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Thermodynamic Characteristics of the Micellization in Droplet and Quasi-Droplet Models of Surfactant Molecular Aggregates with Account of Experimental Data on Equilibrium Micelle Distribution

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Abstract—Formuals for the thermodynamic characteristics of micellization in the droplet and quasi-droplet models of surfactant molecular aggregates are derived. These formulas account for the experimental data on the mean size of micelles and average statistical scatter of their sizes in the equilibrium state. These formulas cover critical micellization concentration corresponded to the onset of surfactant accumulation in micelles and higher (than CMC) concentrations at which micelles incorporate noticeable or even the largest portion of surfactant in micellar solution. Analytical dependence of thermodynamic characteristics of micellization on the initial parameters of droplet and quasi-droplet models of molecular aggregates at critical micellization concentration is disclosed.

INTRODUCTION

Thermodynamic characteristics that can be determined from the dependence of the work of molecular aggregate formation in surfactant solution on the aggregation number (the number of surfactant molecules in aggregate) and the concentration of surfactant monomers in solution were significant for studying the kinetics of micellization in surfactant solution [1–5]. These characteristics as the functions of monomer concentration are: the positions of potential barrier and potential well of the work on the aggregation number axis, the half-widths of potential barrier and potential well on the aggregation number axis, the height of potential barrier, and the depth of potential well.

The problem of the dependence of the work of molecular aggregate formation in surfactant solution on the aggregation number and the concentration of surfactant monomers in solution was in general solved within the framework of the droplet [6–14] and quasi-droplet [15] models of surfactant molecular aggregates. Both models result in different (albeit qualitatively correct) dependences of the work of molecular aggregate formation in surfactant solution on the aggregation number and the concentration of surfactant monomers. At the same time, simplified assumptions (used of necessity in models) concerning both the structure of molecular aggregates and the procedures accounting for basic interactions of surfactant molecules constituting aggregate introduce indefiniteness to the quantitative data obtained by using these models. It seems natural to interpret this indefiniteness as resulted from the insufficiently correct understanding of the initial parameters of the models of molecular aggregates. The predictive force of the models can be increased by introducing representative experimental characteristics of micellization, provided that interrelations between the initial parameters of models and the observable values are understood in this case as exact quantities.

By now, relatively reliable experimental data on the position of the potential well of the work of surfactant molecular aggregate formation on the aggregation number axis (on the mean micelle size), as well as on the half-width of this well (the average statistical scatter of micelle sizes) for various micellar solutions are available in published literature [6, 16, 17]. These data can be refined in the course of further experimental study of the equilibrium distribution over the micelle aggregation numbers. The main aim of this work is to demonstrate how, knowing the experimental position and half-width of potential well, one can find all other thermodynamic characteristics of micellization, in particular, those referring to molecular aggregates in premicellar region of their sizes and that are not easily accessible in experiment. Special interest to such aggregates is explained by the fact that it is these aggregates that, as was shown in [16, 17], play the key role in the relaxation processes of micellization.

The formulas for thermodynamic characteristics of micellization proposed in this work are based on the droplet model of molecular aggregates (studied in [14]) and quasi-droplet model of surfactant molecular aggregates (proposed and studied in [15]). The formula derived in [14] seems to be significant irrespective of the simulation of molecular aggregates. This formula relates [at the critical micellization concentration (CMC)] the depth of potential well to its position and half-width, as well as to the critical degree of micellization.

In their physical meaning, the initial parameters of droplet and quasi-droplet models of molecular aggregates cannot be determined directly from the experiment or by molecular simulation. At high sensitivity of thermodynamic characteristics of micellization to these parameters demonstrated in [14, 15], it is more convenient to initially take into account in the theory the position and half-width of the potential well of aggregation work that can be found quite exactly from the experimental observation of equilibrium micelle distribution over their aggregation numbers, just as proposed in this work. As a result, this allows us to relate theory to experiment, moreover, as applied to specific micellar solutions.

It will be shown here that the thermodynamic characteristics of micellization expressed via the position and half-width of the potential well are rather similar in the droplet and quasi-droplet models of molecular aggregates despite a quite different dependence of the work of aggregate formation on the aggregation numbers in these models. This argues in favor of the plausibility of the droplet and quasi-droplet models in micellization and thereby allows us to perform also quantitative comparison of these models.

The secondary result of this work will be the elucidation of the analytical dependence (at the CMC) of the thermodynamic characteristics of micellization on the initial parameters of the droplet and quasi-droplet models of molecular aggregates.

Formulas for the thermodynamic characteristics of micellization in the droplet and quasi-droplet models will be derived not only at the CMC but also at higher concentrations of micellar solution (that are of interest to experimenters) at which micelles can incorporate almost the entire surfactant.

An important role will be played by typical, by the order of magnitudes according to [6, 16, 17], estimates of the position and half-width of the potential well of aggregation work on the aggregation number axis and the existence of rather small parameter (resulted from these estimates) set by the squared ratio of the half-width of potential well to its position.

1. GENERAL CONCEPTS OF THE WORK OF MOLECULAR AGGREGATE FORMATION

Let us formulate general concepts of the properties of the work of surfactant molecular aggregate formation needed for further discussion. We use notations accepted in [1–5]. The aggregation number of molecular aggregate in micellar solution is denoted by n. The work of aggregate formation is expressed in thermal energy units kT (k is Boltzmann's constant and T is the solution temperature) and denoted by W_n. At $n = 1$, aggregates are represented by surfactant monomers. Their concentration (the number per solution unit volume) is denoted by c_1. Positions of maximum and minimum of work W_n on the n axis, i.e., the aggregation numbers of critical and stable molecular aggregates, are denoted by n_c and n_s, respectively. Then, we have

$$(\partial W_n/\partial n)_{n = n_c} = 0, \quad (\partial W_n/\partial n)_{n = n_s} = 0. \qquad (1.1)$$

Maximum and minimum of work W_n, i.e., the height of potential barrier and the depth of potential well of work W_n, are denoted by $W_c \equiv W_n|_{n = n_c}$ and $W_s \equiv W_n|_{n = n_s}$, respectively. The inflection point of work W_n on the aggregation number axis we denote by n_0. Hence

$$(\partial^2 W_n/\partial n^2)_{n = n_0} = 0. \qquad (1.2)$$

The monomer concentration corresponding to the appearance of barrier and well of work W_n is denoted by c_{10}. Subscript m refers to the values at the CMC. It is evident that $c_{1m} > c_{10}$. We are interested in the $c_1 \geq c_{1m}$ region where the barrier and well are markedly pronounced. At $c_1 = c_{10}$, the maximum and minimum of work W_n are merged in the inflection point n_0. Then, it follows from Eq. (1.1) that

$$(\partial W_n/\partial n)_{c_1 = c_{10},\, n = n_0} = 0. \qquad (1.3)$$

In accordance with the equality (1.12) in [1] followed from the law of mass action, work W_n satisfies the relation

$$\partial W_n/\partial c_1 = -(n-1)/c_1. \qquad (1.4)$$

In view of definitions $W_c \equiv W_n|_{n = n_c}$ and $W_s \equiv W_n|_{n = n_s}$ and equalities (1.1), relation (1.4) secures also the fulfillment of relations

$$\begin{aligned} \partial W_c/\partial c_1 &= -(n_c - 1)/c_1, \\ \partial W_s/\partial c_1 &= -(n_s - 1)/c_1. \end{aligned} \qquad (1.5)$$

Half-widths of potential barrier and potential well of work W_n on the n axis determined by equalities

$$\begin{aligned} \Delta n_c &= [2/|\partial^2 W_n/\partial n^2|_{n = n_c}]^{1/2}, \\ \Delta n_s &= [2/(\partial^2 W_n/\partial n^2)_{n = n_s}]^{1/2} \end{aligned} \qquad (1.6)$$

are significant in the theory developed in [2–5].

Writing Taylor's series expansion of $W_n = W_s + \left(\frac{n - n_s}{\Delta n_s}\right)^2 + \ldots$ with allowance for the second equalities of Eqs. (1.1) and (1.6), we see that, according to Boltzmann's principle for solution equilibrium, the following distribution

$$c_n = c_1 e^{-W_s} e^{-\left(\frac{n - n_s}{\Delta n_s}\right)^2} \quad (|n - n_s| \lesssim \Delta n_s) \qquad (1.7)$$

is valid for the concentration c_n of aggregates with aggregation number n within the $|n - n_s| \lesssim \Delta n_s$ region of the potential well of work W_n where the micelles are accumulated (concentrations c_n are understood as the number of aggregates per solution unit volume). Distribution (1.7) demonstrates that the n_s and Δn_s values setting the position and half-width of potential well of aggregation work determine the average value and average statistical scatter of micelle aggregation numbers in equilibrium solution.

Equilibrium distribution of micelles is observed in experiment. Being the most direct characteristics of equilibrium distribution (1.7), the n_s and Δn_s values are accessible for experimental determination [6, 16, 17]. Note that, according to [16], the Δn_s value can be found experimentally by measuring the time of fast relaxation of micellar solution.

The n_s and Δn_s values can be easily measured experimentally, because, as was shown by the discussion of experiment [16, 17] and will be confirmed by equalities (6.1) in Section 6, they undergo [in contrast to exponent $\exp(-W_s)$ in (1.7)] only relatively small changes of concentration c_1 within the entire region $c_1 \geq c_{1m}$ (which is of interest to us), beginning with the CMC where the surfactant starts to be accumulated in micelles and ending with the concentrations at which almost the whole of surfactant is accumulated in micelles. As c_1 increases from c_{1m} at the CMC, exponent $\exp(-W_s)$ rapidly rises in view of the second relation of Eq. (1.5) and $n_s \gg 1$ that makes distribution c_n in Eq. (1.7) extremely sensitive to the n_s and Δn_s values, thereby decreasing the error of experimental determination of these values using Eq. (1.7).

Let us denote by c_M the micelle total concentration in the region of potential well of work W_n upon solution equilibrium. Recognizing concentration c_n as the number of micelles with aggregation number n per solution unit volume and integrating distribution (1.7) over the region of potential well of work W_n (the infinite limits can be set for n upon integration due to a fast decrease of integrand function), we obtain

$$c_M = \pi^{1/2} c_1 \Delta n_s e^{-W_s}. \qquad (1.8)$$

From Eq. (1.8) and the second of relations in Eq. (1.5), we arrive (neglecting the weak dependence of half-width Δn_s on c_1) at useful relation

$$\partial \ln c_M / \partial c_1 = n_s / c_1, \qquad (1.9)$$

which makes it possible to experimentally find the n_s value, provided that the dependence of c_M on c_1 is known.

At the bimodal distribution of monomers and micelles in solution, we have [6]

$$c_1 + n_s c_M = c, \qquad (1.10)$$

where c is the overall surfactant concentration (the total number of surfactant molecules per solution unit volume).

According to [6], let us introduce the degree of micellization α

$$\alpha = n_s c_M / c. \qquad (1.11)$$

From Eqs. (1.10) and (1.11), we have

$$n_s c_M / c_1 = \alpha/(1-\alpha). \qquad (1.12)$$

Substituting Eq. (1.8) into Eq. (1.12) and taking the logarithm, we arrive at the following relation:

$$W_s = \ln\left(\pi^{1/2}\frac{1-\alpha}{\alpha} n_s \Delta n_s\right). \qquad (1.13)$$

Typical for the CMC is the fact (see [6]) that, at the CMC, the amount of substance $n_s c_M$ in micelles is still small compared with the amount of substance c_1 in monomers; however, it is still so notable that even the amount of substance $n_s c_M$ in micelles at solution concentration slightly higher than the CMC will already exceed the amount of substance $n_s \gg 1$ in monomers in view of Eq. (1.8) and extremely sharp dependence of $\exp(-W_s)$ on c_1 at $n_s \gg 1$ resulted from the second of relations (1.5). Hence, at the CMC, the role of potential well of work W_n where the micelles are accumulated becomes significant. Then, bimodal formula (1.10) becomes also significant.

Critical degree of micellization α_m corresponding to the CMC is estimated, according to [6], as $\alpha_m \approx 0.1$. Then, according to Eq. (1.12), we have $n_{sm} c_{Mm} / c_{1m} \approx 1/9$ so that the relative amount of substance in micelles at the CMC is still small, although it is already noticeable. In order to increase $n_s c_M / c_1$ ratio approximately tenfold and, hence, the relative amount of substance in micelles to exceed unity upon an increase in concentration c_1 from c_{1m} by Δc_1 (small compared to c_{1m}), it is necessary, as is seen from Eq. (1.8) and extremely sharp dependence of $\exp(-W_s)$ on c_1 at $n_s \gg 1$ resulted from relations (1.5), that $\Delta c_1 / c_{1m} \approx \ln(10)/(n_{sm} - 1)$. Thus, at $n_{sm} \gg 1$, an increase in concentration c_1 even by fairly small (compared to c_{1m}) value Δc_1 is already sufficient. Note that, as we will see from Eqs. (2.11), (2.12), and (4.11), (4.12), the Δc_1 value turned out also to be small compared with an increase $c_{1m} - c_{10}$ in concentration c_1 required to achieve the CMC after the appearance of potential barrier and potential well of work W_n. This is supported by the approximate value $\alpha_m \approx 0.1$ of the critical degree of micellization and corresponding approximate CMC value accepted in [6].

According to Eq. (1.13)

$$W_{sm} = \ln\left(\pi^{1/2}\frac{1-\alpha_m}{\alpha_m} n_{sm} \Delta n_{sm}\right) \quad (\alpha_m \approx 0.1). \qquad (1.14)$$

Possible small deviations of the α_m value from $\alpha_m \approx 0.1$ are slightly manifested in Eq. (1.14) due to the low sensitivity of logarithm in Eq. (1.14) to its argument at $n_{sm} \Delta n_{sm} \gg 1$. Then, the α_m value in Eq. (1.14) can be considered as virtually preset coinciding with its approximate value $\alpha_m \approx 0.1$. This very significant circumstance simplifies further study.

Formula (1.14) derived by us in [14] gives the formation work of stable surfactant molecular aggregate at the CMC irrespective of the simulation of molecular aggregates. We reproduced briefly the derivation of Eq. (1.14) described in [14] and reminded, in accordance with [6], the complex meaning of concepts of the CMC and critical degree of micellization, in order to show that formula (1.14) allows us to adequately introduce these concepts into the theory of micellization.

Formula (1.14) represents, at the CMC, the depth W_{sm} of the potential well of aggregation work via the experimentally set position n_{sm} and half-width Δn_{sm} of this well on the aggregation number axis.

2. THERMODYNAMIC CHARACTERISTICS OF MICELLIZATION AT THE CMC AS A FUNCTION OF THE POSITION AND HALF-WIDTH OF POTENTIAL WELL OF AGGREGATION WORK IN THE DROPLET MODEL OF MOLECULAR AGGREGATES

In the droplet model of molecular aggregates studied in [14], we derived, at $n \gg 1$, the following expression:

$$\begin{aligned} W_n &= b_1 n^{4/3} \\ &- \left[\ln(c_1/c_{10}) + \frac{4}{3}(2b_1b_3)^{1/2}\right]n + b_3 n^{2/3} \end{aligned} \tag{2.1}$$

(expression (3.12) in [14]). It will be significant that parameters b_1 and b_3 will be positive and independent of n and c_1. Physical meaning of these parameters elucidated in [14] that allows us to find them only approximately from the available rough quantitative data on micellization will not be significant for further discussion.

According to Eqs. (1.2) and (2.1), we have

$$n_0 = (b_3/2b_1)^{3/2}, \tag{2.2}$$

showing that n_0 is independent of concentration c_1. Expressions (2.1) and (2.2) secure the fulfillment of equality (1.3). In the $n \gg 1$ region, expression (2.1) satisfies relations (1.4) and (1.5).

The second equalities of Eqs. (1.1) and (1.6) and relation (1.14) form, together with Eq. (2.1) and $W_{sm} \equiv W_n|_{c_1 = c_{1m},\, n = n_{sm}}$, three transcendental equations that allow to analytically express three values b_1, b_3, and $\ln(c_{1m}/c_{10})$ via n_{sm}, Δn_{sm}, and α_m. Solving thee equations, we obtain

$$b_1 = 9n_{sm}^{2/3}(\Delta n_{sm})^{-2}(1+\epsilon), \tag{2.3}$$

$$b_3 = 9n_{sm}^{4/3}(\Delta n_{sm})^{-2}(1+2\epsilon), \tag{2.4}$$

$$\ln(c_{1m}/c_{10}) = 1.1n_{sm}(\Delta n_{sm})^{-2}(1-1.3\epsilon), \tag{2.5}$$

where the ϵ value dependent on n_{sm}, Δn_{sm}, and α_m is set by the equality

$$\epsilon = \frac{1}{3}\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2 \ln\left(\pi^{1/2}\frac{1-\alpha_m}{\alpha_m}n_{sm}\Delta n_{sm}\right). \tag{2.6}$$

At $\alpha_m \approx 0.1$ and typical (by the order of magnitude) estimates of $n_{sm} \sim 10^2$ and $\Delta n_{sm} \sim 10$, we have from Eq. (2.6)

$$\epsilon \sim 0.03 \quad (\alpha_m \approx 0.1,\ n_{sm} \sim 10^2,\ \Delta n_{sm} \sim 10), \tag{2.7}$$

so that the ϵ value can be considered as small compared to unity. Hence, we account only for the principal (linear with respect to ϵ) correction, ignoring quadratic and higher-order corrections with respect to ϵ. We emphasize that the existence of fairly small parameter $(\Delta n_{sm}/n_{sm})^2$ is responsible for strong inequality $\epsilon \ll 1$. Note that Eqs. (2.3) and (2.4) are not related to constraint $\epsilon \ll 1$.

Using Eqs. (2.1) and (2.3)–(2.5), we find the analytical dependence of the n_{cm}, Δn_{cm}, and W_{cm} values on n_{sm}, Δn_{sm}, and α_m. Taking into account only the first equalities of Eqs. (1.1) and (1.6), as well as $W_{cm} \equiv W_n|_{c_1 = c_{1m},\, n = n_{cm}}$, we arrive at

$$n_{cm} = \frac{n_{sm}}{8}(1+3\epsilon), \tag{2.8}$$

$$\Delta n_{cm} = \frac{\Delta n_{sm}}{2^{1/2}2}\left(1+\frac{3}{2}\epsilon\right), \tag{2.9}$$

$$W_{cm} = \frac{9}{16}\left(\frac{n_{sm}}{\Delta n_{sm}}\right)^2\left(1+\frac{11}{3}\epsilon\right). \tag{2.10}$$

Formulas (1.14), (2.5), (2.6), and (2.8)–(2.10) express thermodynamic characteristics of micellization at the CMC via n_{sm}, Δn_{sm}, and α_m in the droplet model of molecular aggregates. Formula (2.5), together with Eq. (3.15) derived in [14] for concentration c_{10}, allows us to find experimentally measurable concentration c_{1m}.

According to Eqs. (2.8) and (2.9), inequalities $\Delta n_{cm} < \Delta n_{sm}$ and $\Delta n_{cm}/n_{cm} > \Delta n_{sm}/n_{sm}$ are valid. Hence, the absolute value of the scatter of aggregation numbers in the region of potential barrier of work W_n is smaller than that of aggregation numbers in the region of potential well of work W_n. However, the relative scatter of aggregation numbers in the region of potential barrier is larger than that of aggregation numbers in the region of potential well.

Formula (2.10) demonstrates fairly strong [approximately proportional to $(9/16)(n_{sm}/\Delta n_{sm})^2$] dependence of the W_{cm} value on large parameter $(n_{sm}/\Delta n_{sm})^2$. Even stronger is the dependence of exponential value $\exp(W_{cm})$ on the same parameter. According to [16, 17] and [5], this exponential value determines experimentally significant time of slow relaxation of micellar solution.

Let us illustrate the preceding by simple numerical calculations. For comparison, we cover two typical cases where $n_{sm} = 100$, $\Delta n_{sm} = 15$, and 20 (for simplicity, we vary only Δn_{sm} out of two parameters, n_{sm} and Δn_{sm}). From Eqs. (1.14) and (2.3)–(2.5) with allowance for Eq. (2.6), at $n_{sm} = 100$ and $\Delta n_{sm} = 15$ we can easily find

$$\begin{aligned} W_{sm} &= 10.1\ (\alpha_m \approx 0.1), \quad b_1 = 0.926, \\ b_3 &= 21.4, \quad c_{1m}/c_{10} = 1.61, \end{aligned} \tag{2.11}$$

for $n_{sm} = 100$ and $\Delta n_{sm} = 20$

$$\begin{aligned} W_{sm} &= 10.4\ (\alpha_m \approx 0.1), \quad b_1 = 0.552, \\ b_3 &= 13.3, \quad c_{1m}/c_{10} = 1.30. \end{aligned} \tag{2.12}$$

Further, from Eqs. (2.8)–(2.10) with allowance for Eq. (2.6) at $n_{sm} = 100$ and $\Delta n_{sm} = 15$, we can easily obtain

$$n_{cm} = 15.3, \quad \Delta n_{cm} = 5.90, \quad W_{cm} = 31.9 \tag{2.13}$$

and for $n_{sm} = 100$ and $\Delta n_{sm} = 20$,

$$n_{cm} = 17.7, \quad \Delta n_{cm} = 8.54, \quad W_{cm} = 21.2. \tag{2.14}$$

Relations (2.11)–(2.14), as well as $n_{sm} = 100$, $\Delta n_{sm} = 15$ and 20 values used in these relations, are quite realistic and, hence, testify the plausibility of the droplet model of molecular aggregates.

Relations (2.11) and (2.12) show the high sensitivity of parameters b_1 and b_3 to parameter Δn_{sm}.

3. DEPENDENCE (AT THE CMC) OF THERMODYNAMIC CHARACTERISTICS OF MICELLIZATION ON THE INITIAL PARAMETERS OF THE DROPLET MODEL OF MOLECULAR AGGREGATES

Let us elucidate the dependence (at the CMC) of the thermodynamic characteristics of micellization on initial parameters b_1 and b_3 of Eq. (2.1) of the droplet model of molecular aggregates. Now it can be easily done, returning in formulas of Section 2 from parameters n_{sm} and Δn_{sm} [which were used in expression (1.14) and, correspondingly, were introduced into the conceptual theory of the CMC and critical degree of micellization] to the initial parameters b_1 and b_3 of Eq. (2.1) of the droplet model of molecular aggregates.

Expressing [with the aid of Eqs. (2.3), (2.4), and (2.6)] parameters n_{sm} and Δn_{sm} via parameters b_1 and b_3 by the perturbation method at $\epsilon \ll 1$, we obtain

$$n_{sm} = \left(\frac{b_3}{b_1}\right)^{3/2}\left(1 - \frac{3}{2}\varepsilon\right), \tag{3.1}$$

$$\Delta n_{sm} = 3b_3^{1/2}/b_1, \tag{3.2}$$

where

$$\epsilon = 3\frac{b_1}{b_3^2}\ln\left(3\pi^{1/2}\frac{1-\alpha_m}{\alpha_m}\frac{b_3^2}{b_1^{5/2}}\right). \tag{3.3}$$

High sensitivity of parameter n_{sm} and lower sensitivity of parameter Δn_{sm} to parameters b_1 and b_3 is evident. In order for Eqs. (3.1) and (3.2) to secure the realistic estimates of $\Delta n_{sm} \sim 10^2$ and $\Delta n_{sm} \sim 10$, and correspondingly, in order for Eq. (3.3) to secure inequality $\epsilon \ll 1$, the values of initial parameters b_1 and b_3 of the droplet model should satisfy rather severe constraints, which are assumed to be fulfilled.

Formulas (3.1)–(3.3), together with formulas (1.14), (2.5), and (2.8)–(2.10), determine (in an analytical form) the desired dependence (at the CMC) of all thermodynamic characteristics of micellization on parameters b_1 and b_3 of the droplet model of molecular aggregates.

In particular, for thermodynamic characteristics n_{sm} and n_{cm}, ignoring correction factor ϵ, we obtain the following approximate expressions:

$$n_{sm} \approx (b_3/b_1)^{3/2}, \tag{3.4}$$

$$n_{cm} \approx \frac{1}{8}(b_3/b_1)^{3/2}. \tag{3.5}$$

From Eqs. (2.2), (3.4), and (3.5), we have the following approximate relations:

$$n_{cm}/n_0 \approx 1/2^{3/2}, \quad n_{sm}/n_0 \approx 2^{3/2}, \tag{3.6}$$

indicating the relative positions (that are independent of parameters b_1 and b_3) of points of maximum, inflection, and minimum of work W_n on the aggregation number axis in the droplet model of molecular aggregates.

4. THERMODYNAMIC CHARACTERISTICS OF MICELLIZATION AT THE CMC AS A FUNCTION OF THE POSITION AND HALF-WIDTH OF THE POTENTIAL WELL OF AGGREGATION WORK IN THE QUASI-DROPLET MODEL OF MOLECULAR AGGREGATES

Lets us extend the results obtained in Section 2 to the quasi-droplet model of molecular aggregates proposed and studied in [15]. In this model, the expression

$$W_n = a_1n^2 - a_3n^{3/2} - \left[\ln(c_1/c_{10}) - \frac{9a_3^2}{32a_1}\right]n \tag{4.1}$$

is valid at $n \gg 1$. Equation (3.23) derived in [15] is reduced to Eq. (4.1) after the renotation of its parameters. It will be significant that parameters a_1 and a_3 will be positive and independent of n and c_1. However, the physical meaning of these parameters that was revealed in [15] and allowed to find (so far rather approximately) these parameters using available rough quantitative data on the micellization will not be significant for further discussion.

Let us mention the formal difference between approximate expression (2.1) and similar approximate expression (4.1). In Eq. (2.1), the work of molecular aggregate formation was represented as an expansion in powers of cubic root of aggregation number, whereas, in Eq. (4.1), it was expressed in powers of quadratic root of aggregation number. This can be considered as the reflection of almost two-dimensional structure of the molecular aggregate composed of surfactant molecules in the quasi-droplet model of aggregate, the structure being similar to that of folded monolayer composed of surfactant molecules.

According to Eqs. (1.2) and (4.1), we have

$$n_0 = 9a_3^2/64a_1^2, \tag{4.2}$$

so that n_0 is independent of concentration c_1. Expressions (4.1) and (4.2) secure the fulfillment of equality (1.3). In the $n \gg 1$ region, expression (4.1) satisfies relations (1.4) and (1.5).

The second equalities of Eqs. (1.1) and (1.6) and relation (1.14), together with Eq. (4.1) and $W_{sm} \equiv W_n|_{c_1 = c_{1m},\, n = n_{sm}}$, form three transcendental equations enabling us to analytically express three a_1, a_3, and $\ln(c_{1m}/c_{10})$ values via n_{sm}, Δn_{sm}, and α_m. Solving these equations, we obtain

$$a_1 = 4(\Delta n_{sm})^{-2}(1+\epsilon), \tag{4.3}$$

$$a_3 = 8n_{sm}^{1/2}(\Delta n_{sm})^{-2}\left(1+\frac{4}{3}\epsilon\right), \tag{4.4}$$

$$\ln(c_{1m}/c_{10}) = \frac{1}{2}n_{sm}(\Delta n_{sm})^{-2}(1-\epsilon), \tag{4.5}$$

where the ϵ value dependent on n_{sm}, Δn_{sm}, and α_m is given by the equality

$$\epsilon = \frac{3}{4}\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2 \ln\left(\pi^{1/2}\frac{1-\alpha_m}{\alpha_m}n_{sm}\Delta n_{sm}\right). \tag{4.6}$$

At $\alpha_m \approx 0.1$ and typical (by the order of magnitude) estimates of $n_{sm} \sim 10^2$ and $\Delta n_{sm} \sim 10$, it follows from Eq. (4.6) that

$$\epsilon \sim 0.07 \quad (\alpha_m \approx 0.1,\ n_{sm} \sim 10^2,\ \Delta n_{sm} \sim 10), \tag{4.7}$$

so that the ϵ value can be considered as small compared to unity. Therefore, we take into account only the principal (linear with respect to ϵ) correction ignoring quadratic and higher-order corrections with respect to ϵ. As in the droplet model of molecular aggregates, rather small parameter $(\Delta n_{sm}/n_{sm})^2$ is responsible for strong inequality $\epsilon \ll 1$. Note that Eqs. (4.3) and (4.4) are not related to constraint $\epsilon \ll 1$.

Using Eqs. (4.1) and (4.3)–(4.5), we find analytically the dependence of n_{cm}, Δn_{cm}, and W_{cm} on n_{sm}, Δn_{sm}, and α_m. Accounting for the first equalities of Eqs. (1.1) and (1.6), as well as for $W_{cm} \equiv W_n|_{c_1 = c_{1m},\, n = n_{cm}}$, we have

$$n_{cm} = \frac{n_{sm}}{4}(1+2\epsilon), \tag{4.8}$$

$$\Delta n_{cm} = \frac{\Delta n_{sm}}{2^{1/2}}\left(1+\frac{1}{2}\epsilon\right), \tag{4.9}$$

$$W_{cm} = \frac{1}{4}\left(\frac{n_{sm}}{\Delta n_{sm}}\right)^2\left(1+\frac{11}{3}\epsilon\right). \tag{4.10}$$

Formulas (1.14), (4.5), (4.6), and (4.8)–(4.10) express the thermodynamic characteristics of micellization at the CMC via n_{sm}, Δn_{sm}, and α_m in the quasi-droplet model of molecular aggregates. Formula (4.5), together with formula (3.24) derived in [15] for concentration c_{10}, allows us to find experimentally measurable concentration c_{1m}.

The fact that the structure of obtained results is fairly similar to their analogs in the droplet model of molecular aggregates found in Section 2 argues for the droplet and quasi-droplet models of molecular aggregates, thereby allowing also to quantitatively compare these models.

Let us perform this comparison. According to Eqs. (4.8) and (4.9), inequalities $\Delta n_{cm} < \Delta n_{sm}$ and $\Delta n_{cm}/n_{cm} > \Delta n_{sm}/n_{sm}$ are still valid in the quasi-droplet model. According to Eq. (4.10), fairly strong dependence of the W_{cm} value on large parameter $(n_{sm}/\Delta n_{sm})^2$ still exists. However, as is now seen from comparison of Eqs. (4.10) and (2.10), this dependence is approximately by 9/4 times weaker than in the droplet model of molecular aggregates. Correspondingly, the extremely strong dependence of exponential value $\exp[(5/16)(n_{sm}/\Delta n_{sm})^2]$, determining, as was already mentioned, experimentally significant time of slow relaxation of micellar solution, on large parameter $(n_{sm}/\Delta n_{sm})^2$ becomes now weaker approximately by many times of $\exp(W_{cm})$. Thus, it can be expected that, for micellar solutions where this time is not so long and, hence, the $\exp(W_{cm})$ value is not very large, the quasi-droplet model of molecular aggregates securing estimate $\exp(W_{cm}) \sim \exp[(1/4)(n_{sm}/\Delta n_{sm})^2]$ seems to be preferable. On the contrary, for micellar solutions where this time is very large and, hence, the $\exp(W_{cm})$ value is also very large, the droplet model of molecular aggregates securing estimate $\exp(W_{cm}) \sim \exp[(9/16)(n_{sm}/\Delta n_{sm})^2]$ seems to be preferable. Note also that, in the quasi-droplet model at the same values of parameters n_{sm} and Δn_{cm}, the n_{cm} and Δn_{cm} values, as is seen from comparison of Eqs. (4.8) and (4.9) with Eqs. (2.8) and (2.9), will be approximately twice as large and, on the contrary, the $\ln(c_{1m}/c_{10})$ value, as is seen from comparison of Eqs. (4.5) and (2.5), will be approximately twice as small as in the droplet model.

Let us illustrate the preceding by simple numerical calculations. For comparison, we cover two typical cases where it is set that $n_{sm} = 100$, $\Delta n_{sm} = 10$, and 15 (for simplicity, only parameter Δn_{sm} is varied out of two parameters, n_{sm} and Δn_{sm}). From Eqs. (1.14), (4.3)–(4.5) with allowance for Eq. (4.6) at $n_{sm} = 100$ and $\Delta n_{sm} = 10$, we easily find

$$\begin{aligned} W_{sm} &= 9.68\ (\alpha_m \approx 0.1), \quad a_1 = 0.0429, \\ a_3 &= 0.877, \quad c_{1m}/c_{10} = 1.59, \end{aligned} \tag{4.11}$$

at $n_{sm} = 100$ and $\Delta n_{sm} = 15$

$$\begin{aligned} W_{sm} &= 10.1\ (\alpha_m \approx 0.1), \quad a_1 = 0.0208, \\ a_3 &= 0.436, \quad c_{1m}/c_{10} = 1.20. \end{aligned} \tag{4.12}$$

Further, from Eqs. (4.8)–(4.10) with allowance for Eq. (4.6) at $n_{sm} = 100$ and $\Delta n_{sm} = 10$, we easily obtain

$$n_{cm} = 28.6, \quad \Delta n_{cm} = 7.33, \quad W_{cm} = 31.7, \tag{4.13}$$

at $n_{sm} = 100$ and $\Delta n_{sm} = 15$

$$n_{cm} = 33.5, \quad \Delta n_{cm} = 11.5, \quad W_{cm} = 18.0. \tag{4.14}$$

Relations (4.11)–(4.14), as well as $n_{sm} = 100$, $\Delta n_{sm} =$ 10 and 15 accepted in these relations, are quite realistic and, hence, support the plausibility of the quasi-droplet model of molecular aggregates.

Relations (4.11) and (4.12) show high sensitivity of parameters a_1 and a_3 to parameter Δn_{sm}.

5. DEPENDENCE (AT THE CMC) OF THERMODYNAMIC CHARACTERISTICS OF MICELLIZATION ON THE INITIAL PARAMETERS OF THE QUASI-DROPLET MODEL OF MOLECULAR AGGREGATES

Let us extend the results obtained in Section 3 to the quasi-droplet model of molecular aggregates.

From Eqs. (4.3), (4.4), and (4.6), by the perturbation method at $\epsilon \ll 1$, we obtain

$$n_{sm} = \left(\frac{a_3}{2a_1}\right)^2 \left(1 - \frac{2}{3}\epsilon\right), \tag{5.1}$$

$$\Delta n_{sm} = \frac{2}{a_1^{1/2}}\left(1 + \frac{1}{2}\epsilon\right), \tag{5.2}$$

where

$$\epsilon = 3 \times 2^4 \frac{a_1^3}{a_3^4} \ln\left(\frac{\pi^{1/2}}{2} \frac{1 - \alpha_m}{\alpha_m} \frac{a_3^2}{a_1^{5/2}}\right). \tag{5.3}$$

High sensitivity of the n_{sm} parameter to parameters a_1 and a_3 and lower sensitivity of the Δn_{sm} parameter to parameter a_1 are seen. In order for Eqs. (5.1) and (5.2) to secure realistic estimates $n_{sm} \sim 10^2$ and $\Delta n_{sm} \sim 10$, and, correspondingly, for Eq. (5.3) to secure inequality $\epsilon \ll 1$, the values of initial parameters a_1 and a_3 of the quasi-droplet model should satisfy rather severe constraints, which are considered as fulfilled.

Formulas (5.1)–(5.3), together with formulas (1.14), (4.5), and (4.8)–(4.10) determine (in the analytical form) the desired dependence (at the CMC) of all thermodynamic characteristics of micellization on parameters a_1 and a_3 of the quasi-droplet model of molecular aggregates.

In particular, for thermodynamic characteristics n_{sm} and n_{cm} with the neglect of correction parameter ϵ, we have approximate expressions

$$n_{sm} \approx (a_3/2a_1)^2, \tag{5.4}$$

$$n_{cm} \approx (a_3/4a_1)^2. \tag{5.5}$$

From Eqs. (4.2), (5.4), and (5.5), we obtain approximate relations

$$n_{cm}/n_0 \approx (2/3)^2, \quad n_{sm}/n_0 \approx (4/3)^2, \tag{5.6}$$

indicating the relative positions (independent of parameters a_1 and a_3) of the points of maximum, inflection, and minimum of work W_n on the aggregation number axis in the quasi-droplet model of molecular aggregates.

6. THERMODYNAMIC CHARACTERISTICS OF MICELLIZATION IN THE CONCENTRATION REGION ABOVE THE CMC

Let us derive formulas for the thermodynamic characteristics of micellization in the region $c_1 > c_{1m}$ of monomer concentration c_1 above the CMC that are valid in the droplet and quasi-droplet models of molecular aggregates. It is natural that, within the framework of the models in question, all conclusions will be referred only to the c_1 region where micelles still retain their spherical shape.

As we will be assured below using Eqs. (6.8)–(6.11) and (6.13)–(6.16), this concentration region can be considered, even upon the accumulation (in micelles) of almost the entire surfactant in micellar solution (when the degree of micellization is close to unity and overall surfactant concentration is much higher than the CMC [18]), as so narrow that equalities

$$n_c \approx n_{cm}, \quad n_s \approx n_{sm}, \quad \Delta n_c \approx \Delta n_{cm}, \quad \Delta n_s \approx \Delta n_{sm} \tag{6.1}$$

are fulfilled in this region with a high accuracy when the error does not exceed several percents. Then, integrating (with respect to c_1) relations (1.5) that are valid at $n_c \gg 1$ and $n_s \gg 1$ in the droplet and quasi-droplet models of molecular aggregates, we obtain with the same high accuracy the following relations:

$$\exp(W_c)/\exp(W_{cm}) \approx (c_{1m}/c_1)^{n_{cm}-1}, \tag{6.2}$$

$$\exp(W_s)/\exp(W_{sm}) \approx (c_{1m}/c_1)^{n_{sm}-1}, \tag{6.3}$$

in view of Eq. (1.8), we also obtain

$$c_1/c_{1m} \approx (c_M/c_{Mm})^{1/n_{sm}}. \tag{6.4}$$

Note that Eq. (6.4) can also be derived from the law of mass action in a quasi-chemical approach when the aggregation number is assumed to be constant [6].

Since parameter n_{sm} is rather large, $n_{sm} \sim 10^2$, it follows from Eq. (6.4) that, even at

$$c_M/c_{Mm} \lesssim 10^3, \qquad (6.5)$$

the inequality

$$c_1/c_{1m} \lesssim 1 + 6.91/n_{sm} \qquad (6.6)$$

is valid.

According to Eq. (1.12), at the upper limit of inequalities (6.5) and (6.6), we have $\alpha \simeq 0.99$ for the degree of micellization α and $\alpha_m \simeq 0.1$ that means that micelles already accumulate the main part of the entire surfactant in micellar solution. Hereafter, we consider constraints (6.5) and (6.6) denoting the narrowness of concentration region $c_1 > c_{1m}$ as being fulfilled.

In the case of droplet model of molecular aggregates, we find (moreover, even in the analytical form) the dependence of n_c, n_s, Δn_c, and Δn_s values on concentration c_1 via $\ln(c_1/c_{10})$, using Eqs. (1.1) and (1.6), as well as model formula (2.1). According to Eq. (2.5), at the upper limit of constraint (6.6), relation

$$\frac{\ln(c_1/c_{10}) - \ln(c_{1m}/c_{10})}{\ln(c_{1m}/c_{10})} \simeq 6.28\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2 \qquad (6.7)$$

is valid. In this equation, we ignore (for the simplicity) correction term ϵ. From Eq. (6.7) and at $(\Delta n_{sm}/n_{sm})^2 \sim 10^{-2}$, we see that the deviation of the $\ln(c_1/c_{10})$ value from its magnitude at the CMC is relatively small. Then, retaining principal (with respect to this deviation) contributions to the dependences of n_c, n_s, Δn_c, and Δn_s on $\ln(c_1/c_{10})$ and taking into account Eqs. (2.3)–(2.6), (2.8), (2.9), and (6.7), we obtain

$$n_c \simeq n_{cm}\left[1 - 3.45\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right], \qquad (6.8)$$

$$n_s \simeq n_{sm}\left[1 + 3.45\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right], \qquad (6.9)$$

$$\Delta n_c \simeq \Delta n_{cm}\left[1 - 3.45\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right], \qquad (6.10)$$

$$\Delta n_s \simeq \Delta n_{sm}\left\{1 - \left[0.77\ln\left(\pi^{1/2}\frac{1-\alpha_m}{\alpha_m}n_{sm}\Delta n_{sm}\right) - 2.65\right]\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^4\right\} \qquad (6.11)$$

[as in Eq. (6.7), correction term ϵ is ignored in Eqs. (6.8)–(6.10)].

Even in the case of the quasi-droplet model of molecular aggregates, we find (moreover, again in the analytical form) the dependences of n_c, n_s, Δn_c, and Δn_s values on concentration c_1 via $\ln(c_1/c_{10})$, using Eqs. (1.1), (1.6), and model formula (4.1). According to Eq. (4.5), at the upper limit of constraint (6.6), the relation

$$\frac{\ln(c_1/c_{10}) - \ln(c_{1m}/c_{10})}{\ln(c_{1m}/c_{10})} \simeq 13.8\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2 \qquad (6.12)$$

is valid, where the correction term ϵ is ignored for simplicity. From Eq. (6.12) and at $(\Delta n_{sm}/n_{sm})^2 \sim 10^{-2}$, we see that the deviation of $\ln(c_1/c_{10})$ from its value at the CMC is still relatively small. Then, retaining principal (with respect to this deviation) contributions to the dependences of n_c, n_s, Δn_c, and Δn_s on $\ln(c_1/c_{10})$, taking Eqs. (4.3)–(4.5), (4.8), (4.9), and (6.12), into account, and ignoring, as in Eq. (6.12) by correction term ϵ, we obtain

$$n_c \simeq n_{cm}\left[1 - 6.91\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right], \qquad (6.13)$$

$$n_s \simeq n_{sm}\left[1 + 3.45\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right], \qquad (6.14)$$

$$\Delta n_c \simeq \Delta n_{cm}\left[1 - 5.18\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right], \qquad (6.15)$$

$$\Delta n_s \simeq \Delta n_{sm}\left[1 - 2.59\left(\frac{\Delta n_{sm}}{n_{sm}}\right)^2\right]. \qquad (6.16)$$

It follows from Eqs. (6.8)–(6.11) and (6.13)–(6.16) at $(\Delta n_{sm}/n_{sm})^2 \sim 10^{-2}$ that equalities (6.1) are fulfilled with high accuracy at the upper limit of constraint (6.6). Evidently, this statement is valid throughout the $c_1 > c_{1m}$ concentration region admitted by constraint (6.6). The existence of small parameter $(\Delta n_{sm}/n_{sm})^2$ is responsible for the fulfillment of equalities (6.1) in the droplet and quasi-droplet models of molecular aggregates. Remind that, in these models, this parameter secures the smallness of correction term ϵ and the smallness of maximal deviation of $\ln(c_1/c_{10})$ from its value at the CMC admitted by constraint (6.6).

Terms of higher orders with respect to small parameter $(\Delta n_{sm}/n_{sm})^2$ could also be accounted for in Eqs. (6.8)–(6.11), (6.13)–(6.16), retaining correction term ϵ and the correction contributions with respect to the deviation of $\ln(c_1/c_{10})$ from its value at the CMC. In particular, setting $n_{sm} = 100$ and $\Delta n_{sm} = 15$, according to Eq. (2.13), we have in the droplet model of molecular aggregates $n_{cm} = 15.3$ and $\Delta n_{cm} = 5.90$ and, with allowances for all corrections, we find $n_c = 14.2$, $n_s = 107.8$, $\Delta n_c = 5.47$, and $\Delta n_s = 14.96$ at the upper limit of inequality (6.6). Similarly, in the quasi-droplet model of molecular aggregates at $n_{sm} = 100$ and $\Delta n_{sm} = 15$, according to Eq. (4.14), we have $n_{sm} = 33.5$, $\Delta n_{cm} = 33.5$ and $\Delta n_{cm} = 11.5$ and, with allowances for all corrections, we find $n_c = 29.79$, $n_s = 107.3$, $\Delta n_c = 10.3$, and $\Delta n_s = 14.11$ at the upper limit of inequality (6.6).

Equalities (6.1)–(6.3) yield (in the analytical form), together with formulas for the thermodynamic characteristics of micellization at the CMC derived in Sections 1–5, the thermodynamic characteristics of micellization in the concentration region above the CMC. In this case, both the droplet and quasi-droplet models of molecular aggregates are covered.

From Eqs. (6.2)–(6.4), at $n_{cm} \sim 10$ and $n_{sm} \sim 10^2$, follow that the $\exp(W_s)$ value cannot become smaller too much, provided that constraints (6.5) and (6.6) are fulfilled in the $c_1 > c_{1m}$ region; however, the $\exp(W_s)$ value can decrease, even by a fairly large factor.

Let us now estimate the time t_r of slow relaxation of micellar solution. According to formula (4.3) [5] that is valid irrespective of the simulation of molecular aggregates, we have

$$t_r \simeq \frac{\Delta n_c}{4\pi^{1/2} n_s^2 c_1 v R_c^2} e^{W_c}, \qquad (6.17)$$

where v is the parameter characterizing the rate of monomer absorption from solution on the surface of molecular aggregate and R_c is the radius of critical molecular aggregate (assumed here as spherical). In accordance with estimates (4.4) of [5] and experimental data of [17], we set approximately

$$c_1 \sim 10^{17}\ \text{cm}^{-3}, \quad v \sim 1\ \text{cm s}^{-1}, \quad R_c \sim 10^{-7}\ \text{cm}. \qquad (6.18)$$

At the upper limit of constraint (6.5), it follows from Eqs. (6.2) and (6.4)

$$e^{W_c} \simeq 10^{-3(n_{cm}-1)/n_{sm}} e^{W_{cm}}. \qquad (6.19)$$

Substituting Eqs. (6.18) and (6.19) into Eq. (6.17), we obtain

$$t_r \sim \frac{10^{-3}}{4\pi^{1/2}} 10^{-3(n_{cm}-1)/n_{sm}} \frac{\Delta n_{cm}}{n_{sm}^2} e^{W_{cm}}, \qquad (6.20)$$

where, in view of Eq. (6.1), it is set that $n_s \simeq n_{sm}$ and $\Delta n_c \simeq \Delta n_{cm}$. In accordance with the discussion in Sections 2 and 4, demonstrated by relation (6.20) strong dependence of the time of slow relaxation on the height W_{cm} of activation barrier of micellization at the CMC results in a considerable constraint to the possible values of the n_{sm} and Δn_{sm} in the droplet and quasi-droplet models of molecular aggregates. In the case of the droplet model of molecular aggregates, we assume that $n_{sm} = 100$ and $\Delta n_{sm} = 20$. Then, substituting Eq. (2.14) into Eq. (6.20), we find $t_r \sim 60$ s that is quite realistic value according to experimental data [16, 17] on the time of slow relaxation of micellar solution. In the case of the quasi-droplet model of molecular aggregates, we assume that $n_{sm} = 100$ and $\Delta n_{sm} = 15$. Then, substituting Eq. (4.14) into Eq. (6.20), we find $t_r \sim 1$ s that is also quite realistic value according to experimental data [16, 17].

Note also the following circumstance. According to Eq. (6.6), a relative increase in monomer concentration c_1 that is needed to accumulate almost the whole of surfactant in micelles after reaching the CMC turned out to be still markedly lower than relative increase in monomer concentration c_1 estimated by relations (2.11), (2.12) and (4.11), (4.12) that is necessary to reach the CMC after the appearance of the potential barrier and potential well of work W_n. This confirms all what have been said in Section 1 on the physical meaning of the CMC.

The fact that, within the entire region (6.6) of concentration c_1, the n_s and Δn_s values, in accordance with Eq. (6.1), coincide with their values at the CMC, makes it possible to assume that n_s and Δn_s in equilibrium micelle distribution (1.7) are virtually constant in the entire region (6.6) (note that this fact is the essence of quasi-chemical approximation in the theory of micellization [6]). Hence, it is the distribution (1.7) that can be used to experimentally determine virtually constant n_s and Δn_s values throughout the region (6.6) of solution concentration, but not only at the CMC. Because, in region (6.6), exponent $\exp(-W_s)$ can be, in view of Eq. (6.3), not so small (as at the CMC), then, in accordance with Section 1, the sensitivity of distribution (1.7) to n_s and Δn_s values becomes extremely high. Hence, this allows us to significantly decrease the error of experimental determination [with the aid of distribution (1.7)] of the n_s and Δn_s values, which in region (6.6) are virtually equal to the n_{sm} and Δn_{sm} values.

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REFERENCES

1. Rusanov, A.I., Kuni, F.M., and Shchekin, A.K., *Kolloidn. Zh.,* 2000, vol. 62, no. 2, p. 199.
2. Kuni, F.M., Shchekin, A.K., Grinin, A.P., and Rusanov, A.I., *Kolloidn. Zh.*, 2000, vol. 62, no. 2, p. 204.
3. Kuni, F.M., Grinin, A.P., Shchekin, A.K., and Rusanov, A.I., *Kolloidn. Zh.*, 2000, vol. 62, no. 4, p. 505.
4. Kuni, F.M., Grinin, A.P., Shchekin, A.K., and Rusanov, A.I., *Kolloidn. Zh.*, 2001, vol. 63, no. 2, p. 220.
5. Kuni, F.M., Shchekin, A.K., Grinin, A.P., and Rusanov, A.I., *Kolloidn. Zh.*, 2001, vol. 63, no. 6, p. 792.
6. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh PAV* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
7. Tanford, C., *J. Phys. Chem.,* 1974, vol. 78, no. 21, p. 2469.
8. Tanford, C., *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Toronto: Wiley, 1980.
9. Israelachvili, J.N., Mitchell, D.J., and Ninham, B.W., *J. Chem. Soc., Faraday Trans. 2*, 1976, vol. 72, no. 9, p. 1525.

10. Nagarajan, R. and Ruckenstein, E., *J. Colloid Interface Sci.*, 1977, vol. 60, p. 221.
11. Nagarajan, R. and Ruckenstein, E., *J. Colloid Interface Sci.,* 1979, vol. 71, p. 580.
12. Nagarajan, R. and Ruckenstein, E., *J. Colloid Interface Sci.,* 1983, vol. 91, no. 2, p. 500.
13. Nagarajan, R., Structure–Performance Relationships in Surfactants, *Surfactant Sci. Ser.*, Usimi, K. and Uena, N., Eds., New York: Marcel Dekker, 1997, vol. 70, p. 1.
14. Rusanov, A.I., Kuni, F.M., Grinin, A.P., and Shchekin, A.K., *Kolloidn. Zh.*, 2002, vol. 64, no. 5, p. 670.
15. Grinin, A.P., Rusanov, A.I., Kuni, F.M., and Shchekin, A.K., *Kolloidn. Zh.*, 2003, vol. 65, no. 2, p. 168.
16. Aniansson, E.A.G., Wall, S.N., Almgren, M., *et al.*, *J. Phys. Chem.*, 1976, vol. 80, no. 9, p. 905.
17. Gormelli, G., Gettins, W.Y., and Wyn-Jones, E., *Molecular Interactions*, Ratajczak, H. and Orville-Thomas, W.Y., Chichester: Wiley, 1981.
18. Rusanov, A.I., *Kolloidn. Zh.*, 1998, vol. 60, no. 2, p. 255.