at  $n_C \gg 1$  and  $n \gg 1$ , the radius  $r$  is so large that it exceeds manifold the thickness of hydrophilic layer of an aggregate and the distance of the separation from the surface of hydrocarbon core. Then,  $R \approx r$ , where  $R$  is the radius of spherical molecular aggregate; from  $c_{1n} = 3n/4\pi R^3$  and  $c^\alpha = 3n/4\pi r^3$  it follows that  $c_{1n} \approx c^\alpha$ . Because for the dilute solution  $c_{1n}/c_1 \sim 10^4 - 10^5$  and  $c^\alpha/c_1 \sim 10^4 - 10^5$ , equality  $\ln(c_{1n}/c_1) \approx \ln(c^\alpha/c_1)$  will be fulfilled with even more accuracy. Taking this equality and  $c^\alpha = \text{const}$  into account, we write Eq. (2.11), after calculating the integral in penultimate term at  $n \gg 1$ , as

$$W_n = \int_1^n w^{\beta\alpha} dn + \int_1^n (2\gamma_0 v_C / rkT) dn - \int_1^n (a\gamma_0 / kT) dn + n \ln(c^\alpha/c_1) + W_n^p. \quad (2.12)$$

There are other, in addition to  $W_n^p$ , contributions to  $W_n$  due to the work of transfer. Some of them are already known in the integral form, the others will be calculated by integrating (during the integration, it is admissible to ignore the lower limit, as was done in penultimate term in Eq. (2.12), because we deal with large  $n$ ).

Let us begin with the hydrophobic contribution to work  $W_n$  of the first term in the right-hand side of Eq. (2.12). For the work of transfer  $w^{\beta\alpha}$  (expressed in

$kT$  units) of the entire hydrophobic part of a single surfactant molecule containing  $n_C$  hydrocarbon groups from the surfactant solution to the hydrocarbon bulk phase through the flat surface, we have an empirical expression

$$w^{\beta\alpha} = -Bn_C, \quad (2.13)$$

which is valid at  $n_C \gg 1$  [13]. Here,  $B$  is positive and dimensionless constant. It is true that Eq. (2.13) does not refer to the zero-valued but rather to atmospheric (identical in both phases) pressure. However, this difference can be ignored due to infinitesimal compressibility of liquids. The positive value of constant  $B$  (i.e., the negative value of the right-hand side of Eq. (2.13)) denotes the hydrophobicity of hydrocarbon groups. According to empirical data [6, 7, 13], constant  $B$  is equal to approximately 1.4 at 20°C. The difference between the work of transfer of one or two segments of hydrocarbon chain nearest to polar group and that of end methyl group from the work  $-B$  does not virtually affect the applicability of expression (2.13) (linear with respect to  $n_C$ ) at  $n_C \gg 1$ . The fact that, in the accepted model of molecular aggregate, the hydrocarbon core is really not the infinite bulk phase but is surrounded by the surface with radius  $r \gg 1$  will be accounted for somewhat later. The integration of Eq. (2.13) in accordance with Eq. (2.12) yields, at  $n \gg 1$ , the desired hydrophobic contribution  $W_n^h$  to work  $W_n$  of the molecular aggregate formation

$$W_n^h = -nBn_C. \quad (2.14)$$

The negative value of  $W_n^h$  demonstrated by expression (2.14) (at  $B > 0$ ) facilitates the formation of molecular aggregates in micellar solution.

When packing into the spherical hydrocarbon core of molecular aggregate, the hydrophobic portion of surfactant molecule is slightly deformed and its conformation, on the average, differs from the conformation in the infinitely large hydrocarbon phase. The difference in conformations generates a positive contribution to the work of molecular aggregate formation. Let us name this contribution the deformation contribution and denote by  $W_n^d$ . The  $W_n^d$  contribution is described elsewhere [12, 14] and, in the accepted designation, is given by formula

$$W_n^d = n \frac{3\pi^2}{80} \frac{r^2}{NL^2}, \quad (2.15)$$

where  $N$  is the number of rigid segments in the hydrophobic portion of surfactant molecule and  $L$  is the length of rigid segment. Evidently, the  $NL$  product is equal to the length  $l_C$  of the hydrophobic portion of surfactant molecule. According to [14], in the case of hydrophobic portions composed of methylene groups,

the rigid segment contains, on the average, 3.6 of such groups [14] so that  $N = n_c/3.6$ . Taking this relation and inequality (1.6) into account, we obtain from Eq. (2.15) the upper estimate

$$W_n^d \leq 0.1nn_c. \quad (2.16)$$

Comparing Eqs. (2.14) and (2.16), we see that, at the value of constant  $B$  indicated above, the  $W_n^d$  contribution appears as small correction to the hydrophobic contribution  $W_n^h$ . Under this condition, hereafter the  $W_n^d$  contribution is not taken into account.

As was mentioned above, the hydrophobic core is actually not the infinite bulk phase with the flat interface. According to Eq. (2.8), the distortion of the latter leads to the appearance of the Laplace pressure drop and corresponding contribution to the work of transfer  $W_n^L$  represented by the second term in the right-hand side of Eq. (2.12). According to Eq. (1.2), in the considered model of surfactant molecular aggregate, for the volume  $v_c$  we have

$$v_c = v(n_c + 1) \quad (2.17)$$

in view of Eq. (1.1), this results in

$$v_c = \frac{4\pi r^3}{3n}. \quad (2.18)$$

Equation (2.18) can also be derived directly with allowance for the meaning of values  $r$  and  $n$ . Using Eq. (2.18) and opening the dependence of  $r$  on  $n$  with the aid of Eq. (1.1), we derive the full-length expression for the integrand of the second term in the right-hand side of Eq. (2.12) as

$$\frac{2\gamma_0 v_c}{rkT} = \frac{8\pi\gamma_0}{3kT} \left[ \frac{3v(n_c + 1)}{4\pi} \right]^{2/3} \frac{1}{n^{1/3}}. \quad (2.19)$$

Only the dependence of  $\gamma_0$  on  $n$  still remains unopened in Eq. (2.19). For simplicity, we consider the surface tension  $\gamma_0$  as constant and equal to its value for the flat surface. The dependence of total surface tension  $\gamma$  on the size of molecular aggregate is further accounted for immediately through the contribution of polar groups.

Integrating now relation (2.19) with the use of Eq. (2.12) with respect to aggregation number  $n$  and ignoring the lower limit of integration at  $n \gg 1$ , we obtain

$$W_n^L = \frac{4\pi\gamma_0}{kT} \left[ \frac{3v(n_c + 1)}{4\pi} \right]^{2/3} n^{2/3} \quad (2.20)$$

for the desired contribution  $W_n^L$  to the work  $W_n$  of aggregate formation from the Laplace pressure in the hydrocarbon core. Relations (1.1) and (2.20) indicate that this contribution is equal to the Gibbs surface

energy  $4\pi\gamma_0 r^2/kT$  of hydrophobic core expressed in  $kT$  units. Using definition (1.3), we represent Eq. (2.20) as

$$W_n^L = b_3 n^{2/3}, \quad (2.21)$$

where  $n$ -independent dimensionless constant  $b_3$  is determined according to

$$b_3 \equiv \frac{4\pi\gamma_0\lambda^2}{kT}. \quad (2.22)$$

From Eq. (2.22) with allowance for  $\gamma_0 > 0$ , we have  $b_3 > 0$ . Then, it follows from Eq. (2.21) that  $W_n^L > 0$ .

Positive values of contribution  $W_n^L$  from the Laplace pressure to work  $W_n$  prevents the formation of molecular aggregates in micellar solution.

Let us consider now the contribution of polar groups  $W_n^p$ . Their forced approach during the transfer of hydrocarbon tails inside the molecular aggregate results in their interaction, whose most typical kind is the mutual electrostatic repulsion of dipoles. Denote the desired electrical contribution to work  $W_n$  by  $W_n^{\text{el}}$  and consider the case when the electrostatic component characterizes rather well the total interaction of polar groups:  $W_n^{\text{el}} \approx W_n^p$ . According to [12–14], we describe briefly the determination of electric contribution to the work of aggregate formation due to the presence of polar groups of surfactant molecules protruding from hydrocarbon core in aggregate. Because molecular aggregates are formed in a solution at constant temperature and external pressure,  $W_n^{\text{el}}$  is nothing other than the Gibbs electric energy  $G_n^{\text{el}}$  of a capacitor formed by the hydrophilic parts of surfactant molecules in molecular aggregate. Hence,

$$W_n^{\text{el}} = G_n^{\text{el}}, \quad (2.23)$$

that results precisely in the contribution from polar groups to the last term of Eq. (2.12) expressed in the integral form.

Assuming that, in our model of molecular aggregate, the capacitor formed by the hydrophilic parts of surfactant molecules in molecular aggregate possesses the spherical symmetry, we arrive at the electrostatic expression (in  $kT$  units)

$$G_n^{\text{el}} = \frac{(ze n)^2 \delta}{8\pi kT \epsilon_0 \epsilon (r + \Delta l)^2}. \quad (2.24)$$

Here,  $ze$  is the electric charge of a single hydrophilic part of surfactant molecule in the dipole ( $e$  is the elementary charge);  $\delta$  is the length of the dipole of the hydrophilic part, i.e., the capacitor thickness);  $\epsilon$  is the effective permittivity of a capacitor medium;  $\epsilon_0$  is the electric constant; and  $\Delta l$  is the bond length connecting the

hydrophobic portion of surfactant molecule with its polar hydrophilic part. It is suggested that Eq. (2.24) contains inequality  $r + \Delta l \gg \delta$ , which, according to Eq. (1.1), is valid at  $n_c \gg 1$  and  $n \gg 1$ .

Suggesting that, at  $n_c \gg 1$  and  $n \gg 1$ , inequality  $r \gg \Delta l$  is also valid, from Eq. (2.24) with allowance for Eq. (1.4), we obtain

$$G_n^{\text{el}} = \frac{(ze)^2 \delta}{8\pi k T \epsilon_0 \epsilon \lambda^2} n^{4/3}. \quad (2.25)$$

According to Eqs. (2.23) and (2.25), we have

$$W_n^{\text{el}} = b_1 n^{4/3}, \quad (2.26)$$

where  $n$ -independent dimensionless constant  $b_1$  is defined as

$$b_1 \equiv \frac{(ze)^2 \delta}{8\pi k T \epsilon_0 \epsilon \lambda^2}. \quad (2.27)$$

It follows from Eq. (2.27) that  $b_1 > 0$ . Then, according to Eq. (2.26),  $W_n^{\text{el}} > 0$ . Positive value of electric contribution  $W_n^{\text{el}}$  to work  $W_n$  prevents the formation of molecular aggregates in micellar solution. It should be mentioned that we calculated the overall contribution of polar interactions from both the chemical potential and surface tension. For our purposes, there is no necessity to separately calculate the contribution of mutual repulsion of polar groups to the surface tension that results, as is known, in a decrease in the surface tension with an increase in micelle size [13].

In addition to electric forces, yet more powerful forces of direct repulsion of polar groups arising at their contact, are possible under very close approach of the hydrophilic parts of surfactant molecules. Such a picture is typical of the case when the molecular packing in micelles is governed by the size of polar groups. However, we focus our attention to the case, when the hydrocarbon chains determine the packing, and polar groups participate in the micellization only via the long-range forces of electric repulsion.

### 3. THE WORK OF MOLECULAR AGGREGATE FORMATION AS A FUNCTION OF AGGREGATION NUMBER AND THE CONCENTRATION OF SURFACTANT MONOMERS IN SOLUTION

We find the work of aggregate formation  $W_n$  by substituting contributions (2.14), (2.21), and (2.26) (disclosed in Section 2) into the right-hand side of expression (2.12) and integrating the third summand with

allowance made for constant  $\gamma_0$  and inequality  $n \gg 1$ . Introducing designation

$$b_2 \equiv B n_c + a \gamma_0 / k T + \ln(c_1 / c^\alpha) \\ = B n_c + (4\pi)^{1/3} (3v)^{2/3} \gamma_0 / k T + \ln(c_1 / c^\alpha), \quad (3.1)$$

we obtain expression

$$W_n = b_1 n^{4/3} - b_2 n + b_3 n^{2/3}, \quad (3.2)$$

where the terms are arranged in decreasing powers of  $n$ . This expression is valid at  $n \gg 1$ .

According to Eqs. (2.27), (3.1), and (2.22), coefficients  $b_1$ ,  $b_2$ , and  $b_3$  in this expression are dimensionless constants independent of the aggregation number  $n$ . In addition, coefficients  $b_1$  and  $b_3$  do not depend on concentration  $c_1$  of surfactant monomers in solution. As was already mentioned, inequalities  $b_1 > 0$  and  $b_3 > 0$  are always valid. Equation (3.2) is consistent with the expression reported in [8, 11]. However, coefficient at  $n$  obtained in [8, 11] does not explicitly include the dependence on solution concentration.

From Eq. (3.2) with allowance for the fact that coefficients  $b_1$ ,  $b_2$ , and  $b_3$  are independent of  $n$ , we obtain

$$\frac{\partial W_n}{\partial n} = \frac{4b_1}{3} n^{1/3} - b_2 + \frac{2b_3}{3} n^{-1/3}, \quad (3.3)$$

$$\frac{\partial^2 W_n}{\partial n^2} = \frac{4b_1}{9} n^{-2/3} - \frac{2b_3}{9} n^{-4/3}. \quad (3.4)$$

Using Eq. (3.3), we can determine the roots  $n = n_c$  and  $n = n_s$  of equations

$$(\partial W_n / \partial n)_{n=n_c} = 0 \quad (3.5)$$

and

$$(\partial W_n / \partial n)_{n=n_s} = 0, \quad (3.6)$$

determining the points  $n_c$  and  $n_s$  of the maximum and minimum of work  $W_n$ , respectively, i.e., the aggregation numbers of critical and stable molecular aggregates. The fact that the largest root  $n_s$  corresponds to the minimum and, respectively, the smallest root  $n_c$ , to the maximum of work  $W_n$  follows, in view of  $b_1 > 0$ , from an asymptotic rise of work  $W_n$  with an increase in aggregation number  $n$  indicated by Eq. (3.2).

The root  $n = n_0$  of equation

$$(\partial^2 W_n / \partial n^2)_{n=n_0} = 0 \quad (3.7)$$

determines the inflection point  $n_0$  of work  $W_n$ . For the considered model of molecular aggregate, we have from Eqs. (3.4) and (3.7) that

$$n_0 = (b_3 / 2b_1)^{3/2}. \quad (3.8)$$

According to Eq. (3.8) [and Eqs. (2.22) and (2.27)], the inflection point  $n_0$  of work  $W_n$  turned out to be iden-

tical at all monomer concentrations  $c_1$  in surfactant solution. Relation (3.8) allows one to reveal the constraint on  $(b_3/2b_1)^{3/2}$  value, at which  $n_0$  fits the region of aggregation numbers  $n$  that is realistic for molecular aggregates.

The considered model of molecular aggregate leads to the existence of the potential maximum and potential well of work  $W_n$  at a sufficiently high monomer concentration  $c_1$  in surfactant solution. Monomer concentration in surfactant solution, at which the potential maximum and potential well of work  $W_n$  appear, is denoted by  $c_{10}$ . Because at  $c_1 = c_{10}$  the maximum and minimum of work  $W_n$  are merged in its inflection point  $n_0$ , it follows from Eqs. (3.5) and (3.6) that

$$(\partial W_n / \partial n)_{c_1 = c_{10}, n = n_0} = 0. \quad (3.9)$$

Note that the concentration  $c_{10}$  is slightly lower than the critical micellization concentration, at which the potential well of work  $W_n$  begins to play a significant role in the consumption of the total amount of surfactant from micellar solution. This phenomenon will be disclosed quantitatively in Section 4.

Let us represent Eq. (3.1) as

$$b_2 = \ln(c_1/c_{10}) + \tilde{b}_2, \quad (3.10)$$

where  $\tilde{b}_2$  is no longer dependent on  $c_1$ . Using Eqs. (3.9), (3.8), and (3.3), we then arrive at

$$\tilde{b}_2 = \frac{4}{3}(2b_1b_3)^{1/2}, \quad (3.11)$$

which, together with Eq. (3.10), sets the correlation between the coefficient  $b_2$  and coefficients  $b_1$  and  $b_3$  in expression (3.2).

Finally, substituting Eqs. (3.10) and (3.11) into Eq. (3.2), we obtain

$$W_n = b_1 n^{4/3} - \left[ \ln(c_1/c_{10}) + \frac{4}{3}(2b_1b_3)^{1/2} \right] n + b_3 n^{2/3}. \quad (3.12)$$

Expression (3.12), which is valid at  $n \gg 1$ , was not earlier cited in the literature. It describes the dependence of work  $W_n$  on the aggregation number  $n$  and surfactant monomer concentration  $c_1$  in solution, which is the most important in the theory of micellar solutions. This expression contains three parameters  $b_1$ ,  $b_3$ , and  $c_{10}$  independent of  $n$  and  $c_1$ . It was already mentioned that inequalities  $b_1 > 0$  and  $b_3 > 0$  are always valid. However, it can be that both  $c_1/c_{10} < 1$  and  $c_1/c_{10} > 1$ . The introduction of parameter  $c_{10}$  allowed us to eliminate, in accordance with Eqs. (3.1), (3.10), and (3.11), the dependence of  $B$  on  $c^\alpha$  in Eq. (3.12). All three parameters  $b_1$ ,  $b_3$ , and  $c_{10}$  have clear physical meaning. Each of these parameters can be determined directly in experiment.

According to Eqs. (3.1), (3.10), and (3.11), parameter  $c_{10}$  is connected with parameters  $B$  and  $c^\alpha$  by the relationship

$$\ln(c_{10}/c^\alpha) = -Bn_c - (4\pi)^{1/3} \times (3v)^{2/3} \gamma_0/kT + \frac{4}{3}(2b_1b_3)^{1/2}. \quad (3.13)$$

Taking into account that, in view of Eq. (2.17) and  $c^\alpha = 1/v_C$ , expression

$$c^\alpha = \frac{1}{v(n_C + 1)} \quad (3.14)$$

is valid, we rewrite Eq. (3.13) as

$$\ln(v_C c_{10}) = -Bn_c - (4\pi)^{1/3} (3v)^{2/3} \gamma_0/kT - \ln(n_C + 1) + \frac{4}{3}(2b_1b_3)^{1/2}. \quad (3.15)$$

This formula will be needed in Section 4.

From Eq. (3.12), for the roots  $n_c$  and  $n_s$  of Eqs. (3.5) and (3.6) (for the aggregation numbers of critical and stable molecular aggregates, respectively), we obtain important analytical formulas

$$n_c = \left( \frac{1}{8b_1} \right)^3 \left\{ 2^{5/2} (b_1b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) - \sqrt{\left[ 2^{5/2} (b_1b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) \right]^2 - 32b_1b_3} \right\}^3 \quad (c_1 > c_{10}), \quad (3.16)$$

$$- \sqrt{\left[ 2^{5/2} (b_1b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) \right]^2 - 32b_1b_3} \right\}^3 \quad (c_1 > c_{10}),$$

$$n_s = \left( \frac{1}{8b_1} \right)^3 \left\{ 2^{5/2} (b_1b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) + \sqrt{\left[ 2^{5/2} (b_1b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) \right]^2 - 32b_1b_3} \right\}^3 \quad (c_1 > c_{10}), \quad (3.17)$$

$$+ \sqrt{\left[ 2^{5/2} (b_1b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) \right]^2 - 32b_1b_3} \right\}^3 \quad (c_1 > c_{10}),$$

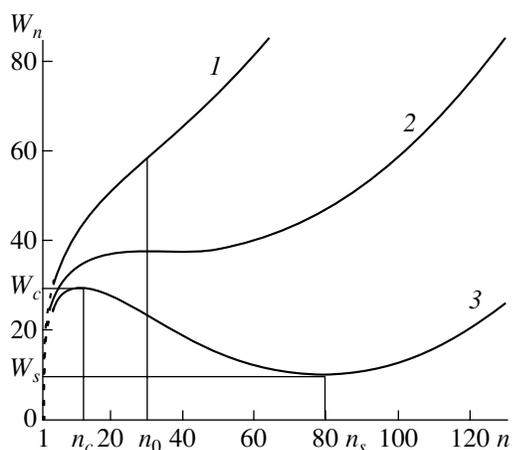
where constraint  $c_1 > c_{10}$ , at which roots  $n_c$  and  $n_s$  exist as real quantities that are responsible for both the maximum and minimum of work  $W_n$ . Equations (3.16) and (3.17) confirm the suggested existence of the potential maximum and potential well of work  $W_n$  at  $c_1 > c_{10}$  used in Eq. (3.9).

Equation (3.12) secures the validity of relation

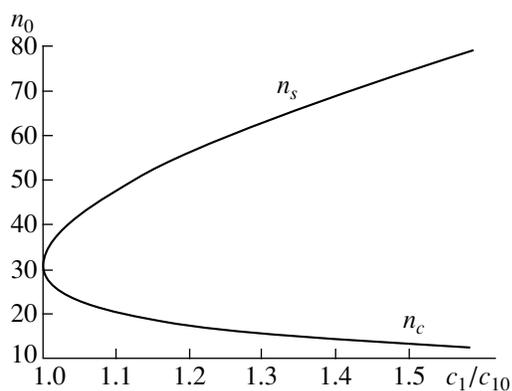
$$\partial W_n / \partial c_1 = -n/c_1, \quad (3.18)$$

which agrees with Eq. (2.12) in the region of  $n \gg 1$  of the applicability of expression (3.12).

The dependence of work  $W_n$  on the aggregation number  $n$  and the concentration of surfactant solution  $c_1$  indicated by Eq. (3.12) is demonstrated in Fig. 1. This dependence corresponds to the available quantitative empirical representations of the behavior of work  $W_n$  and it was plotted with the specific set of parame-



**Fig. 1.** Dependence of work  $W_n$  on the aggregation number  $n$  and concentration  $c_1$  of surfactant solution. Curves 1, 2, 3 correspond to  $c_1 < c_{10}$ ,  $c_1 = c_{10}$ , and  $c_1 > c_{10}$ , respectively.



**Fig. 2.** Dependences of  $n_c$  and  $n_s$  on  $c_1/c_{10}$  ratio.

ters, which is to be commented in the next section. Equality  $W_1 = 0$  corresponding to Eq. (2.2) is taken into account in Fig. 1. Undoubtedly, this equality cannot be evident from expression (3.12), which is valid only at  $n \gg 1$ ; hence, the behavior of  $W_n$  near  $n = 1$  is shown by the dashed portions of curves.

#### 4. MODEL CALCULATIONS

We concern only with the range of concentration  $c_1$  of surfactant solution where  $c_1/c_{10} > 1$ . In addition to values  $n_c$  and  $n_s$ , significant for the kinetics of micellization [1–5] in the  $c_1/c_{10} > 1$  region are the quantities

$$W_c = W_n|_{n=n_c}, \quad W_s = W_n|_{n=n_s}, \quad (4.1)$$

which are shown in Fig. 1 and determine the height of potential maximum and the depth of potential well of

work  $W_n$ , as well as the quantities

$$\Delta n_c = \left[ 2 / \left| \frac{\partial^2 W_n}{\partial n^2} \right|_{n=n_c} \right]^{1/2}, \quad (4.2)$$

$$\Delta n_s = \left[ 2 / \left( \frac{\partial^2 W_n}{\partial n^2} \right) \right]_{n=n_s}^{1/2},$$

determining the half-widths of potential maximum and potential well of work  $W_n$  at the  $n$ -axis.

Let us calculate thermodynamic characteristics of the kinetics of micellization such as  $n_c$ ,  $n_s$ ,  $W_c$ ,  $W_s$ ,  $\Delta n_c$ , and  $\Delta n_s$  in the droplet model of surfactant spherical molecular aggregate. Let us set the following values of the initial parameters of a model:

$$\lambda = 5.0 \times 10^{-10} \text{ m}, \quad \gamma_0 = 30 \text{ mN m}^{-1}, \quad \varepsilon = 30,$$

$$\delta = 3 \times 10^{-10} \text{ m}, \quad z = 1, \quad T = 293 \text{ K}. \quad (4.3)$$

The accepted value of parameter  $\lambda$  introduced by definition (1.3) corresponds to the representative case when  $n_c = 18$  (it can be octadecyl radical that can be completely packed into the hydrocarbon core or the fragment of longer aliphatic hydrocarbon radical). In this case, constraint (1.7) is reduced to  $n < 108$ . Accepted values of parameters  $\gamma_0$ ,  $\varepsilon$ , and  $\delta$  are quite admissible in view of rather approximate quantitative data on the micellization that are available in published literature and that were used when plotting Fig. 1. Results of calculations reported below are quite sensitive to the values of parameters  $\gamma_0$ ,  $\varepsilon$ , and  $\delta$ . In order to have more realistic results, the values of these parameters should be carefully correlated.

From Eqs. (2.22), (2.27), and (3.8) with allowance for Eq. (4.3), we have

$$b_1 = 1.13, \quad b_3 = 22.4, \quad n_0 = 31.2. \quad (4.4)$$

The value of parameter  $n_0$  shown in Eq. (4.4) lies in the realistic (for molecular aggregates) region of aggregation numbers  $n$  admitted at  $n_c = 18$  by the constraint  $n < 108$  and followed from Eq. (1.7). Once the values of parameters  $\gamma_0$ ,  $\varepsilon$ , and  $\delta$  admitted in Eq. (4.3) are slightly changed, one can easily overcome the domain of applicability of required constraints  $n_0 < 108$  and  $n_0 \gg 1$ .

The subsequent calculations depend on to what extent the  $c_1/c_{10}$  ratio exceeds unity. Results of the calculation of the dependence of  $n_c$  and  $n_s$  on  $c_1/c_{10}$  obtained with the aid of Eqs. (3.16), (3.17), and (4.4) are shown in Fig. 2. At  $c_1/c_{10} = 1$ , the values of  $n_c$  and  $n_s$  coincide and are equal to  $n_0$ . As the  $c_1/c_{10}$  ratio increases, the value of  $n_c$  decreases monotonically and the value of  $n_s$  increases monotonically; moreover,  $n_s$  increases faster than  $n_c$  decreases so that the curve has the form of asymmetric loop. In this case, constraints

$n_s < 108$  and  $n_c \gg 1$  that are necessary for the applicability of the droplet model of molecular aggregate at  $n_c = 18$  are fulfilled to lower and lower extent. Figure 3 demonstrates the dependences of  $W_c$  and  $W_s$  on  $c_1/c_{10}$  ratio obtained using Eqs. (3.12), (3.16), (3.17), (4.1), and (4.4). At  $c_1/c_{10} = 1$ , the values of  $W_c$  and  $W_s$  coincide with each other. As  $c_1/c_{10}$  ratio increases, the values of  $W_c$  and  $W_s$  decrease monotonically; moreover,  $W_c$  decreases much slower than  $W_s$ . Finally, the results of calculations of the dependences of  $\Delta n_c$  and  $\Delta n_s$  on  $c_1/c_{10}$  ratio obtained using Eqs. (3.12), (3.16), (3.17), (4.2), and (4.4) are shown in Fig. 4. At  $c_1/c_{10} = 1$ , the values of  $\Delta n_c$  and  $\Delta n_s$  are reduced to infinity. As  $c_1/c_{10}$  ratio increases, the values of  $\Delta n_c$  and  $\Delta n_s$  decrease monotonically; however, inequality  $\Delta n_c < \Delta n_s$  is fulfilled (the peak of activation energy becomes noticeably narrower than potential well of micelles). Figures 2–4 agree with Fig. 1.

Let us introduce the CMC into consideration. The values at the CMC are marked by subscript  $m$ . Using Boltzmann's formula  $c_n = c_1 \exp(-W_n)$  for the equilibrium concentration  $c_n$  of aggregates with aggregation number  $n$  and accounting for Eq. (3.6) and the second relations of Eqs. (4.1) and (4.2), we obtain, by integrating with respect to the region of the potential well of work  $W_n$ , the expression  $c_M = \pi^{1/2} c_1 \Delta n_s \exp(-W_s)$  for the total equilibrium concentration  $c_M$  of micelles accumulating at the bottom of potential well. According to [13], we can determine the degree of micellization  $\alpha$  using relation  $\alpha = n_s c_M / c$ , where  $c$  is the overall surfactant concentration (the total number of surfactant molecules per solution unit volume). Passing to the CMC in the expression for  $c_M$  indicated above and using bimodal approximation  $c_{1m} + n_{sm} c_{Mm} = c$ , we obtain

$$W_{sm} = \ln \left( \pi^{1/2} \frac{1 - \alpha_m}{\alpha_m} n_{sm} \Delta n_{sm} \right). \quad (4.5)$$

As was shown in [18], the critical degree of micellization  $\alpha_m$  depends on the choice of CMC definition and, in particular, it can be equal to approximately 0.1. Possible deviations of the value of  $\alpha_m$  from 0.1 are slightly manifested in Eq. (4.5) due to weaker sensitivity of logarithm in Eq. (4.5) to its argument shown below.

The substitution of Eq. (3.17) into Eq. (3.12) at  $c_1 = c_{1m}$  makes it possible to express the value of  $W_{sm}$  in the left-hand side of equality (4.5) as the known function of the  $c_{1m}/c_{10}$  ratio. Using Eqs. (3.17) and (3.12) and the second formula of Eq. (4.2) at  $c_1 = c_{1m}$ , we can also represent the right-hand side of Eq. (4.5) as the known function of the  $c_{1m}/c_{10}$  ratio. As a result, the transcendental equation for determining  $c_{1m}/c_{10}$  ratio can be derived from Eq. (4.5). Solving this equation, we have

$$c_{1m}/c_{10} = 1.58. \quad (4.6)$$

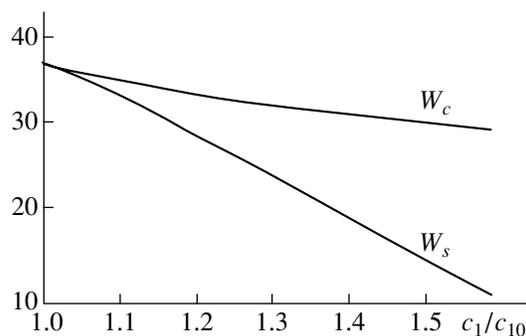


Fig. 3. Dependences of  $W_c$  and  $W_s$  on  $c_1/c_{10}$  ratio.

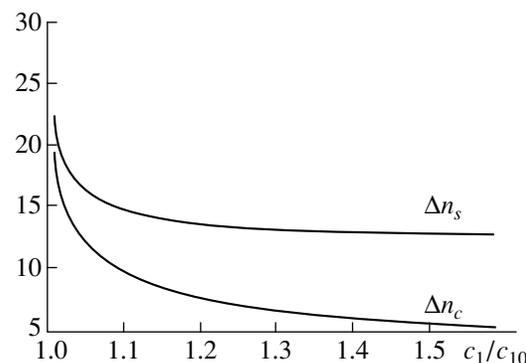


Fig. 4. Dependences of  $\Delta n_c$  and  $\Delta n_s$  on  $c_1/c_{10}$  ratio.

Substituting Eq. (4.6) into Eqs. (3.17) and (3.12) and into the second equation of relations (4.2), we find

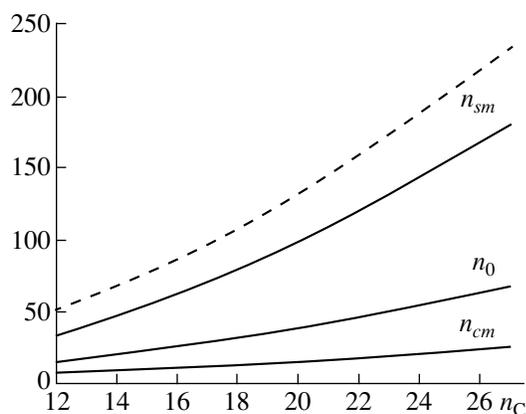
$$n_{sm} = 79.0, \quad W_{sm} = 9.67, \quad \Delta n_{sm} = 12.6. \quad (4.7)$$

Similarly, substituting Eq. (4.6) into Eqs. (3.16) and (3.12) and into the first equation of relations (4.2), we obtain

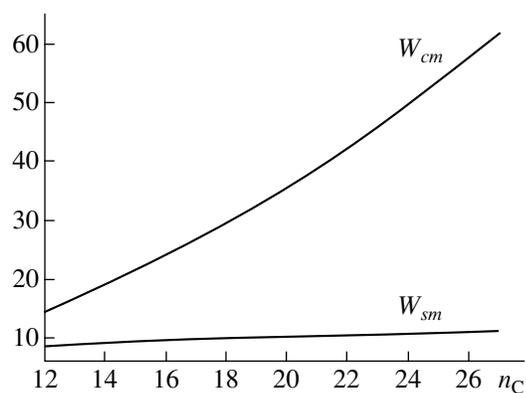
$$n_{cm} = 12.3, \quad W_{cm} = 29.1, \quad \Delta n_{cm} = 4.97. \quad (4.8)$$

In Eqs. (4.6)–(4.8), we took into account the values of  $b_1$  and  $b_3$  at  $n_c = 18$  shown in (4.4).

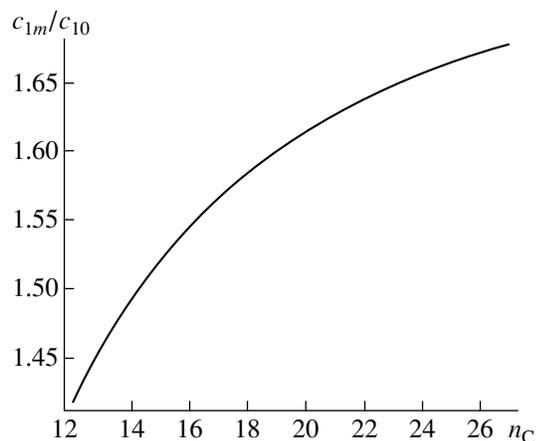
As is seen from Eqs. (4.7) and (4.8), at the CMC, the values of  $n_{sm}$  and  $n_{cm}$  for the droplet model lie in the realistic region of aggregation numbers admitted by the constraint  $n < 108$  followed from Eq. (1.7) at  $n_c = 18$ . It is also seen that inequality  $n_{sm} \gg 1$  and even inequality  $n_{cm} \gg 1$ , which are necessary for the applicability of the theory (asymptotic at  $n \gg 1$ ), are valid. As a result, the model calculations of the thermodynamic characteristics of the kinetics of micellization involve the CMC. The fact that  $n_{sm} \Delta n_{sm}$  product is much smaller than unity is indicative of the weak sensitivity of logarithm in Eq. (4.5) to its argument. Let us emphasize that it is the relation (4.5), which was not used earlier in the literature, sets the relation between the CMC and model parameters.



**Fig. 5.** Dependences of  $n_{cm}$ ,  $n_0$ , and  $n_{sm}$  on  $n_C$ . The dotted curve denotes the upper boundary of the values of aggregation number for the spherical model of molecular aggregate corresponding to right-hand part of constraint (1.7).



**Fig. 6.** Dependences of  $W_{cm}$  and  $W_{sm}$  on  $n_C$ .



**Fig. 7.** Dependence of concentration ratio  $c_{1m}/c_{10}$  on  $n_C$ .

The dependence of thermodynamic characteristics of micellization on the number of hydrocarbon groups,  $n_C$ , in the hydrophobic portion of surfactant molecule is

also important for any model of molecular aggregates. Figures 5–7 show the behavior of  $n_{cm}$ ,  $n_0$ , and  $n_{sm}$  values, as well as the values of  $W_{cm}$ ,  $W_{sm}$ , and  $c_{1m}/c_{10}$  ratio as functions of number  $n_C$  (the length of hydrocarbon chain) for the considered droplet model in the range of  $12 \leq n_C \leq 27$ . Although the parameter  $\lambda$  in Eq. (4.3) varies in this case [according to its definition (1.3)], the other parameters of Eq. (4.3) are assumed, for definiteness, to be constant. As is seen from Fig. 5, regardless of the rapid increase in  $n_{sm}$  value with an increase in  $n_C$ , constraint (1.7) is fulfilled at  $n = n_{sm}$  well in advance. This is explained by a rather rapid increase in the right-hand side of Eq. (1.7) with an increase in  $n_C$ .

According to definitions (2.22) and (2.27), the  $b_1 b_3$  product is independent of  $n_C$ . Calculating this product with the aid of Eq. (4.4) and using Eq. (3.15), we obtain

$$\ln(\nu c_{10}) = -Bn_C - (4\pi)^{1/3} (3\nu)^{2/3} \gamma_0/kT - \ln(n_C + 1) + 9.4. \quad (4.9)$$

Within the entire range  $12 \leq n_C \leq 27$ , inequality  $\ln(\nu c_{10}) < -10$  follows from Eq. (4.9) and  $B = 1.4$ . As is shown by Fig. 7, within the same range,  $c_{1m}/c_{10}$  ratio is equal approximately to 1.6. At a rather high accuracy, we then have  $\ln(\nu c_{1m}) = \ln(\nu c_{10}) + \ln(1.6)$ . Therefore, in addition to Eq. (4.9), relation

$$\ln(\nu c_{1m}) = -Bn_C - (4\pi)^{1/3} (3\nu)^{2/3} \gamma_0/kT - \ln(n_C + 1) + 9.9 \quad (4.10)$$

is also valid.

According to Eq. (4.10), the logarithm of concentration  $c_{1m}$ , i.e., the logarithm of the CMC, decreases with an increase in  $n_C$  almost linearly at  $n_C \gg 1$  that is confirmed by the known experimental data [7, 12–14].

## ACKNOWLEDGMENTS

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