

Relations for Extrema of the Work of Aggregation in Micellar Solutions

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Abstract—Exact relations for the dependence of the positions of extrema of the aggregation work on the aggregation number axis on the surfactant monomer concentration are found for a dilute micellar solution. Relations for the half-widths of the vicinities of the extrema of the aggregation work are determined also. These half-widths are determined by the condition that, within the boundaries of their values, the aggregation work deviates from its extreme values by a thermal unit. The relations derived are illustrated by calculations based on the droplet and quasi-droplet models of spherical aggregates of nonionic surfactant. Some important applications of the obtained results to the theory of relaxation in micellar solutions are considered.

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INTRODUCTION

Characteristics of the extrema of the work of aggregation in surfactant micellar solutions may be experimentally determined from the data on the times of “fast” and “slow” relaxation in solutions [1–5]. These characteristics include positions of extrema on the aggregation number axis and the half-widths of the vicinities of extrema, with these half-widths being determined by the condition that, within the ranges of these parameters, the work of aggregation deviates from its extreme magnitudes by a thermal unit. The determination of relations for these characteristics allows us to experimentally verify the kinetics and thermodynamics of micellization and also to obtain additional information from experimental data on such parameters as the rate of surfactant monomer addition to micelles and the height of a maximum and the depth of a minimum of the aggregation work.

In this paper, we confine ourselves to the consideration of an ideal associated system (the interactions between particles of all sizes are ignored). For such a system, exact relations will be obtained for derivatives of the positions of the maximum and minimum of the work of aggregation and half-widths of their vicinities with respect to monomer concentrations in micellar solutions. These relations are not associated with the material isolation of a solution and the fact whether the solution is in the equilibrium state or not. These relations have identical forms for nonionic and ionic surfactant aggregates not only above the first (CMC_1) but also above the second (CMC_2) critical micellization concentration, when, in addition to spherical micelles, cylindrical and other micelles are present in a solution

(provided that the interaction between them is still negligible). In this paper, the relations obtained will be illustrated by calculations performed on the basis of droplet [5, 6] and quasi-droplet [5, 7] models of spherical nonionic surfactant aggregates, as applied to the work of aggregation. In the final part of the paper, we consider some applications of the derived relations to the theory of relaxation in micellar solutions.

1. DERIVATIVES OF THE POSITIONS OF EXTREMA OF THE WORK OF AGGREGATION AND HALF-WIDTHS OF THEIR VICINITIES WITH RESPECT TO MONOMER CONCENTRATION

The aggregation number of a molecular aggregate in a micellar solution is denoted by n . The minimal work of the formation of a surfactant molecular aggregate (hereafter for brevity, the work of aggregation) is expressed in thermal units of energy kT (k is Boltzmann's constant and T is the solution temperature) and denoted by W_n . At $n = 1$, the aggregates represent surfactant monomers. Their concentration (the number of monomers in the unit volume of the solution) is denoted by c_1 . Work W_n depends not only on aggregation number n but also on monomer concentration c_1 . The positions of the maximum and minimum of work W_n on the axis of variable n are denoted by n_c and n_s , respectively. The height of the potential barrier and the depth of the potential well are denoted by $W_c \equiv W_n|_{n=n_c}$ and $W_s \equiv W_n|_{n=n_s}$, respectively. Let us introduce the half-widths

[†] Deceased.

of the potential barrier and well of work W_n on the axis and of variable n determined by the equalities

$$\begin{aligned}\Delta n_c &= [-2/(\partial^2 W_n/\partial n^2)_{n=n_c}]^{1/2}, \\ \Delta n_s &= [2/(\partial^2 W_n/\partial n^2)_{n=n_s}]^{1/2}.\end{aligned}\quad (1.1)$$

Signs minus and plus under radicals suggest that W_n has a maximum at $n = n_c$ and a minimum at $n = n_s$. Values n_c , n_s , W_c , W_s , Δn_c , and Δn_s are functions of surfactant monomer concentration c_1 .

With allowance for definitions (1.1), quadratic approximations for work W_n in the vicinity of its maximum and minimum can be written as

$$\begin{aligned}W_n - W_c &= -\left(\frac{n - n_c}{\Delta n_c}\right)^2 \\ (n_c - \Delta n_c \leq n \leq n_c + \Delta n_c),\end{aligned}\quad (1.2)$$

and

$$\begin{aligned}W_n - W_s &= \left(\frac{n - n_s}{\Delta n_s}\right)^2 \\ (n_s - \Delta n_s \leq n \leq n_s + \Delta n_s),\end{aligned}\quad (1.3)$$

whose accuracy is the higher, the smaller the selected deviations $|n - n_c|$ and $|n - n_s|$ compared to Δn_c and Δn_s , respectively. According to (1.2), work W_n decreases by a thermal unit, when variable n deviates from n_c by Δn_c . According to (1.3), work W_n increases by a thermal unit, when variable n deviates from n_s by Δn_s . These facts disclose the physical meaning of introduced half-widths Δn_c and Δn_s . We take into account that, in the absence of interaction between molecular aggregates, the dependence of the work of aggregation, W_n , on surfactant monomer concentration c_1 has a universal (independent of a model selected for molecular aggregates) form and is determined by term $-(n - 1)\ln c_1$ [4, 5]. Therefore, the following relations:

$$\begin{aligned}\partial W_n/\partial c_1 &= -(n - 1)/c_1, \quad \partial W_c/\partial c_1 = -(n_c - 1)/c_1, \\ \partial W_s/\partial c_1 &= -(n_s - 1)/c_1,\end{aligned}\quad (1.4)$$

are valid.

Let us differentiate $W_n - W_c$ and $W_n - W_s$ with respect to c_1 using relations (1.2), (1.3), and (1.4). Equating the results, we obtain

$$\begin{aligned}-\frac{(n - n_c)}{c_1} &= 2\frac{n - n_c}{\Delta n_c^2} \frac{\partial n_c}{\partial c_1} + 2\frac{(n - n_c)^2}{\Delta n_c^3} \frac{\partial \Delta n_c}{\partial c_1} \\ (|n - n_c| < \Delta n_c),\end{aligned}\quad (1.5)$$

$$\begin{aligned}-\frac{(n - n_s)}{c_1} &= -2\frac{n - n_s}{\Delta n_s^2} \frac{\partial n_s}{\partial c_1} - 2\frac{(n - n_s)^2}{\Delta n_s^3} \frac{\partial \Delta n_s}{\partial c_1} \\ (|n - n_s| < \Delta n_s).\end{aligned}\quad (1.6)$$

In the limiting case, at $n \rightarrow n_c$ and $n \rightarrow n_s$, from Eqs. (1.5) and (1.6), we arrive exactly at

$$\frac{\partial \ln n_c}{\partial \ln c_1} = -\frac{\Delta n_c^2}{2n_c},\quad (1.7)$$

and

$$\frac{\partial \ln n_s}{\partial \ln c_1} = \frac{\Delta n_s^2}{2n_s},\quad (1.8)$$

where the result is expressed via logarithmic derivatives.

Note that the problem of determining the positions of extrema of an equilibrium distribution over the aggregation number of molecular aggregates as functions of c_1 (in a general case, of the chemical potential of surfactant monomers) was solved for the first time in [8] (see also [9]). At low concentrations of monomers and molecular aggregates (when their activities may be replaced by concentrations), the result obtained previously ([9], formula (50.7)) is equivalent to Eqs. (1.7) and (1.8), as applied to the equilibrium distribution. Relation (1.8) was also derived from the definition of the average aggregation number of micelles assuming the Gaussian quasi-equilibrium distribution of aggregates in the micellar region $n_s - \Delta n_s \leq n \leq n_s + \Delta n_s$ [1]. As follows from Eqs. (1.7) and (1.8), $\partial n_c/\partial c_1 < 0$ and $\partial n_s/\partial c_1 > 0$; hence, n_c decreases and n_s increases with an increase in c_1 . This regularity, which had been for the first time formulated in [8, 9], was verified employing the droplet and quasi-droplet models of spherical aggregates of a nonionic surfactant [6, 7, 10].

Now, let us find derivative $\partial \Delta n_c/\partial c_1$. We differentiate the first of definitions (1.1) with respect to c_1 . Then, using this definition once more, we obtain

$$\frac{\partial \Delta n_c}{\partial c_1} = \frac{\Delta n_c^3}{4} \frac{\partial}{\partial c_1} \left(\frac{\partial^2 W_n}{\partial n^2} \right)_{n=n_c}.\quad (1.9)$$

Further, we twice differentiate the first of relations (1.4) with respect to n . In the resultant equality, let us change the order of the differentiation with respect to independent variables c_1 and n . We conclude that second derivative $\partial^2 W_n/\partial n^2$ is independent of c_1 . In this case, the dependence of $(\partial^2 W_n/\partial n^2)_{n=n_c}$ on c_1 is

entirely determined by the dependence of n_c on c_1 , and we have

$$\frac{\partial}{\partial c_1} \left(\frac{\partial^2 W_n}{\partial n^2} \right)_{n=n_c} = \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_c} \frac{\partial n_c}{\partial c_1}. \quad (1.10)$$

Substituting Eq. (1.10) into (1.9), we obtain

$$\frac{\partial \Delta n_c}{\partial c_1} = \frac{\Delta n_c^3}{4} \frac{\partial n_c}{\partial c_1} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_c}. \quad (1.11)$$

Substituting equality (1.7) into (1.11), we derive exactly

$$\frac{\partial \ln \Delta n_c}{\partial \ln c_1} = -\frac{\Delta n_c^4}{8} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_c}, \quad (1.12)$$

where the result is expressed via the logarithmic derivative.

Analogously, repeating the above speculations as applied to half-width Δn_s and employing the second of definitions (1.1), we arrive at

$$\frac{\partial \Delta n_s}{\partial c_1} = -\frac{\Delta n_s^3}{4} \frac{\partial n_s}{\partial c_1} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_s}. \quad (1.13)$$

Substituting equality (1.8) into (1.13), we obtain exactly

$$\frac{\partial \ln \Delta n_s}{\partial \ln c_1} = -\frac{\Delta n_s^4}{8} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_s}. \quad (1.14)$$

Relations (1.12) and (1.14) were previously unknown.

It is obvious that equalities (1.7), (1.8), (1.12), and (1.14) are not related with the material isolation of a solution and the fact whether the solution is in the equilibrium state or not. These equalities are valid for aggregates of both nonionic and ionic surfactants. They are true even above the CMC₂, when, in addition to spherical micelles, cylindrical and micelles of other shapes are present in the solution (provided that their interaction can be ignored).

The following formula is derived from Eqs. (1.7) and (1.12):

$$\frac{\partial \ln(\Delta n_c/n_c)}{\partial \ln c_1} = \frac{\Delta n_c^2}{2n_c} - \frac{\Delta n_c^4}{8} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_c}. \quad (1.15)$$

Analogously, from Eqs. (1.8) and (1.14), we obtain

$$\frac{\partial \ln(\Delta n_s/n_s)}{\partial \ln c_1} = -\frac{\Delta n_s^2}{2n_s} - \frac{\Delta n_s^4}{8} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n=n_s}. \quad (1.16)$$

In the next paragraph, using equations (1.15) and (1.16), we shall clarify the behavior of relative half-

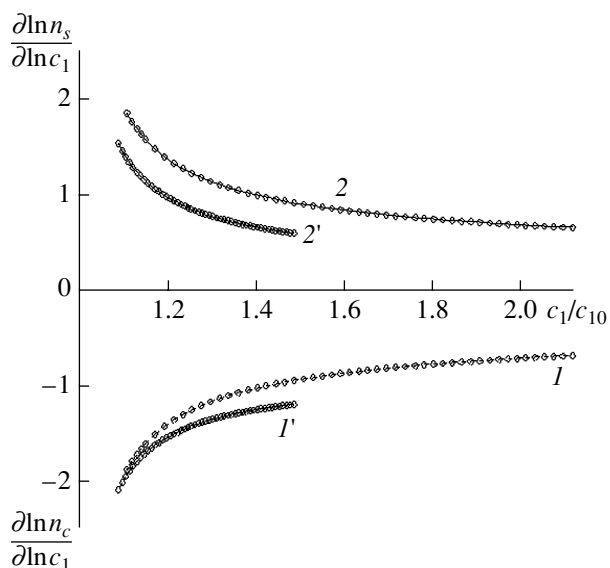


Fig. 1. Logarithmic derivatives (I, I') $\partial \ln n_c / \partial \ln c_1$ and ($2, 2'$) $\partial \ln n_s / \partial \ln c_1$ as functions of surfactant monomer concentration c_1 expressed in c_{10} units for ($I, 2$) droplet and ($I', 2'$) quasi-droplet models of spherical surfactant aggregates.

widths, $\Delta n_c/n_c$ and $\Delta n_s/n_s$, of the vicinities of the maximum and minimum of aggregation work upon an increase in surfactant monomer concentration.

2. CALCULATIONS ON THE BASIS OF DROPLET AND QUASI-DROPLET MODELS OF SURFACTANT AGGREGATES

According to the droplet model of spherical molecular aggregates of a nonionic surfactant, in the range $n \gg 1$, albeit to the left of the region of existence of cylindrical micelles, the dependence of the aggregation work on aggregation number n has the form [5, 6]:

$$W_n^{(d)} = b_1 n^{4/3} - \left[\ln(c_1/c_{10}^{(d)}) + \frac{4}{3}(2b_1 b_3)^{1/2} \right] n + b_3 n^{2/3}. \quad (2.1)$$

Similarly, in the quasi-droplet model of spherical molecular aggregates of a nonionic surfactant, in the range $n \gg 1$, albeit to the left of the region of existence of cylindrical micelles, we have [5, 7]

$$W_n^{(q)} = a_1 n^2 - a_3 n^{3/2} - \left[\ln \left((c_1/c_{10}^{(q)}) - \frac{9a_3^2}{32a_1} \right) \right] n. \quad (2.2)$$

Hereafter, superscripts (d) and (q) refer to the droplet and quasi-droplet models, respectively. Parameters $b_1, b_3, c_{10}^{(d)}, a_1, a_3,$ and $c_{10}^{(q)}$ of the models are positive and independent of n and c_1 . The physical meaning of these parameters revealed in [5–7] allows us to find their values, only quite approximately, from the quanti-

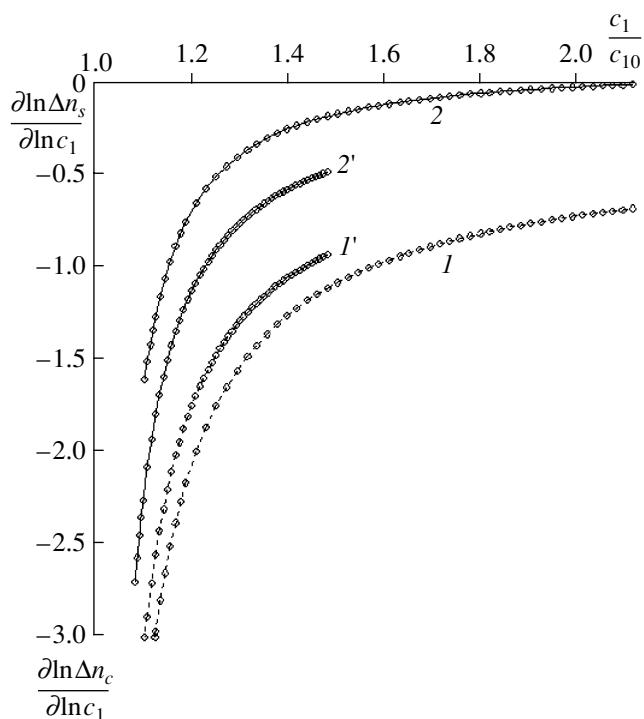


Fig. 2. Logarithmic derivatives ($1, 1'$) $\partial \ln \Delta n_c / \partial \ln c_1$ and ($2, 2'$) $\partial \ln n_s / \partial \ln c_1$ as functions of surfactant monomer concentration c_1 expressed in c_{10} units for ($1, 2$) droplet and ($1', 2'$) quasi-droplet models of spherical surfactant aggregates.

tative published data available on the micellization. Note that, in both models, parameter c_{10} represents monomer concentrations corresponding to the appearance of the height and well of work W_n . The magnitudes of b_1, b_3, a_1 , and a_3 selected below for numerical calculations fit the ranges, which, according to [5–7], are possible for these parameters.

Using model equations (2.1) and (2.2), values of n_c and n_s are calculated as the roots of equations $(\partial W_n / \partial n)_{n=n_c} = 0$ and $(\partial W_n / \partial n)_{n=n_s} = 0$. Then, from definitions (1.1), Δn_c and Δn_s , as well as $(\partial^3 W_n / \partial n^3)_{n=n_c}$ and $(\partial^3 W_n / \partial n^3)_{n=n_s}$ are calculated. Figures 1 and 2 show the corresponding dependences of logarithmic derivatives $\partial \ln n_c / \partial \ln c_1$, $\partial \ln n_s / \partial \ln c_1$, $\partial \ln \Delta n_c / \partial \ln c_1$, and $\partial \ln \Delta n_s / \partial \ln c_1$ on surfactant monomer concentration c_1 expressed in c_{10} units. The points in the plots refer to the values calculated through exact equations (1.7) and (1.8), as well as (1.12) and (1.14). The following values were taken for the model parameters: $b_1 = 1.625$, $b_3 = 29.25$, $a_1 = 0.0457$, and $a_3 = 0.797$. At these parameter values and the surfactant monomer concentration corresponding to CMC_1 , we have the following characteristics of the extrema:

$$\begin{aligned} \text{(d)} \quad n_c &\approx 10.4, \quad \Delta n_c \approx 3.9, \quad W_c \approx 34.2, \\ n_s &\approx 70, \quad \Delta n_s \approx 10, \quad W_s \approx 9.3, \end{aligned} \quad (2.3)$$

and

$$\begin{aligned} \text{(q)} \quad n_c &\approx 22.1, \quad \Delta n_c \approx 7.5, \quad W_c \approx 19.1, \\ n_s &\approx 70, \quad \Delta n_s \approx 10, \quad W_s \approx 9.3, \end{aligned} \quad (2.4)$$

where (d) and (q) indicate that the characteristics refer to the droplet and quasi-droplet models, respectively. Values of surfactant monomer concentration were taken in the interval extending from the value, at which difference $n_s - n_c$ is equal to the sum $\Delta n_c + \Delta n_s$ of half-widths, to the value, at which minimum aggregation work W_s decreases to 3. Although, at $n_s - n_c = \Delta n_s + \Delta n_c$, monomer concentration c_1 is below CMC_1 (when, at the equilibrium state of the solution, the relative fraction of the substance in micelles is 0.1, and the minimum of the work of aggregation is equal to approximately 10), this magnitude determines the lower boundary of c_1 values, at which the maximum and minimum of aggregation work are already sufficiently separated on the aggregation number axis, and the half-widths of their vicinities are not overlapped. At monomer concentrations higher than the concentration at $W_s = 3$, a passage to micelles of other shapes is usually observed in an equilibrium solution. Note that, for the applicability to the droplet and quasi-droplet models to spherical aggregates, quantity $n_s + \Delta n_s$ as a function of c_1 must satisfy conditions of the spherical packing throughout the monomer concentration range [5–7]. At taken values of parameters, this is really the case.

As a result, for the droplet and quasi-droplet models, concentration ranges of surfactant monomers turn out to be fairly wide: $c_1/c_{10}^{(d)} = 1.104\text{--}2.114$ and $c_1/c_{10}^{(q)} = 1.084\text{--}1.483$, respectively. The plots in Figs. 1 and 2 relate precisely to these intervals. Note also that, at the solution equilibrium, corresponding ranges of overall concentration c are rather wide: $c/c_{10}^{(d)} = 1.104\text{--}140.7$ and $c/c_{10}^{(q)} = 1.084\text{--}93.95$.

It is seen that the plots in Figs. 1 and 2 are identical to the results obtained through exact equations (1.7) and (1.8) as well as (1.12) and (1.14). This circumstance testifies that model equations (2.1) and (2.2) are consistent.

In order to estimate the right-hand sides of Eqs. (1.12) and (1.14), we need to know the third derivatives $(\partial^3 W_n / \partial n^3)_{n=n_c}$ and $(\partial^3 W_n / \partial n^3)_{n=n_s}$ in these expressions. From the general rules for the differentiation of a power function of n (according to Eqs. (2.1) and (2.2), $\partial^2 W_n / \partial n^2$ is such a function) with respect to n , we have

$$\left| \partial^3 W_n / \partial n^3 \right|_{n=n_c} \sim \frac{1}{n_c} \left| \partial^2 W_n / \partial n^2 \right|_{n=n_c} \quad (2.5)$$

and

$$|\partial^3 W_n / \partial n^3|_{n=n_s} \sim \frac{1}{n_s} (\partial^2 W_n / \partial n^2)_{n=n_s}. \quad (2.6)$$

Calculations performed through model equation (2.2) reveal that, in all cases, $\partial^3 W_n^{(q)} / \partial n^3 > 0$. At the same time, calculations, performed through model equation (2.1) at the aforementioned values of parameters $b_1 = 1.625$ and $b_3 = 29.25$, disclose that $\partial^3 W_n^{(d)} / \partial n^3 > 0$ at $n < 75$ and $W_n^{(d)} / \partial n^3 < 0$ at $n > 75$. Number n_s approaches the value $n_s = 75$ only when surfactant monomer concentration reaches the right-hand boundary of the interval $c_1/c_{10}^{(d)} = 1.104\text{--}2.114$. With allowance for estimate (2.5), the first of definitions (1.1), and the plots in Figs. 1 and 2, instead of exact relation (1.12), in both models we may use the estimate

$$\frac{\partial \ln \Delta n_c}{\partial \ln c_1} \sim -\frac{\Delta n_c^2}{n_c}. \quad (2.7)$$

At the same time, with allowance for estimate (2.6), the first of definitions (1.1), relation (1.8), and the plots in Figs. 1 and 2, instead of exact relation (1.14), we may use the estimates

$$\frac{\partial \ln \Delta n_s}{\partial \ln c_1} \sim -\frac{\Delta n_s^2}{n_s} \quad (\text{q}), \quad (2.8)$$

and

$$\frac{\partial \ln \Delta n_s}{\partial \ln c_1} \sim -\frac{\Delta n_s^2}{2n_s} \quad (\text{d}). \quad (2.9)$$

in the quasi-droplet and the droplet models, respectively.

Taking into account relations (2.7)–(2.9), the following estimates are obtained from exact equations (1.15) and (1.16):

$$\frac{\partial \ln(\Delta n_c/n_c)}{\partial \ln c_1} \sim -\frac{\Delta n_c^2}{2n_c}, \quad (2.10)$$

for both models

$$\frac{\partial \ln(\Delta n_s/n_s)}{\partial \ln c_1} \sim -\frac{3\Delta n_s^2}{2n_s} \quad (\text{q}), \quad (2.11)$$

for the quasi-droplet model, and

$$\frac{\partial \ln(\Delta n_s/n_s)}{\partial \ln c_1} \sim -\frac{\Delta n_s^2}{n_s} \quad (\text{d}), \quad (2.12)$$

for the droplet model.

Equations (2.10)–(2.12) with allowance for Eqs. (2.3) and (2.4), show that, in both models, $\Delta n_c/n_c$ decreases with an increase in surfactant monomer concentration slower than $\Delta n_s/n_s$; hence, the relative half-

width of the vicinity of the minimum of the work of aggregation narrows faster than that of its vicinity of a maximum.

Let us combine these conclusions with the conclusion made in [10] that, at CMC_1 , in both the droplet and quasi-droplet models, the inequality $\Delta n_c/n_c > \Delta n_s/n_s$ is valid, in spite of the fact that, in this inequality, $\Delta n_c < \Delta n_s$. Then, we can see that, beginning with the CMC_1 , the $\Delta n_c/n_c > \Delta n_s/n_s$ inequality is valid for both the droplet and quasi-droplet models and becomes stronger with an increase in the surfactant concentration in a solution.

3. APPLICATIONS TO THE RELAXATION THEORY OF SURFACTANT SOLUTIONS

Let us mark the quantities relevant to the final equilibrium state of a solution with a wavy bar above. Symbol δ at the values refers to their deviations from the values corresponding to the final equilibrium state of a solution (the deviations may have any sign).

At overall surfactant concentrations c above the CMC_1 and throughout the concentration interval at which only spherical micelles are present in the solution, the material balance equation for surfactant has the form,

$$c_1 + n_s c_M = c, \quad (3.1)$$

where c_M is the concentration of micelles (the total number of micelles in solution unit volume). In a materially isolated solution, overall concentration c remains virtually unchanged. Let us find the conditions for the linearization of material balance equation (3.1) in the vicinity of the final equilibrium state of a materially isolated solution. For product $n_s c_M$ as a function of independent variables c_1 and c_M , with an accuracy to the terms on the order of $(\delta c_1)^2$ and $\delta c_1 \delta c_M$ inclusive, we have

$$\begin{aligned} \delta(n_s c_M) &= \left(\frac{\partial n_s}{\partial c_1} \right)_{c_1 = \bar{c}_1} \bar{c}_M \delta c_1 + \bar{n}_s \delta c_M \\ &+ \frac{1}{2} \left(\frac{\partial^2 n_s}{\partial c_1^2} \right)_{c_1 = \bar{c}_1} \bar{c}_M (\delta c_1)^2 + \left(\frac{\partial n_s}{\partial c_1} \right)_{c_1 = \bar{c}_1} \delta c_1 \delta c_M, \end{aligned} \quad (3.2)$$

where the material isolation of the solution is not required. For the linearization of Eq. (3.2), it is sufficient that the absolute values of the third and fourth terms of the right-hand sides will be much smaller than the first and second terms, respectively. The conditions for this situation are:

$$\left| \frac{1}{2} \left(\frac{\partial^2 n_s}{\partial c_1^2} \right)_{c_1 = \bar{c}_1} \delta c_1 \right| \ll \left| \frac{\partial n_s}{\partial c_1} \right|_{c_1 = \bar{c}_1}, \quad (3.3)$$

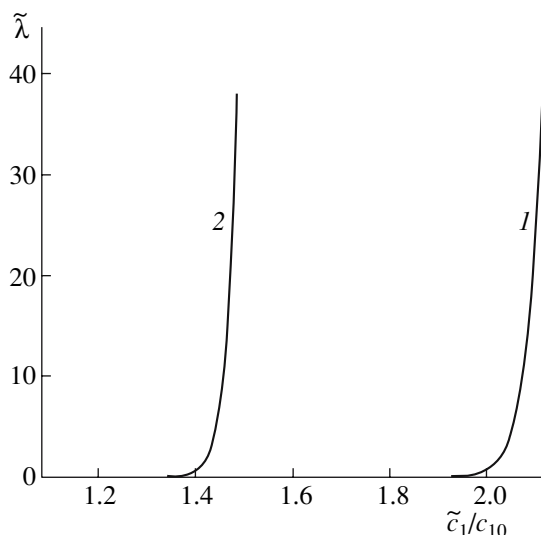


Fig. 3. Parameter $\tilde{\lambda}$ as a function of surfactant monomer concentration \tilde{c}_1 expressed in c_{10} units for (1) droplet and (2) quasi-droplet models of spherical surfactant aggregates.

and

$$\left| \left(\frac{\partial n_s}{\partial c_1} \right)_{c_1 = \tilde{c}_1} \delta c_1 \right| \ll \tilde{n}_s. \quad (3.4)$$

With allowance for relations (1.8), (2.8), and (2.9), conditions (3.3) and (3.4) may be rewritten as

$$\frac{|\delta c_1|}{\tilde{c}_1} \ll \frac{2}{2\Delta\tilde{n}_s^2/\tilde{n}_s + 1}, \quad (3.5)$$

and

$$\frac{|\delta c_1|}{\tilde{c}_1} \ll \frac{2\tilde{n}_s}{\Delta\tilde{n}_s^2}. \quad (3.6)$$

Using characteristics (2.3) and (2.4), we obtain that the right-hand sides of inequalities (3.5) and (3.6) are equal to 0.5 and 1.4, respectively. It is seen that both conditions (3.5) and (3.6) are quite weak, and Eq. (3.1) can be linearized with respect to the final equilibrium state of the solution almost throughout the admissible intervals $c_1/c_{10}^{(d)} = 1.104\text{--}2.114$ and $c_1/c_{10}^{(q)} = 1.084\text{--}1.483$.

After the linearization of Eq. (3.1) for materially isolated solution with account of Eq. (3.2), we obtain [3]:

$$\delta c_M = -\frac{1 + \tilde{\lambda}}{\tilde{n}_s} \delta c_1, \quad (3.7)$$

where parameter $\tilde{\lambda}$ is defined as

$$\tilde{\lambda} \equiv \tilde{c}_M (\partial n_s / \partial c_1)_{c_1 = \tilde{c}_1}. \quad (3.8)$$

In the final equilibrium state, micelle concentration \tilde{c}_M of a materially isolated micellar solution satisfies the relation [3–5]

$$\tilde{c}_M = \pi^{1/2} \tilde{c}_1 \Delta\tilde{n}_s \exp(-\tilde{W}_s). \quad (3.9)$$

The following equality determining parameter $\tilde{\lambda}$ results from Eqs. (3.8), (3.9), and (1.8):

$$\tilde{\lambda} = \frac{\pi^{1/2} \Delta\tilde{n}_s^3 \exp(-\tilde{W}_s)}{2}. \quad (3.10)$$

The third of relations (1.4) and estimates (2.8) and (2.9) indicate that, as the surfactant monomer concentration increases, $\tilde{\lambda}$ grows (because of the effect of $\exp(-\tilde{W}_s)$ term in Eq. (3.10)), and, at $\Delta n_s > 10$ and $W_s < 10$, it may be that $\tilde{\lambda} > 1$. Figure 3 illustrates the dependences of $\tilde{\lambda}$ on the surfactant monomer concentration for the droplet and quasi-droplet models at the same magnitudes of parameters as in Figs. 1 and 2. It is seen that $\tilde{\lambda}$ may achieve very high values with an increase in monomer concentration within admissible ranges $c_1/c_{10}^{(d)} = 1.104\text{--}2.114$ and $c_1/c_{10}^{(q)} = 1.084\text{--}1.483$. The points on the \tilde{c}_1/c_{10} axis, where $\tilde{\lambda}$ begins to increase rapidly, lie slightly above the surfactant monomer concentration at the CMC_1 for a corresponding model.

Let us formulate the conditions for the linearization of W_s and W_c magnitudes with respect to δc_1 . With allowance for Eqs. (1.4), (1.7), and (1.8), with an accuracy to the terms on the order of $(\delta c_1)^2$ inclusive, we have

$$\delta W_s = -\frac{\tilde{n}_s - 1}{\tilde{c}_1} \delta c_1 + \frac{1}{2\tilde{c}_1^2} \left(\tilde{n}_s - 1 - \frac{\Delta\tilde{n}_s^2}{2} \right) (\delta c_1)^2, \quad (3.11)$$

and

$$\delta W_c = -\frac{\tilde{n}_c - 1}{\tilde{c}_1} \delta c_1 + \frac{1}{2\tilde{c}_1^2} \left(\tilde{n}_c - 1 + \frac{\Delta\tilde{n}_c^2}{2} \right) (\delta c_1)^2. \quad (3.12)$$

According to Eqs. (3.11) and (3.12), the conditions for the linearization of δW_s and δW_c have the forms

$$\frac{|\delta c_1|}{\tilde{c}_1} \ll \frac{2}{\left| 1 - \frac{\Delta\tilde{n}_s^2}{2\tilde{n}_s} \right|}, \quad (3.13)$$

and

$$\frac{|\delta c_1|}{\tilde{c}_1} \ll \frac{2}{1 + \frac{\Delta \tilde{n}_c}{2\tilde{n}_c}}, \quad (3.14)$$

respectively.

Using Eqs. (2.3) and (2.4), we find that the right-hand sides of inequalities (3.13) and (3.14) are equal to 6.7 and 0.9, respectively. It is seen that condition (3.13) is much weaker than inequalities (3.5) and (3.6), but condition (3.14) is slightly weaker than (3.5). Hence, W_s and W_c can be linearized with respect to δc_1 even in wider parts of admissible intervals $c_1/c_{10}^{(d)} = 1.104$ – 2.114 and $c_1/c_{10}^{(q)} = 1.084$ – 1.483 than for material balance equation (3.1). Linearizing Eqs. (3.11) and (3.12) with respect to δc_1 and accounting for the meaning of symbol δ , we arrive at

$$W_s - \tilde{W}_s = -(\tilde{n}_s - 1)\delta c_1/\tilde{c}_1, \quad (3.15)$$

and

$$W_c - \tilde{W}_c = -(\tilde{n}_c - 1)\delta c_1/\tilde{c}_1. \quad (3.16)$$

As was shown in [3], for the applicability of the notions of forward and reverse fluxes of molecular aggregates over the potential barrier of work W_n , it is necessary to fulfill inequalities $\exp(W_c - W_s) \gg 1$ and $\exp(\tilde{W}_c - \tilde{W}_s) \gg 1$. Let us clarify the constraint on δc_1 , at which the fulfillment of inequality $\exp(\tilde{W}_c - \tilde{W}_s) \gg 1$ ensures the fulfillment of inequality $\exp(W_c - W_s) \gg 1$. Because these inequalities are highly sensitive to concentration c_1 , let us replace them by inequalities $\tilde{W}_c - \tilde{W}_s > 2$ and $W_c - W_s > 2$, which, according to Eqs. (1.2) and (1.3), correspond to the fact that the half-widths of the vicinities of the maximum and minimum of the work of aggregation are already far apart from each other. From Eqs. (3.15) and (3.16), we obtain

$$W_c - W_s = \tilde{W}_c - \tilde{W}_s + (\tilde{n}_s - \tilde{n}_c)\delta c_1/\tilde{c}_1. \quad (3.17)$$

According to Eq. (3.17), to satisfy inequality $W_c - W_s > 2$, it is necessary to have

$$\delta c_1/\tilde{c}_1 > (2 - \tilde{W}_c + \tilde{W}_s)/(\tilde{n}_s - \tilde{n}_c), \quad (3.18)$$

that, upon the fulfillment of inequality $\tilde{W}_c - \tilde{W}_s > 2$, yields precisely the desired constraint on $\delta c_1/\tilde{c}_1$. Applying relations (2.3) and (2.4) to the final equilibrium state of a solution, we have: (i) in the droplet model, $\tilde{W}_c - \tilde{W}_s = 24.9$ and $\tilde{n}_s - \tilde{n}_c \approx 59.6$; (ii) in the quasi-droplet model, $\tilde{W}_c - \tilde{W}_s = 9.8$ and $\tilde{n}_s - \tilde{n}_c \approx 47.9$. Thus, inequality $\tilde{W}_c - \tilde{W}_s > 2$ is satisfied with a fairly large excess, especially, in the case of the droplet

model. With account of the aforementioned data, constraint (3.18) is presented as

$$\delta c_1/\tilde{c}_1 > -0.16. \quad (3.19)$$

In inequality (3.19), we took into account the case of the quasi-droplet model, in which constraint (3.18) is somewhat stronger than in the case of the droplet model. This may be explained as follows. The weaker the fulfillment of inequality $\tilde{W}_c - \tilde{W}_s > 2$, the stronger the constraint (3.18). Constraint (3.19) is satisfied in advance at $\delta c_1 > 0$. When $\delta c_1 < 0$, $\delta c_1 = -|\delta c_1|$, and constraint (3.19) may be written as $|\delta c_1|/\tilde{c}_1 < 0.16$. This is approximately equivalent to the constraint imposed by condition (3.14) on the applicability of linearized relation (3.16), and markedly stronger than the constraint imposed by condition (3.13) on the applicability of linearized expression (3.15). Thus, the obtained constraint $|\delta c_1|/\tilde{c}_1 < 0.16$ fits the validity range of relations (3.16) and (3.15).

In the theory of exponential relaxation of micellar solutions (even containing not only spherical micelles), an important role is played by the linearization of quantity $\exp(W_s)$ (that is rather sensitive to concentration c_1) with respect to δc_1 in the vicinity of the final equilibrium state of a solution. Let us consider this linearization and also clarify and discuss the conditions of its applicability.

Using the third of relations (1.4) and taking into account that $n_s \gg 1$, with a high accuracy, we obtain

$$\frac{\partial}{\partial c_1} e^{W_s} = -e^{W_s} \frac{n_s}{c_1}, \quad (3.20)$$

and

$$\frac{\partial^2}{\partial c_1^2} e^{W_s} = e^{W_s} \left[\left(\frac{n_s}{c_1} \right)^2 - \frac{1}{c_1} \frac{\partial n_s}{\partial c_1} \right], \quad (3.21)$$

moreover, the material isolation of the solution is not required. Expansion in a Taylor series employing Eqs. (3.20) and (3.21) yields

$$\begin{aligned} \delta e^{W_s} = & -e^{\tilde{W}_s} \left[\frac{\tilde{n}_s}{\tilde{c}_1} \delta c_1 - \frac{1}{2} \left(\frac{\tilde{n}_s}{\tilde{c}_1} \right)^2 (\delta c_1)^2 \right. \\ & \left. + \frac{1}{2\tilde{c}_1} \left(\frac{\partial n_s}{\partial c_1} \right)_{c_1=\tilde{c}_1} (\delta c_1)^2 \right], \end{aligned} \quad (3.22)$$

where we excluded the terms of the third and higher orders with respect to δc_1 .

The linearization of Eq. (3.22) with respect to δc_1 is applicable, provided that the absolute values of the second and third bracketed terms of Eq. (3.22) are much smaller than the first bracketed term. The conditions for this situation are

$$|\delta c_1|/\tilde{c}_1 \ll 2/\tilde{n}_s, \quad (3.23)$$

and

$$\frac{1}{\tilde{n}_s} \left| \left(\frac{\partial n_s}{\partial c_1} \right)_{c_1 = \tilde{c}_1} \delta c_1 \right| \ll 2. \quad (3.24)$$

Because $\tilde{n}_s \gg 1$, condition (3.23) formulated earlier in [11] imposes quite a strong constraint on $|\delta c_1/\tilde{c}_1|$. Let us show that, when condition (3.23) is met, condition (3.24) will already be satisfied. Using equality (1.8) and condition (3.23), we obtain the inequality

$$\frac{1}{\tilde{n}_s} \left| \left(\frac{\partial n_s}{\partial c_1} \right)_{c_1 = \tilde{c}_1} \delta c_1 \right| \ll \frac{\Delta \tilde{n}_s^2}{\tilde{n}_s^2}, \quad (3.25)$$

which, in combination with the obvious inequality $\Delta \tilde{n}_s^2/\tilde{n}_s^2 \ll 1$, indicates that condition (3.24) is really met and even with a large excess, given that condition (3.23) is satisfied. Taking into account the meaning of symbol δ , inequality (3.25) may be rewritten as the inequality

$$|\delta n_s|/\tilde{n}_s \ll \Delta \tilde{n}_s^2/\tilde{n}_s^2, \quad (3.26)$$

that imposes the constraint on $|\delta n_s|/\tilde{n}_s$ admitted by condition (3.23). The fact that, at $\tilde{n}_s \gg 1$, condition (3.23) is rather strong, allows us to ignore the dependence of n_s on c_1 when linearizing δc_1 value with respect to $\exp(W_s)$, was mentioned in [11]. However, this could be exactly substantiated only when using relation (1.8).

In the theory of exponential relaxation in micellar solutions (even containing not only spherical micelles), when linearizing (with respect to δc_1) the sum of fluxes of molecular aggregates over the potential barrier of the work of aggregation, W_n , it is assumed that, in addition to conditions (3.23) and (3.24), there is yet one more condition [11]:

$$|\delta(\Delta n_s)|/\Delta \tilde{n}_s \ll 1. \quad (3.27)$$

Let us demonstrate that this condition is satisfied when condition (3.23) is met. We use estimate (2.8) and condition (3.23). Taking into account that estimate (2.8) may be even overestimated, we have

$$\frac{|\delta(\Delta n_s)|}{\Delta \tilde{n}_s} = \left| \left(\frac{\partial \ln \Delta n_s}{\partial c_1} \right)_{c_1 = \tilde{c}_1} \delta c_1 \right| \ll 2 \frac{\Delta \tilde{n}_s^2}{\tilde{n}_s^2}. \quad (3.28)$$

This inequality, in combination with the obvious inequality $\Delta \tilde{n}_s^2/\tilde{n}_s^2 \ll 1$, testifies that, when condition (3.23) is met, condition (3.27) is really satisfied, even with a rather large excess. Inequality (3.28) imposes the constraint on $|\delta(\Delta n_s)|/\Delta \tilde{n}_s$ admitted by condition (3.23). The fact that condition (3.23), which is rather strong at $\tilde{n}_s \gg 1$, enables us to ignore the dependence of $\Delta \tilde{n}_s$ on c_1 upon the linearization of the sum of fluxes of molecular aggregates with respect to δc_1 , was noted in [11].

However, this could be exactly substantiated only using estimate (2.8).

As was already mentioned, all what have been said above about conditions (3.23), (3.24), and (3.27) is valid not only for solutions containing spherical micelles. However, only in the case of solutions containing spherical micelles, relation (3.23) becomes the main condition determining the degree of the closeness of the state of a solution to the equilibrium that is theoretically admitted for the stage of exponential relaxation. When the solution simultaneously contains both spherical and cylindrical micelles, in addition to condition (3.23), there is a still stronger condition [11] concerning the smallness of relative deviation δc_1 .

Finally, according to the theory of the exponential relaxation in micellar solutions (even containing not only spherical micelles), when linearizing the sum of fluxes of molecular aggregates over the potential barrier of work W_n with respect to δc_1 , the following inequality is assumed [3]:

$$\frac{1}{\tilde{n}_s} \left| \frac{\partial \ln \Delta n_s}{\partial \ln c_1} \right|_{c_1 = \tilde{c}_1} \ll 1. \quad (3.29)$$

In designations of [3], this relation is equivalent to inequality $|\eta|/\tilde{n}_s \ll 1$, which makes it possible in general to ignore parameter η in the theory of exponential relaxation [3]. Using estimate (2.8), and taking into account that it can be even overestimated, we arrive at the inequality

$$\frac{1}{\tilde{n}_s} \left| \frac{\partial \ln \Delta n_s}{\partial \ln c_1} \right|_{c_1 = \tilde{c}_1} \lesssim \frac{\Delta \tilde{n}_s^2}{\tilde{n}_s^2}, \quad (3.30)$$

which, in combination with obvious inequality $\Delta \tilde{n}_s^2/\tilde{n}_s^2 \ll 1$, ensures the fulfillment of inequality (3.29) with a large excess. In [3], this fulfillment was motivated qualitatively. Note that condition (3.23) was not used in inequalities (3.29) and (3.30).

Let us emphasize that the material isolation of a solution was required only for relation (3.7). The remaining content of this section is not directly associated with the material isolation of the solution. The presence of only spherical micelles in the solution was significant only for relation (3.7) (and Eq. (3.1)).

The domain of the applicability of relations (1.7), (1.8), (1.12), and (1.14) and estimates (2.7) and (2.8) to the relaxation theory of micellar solutions is, in fact, much wider than that used above. For example, when considering the stage of power relaxation preceding the final stage of exponential relaxation [3–5], together with the dependence of the position and half-width of the vicinity of the minimum of the work of aggregation, an analogous dependence for the position and half-width of the vicinity of work maximum is also significant. The regularities of the stage of power relaxation and the applicability of exact relations obtained in this

work to this stage will be considered in the next communication.

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