

Kinetics of Slow Relaxation upon the Competition between Globular and Small Spherocylindrical Micelles

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Abstract—Kinetic description of the slow establishment of complete equilibrium in surfactant solutions with concentrations exceeding the first critical micellization concentration is constructed for the case when surfactant monomers, premicellar spherical aggregates, and globular and small spherocylindrical micelles coexist. The model proposed suggests the presence of two separate branches with minima for the aggregation work of aggregates with aggregation numbers above the limiting spherical packing of surfactant molecules. One of these branches corresponds to globular micelles, while the other corresponds to small spherocylindrical micelles. Transitions between aggregates at each of the branches are taken into account with the absence of direct transitions between aggregates on different branches. Relations obtained reflect correlations between the current values of the concentrations of surfactant monomers and total concentrations of globular and small spherocylindrical micelles and determine the characteristic time of slow relaxation.

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INTRODUCTION

It is known [1, 2] that, in highly concentrated micellar surfactant solutions, when aggregation numbers exceed the limit of the spherical packing of monomers, the formation of globular micelles (which can be considered as the prototype of bilayers) or small spherocylindrical micelles (the prototype of long cylindrical micelles) proceeds. It was shown for nonionic surfactants [3] that globular and spherocylindrical micelles can simultaneously present in a solution; in this case, the dependence of aggregation work on the number of monomers in micelles is divided into two single branches. The division begins at aggregation numbers above the limit of the spherical packing of monomers. One of these branches represents globular micelles, while the other one represents spherocylindrical micelles. As the overall surfactant concentration increases, globular and spherocylindrical micelles compete with one another in the absorption of surfactant monomers in solution.

Usually, the absence of small spherocylindrical micelles at the overall surfactant concentration between the first (CMC_1) and second (CMC_2) critical micellization concentrations is explained by the existence of potential barrier for the formation of cylindrical micelles from spherical aggregates [4, 5]. It is implied that this barrier only becomes fairly low above the CMC_2 . The presence of two branches of aggregation work and, correspondingly, two branches of aggregate distribution over aggregation numbers suggests that additional factor explaining the absence of small

spherocylindrical micelles below CMC_2 is their competition with globular micelles.

Numerical calculations demonstrate [3] that the situation is possible when there is no minimum for the work of spherical aggregate formation, because the limit of the spherical packing of monomers is achieved at its descending part. In such a situation, spherical micelles, which are stable aggregates, are not formed at all. In this case, minima of aggregation work can exist at both the globular and spherocylindrical branches of aggregation work. The branch of aggregation work for globular micelles is characterized by a deeper minimum compared to the branch for spherocylindrical micelles; at the same time, the formation of large globular micelles is energetically less advantageous than the formation of large cylindrical micelles. Therefore, at overall concentrations between CMC_1 and CMC_2 , globular micelles are primarily observed; at higher concentrations, the role of spherocylindrical aggregates becomes noticeable.

This study is devoted to the kinetic description of the slow establishment of complete equilibrium in solutions where premicellar spherical aggregates and globular and small spherocylindrical micelles exist simultaneously, but spherical micelles are absent. The solutions to the problem of slow relaxation in surfactant solutions are known only for the cases when there are only spherical aggregates [6–9] or coexisting spherical and cylindrical micelles [10–13]. The dynamics of the transfer of aggregates over activation barriers at one of the branches of aggregation work has been considered in these publications. We will take into account the transitions between aggregates at different branches.

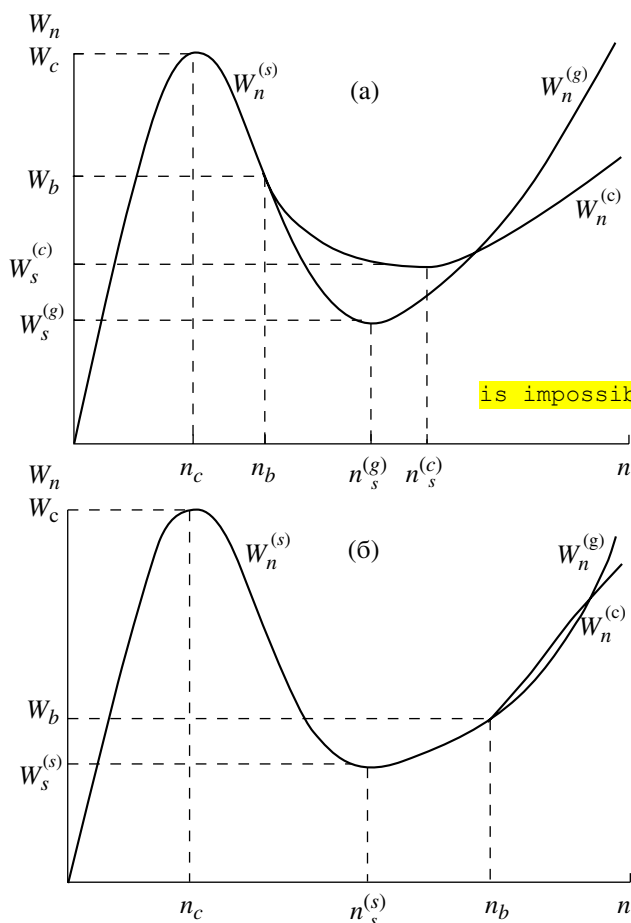


Fig. 1. Approximate pattern of the dependence of aggregation work for molecular aggregate on its size n (a) in the absence and (b) in the presence of stable spherical micelles. At $n \leq n_b$, only spherical molecular aggregates exist (curve $W_n^{(s)}$); at $n > n_b$, globular (curve $W_n^{(g)}$) and spherocylindrical (curve $W_n^{(c)}$) exist simultaneously.

Such a problem has not been previously considered. We establish relations between the current values of the concentrations of monomeric surfactants and total concentrations of globular and small spherocylindrical micelles and determine the characteristic time of slow relaxation.

1. FORMULATION OF A PROBLEM

Let us denote the aggregation number (the number of surfactant molecules in molecular aggregate) by n . The position of bifurcation point at $n = n_b$ at the curve of the dependence of the formation work of molecular aggregate on the aggregation number is determined by the characteristic sizes of surfactant molecules. At $n < n_b$ to the left of the branching point, all molecular aggregates are spherical. To the right of the branching point, at $n > n_b$, molecular aggregates acquire the shape of

either globules or spherocylinders. The transition of aggregates from one branch to another can occur only through the bifurcation point. According to numerical calculations [3], immediately after the bifurcation point at $n > n_b$, the curve of aggregation work for globular micelles lies below the curve for spherocylindrical micelles.

Two characteristic dependences of aggregation work on the aggregation numbers are shown in Fig. 1; Fig. 1a corresponds to the case when the limit of spherical packing lies at the descending part of the formation work that corresponds to the impossible formation of stable spherical micelles and Fig. 1b corresponds to the case when the limit of spherical packing is achieved beyond the minimum of the aggregation work for spherical micelles. On these figures, W_n is the minimal formation work of molecular aggregate with the aggregation number n expressed in thermal units $k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature of solution; superscripts (s), (g), and (c) denote the values referred to spherical, globular, and spherocylindrical aggregates, respectively; subscript b indicates the bifurcation point and subscripts c and s indicate the points of maximum and minimum, respectively.

Results of the kinetics of slow relaxation obtained previously in [6–13] refer precisely to the case shown in Fig. 1b. In this case, the globular branch of aggregation work does not have a minimum and, with an increase in the aggregation number, becomes noticeably higher than the spherocylindrical branch so that the fraction of surfactant in globular micelles is insignificant.

In accordance with the preceding, we consider conditions complying with Fig. 1a. In this case, the fraction of surfactant molecules forming pre-micellar spherical aggregates will be negligible and its main amount is distributed over monomers, globular and small spherocylindrical micelles.

2. EQUATIONS OF SLOW RELAXATION FOR GLOBULAR AND SPHEROCYLINDRICAL MICELLES AND SURFACTANT MONOMERS

Let us describe the process of the establishment of total equilibrium in a solution containing surfactant monomers, pre-micellar spherical aggregates, and globular and spherocylindrical micelles. We assume that the relaxation proceeds rather slowly so that, at current values of monomer concentrations and total concentrations of globular and spherocylindrical micelles, single quasi-equilibrium states over aggregation numbers between systems on both sides of the maximum of aggregation work would have time to be established (see Fig. 1a). Let us denote the concentration of aggregates (the number of aggregates in solution unit volume) with aggregation number n by c_n ; in this case, c_1 represents the concentration of surfactant monomers.

According to Boltzmann's principle, quasi-equilibrium distributions of monomers and small pre-micellar spherical surfactant aggregates over the aggregation numbers to the left of potential barrier of aggregation work is given by the expression

$$c_n = c_1 e^{-W_n} \quad (2.1)$$

According to the same considerations, with allowance for the forbidding of direct transitions between globular and spherocylindrical micelles, the distribution of molecular aggregates over the aggregation numbers at $n > n_b$ on the globular and spherocylindrical branches can be presented as

$$c_n^{(g)} = c_b e^{-(W_n^{(g)} - W_b)}, \quad c_n^{(c)} = c_b e^{-(W_n^{(c)} - W_b)}, \quad (2.2)$$

where W_b and c_b are the aggregation work and the concentration of spherical aggregates in the bifurcation point $n = n_b$, respectively. Note that identical pre-exponential factors in distributions (2.2) indicate the existence of quasi-equilibrium between the branches of globular and spherocylindrical branches. In turn, the difference between c_1 and $c_b e^{W_b}$ speaks of the absence of total equilibrium in a solution, i.e., of the absence of the mutual equilibrium of aggregates with any aggregation numbers.

In the system under consideration, the equation of surfactant material balance (for unit volume) with allowance for the distribution over the branches (Eq. (2.2)) has the following form (with disregard to the contribution from pre-micellar spherical aggregates):

$$c_1 + \int_{n_b}^{\infty} n c_n^{(g)} dn + \int_{n_b}^{\infty} n c_n^{(c)} dn = c, \quad (2.3)$$

where c is the overall surfactant concentration in solution. For convenience, let us introduce the following designations:

$$\begin{aligned} c_M^{(g)} &= \int_{n_b}^{\infty} c_n^{(g)} dn, & n^{(g)} &= \frac{1}{c_M^{(g)}} \int_{n_b}^{\infty} n c_n^{(g)} dn, \\ (\Delta n^{(g)})^2 &= \frac{1}{c_M^{(g)}} \int_{n_b}^{\infty} (n - n^{(g)})^2 c_n^{(g)} dn, \\ c_M^{(c)} &= \int_{n_b}^{\infty} c_n^{(c)} dn, & n^{(c)} &= \frac{1}{c_M^{(c)}} \int_{n_b}^{\infty} n c_n^{(c)} dn, \\ (\Delta n^{(c)})^2 &= \frac{1}{c_M^{(c)}} \int_{n_b}^{\infty} (n - n^{(c)})^2 c_n^{(c)} dn, \end{aligned} \quad (2.4)$$

where $c_M^{(g)}$ and $c_M^{(c)}$ are the total concentrations of globular and spherocylindrical micelles, respectively; $n^{(g)}$, $n^{(c)}$, and $\Delta n^{(g)}$, $\Delta n^{(c)}$ are their average aggregation numbers and rms deviations of aggregation numbers, respectively. Using relations (2.4), material balance equation (2.3) can be rewritten in the following form:

$$c_1 + c_M^{(g)} n^{(g)} + c_M^{(c)} n^{(c)} = c. \quad (2.5)$$

The kinetics of slow relaxation is determined by the direct and back transitions of aggregates over the potential barrier of aggregation work in the vicinity of $n = n_c$ that are established after fast relaxation [14]. Changes in the total number of supercritical aggregates with time t , which is approximately equal to the sum of $c_M^{(g)}$ and $c_M^{(c)}$, can be described by the scheme used in [4]

$$\frac{d}{dt}(c_M^{(g)} + c_M^{(c)}) = J - J'', \quad (2.6)$$

where J and J'' are the direct and back fluxes of aggregates over the potential barrier of aggregation work (rates of aggregation and disaggregation), respectively. For quasi-equilibrium distributions (2.1) and (2.2), these fluxes are quasi-stationary and, by analogy with relations (5.8) and (5.10) from [14], they can be represented as

$$J = \frac{j_c^+}{\sqrt{\pi} \Delta n_c} c_1 e^{-W_c}, \quad J'' = \frac{j_c^+}{\sqrt{\pi} \Delta n_c} c_b e^{-(W_c - W_b)}, \quad (2.7)$$

where W_c is the value of aggregation work in point n_c , Δn_c is the half-width of aggregation work in the vicinity of point n_c , and j_c^+ is the amount of monomers absorbed by the aggregate with aggregation number n_c per unit time. For convenience, the second of relations (2.7) was made different from formula (5.10) from [14]: the quasi-equilibrium state of aggregates to the right of $n = n_c$ is established already at $n > n_c + \Delta n_c$ and is valid in advance at $n = n_b$.

Equations (2.5) and (2.6) at preset overall concentration c and known dependences of n_c , Δn_c , W_c , and W_b parameters on the concentration of surfactant monomers yield, with allowance for relations (2.2), (2.4), and (2.7), the closed nonlinear system of equations relative to two unknown concentrations c_1 and c_b . The value of n_b is defined by the characteristics of surfactant molecules in the thermodynamic model of molecular aggregate and is independent of the concentration of surfactant monomers.

3. EXACT RELATIONS AT QUASI-EQUILIBRIUM STATE OF GLOBULAR AND SPHEROCYLINDRICAL MICELLES AND THE SYSTEM OF LINEARIZED EQUATIONS OF SLOW RELAXATION

At the state of complete equilibrium of micellar solution, the direct J' and back J'' fluxes of aggregates should be equal

$$\tilde{J}' = \tilde{J}'' \quad (3.1)$$

Hereafter, all values at the state of complete equilibrium are denoted by a wavy bar placed above them. From Eqs. (2.7) and (3.1), we derive the relation between the equilibrium values of concentrations \tilde{c}_1 and \tilde{c}_b

$$\tilde{c}_b = \tilde{c}_1 e^{-\tilde{W}_b} \quad (3.2)$$

which can also be derived under the conditions of complete equilibrium from equalities (2.1) and (2.2). Using balance condition (2.3) as it applies to the final equilibrium state and accounting for equalities (2.2) and (3.2), we arrive at the transcendental equation, which, at known dependences $W_n^{(g)}$ and $W_n^{(c)}$ on n and c_1 , determines equilibrium concentration \tilde{c}_1 from the preset value of overall surfactant concentration c

$$\tilde{c}_1 \left[1 + \int_{n_b}^{\infty} n (e^{-\tilde{W}_n^{(g)}} + e^{-\tilde{W}_n^{(c)}}) dn \right] = c \quad (3.3)$$

We consider small deviations of our system from the equilibrium state. In this case, we can represent monomer concentration c_1 , as well as total concentrations of globular micelles $c_M^{(g)}$ and spherocylindrical micelles $c_M^{(c)}$ as

$$\begin{aligned} c_1 &= \tilde{c}_1 + \delta c_1, & c_M^{(g)} &= \tilde{c}_M^{(g)} + \delta c_M^{(g)}, \\ c_M^{(c)} &= \tilde{c}_M^{(c)} + \delta c_M^{(c)}, \end{aligned} \quad (3.4)$$

where, hereafter, symbol δ denotes deviations of the corresponding value from its value at the equilibrium state. According to the general thermodynamic principles and ignoring interactions between micelles, we can arrive at the following equalities [9]:

$$\delta W_n^{(g)} = -(n-1) \frac{\delta c_1}{c_1}, \quad \delta W_n^{(c)} = -(n-1) \frac{\delta c_1}{c_1} \quad (3.5)$$

Deviations $\delta c_M^{(g)}$ and $\delta c_M^{(c)}$ appeared to be interconnected through these equalities and relations (2.2) and

(2.4). Later, we derive explicit coupling equation for these values. quantities ✓

Because, at the material isolation of solution, deviation δc of the overall concentration c can be considered to be equal almost to zero, the first variation of balance ratio (2.5) at the arbitrary moment leads to the equation of time ✓

$$\begin{aligned} \delta c_1 + n^{(g)} \delta c_M^{(g)} + n^{(c)} \delta c_M^{(c)} \\ + c_M^{(g)} \delta n^{(g)} + c_M^{(c)} \delta n^{(c)} = 0. \end{aligned} \quad (3.6)$$

Taking into account definitions (2.4) and equalities (2.2) and (3.5), it is easy to demonstrate that, at the arbitrary pattern of curves $W_n^{(g)}$ and $W_n^{(c)}$, we derive the exact relations

$$\delta n^{(g)} = \frac{\delta c_1}{c_1} (\Delta n^{(g)})^2, \quad \delta n^{(c)} = \frac{\delta c_1}{c_1} (\Delta n^{(c)})^2 \quad (3.7)$$

These relations are valid in the presence of quasi-equilibrium state of globular and spherocylindrical micelles even far from the state of solution equilibrium. In the vicinity of equilibrium state at $\delta c_1 / \tilde{c}_1 \ll 1$, relations (3.7) are transformed into the following equations:

$$\delta n^{(g)} = \frac{\delta c_1}{\tilde{c}_1} (\Delta \tilde{n}^{(g)})^2, \quad \delta n^{(c)} = \frac{\delta c_1}{\tilde{c}_1} (\Delta \tilde{n}^{(c)})^2 \quad (3.8)$$

Substituting Eq. (3.8) into (3.6), we obtain

$$\begin{aligned} \delta c_1 + \tilde{n}^{(g)} \delta c_M^{(g)} + \tilde{n}^{(c)} \delta c_M^{(c)} \\ + \frac{\delta c_1}{c_1} [\tilde{c}_M^{(g)} (\Delta \tilde{n}^{(g)})^2 + \tilde{c}_M^{(c)} (\Delta \tilde{n}^{(c)})^2] = 0. \end{aligned} \quad (3.9)$$

Let us now consider the first variation of Eq. (2.6). For this purpose, we first rewrite Eq. (2.6) with allowance for expressions (2.7) in the following form, which is convenient for analysis:

$$\frac{d}{dt} (c_M^{(g)} + c_M^{(c)}) = \frac{J_c^+ e^{-W_c}}{\sqrt{\pi \Delta n_c}} (c_1 - c_b e^{W_b}) \quad (3.10)$$

According to distribution (3.2) the right-hand side of equality (3.10) is nullified; hence, in the vicinity of equilibrium state, Eq. (3.10) can be linearized as follows: ✓

$$\frac{d}{dt} (\delta c_M^{(g)} + \delta c_M^{(c)}) = \frac{\tilde{J}_c^+ e^{-\tilde{W}_c}}{\sqrt{\pi \Delta \tilde{n}_c}} [\delta c_1 - \delta (c_b e^{W_b})] \quad (3.11)$$

Let us take into account the identities

$$c_b e^{W_b} = \frac{\int_{n_b}^{\infty} c_b e^{-(W_n^{(g)} - W_b)} dn}{\int_{n_b}^{\infty} e^{-W_n^{(g)}} dn} = \frac{c_M^{(g)}}{\int_{n_b}^{\infty} e^{-W_n^{(g)}} dn}, \quad (3.12)$$

$$c_b e^{W_b} = \frac{\int_{n_b}^{\infty} c_b e^{-(W_n^{(c)} - W_b)} dn}{\int_{n_b}^{\infty} e^{-W_n^{(c)}} dn} = \frac{c_M^{(c)}}{\int_{n_b}^{\infty} e^{-W_n^{(c)}} dn},$$

which stem from definitions (2.4) and relations (2.2) and are valid at any moment during the slow relaxation. Let us vary identities (3.12). We take into account that $\delta n_b = 0$, as number n_b is determined only by the geometric parameters of surfactant molecules. Using formulas (3.5) and (2.4), we find the following exact relations:

$$\delta \ln(c_b e^{W_b}) = \delta \ln c_M^{(g)} - (n^{(g)} - 1) \delta \ln c_1, \quad (3.13)$$

$$\delta \ln(c_b e^{W_b}) = \delta \ln c_M^{(c)} - (n^{(c)} - 1) \delta \ln c_1.$$

From Eq. (3.13), we arrive at the exact equality

$$\delta \ln c_M^{(g)} - n^{(g)} \delta \ln c_1 = \delta \ln c_M^{(c)} - n^{(c)} \delta \ln c_1. \quad (3.14)$$

This equality defines, in explicit form, the aforementioned relationship between variations $\delta c_M^{(g)}$ and $\delta c_M^{(c)}$.

As follows from exact relations (3.13), with allowance for the pattern of distribution (3.2), Eq. (3.11) in the vicinity of equilibrium state can be rewritten as

$$\frac{d}{dt} (\delta c_M^{(g)} + \delta c_M^{(c)}) = \frac{\tilde{J}_c \tilde{c}_1 e^{-\tilde{W}_c}}{\sqrt{\pi} \Delta \tilde{n}_c} \left(\tilde{n}^{(g)} \frac{\delta c_1}{\tilde{c}_1} - \frac{\delta c_M^{(g)}}{\tilde{c}_M^{(g)}} \right). \quad (3.15)$$

Additionally, from Eq. (3.14), in the vicinity of equilibrium state of solution at $\delta c_M^{(g)} / \tilde{c}_M^{(g)} \ll 1$, $\delta c_M^{(c)} / \tilde{c}_M^{(c)} \ll 1$ and $\delta c_1 / \tilde{c}_1 \ll 1$, we find

$$\frac{\delta c_M^{(g)}}{\tilde{c}_M^{(g)}} - \tilde{n}^{(g)} \frac{\delta c_1}{\tilde{c}_1} = \frac{\delta c_M^{(c)}}{\tilde{c}_M^{(c)}} - \tilde{n}^{(c)} \frac{\delta c_1}{\tilde{c}_1}. \quad (3.16)$$

Equations (3.9), (3.15), and (3.16) form the closed system of linear differential first-order equation for unknown deviations δc_1 , $\delta c_M^{(g)}$, and $\delta c_M^{(c)}$.

4. CHARACTERISTIC TIME OF SLOW RELAXATION UPON THE COMPETITION BETWEEN GLOBULAR AND SPHERE-CYLINDRICAL MICELLES

Let us find the solution to the system of equations (3.9), (3.15), and (3.16). At the first step, we express linear variations $\delta c_M^{(g)}$ and $\delta c_M^{(c)}$ via δc_1 . Solving Eqs. (3.9) and (3.16) with respect to $\delta c_M^{(g)}$ and $\delta c_M^{(c)}$, we arrive at

$$\frac{\delta c_M^{(g)}}{\tilde{c}_M^{(g)}} = \left(\tilde{n}^{(g)} - \frac{\tilde{c}_1 + \tilde{c}_M^{(g)} [(\tilde{n}^{(g)})^2 + (\Delta \tilde{n}^{(g)})^2] + \tilde{c}_M^{(c)} [(\tilde{n}^{(c)})^2 + (\Delta \tilde{n}^{(c)})^2]}{\tilde{n}^{(g)} \tilde{c}_M^{(g)} + \tilde{n}^{(c)} \tilde{c}_M^{(c)}} \right) \frac{\delta c_1}{\tilde{c}_1}, \quad (4.1)$$

$$\frac{\delta c_M^{(c)}}{\tilde{c}_M^{(c)}} = \left(\tilde{n}^{(c)} - \frac{\tilde{c}_1 + \tilde{c}_M^{(g)} [(\tilde{n}^{(g)})^2 + (\Delta \tilde{n}^{(g)})^2] + \tilde{c}_M^{(c)} [(\tilde{n}^{(c)})^2 + (\Delta \tilde{n}^{(c)})^2]}{\tilde{n}^{(g)} \tilde{c}_M^{(g)} + \tilde{n}^{(c)} \tilde{c}_M^{(c)}} \right) \frac{\delta c_1}{\tilde{c}_1}. \quad (4.2)$$

It is evident that Eqs. (4.1) and (4.2) are consistent with Eq. (3.16).

After the substitution of expressions (4.1) and (4.2) into Eq. (3.15), we can easily solve this equation relative to δc_1

$$\delta c_1 = \delta c_1(0) e^{-t/t_r}, \quad (4.3)$$

where $\delta c_1(0)$ is a certain deviation of the concentration of surfactant monomers at the final stage of slow relaxation at $\delta c_M^{(g)} / \tilde{c}_M^{(g)} \ll 1$, $\delta c_M^{(c)} / \tilde{c}_M^{(c)} \ll 1$, and $\delta c_1 / \tilde{c}_1 \ll 1$ at the moment taken as zero-valued. The characteristic time of slow relaxation t_r is defined by the equality

$$t_r = \frac{1}{\tilde{J}} \frac{(\tilde{c}_M^{(g)} + \tilde{c}_M^{(c)}) [\tilde{c}_1 + \tilde{c}_M^{(g)} (\Delta \tilde{n}^{(g)})^2 + \tilde{c}_M^{(c)} (\Delta \tilde{n}^{(c)})^2] + \tilde{c}_M^{(g)} \tilde{c}_M^{(c)} [\tilde{n}^{(g)} - \tilde{n}^{(c)}]^2}{\tilde{c}_1 + \tilde{c}_M^{(g)} [(\tilde{n}^{(g)})^2 + (\Delta \tilde{n}^{(g)})^2] + \tilde{c}_M^{(c)} [(\tilde{n}^{(c)})^2 + (\Delta \tilde{n}^{(c)})^2]}. \quad (4.4)$$

In view of positive definiteness of all values in the right-hand side of Eq. (4.4), it is evident that $t_r > 0$.

Solution (4.3) is one of three solutions (3.9)–(3.15) and (3.16) of a system of equations. Two remaining solutions for

$\delta c_M^{(g)}$ and $\delta c_M^{(c)}$ can be readily found after the substitution of solution (4.3) into equalities (4.1) and (4.2). Then, we have

$$\delta c_M^{(g)} = \frac{\tilde{c}_M^{(g)}}{\tilde{c}_1} \left(\tilde{n}^{(g)} - \frac{\tilde{c}_1 + \tilde{c}_M^{(g)} [(\tilde{n}^{(g)})^2 + (\Delta\tilde{n}^{(g)})^2] + \tilde{c}_M^{(c)} [(\tilde{n}^{(c)})^2 + (\Delta\tilde{n}^{(c)})^2]}{\tilde{n}^{(g)}\tilde{c}_M^{(g)} + \tilde{n}^{(c)}\tilde{c}_M^{(c)}} \right) \delta c_1(0) e^{-t/t_r}, \quad (4.5)$$

$$\delta c_M^{(c)} = \frac{\tilde{c}_M^{(c)}}{\tilde{c}_1} \left(\tilde{n}^{(c)} - \frac{\tilde{c}_1 + \tilde{c}_M^{(g)} [(\tilde{n}^{(g)})^2 + (\Delta\tilde{n}^{(g)})^2] + \tilde{c}_M^{(c)} [(\tilde{n}^{(c)})^2 + (\Delta\tilde{n}^{(c)})^2]}{\tilde{n}^{(g)}\tilde{c}_M^{(g)} + \tilde{n}^{(c)}\tilde{c}_M^{(c)}} \right) \delta c_1(0) e^{-t/t_r}. \quad (4.6)$$

Pre-exponential factors in Eqs. (4.5) and (4.6) determine deviations of the total concentrations of globular and spherocylindrical micelles at the final stage of slow relaxation at the moment taken as zero-valued.

Let us study the mutual effect of coexisting globular and spherocylindrical micelles. This effect is exhibited via time t_r and pre-exponential factors in Eqs. (4.5) and (4.6). It is seen that the values referred to globular and spherocylindrical micelles enter into Eqs. (4.4)–(4.6) in a symmetric manner. The mutual effect of coexisting globular and spherocylindrical micelles is determined not only by the relation between the total concentration of micelles at the equilibrium state, but also relations between their average aggregation numbers and rms deviations in this state.

Equalities (2.2), (2.4), and (3.2) suggest that total equilibrium concentration $\tilde{c}_M^{(g)}$ and $\tilde{c}_M^{(c)}$ are functionals of $\tilde{W}_n^{(g)}$ and $\tilde{W}_n^{(c)}$ branches of aggregation work. Let us consider further the case when, in the vicinity of minima $n = \tilde{n}_s^{(g)}$ and $n = \tilde{n}_s^{(c)}$ of $\tilde{W}_n^{(g)}$ and $\tilde{W}_n^{(c)}$ branches of aggregation work (see Fig. 1a), the quadratic approximations

$$\tilde{W}_n^{(g)} \approx \tilde{W}_s^{(g)} + \frac{(n - \tilde{n}_s^{(g)})^2}{(\Delta\tilde{n}_s^{(g)})^2}, \quad (4.7)$$

$$\tilde{W}_n^{(c)} \approx \tilde{W}_s^{(c)} + \frac{(n - \tilde{n}_s^{(c)})^2}{(\Delta\tilde{n}_s^{(c)})^2}, \quad (4.8)$$

can be used, where $\tilde{W}_s^{(g)}$ and $\tilde{W}_s^{(c)}$ are the minima of corresponding branches (the depths of potential wells for globular and spherocylindrical micelles; $\Delta\tilde{n}_s^{(g)}$ and $\Delta\tilde{n}_s^{(c)}$ are the half-widths of aggregation work in the vicinity of points $n = \tilde{n}_s^{(g)}$ and $n = \tilde{n}_s^{(c)}$ (half-widths of

potential wells), respectively. Equalities (2.2), (2.4), (3.2), (4.7), and (4.8) yield relations

$$\begin{aligned} \tilde{c}_M^{(g)} &= \tilde{c}_1 \sqrt{\pi} \Delta\tilde{n}_s^{(g)} e^{-\tilde{W}_s^{(g)}}, & \tilde{n}^{(g)} &= \tilde{n}_s^{(g)}, \\ \Delta\tilde{n}^{(g)} &= \Delta\tilde{n}_s^{(g)} / \sqrt{2}, \\ \tilde{c}_M^{(c)} &= \tilde{c}_1 \sqrt{\pi} \Delta\tilde{n}_s^{(c)} e^{-\tilde{W}_s^{(c)}}, & \tilde{n}^{(c)} &= \tilde{n}_s^{(c)}, \\ \Delta\tilde{n}^{(c)} &= \Delta\tilde{n}_s^{(c)} / \sqrt{2}. \end{aligned} \quad (4.9)$$

Alongside formulas (4.4)–(4.6), these relations make it possible, using experimental data on slow relaxation, to estimate the $\tilde{W}_s^{(g)}$ and $\tilde{W}_s^{(c)}$ values. As follows from Eq. (4.9), for the prevalence of globular micelles at overall concentrations between CMC_1 and CMC_2 , the strong inequality

$$e^{\tilde{W}_s^{(c)} - \tilde{W}_s^{(g)}} \gg \frac{\Delta\tilde{n}^{(c)}}{\Delta\tilde{n}^{(g)}}. \quad (4.10)$$

should be fulfilled. Because inequality $\Delta\tilde{n}^{(c)} \gg \Delta\tilde{n}^{(g)}$ is usually true (this is qualitatively reflected in Fig. 1a), the $\tilde{W}_s^{(c)} - \tilde{W}_s^{(g)}$ difference should be sufficiently large such that to ensure strong inequality (4.10).

If we assume, in formulas (4.1)–(4.6), that $\tilde{c}_M^{(g)} = 0$, these formulas are transformed into relations for the case when the aggregation work has only one spherocylindrical branch. Corresponding formulas for the case of solutions with merely spherical micelles (at overall surfactant concentration above CMC_1) are shown, for example, in [9] and, with allowance for Eq. (4.9), virtually coincide with those that follow from equalities (4.1)–(4.6).

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