

Power-Law Stage of Slow Relaxation in Solutions with Spherical Micelles

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Abstract—General (independent of models selected for surfactant molecular aggregates) analytical relations are derived to describe the initial stage of slow relaxation in micellar solutions with spherical micelles. This stage precedes the final stage of the relaxation occurring via an exponential decay of disturbances with time. The relations obtained are applicable throughout the interval of micellar solution concentrations from the first to the second critical micellization concentration. It is shown that the initial stage is characterized by power laws of variations in the concentrations of monomers and micelles with time, these laws being different for the relaxation processes proceeding from above and below toward equilibrium values of micellar solution parameters. Relations are derived for the duration of this stage, and the effect of initial conditions is studied. Characteristic times of the power-law stage are determined and compared with the characteristic time of the final exponent-law relaxation stage. The behavior of these times is investigated at surfactant solution concentrations in the vicinity of, and noticeably above, the first critical micellization concentration. On the basis of the droplet and quasi-droplet thermodynamic models of surfactant molecular aggregates, numerical solutions are found for nonlinearized equations of slow relaxation for the time dependence of surfactant monomer concentrations at all stages of the slow relaxation. Numerical results obtained from the models are compared with the results of a general analytical study.

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INTRODUCTION

The concept of “slow” relaxation processes in micellar solutions as processes relevant to the establishment of complete equilibrium by the formation and disintegration of micelles, which are accompanied by the forward and back fluxes of molecular aggregates through a potential barriers of micellization, was formulated for the first time in Aniansson’s and Wall’s works [1, 2] and is generally accepted today. Usually, when speaking of a slow relaxation time, they mean the characteristic time of the exponential decay of a disturbance in monomer concentration or total micelle concentration [3]. However, the exponential decay regime is only developed at the final stage of the relaxation process, when the deviations from the equilibrium concentrations of surfactant monomers and micelles become very small [4–6]. The final stage of the slow relaxation occurring via the exponential decay of concentration disturbances with time is hereafter referred to as “exponent-law relaxation” for short. In the total relaxation process, a marked role is also played by the stage of power-law variations in the concentrations with time. This stage precedes the exponent-law relaxation. Accordingly, this initial stage of slow relaxation is hereafter referred to as a “power-law relaxation stage.” It is during the power-law stage that relaxing parameters of a solution undergo main nonlinear variations. An important peculiarity of the power-law stage is, in con-

trast to the exponent-law stage, the dependence of the characteristic times and the duration of the power-law stage itself on whether the relaxing parameters of a micellar solution approach their equilibrium values from above or below. The relations between the relaxation times of the exponent- and power-law relaxation processes were, in general, estimated in [4–6] for the situation in which, after an initial disturbance, the concentrations of surfactant monomers and micelles decrease and increase, respectively. An opposite situation when the surfactant monomer and micelle concentrations rise and diminish, respectively, is also of experimental and theoretical interest. This situation will be considered in this paper.

In this paper, analytical relations will be derived for the time dependences of surfactant monomer concentration at the power-law stage of slow relaxation in solutions at arbitrary initial conditions. The aforementioned relations will be obtained on the basis of exact formulas describing the dependences of the positions and half-widths of the vicinities of extreme work values on surfactant monomer concentrations in dilute micellar solutions [7]. It will be shown that the derived relations have a general form independent of the model, which is selected for surfactant molecular aggregates, and are applicable throughout the range of micellar solution concentrations from the first to the second critical micellization concentration (CMC_1 and CMC_2 ,

respectively). The influence of initial conditions will be investigated. The characteristic times of the power-law stage will be found and compared with the characteristic time of the final exponent-law stage of relaxation. The behavior of these times will be analyzed at surfactant concentrations close to and well above CMC₁. The derived general relations will be verified using the droplet [8, 6] and quasi-droplet [9, 6] thermodynamic models of surfactant molecular aggregates. In terms of these models, numerical solutions will be formulated for nonlinearized equations of the slow relaxation for the time dependences of surfactant monomer and micelle concentrations at all stages of slow relaxation. Characteristic times and their dependences on the overall solution concentration will be calculated.

1. GENERAL CONCEPTS OF SLOW RELAXATION KINETICS IN NONIONIC SURFACTANT SOLUTIONS WITH SPHERICAL MICELLES

Let us introduce the denotations and formulate the general concepts of slow relaxation in nonionic surfactant solutions with spherical micelles that are necessary for further consideration. The aggregation number of a molecular aggregate in a micellar solution is denoted as n . The minimum work of surfactant molecular aggregate formation (hereafter it is referred to as the aggregation work for short) is expressed in thermal units of energy kT (k is the Boltzmann constant and T is solution temperature) and denoted as W_n . At $n = 1$, aggregates represent surfactant monomers. Their concentration in a solution is denoted as c_1 . The positions of the maximum and minimum of work W_n in the axis of variable n are denoted as n_c and n_s , respectively. The maximum and minimum of W_n themselves, that is, the height of the potential barrier and the depth of the potential well of the aggregation work, are denoted as $W_c \equiv W_n|_{n=n_c}$

and $W_s \equiv W_n|_{n=n_s}$, respectively. The half-widths of the potential barrier and the potential well of work W_n along the axis of variable n are determined as follows:

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

Let us introduce the quasi-steady-state forward and back fluxes (J' and J'' , respectively) of molecular aggregates through the potential barrier of the aggregation work per unit time and unit volume as follows [4–6]:

$$J' = c_1 j_c^+ \exp(-W_c)/\pi^{1/2} \Delta n_c, \quad (1.2)$$

$$J'' = -c_M j_c^+ \exp[-(W_c - W_s)]/\pi \Delta n_c \Delta n_s, \quad (1.3)$$

where j_c^+ is the number of surfactant monomers absorbed by a molecular aggregate per unit time at $n =$

n_c and c_M is the total micelle concentration (the total number of aggregates with aggregation numbers $n > n_c + \Delta n_c$ in unit volume of a solution).

At the slow relaxation stage, the balance of the forward and back transitions of molecular aggregates [4–6] is expressed as

$$\partial c_M/\partial t = J' + J''. \quad (1.4)$$

At overall surfactant concentrations c ranging from CMC₁ to CMC₂ (that is, when only monomers and spherical micelles are present in a solution), in addition to Eq. (1.4), we have an equation describing surfactant material balance in unit volume:

$$c_1 + n_s c_M = c. \quad (1.5)$$

For a materially isolated solution (when the overall surfactant concentration is virtually constant), using Eq. (1.5) and explicit expressions (1.2) and (1.3) for fluxes J' and J'' , formula (1.4) is reduced to a relation for surfactant monomer concentration $c_1(t)$ that depends on time. This relation is a nonlinear differential equation of the first order with respect to time. For any time moment during the slow relaxation stage, the integration of this relation yields

$$t = - \int_{c_1(0)}^{c_1(t)} dc_1 \frac{\pi^{1/2} \Delta n_c (c_M \partial n_s / \partial c_1 + 1) \exp(W_c)}{j_c^+ n_s c_1 [1 - (c_M/c_1) \exp(W_s)/\pi^{1/2} \Delta n_s]}, \quad (1.6)$$

where $c_1(0)$ is an initial surfactant monomer concentration at the onset of the slow relaxation (time moment $t = 0$). When W_c , W_s , n_c , n_s , Δn_c , Δn_s , and j_c^+ are specified as functions of c_1 , Eqs. (1.5) and (1.6) determine the behavior of monomer concentration and the total concentration of micelles with time during the slow relaxation.

Let us denote the values relevant to the final equilibrium state of the micellar solution by a wavy bar above. At the final equilibrium, and taking into account relations (1.2), (1.3), and (1.5), the equality of the right-hand side of Eq. (1.4) to zero leads to the following relations [3–5]:

$$\tilde{c}_M = \pi^{1/2} \tilde{c}_1 \Delta \tilde{n}_s \exp(-\tilde{W}_s), \quad (1.7)$$

$$\tilde{c}_1 + \pi^{1/2} \tilde{c}_1 \tilde{n}_s \Delta \tilde{n}_s \exp(-\tilde{W}_s) = c. \quad (1.8)$$

At specified overall concentration c and known dependences of n_s , Δn_s and W_s on concentration c_1 , Eqs. (1.7) and (1.8) enable us to find the equilibrium values of \tilde{c}_M and \tilde{c}_1 .

Let us denote deviations of the parameters from their values at the final equilibrium state by symbol δ before these parameters. As was shown earlier [4–6], for times at which concentrations c_1 and c_M are already

close to the \tilde{c}_1 and \tilde{c}_M values at the final equilibrium state of the solution, the following relations are valid:

$$\begin{aligned}\delta c_1(t) &= \delta c_1(t_0)e^{-(t-t_0)/t_r}, \\ \delta c_M(t) &= \delta c_M(t_0)e^{-(t-t_0)/t_r} \quad (t \geq t_0).\end{aligned}\quad (1.9)$$

Here, $\delta c_1(t_0)$ and $\delta c_M(t_0)$ are the deviations of the concentrations of surfactant monomers and micelles at the onset of the final exponent-law stage of the slow relaxation ($t = t_0$). The characteristic time of the exponent-law relaxation t_r is found as follows [4–6]:

$$t_r = \frac{(1 - \tilde{\lambda})\tilde{c}_1}{\tilde{n}_s \tilde{J}'} \left(1 + \tilde{\gamma} + \tilde{\eta}_s + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}} \right)^{-1}, \quad (1.10)$$

where dimensionless parameters $\tilde{\gamma}$, $\tilde{\eta}_s$, and $\tilde{\lambda}$ are equal to

$$\begin{aligned}\tilde{\gamma} &\equiv -\tilde{c}_1 (\partial W_s / \partial c_1) |_{c_1 = \tilde{c}_1}, \\ \tilde{\eta}_s &\equiv \tilde{c}_1 (\partial \ln \Delta n_s / \partial c_1) |_{c_1 = \tilde{c}_1}, \\ \tilde{\lambda} &\equiv \tilde{c}_M (\partial n_s / \partial c_1) |_{c_1 = \tilde{c}_1}\end{aligned}\quad (1.11)$$

and dimensionless value α is introduced as

$$\tilde{\alpha} \equiv \frac{\tilde{n}_s \tilde{c}_M}{\tilde{c}_1} \quad (1.12)$$

(at CMC_1 , the $\tilde{\alpha}$ value is close to degree $\tilde{n}_s \tilde{c}_M / c$ of micellization and is usually assumed to be equal to 0.1). With allowance for exact relations (1.4), (1.14), and (3.10) presented in [7] and (1.7) and (1.12), the formulas for $\tilde{\gamma}$, $\tilde{\eta}_s$, $\tilde{\lambda}$, and $\tilde{\alpha}$ are transformed into the following relations:

$$\tilde{\gamma} = \tilde{n}_s - 1, \quad (1.13)$$

$$\tilde{\eta}_s = -\frac{\Delta \tilde{n}_s^4}{8} \left(\frac{\partial^3 W_n}{\partial n^3} \right)_{n = \tilde{n}_s}, \quad (1.14)$$

$$\tilde{\lambda} = \frac{\tilde{\alpha} \Delta \tilde{n}_s^2}{2 \tilde{n}_s} = \frac{\pi^{1/2} \Delta \tilde{n}_s^3 \exp(-\tilde{W}_s)}{2}, \quad (1.15)$$

$$\tilde{\alpha} = \pi^{1/2} \tilde{n}_s \Delta \tilde{n}_s \exp(-\tilde{W}_s). \quad (1.16)$$

Taking into account Eqs. (1.13) and (1.15), formula (1.10) for time t_r may be rewritten as

$$t_r = \frac{\left(1 + \frac{\tilde{\alpha} \Delta \tilde{n}_s^2}{2 \tilde{n}_s} \right) \tilde{c}_1}{\tilde{n}_s^2 \tilde{J}'} \left(1 + \frac{\tilde{\eta}_s}{\tilde{n}_s} + \frac{1}{\tilde{\alpha} \tilde{n}_s} + \frac{\Delta \tilde{n}_s^2}{2 \tilde{n}_s^2} \right)^{-1}. \quad (1.17)$$

Note that time t_r is sometimes unreasonably considered to be the characteristic time of the whole slow relaxation process in a solution with spherical micelles.

2. INTERVALS OF VARIATIONS IN SURFACTANT MONOMER AND MICELLE CONCENTRATIONS DURING SLOW RELAXATION IN A SOLUTION

Let us consider a micellar solution disturbed by an external action (the nature of the action is here ignored). After the disturbance, the solution is assumed to be materially isolated and to have an overall surfactant concentration c lying between CMC_1 and CMC_2 and constant temperature and pressure. As micelle concentration remains virtually unchanged at the fast relaxation stage, total micelle concentration $c_M(0)$ at the onset of the slow relaxation coincides with that at the onset of the fast relaxation immediately after the solution is disturbed. Further, this parameter is assumed to be known. Accordingly, taking into account Eqs. (1.8) and (1.7), deviation $\delta c_M(0)$ is also considered to be known (at specified c and $c_M(0)$ parameters).

When the fast relaxation is completed, the state of the solution is determined only by concentrations $c_M(t)$ and $c_1(t)$, with one of them decreasing with time and the other increasing to final equilibrium values. As was shown in [7], for monomer concentration c_1 , lying in the range from its value at which c is even slightly lower than CMC_1 and the difference $n_s - n_c$ is equal to the sum of half-widths $\Delta n_c + \Delta n_s$ to its value at which the minimum of aggregation work W_s diminishes to 3 (or CMC_2 is reached), material balance equation (1.5) may be linearized in the form

$$\delta c_M = -\frac{1 + \tilde{\lambda}}{\tilde{n}_s} \delta c_1. \quad (2.1)$$

In order to make Eq. (2.1) valid within the aforementioned interval, it is sufficient to fulfill the strong inequality $|\delta c_1|/\tilde{c}_1 \ll 1$ [7].

Although the strong inequality $|\delta c_M|/\tilde{c}_M \ll 1$ is not necessary for relation (2.1), it will be necessary to limit the $|\delta c_M|/\tilde{c}_M$ value from above. Preliminarily, the following circumstances should be noted. As the final concentration of spherical micelles \tilde{c}_M rapidly rises with the overall micellar solution concentration, the strong inequality $|\delta c_M|/\tilde{c}_M \ll 1$ and, as a consequence, the inequality $(1 + \tilde{\lambda})|\delta c_1|/\tilde{\alpha} \tilde{c}_1 \ll 1$, (in view of relations (2.1) and (1.12)), may be unsatisfied (despite $|\delta c_1|/\tilde{c}_1 \ll 1$) only at sufficiently small \tilde{c}_M values in the vicinity of CMC_1 . To avoid a situation in which current micelle concentration c_M may be reduced to zero, let us impose the additional condition $(1 + \tilde{\lambda})\delta c_1/\tilde{\alpha} \tilde{c}_1 < 1$ when $\delta c_1 > 0$. At $\delta c_1 < 0$, this situation is impossible.

As, in general, the time dependences of monomer concentrations increasing and decreasing in the course of relaxation are different, let us distinguish between them employing superscripts (*u*) and (*b*). The initial

values of $\delta c_1^{(u)}(0)$ and $\delta c_1^{(b)}(0)$ of deviation $\delta c_1^{(u)}(t)$ and $\delta c_1^{(b)}(t)$ in surfactant monomer concentration are expressed as

$$\delta c_1^{(u)}(0) = \frac{\beta_u \tilde{c}_1}{\tilde{n}_s}, \quad \delta c_1^{(b)}(0) = -\frac{\beta_b \tilde{c}_1}{\tilde{n}_s}, \quad (2.2)$$

where β_u and β_b are some positive numerical parameters. Then, according to relations (2.1) and (2.2), initial $\delta c_M^{(u)}(0)$ and $\delta c_M^{(b)}(0)$ values of deviations $\delta c_M^{(u)}(t)$ and $\delta c_M^{(b)}(t)$ in micelle concentration are equal to

$$\begin{aligned} \delta c_M^{(u)}(0) &= -\frac{\beta_u \tilde{c}_1}{\tilde{n}_s^2} (1 + \tilde{\lambda}), \\ \delta c_M^{(b)}(0) &= \frac{\beta_b \tilde{c}_1}{\tilde{n}_s^2} (1 + \tilde{\lambda}). \end{aligned} \quad (2.3)$$

As follows from relations (2.3) and (2.2), by specifying initial deviation $\delta c_M^{(u)}(0)$ and $\delta c_M^{(b)}(0)$, we determine positive magnitudes β_u and β_b , as well as initial deviations $\delta c_1^{(u)}(0)$ and $\delta c_1^{(b)}(0)$. Vice versa, by specifying numbers β_u and β_b , we perform the parameterization of the initial disturbances of a micellar solution. The larger β_u and β_b the stronger the initial disturbance of a solution.

In view of (2.2), the range of variations in surfactant monomer concentration must obey the following inequality when this concentration diminishes in a micellar solution:

$$0 \leq \delta c_1^{(u)}(t) \leq \frac{\beta_u \tilde{c}_1}{\tilde{n}_s}. \quad (2.4)$$

When the concentration increases, the interval must obey the inequality

$$-\frac{\beta_b \tilde{c}_1}{\tilde{n}_s} \leq \delta c_1^{(b)}(t) \leq 0. \quad (2.5)$$

As was shown in [7], in order to make relations (1.9), which describe the exponent-law stage of relaxation, to be applicable, the following strong inequality must be fulfilled:

$$\frac{|\delta c_1(t_0)|}{\tilde{c}_1} \ll \frac{2}{\tilde{n}_s}. \quad (2.6)$$

As the exponent-law relaxation is reached asymptotically, the onset of the exponent-law stage is determined, to some extent, arbitrarily. Let us specify moments $t_0^{(u)}$ and $t_0^{(b)}$ of the onset of the exponent-law relaxation stage upon a reduction and an increase in the monomer

concentration, respectively, by the following conditions corresponding to relation (2.6):

$$\frac{\delta c_1^{(u)}(t_0^{(u)})}{\tilde{c}_1} = \frac{1}{2\tilde{n}_s}, \quad \frac{|\delta c_1^{(b)}(t_0^{(b)})|}{\tilde{c}_1} = \frac{1}{2\tilde{n}_s}. \quad (2.7)$$

Then, within the time intervals $0 \leq t \leq t_0^{(u)}$ and $0 \leq t \leq t_0^{(b)}$, which precede the onset of the exponent-law stage of relaxation, with allowance for relations (2.2) and (2.4)–(2.7), deviations in the surfactant monomer concentration vary over the ranges

$$\delta c_1^{(u)}(t_0^{(u)}) = \frac{1}{2\tilde{n}_s} \tilde{c}_1 < \delta c_1^{(u)}(t) \leq \frac{\beta_u \tilde{c}_1}{\tilde{n}_s} = \delta c_1^{(u)}(0), \quad (2.8)$$

$$\begin{aligned} \delta c_1^{(b)}(0) &= -\frac{\beta_b \tilde{c}_1}{\tilde{n}_s} \leq \delta c_1^{(b)}(t) \\ &< -\frac{1}{2\tilde{n}_s} \tilde{c}_1 = \delta c_1^{(b)}(t_0^{(b)}). \end{aligned} \quad (2.9)$$

Accordingly, deviations $\delta c_M^{(u)}(t)$ and $\delta c_M^{(b)}(t)$ in micelle concentrations upon a decrease and a rise in monomer concentration will, with allowance for relations (2.1) and (2.3), vary within ranges

$$\delta c_M^{(u)}(0) = -\frac{\beta_u (1 + \tilde{\lambda}) \tilde{c}_1}{\tilde{n}_s^2} \leq \delta c_M^{(u)}(t) \quad (2.10)$$

$$< -\frac{1 + \tilde{\lambda}}{2\tilde{n}_s^2} \tilde{c}_1 = \delta c_M^{(u)}(t_0^{(u)}),$$

$$\begin{aligned} \delta c_M^{(b)}(t_0^{(b)}) &= \frac{1 + \tilde{\lambda}}{2\tilde{n}_s^2} \tilde{c}_1 < \delta c_M^{(b)}(t) \\ &\leq \frac{\beta_b (1 + \tilde{\lambda}) \tilde{c}_1}{\tilde{n}_s^2} = \delta c_M^{(b)}(0). \end{aligned} \quad (2.11)$$

3. ANALYTICAL SOLUTION OF THE PROBLEM OF THE INITIAL STAGE OF THE SLOW RELAXATION

Let us consider the integral in the right-hand part of relation (1.6) within the time interval preceding the exponent-law relaxation stage. The main contribution to the dependence of the integrand in relation (1.6) on the concentration of surfactant monomers c_1 is made by exponents $\exp(W_c)$ and $\exp(W_s)$. As was shown in [7] by means of inequalities (3.13) and (3.14), W_c and W_s values may be linearized relative to δc_1 provided that the inequality $|\delta c_1|/\tilde{c}_1 \ll 1$ is satisfied. Relation (2.1) may be linearized under the same condition. Hereafter, we assume that this inequality is fulfilled within ranges (2.8) and (2.9). Later on, we clarify the conditions imposed on values β_u and β_b in this case. Using formu-

las (3.15) and (3.16) presented in [7], we write the following equations:

$$\begin{aligned} W_c &= \tilde{W}_c - (\tilde{n}_c - 1)\delta c_1/\tilde{c}_1, \\ W_s &= \tilde{W}_s - (\tilde{n}_s - 1)\delta c_1/\tilde{c}_1 \quad (|\delta c_1|/\tilde{c}_1 \ll 1). \end{aligned} \quad (3.1)$$

Assuming that the inequalities

$$\begin{aligned} |\delta c_1|/\tilde{c}_1 \ll 1, \quad |\delta c_M|/\tilde{c}_M < 1/2, \quad |\eta_c \delta c_1|/\tilde{c}_1 \ll 1, \\ |\eta_s \delta c_1|/\tilde{c}_1 \ll 1, \quad \frac{\Delta n_c^2 |\delta c_1|}{2n_c \tilde{c}_1} \ll 1, \quad \frac{\Delta n_s^2 |\delta c_1|}{2n_s \tilde{c}_1} \ll 1 \end{aligned} \quad (3.1a)$$

are satisfied, it is easy to understand that the following approximate inequalities take place:

$$c_1 \approx \tilde{c}_1 \exp\left(\frac{\delta c_1}{\tilde{c}_1}\right), \quad (3.2)$$

$$c_M \equiv \tilde{c}_M \exp\left[\ln\left(1 + \frac{\delta c_M}{\tilde{c}_M}\right)\right] \approx \tilde{c}_M \exp\left(-\frac{1 + \tilde{\lambda} \delta c_1}{\tilde{\alpha} \tilde{c}_1}\right),$$

$$\Delta n_c \approx \Delta \tilde{n}_c \exp\left(\frac{\partial \ln(\Delta n_c)}{\partial c_1} \Big|_{c_1 = \tilde{c}_1} \delta c_1\right) \approx \Delta \tilde{n}_c \exp\left(\tilde{\eta}_c \frac{\delta c_1}{\tilde{c}_1}\right), \quad (3.3)$$

$$\Delta n_s \approx \Delta \tilde{n}_s \exp\left(\tilde{\eta}_s \frac{\delta c_1}{\tilde{c}_1}\right),$$

$$n_c \approx \tilde{n}_c \exp\left(\frac{\partial \ln(n_c)}{\partial c_1} \Big|_{c_1 = \tilde{c}_1} \delta c_1\right) \approx \tilde{n}_c \exp\left(-\frac{\Delta \tilde{n}_c^2 \delta c_1}{2\tilde{n}_c \tilde{c}_1}\right), \quad (3.4)$$

$$n_s \approx \tilde{n}_s \exp\left(\frac{\Delta \tilde{n}_s^2 \delta c_1}{2\tilde{n}_s \tilde{c}_1}\right),$$

where relations (2.1) and (1.12) are taken into account, parameter $\tilde{\eta}_c \equiv \tilde{c}_1 (\partial \ln \Delta n_c / \partial c_1)|_{c_1 = \tilde{c}_1}$, is introduced analogously to the second one of relations (1.11), and the equalities $\frac{\partial \ln n_c}{\partial \ln c_1} = -\frac{\Delta n_c^2}{2n_c}$, and $\frac{\partial \ln n_s}{\partial \ln c_1} = \frac{\Delta n_s^2}{2n_s}$ (equalities (1.7) and (1.8) in [7]) are taken into account.

With allowance for relations (3.1)–(3.3) and (1.7) and employing geometric progression formula, the following expansions are derived within intervals (2.8) and (2.9) for the factor $[1 - (c_M/c_1)\exp(W_s)/\pi^{1/2}\Delta n_s]^{-1}$ in the integrand of relation (1.6):

$$\begin{aligned} & \frac{1}{1 - (c_M/c_1)\exp(W_s)/\pi^{1/2}\Delta n_s} \\ &= \sum_{m=0}^{\infty} \exp\left[-m\left(\tilde{n}_s + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}} + \tilde{\eta}_s\right)\frac{\delta c_1}{\tilde{c}_1}\right] \\ & \left(\frac{1}{2\tilde{n}_s} \leq \frac{\delta c_1}{\tilde{c}_1} \leq \frac{\beta_u}{\tilde{n}_s}\right), \end{aligned} \quad (3.5)$$

$$\begin{aligned} & \frac{1}{1 - (c_M/c_1)\exp(W_s)/\pi^{1/2}\Delta n_s} \\ &= -\sum_{m=0}^{\infty} \exp\left[(m+1)\left(\tilde{n}_s + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}} + \tilde{\eta}_s\right)\frac{\delta c_1}{\tilde{c}_1}\right] \\ & \left(-\frac{\beta_b}{\tilde{n}_s} \leq \frac{\delta c_1}{\tilde{c}_1} \leq \frac{1}{2\tilde{n}_s}\right). \end{aligned} \quad (3.6)$$

The series in relations (3.5) and (3.6) are rapidly convergent because $|\delta c_1|/\tilde{c}_1 \geq 1/2\tilde{n}_s$. In this situation, it is sufficient to take into account only two initial terms.

Analogously, with allowance for (3.1)–(3.4), (1.2), and (1.11), we have the following equality for the second factor in the integrand of relation (1.6):

$$\begin{aligned} & \frac{\pi^{1/2}\Delta n_c}{j_c^+ n_s c_1} \left(c_M \frac{\partial n_s}{\partial c_1} + 1\right) e^{W_c} = \frac{1 + \tilde{\lambda} e^{-\left(1 + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}} - 2\tilde{\eta}_s\right)\frac{\delta c_1}{\tilde{c}_1}}}{\tilde{n}_s \tilde{J}'} \\ & \times \exp\left[-\left(\tilde{n}_c - \tilde{\eta}_c + 1 + \frac{\Delta \tilde{n}_s^2}{2\tilde{n}_s} - \frac{\Delta \tilde{n}_c^2}{3\tilde{n}_c}\right)\frac{\delta c_1}{\tilde{c}_1}\right]. \end{aligned} \quad (3.7)$$

Equation (3.7) is valid in both ranges (2.8) and (2.9). Relation (3.7) takes into account that the j_c^+ value is proportional to surfactant monomer concentration c_1 and micelle surface area $\propto n_c^{2/3}$.

It was found that $\Delta \tilde{n}_c^2/2\tilde{n}_c \sim 1$, $\Delta \tilde{n}_s^2/2\tilde{n}_s \sim 1$, $\tilde{\eta}_c$, and $\tilde{\eta}_s$ are negative values $|\tilde{\eta}_c| \approx 0.1$ – 1 and $|\tilde{\eta}_s| \approx 1$ – 2 [7]. The aforementioned estimations suggest that the latter four inequalities in (3.1a) are well fulfilled at $|\delta c_1|/\tilde{c}_1 \ll 1$. In view of relation (1.15), $\tilde{\lambda}$ increases with monomer concentration from $\tilde{\lambda} \sim 0.1$ at CMC_1 (at $\tilde{\alpha} = 0.1$) to large values $\tilde{\lambda} \gg 1$ (at $\tilde{\alpha} \gg 1$) so that the ratio $(1 + \tilde{\lambda})/\tilde{\alpha}$ appears to be on the order of ten at overall concentrations close to CMC_1 and on the order of $\Delta \tilde{n}_s^2/2\tilde{n}_s \sim 1$ at concentrations noticeably higher than CMC_1 . As the inequality $\tilde{n}_s \gg 1$ is always satisfied with a large excess for micelles, the contribution of term $\tilde{\eta}_s$ to the power indices of the exponents in the right-hand parts of relations (3.5) and (3.6) is small as compared to \tilde{n}_s . Further, we shall ignore this term to compare with \tilde{n}_s in the power indices of the exponents in relations (3.5) and (3.6). Term $(1 + \tilde{\lambda})/\tilde{\alpha}$ in these indices should be retained at overall concentrations close to CMC_1 . Taking into account the aforementioned behavior of $\tilde{\lambda}$ and $(1 + \tilde{\lambda})/\tilde{\alpha}$ values, factor $1 + \tilde{\lambda}$

$\exp\left[-\left(1 + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}} - 2\tilde{\eta}_s\right)\frac{\delta c_1}{\tilde{c}_1}\right]$ in Eq. (3.7) may be

replaced by $1 + \tilde{\lambda}$. Indeed, the absolute value of the power index of the exponent in this factor may be noticeable as compared with unity in the vicinity of CMC_1 despite the fact that $|\delta c_1|/\tilde{c}_1 \ll 1$; however, factor $\tilde{\lambda}$ at the exponent will, in this case, be much smaller than unity. Upon a rise in the overall concentration above CMC_1 , when $\tilde{\lambda}$ begins to rapidly grow, the absolute value of the power index of the exponent becomes small as compared to unity at $|\delta c_1|/\tilde{c}_1 \ll 1$ and the exponent itself approaches unity. Thus, the aforementioned replacement is valid at concentrations both close to and above CMC_1 . At $\tilde{n}_c \gg 1$ (even slightly larger than unity), the role of the difference $\Delta\tilde{n}_s^2/2\tilde{n}_s - \Delta\tilde{n}_c^2/3\tilde{n}_c$ in the power index of the exponent, which is the second term of relation (3.7), may be ignored as compared to \tilde{n}_c . However, as \tilde{n}_c may be on the order of ten, the role of term $|\tilde{\eta}_c| + 1$ in relation (3.7) may be noticeable. Therefore, further, we will retain $|\tilde{\eta}_c| + 1$ as an addend to the main terms on the order of \tilde{n}_c .

With allowance for all the mentioned above, substituting (3.5)–(3.7) into the integrand in relation (1.6) and retaining only first two members of the rapidly converging series in relations (3.5) and (3.6), after integration, we obtain

$$t = \frac{1 + \tilde{\lambda}}{\tilde{n}_s(\tilde{n}_c + 1 + |\tilde{\eta}_c|)} \tilde{c}_1 e^{-\tilde{\eta}_c + 1 + |\tilde{\eta}_c|} \frac{\delta c_1^{(u)}(t)}{\tilde{c}_1} \times \left[1 - e^{-\tilde{\eta}_c + 1 + |\tilde{\eta}_c|} \frac{\delta c_1^{(u)}(0) - \delta c_1^{(u)}(t)}{\tilde{c}_1} + \frac{(\tilde{n}_c + 1 + |\tilde{\eta}_c|)}{\tilde{n}_s + \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} e^{-\tilde{\eta}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \frac{\delta c_1^{(u)}(t)}{\tilde{c}_1} \right] \times \left(1 - e^{-\tilde{\eta}_c + \tilde{n}_s + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \frac{\delta c_1^{(u)}(0) - \delta c_1^{(u)}(t)}{\tilde{c}_1} \right) \quad (0 \leq t \leq t_0^{(u)}), \quad (3.8)$$

$$t = \frac{1 + \tilde{\lambda}}{\tilde{n}_s(\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}})} \tilde{c}_1 e^{-\tilde{\eta}_c - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \frac{\delta c_1^{(b)}(t)}{\tilde{c}_1} \times \left[1 - e^{-\tilde{\eta}_c - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \frac{\delta c_1^{(b)}(0) - \delta c_1^{(b)}(t)}{\tilde{c}_1} + \frac{\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}}{\left(2\tilde{n}_s - \tilde{n}_c + 2\frac{1 + \tilde{\lambda}}{\tilde{\alpha}}\right)} e^{-\tilde{\eta}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \frac{\delta c_1^{(b)}(t)}{\tilde{c}_1} \right] \times \left(1 - e^{-\left(2\tilde{n}_s - \tilde{n}_c + 2\frac{1 + \tilde{\lambda}}{\tilde{\alpha}}\right) \frac{\delta c_1^{(b)}(0) - \delta c_1^{(b)}(t)}{\tilde{c}_1}} \right) \quad (0 \leq t \leq t_0^{(b)}). \quad (3.9)$$

Here, we have ignored $1 + \tilde{\eta}_c$ as compared to \tilde{n}_s . It is the constraint from above on variations in time t presented in relations (3.8) and (3.9) that is the reason for the rapid convergence of the series in relations (3.5) and (3.6).

As is seen from formula (3.8), the effect of the initial $\delta c_1^{(u)}(0)$ value on the relaxation at $\delta c_1^{(u)}(t) > 0$ will be slight when the following condition is fulfilled:

$$e^{-\tilde{\eta}_c + 1 + |\tilde{\eta}_c|} \frac{\delta c_1^{(u)}(0) - \delta c_1^{(u)}(t)}{\tilde{c}_1} \ll 1. \quad (3.10)$$

At $t \approx t_0^{(u)}$, condition (3.10) is, with allowance for relation (2.8), reduced with a large excess to the inequality $\exp\left(-\tilde{n}_c \frac{\beta_u - 1/2}{\tilde{n}_s}\right) \ll 1$, which is satisfied at

$$\beta_u > 2\frac{\tilde{n}_s}{\tilde{n}_c} + \frac{1}{2}. \quad (3.11)$$

Similarly, as is seen from formula (3.9), the influence of the initial $\delta c_1^{(b)}(0)$ value on the relaxation at $\delta c_1^{(b)}(t) < 0$ will be slight when the following condition is fulfilled:

$$e^{-\tilde{\eta}_c - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \frac{\delta c_1^{(b)}(0) - \delta c_1^{(b)}(t)}{\tilde{c}_1} \ll 1. \quad (3.12)$$

At $t \approx t_0^{(b)}$, condition (3.12) is, with allowance for (2.9), reduced to inequality

$\exp\left[-\left(\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}\right) \frac{\beta_b - 1/2}{\tilde{n}_s}\right] \ll 1$, which is satisfied at

$$\beta_b > 2 \frac{\tilde{n}_s}{\tilde{n}_s - \tilde{n}_c + (1 + \tilde{\lambda})/\tilde{\alpha}} + \frac{1}{2}. \quad (3.13)$$

At $t < t_0^{(u)}$ and $t < t_0^{(b)}$, inequalities (3.11) and (3.13) would naturally be even stronger.

At a reasonable estimate $\tilde{n}_s/\tilde{n}_c \approx 3$, inequality (3.11) is already fulfilled at $\beta_u \approx 6.5$, while inequality (3.13), at overall concentrations noticeably higher than and close to CMC_1 , is already satisfied at $\beta_b \approx 3.5$ and 2.5, respectively. As follows from relations (2.8), (2.9), and $\tilde{n}_s \approx 10^2$, at these β_u and β_b values, inequality $|\delta c_1|/\tilde{c}_1 \ll 1$, which was required to analytically calculate the integral in relation (1.6), will be fulfilled with an excess throughout the interval of integration. Since, according to relations (2.10), (2.11), and (1.12), inequalities $|\delta c_M^{(u)}|/\tilde{c}_M < \beta_u(1 + \tilde{\lambda})/\tilde{\alpha}\tilde{n}_s$ and $|\delta c_M^{(b)}|/\tilde{c}_M < \beta_b(1 + \tilde{\lambda})/\tilde{\alpha}\tilde{n}_s$, are valid and, as inequality $(1 + \tilde{\lambda})/\tilde{\alpha} < 10$ is satisfied, even in the vicinity of CMC_1 , at the aforementioned estimates ($\beta_u \approx 6.5$, $\beta_b \approx 2.5$, and $\tilde{n}_s \approx 10^2$) inequality $|\delta c_M|/\tilde{c}_M < 1/2$ in relation (3.1a) will also be fulfilled (at $\beta_u \approx 6.5$ it is barely satisfied). Finally, all of the inequalities (3.1a) will be fulfilled.

The role of the third contributions in the brackets in relations (3.8) and (3.9), which are due to the second expansion terms in (3.5) and (3.6), is greatest at $t \approx t_0^{(u)}$ and $t \approx t_0^{(b)}$, as is evident from relations (2.8) and (2.9). However, even in this case, with allowance for relations (2.7), at $\tilde{n}_s/\tilde{n}_c \approx 3$, we obtain that the correction resultant from the third contributions in relation (3.8), as compared to the main contribution, is rather adequately estimated as

$$\frac{\tilde{n}_c}{\tilde{n}_s + \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} e^{-\frac{1}{2}\left(1 + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}\tilde{n}_s}\right)} < 0.15. \quad (3.14)$$

In relation (3.9), it is assessed as

$$\frac{\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}}{2\tilde{n}_s - \tilde{n}_c + 2\frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} e^{-\frac{1}{2}\left(1 + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}\tilde{n}_s}\right)} < 0.25. \quad (3.15)$$

Thus, the role of these contributions is slight. At $t < t_0^{(u)}$ and $t < t_0^{(b)}$, their role becomes still slighter.

4. CHARACTERISTIC TIMES OF SLOW RELAXATION

Solving relations (3.8) and (3.9) relative to $c_1^{(u)}(t)$ and $c_1^{(b)}(t)$ at $0 \leq t < t_0^{(u)}$ and $0 \leq t < t_0^{(b)}$, when the third contributions in the brackets in relations (3.8) and (3.9) may be ignored, taking into account the first of equalities (3.2), we, with sufficient accuracy, find the following power relations for monomer concentrations as the basic approximations:

$$c_1^{(u)}(t) = \tilde{c}_1 \left[t/t_r^{(u)} + (\tilde{c}_1/c_1^{(u)}(0))^{\tilde{n}_c + 1 + |\tilde{\eta}_c|} \right]^{-\frac{1}{\tilde{n}_c + 1 + |\tilde{\eta}_c|}} \quad (4.1)$$

$$(0 \leq t < t_0^{(u)}),$$

$$c_1^{(b)}(t) = \tilde{c}_1 \left[t/t_r^{(b)} + (c_1^{(b)}(0)/\tilde{c}_1)^{\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}} \right]^{-\frac{1}{\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}}} \quad (4.2)$$

$$(0 \leq t < t_0^{(b)}),$$

where $t_r^{(u)}$ and $t_r^{(b)}$ are defined as

$$t_r^{(u)} \equiv \frac{(1 + \tilde{\lambda})\tilde{c}_1}{\tilde{n}_s(\tilde{n}_c + 1 + |\tilde{\eta}_c|)\tilde{J}'}, \quad (4.3)$$

$$t_r^{(b)} \equiv \frac{(1 + \tilde{\lambda})\tilde{c}_1}{\tilde{n}_s\left(\tilde{n}_s - \tilde{n}_c + \frac{1 + \tilde{\lambda}}{\tilde{\alpha}}\right)\tilde{J}'}. \quad (4.4)$$

Having, unlike relations (1.9), the power (rather than exponential) form of the time dependence, formulas (4.1) and (4.2) justify the name of the study to which they are applicable, i.e., the power-law stage of the slow relaxation. Moreover, the $t_r^{(u)}$ and $t_r^{(b)}$ values have the meaning of the characteristic times of the power-law relaxation stage. Note that it is this stage in which the amount of a surfactant markedly varies in micelles due to, first of all, variations in concentration c_M (at the final exponent-law stage of micellization, this variation is already negligible).

Let us compare the characteristic times $t_r^{(u)}$ and $t_r^{(b)}$ of the power-law relaxation with the characteristic time t_r of the exponent-law relaxation. Taking into account relation (1.17) at $\tilde{n}_s \gg |\eta_s|$ and relation (1.15), from equalities (4.3) and (4.4), we arrive at

$$t_r^{(u)} = \frac{\tilde{n}_s \left(1 + \frac{1}{\tilde{\alpha}\tilde{n}_s} + \frac{\Delta\tilde{n}_s^2}{2\tilde{n}_s^2} \right)}{\tilde{n}_c \left(1 + \frac{1 + |\tilde{\eta}_c|}{\tilde{n}_c} \right)} t_r, \quad (4.5)$$

$$t_r^{(b)} = \frac{\tilde{n}_s \left(1 + \frac{1}{\tilde{\alpha}\tilde{n}_s} + \frac{\Delta\tilde{n}_s^2}{2\tilde{n}_s^2} \right)}{(\tilde{n}_s - \tilde{n}_c) \left(1 + \frac{1}{\tilde{\alpha}(\tilde{n}_s - \tilde{n}_c)} + \frac{\Delta\tilde{n}_s^2}{2\tilde{n}_s(\tilde{n}_s - \tilde{n}_c)} \right)} t_r. \quad (4.6)$$

Formulas (4.5) and (4.6) testify that the characteristic times of the power-law stage are always longer than the characteristic time of the exponent-law stage. This is especially pronounced for time $t_r^{(u)}$. Experimental determination of times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ allows us to independently find aggregation numbers \tilde{n}_c , and \tilde{n}_s and the extrema \tilde{W}_c and \tilde{W}_s of the aggregation work.

Let us investigate the characteristic times of slow relaxation t_r , $t_r^{(u)}$, and $t_r^{(b)}$ as functions of the final concentration \tilde{c}_1 of surfactant monomers in a solution. Note that, according to the facts mentioned in the beginning of Section 2, relations (1.17), (4.3), and (4.4) for times t_r , $t_r^{(u)}$, and $t_r^{(b)}$, are valid, not only above, but also slightly below CMC₁ provided that the potential well and barrier are distanced from each other over the aggregation number axis and the concepts of the forward and back fluxes of molecular aggregates are valid. Usually, inequalities $|\tilde{\eta}_s|/\tilde{n}_s \ll 1$, $\Delta\tilde{n}_s^2/2\tilde{n}_s^2 \ll 1$, and $(1 + |\tilde{\eta}_c|)/\tilde{n}_c \ll 1$ are valid throughout the range of solution overall concentrations from concentrations slightly lower than CMC₁ to CMC₂. Then, for concentrations from slightly below CMC₁ to CMC₂, from relations (1.17), (4.5), and (4.6), we obtain the following simplified expressions:

$$t_r \approx \frac{\tilde{c}_1}{\tilde{n}_s \tilde{J}'} \frac{1 + \frac{\tilde{\alpha}\Delta\tilde{n}_s^2}{2\tilde{n}_s}}{\tilde{n}_s + \tilde{\alpha}^{-1}}, \quad (4.7)$$

$$t_r^{(u)} \approx \frac{\tilde{c}_1}{\tilde{n}_s \tilde{n}_c \tilde{J}'} \left(1 + \frac{\tilde{\alpha}\Delta\tilde{n}_s^2}{2\tilde{n}_s} \right), \quad (4.8)$$

$$t_r^{(b)} \approx \frac{\tilde{c}_1}{\tilde{n}_s \tilde{J}' (\tilde{n}_s - \tilde{n}_c + \tilde{\alpha}^{-1})} \left(1 + \frac{\tilde{\alpha}\Delta\tilde{n}_s^2}{2\tilde{n}_s} \right). \quad (4.9)$$

According to relations (1.16) and (1.2), the dependences of $\tilde{\alpha}$ and \tilde{J}' on \tilde{c}_1 manifest themselves mainly through exponents $\exp(-\tilde{W}_s)$ and $\exp(-\tilde{W}_c)$, respectively. Having obtained from (3.1) formulas $\partial\tilde{W}_s/\partial\tilde{c}_1 =$

$-(\tilde{n}_s - 1)/\tilde{c}_1$, and $\partial\tilde{W}_c/\partial\tilde{c}_1 = -(\tilde{n}_c - 1)/\tilde{c}_1$, we, from relations (1.16) and (1.2), arrive at

$$\partial\tilde{\alpha}/\partial\ln\tilde{c}_1 \approx \tilde{\alpha}\tilde{n}_s, \quad \partial\ln\tilde{J}'/\partial\ln\tilde{c}_1 \approx \tilde{n}_c. \quad (4.10)$$

Finding the logarithms of relations (4.7)–(4.9) and differentiating with respect to $\ln\tilde{c}_1$, taking into account the dependence on \tilde{c}_1 of only most sensitive to \tilde{c}_1 $\tilde{\alpha}$ and \tilde{J}' values and using relations (4.10), we obtain

$$\frac{d\ln t_r}{d\ln\tilde{c}_1} \approx -\tilde{n}_c + \frac{\tilde{\alpha}\tilde{n}_s\Delta\tilde{n}_s^2}{2\tilde{n}_s + \tilde{\alpha}\Delta\tilde{n}_s^2} + \frac{\tilde{n}_s}{1 + \tilde{\alpha}\tilde{n}_s}, \quad (4.11)$$

$$\frac{d\ln t_r^{(u)}}{d\ln\tilde{c}_1} \approx -\tilde{n}_c + \frac{\tilde{\alpha}\tilde{n}_s\Delta\tilde{n}_s^2}{2\tilde{n}_s + \tilde{\alpha}\Delta\tilde{n}_s^2}, \quad (4.12)$$

$$\frac{d\ln t_r^{(b)}}{d\ln\tilde{c}_1} \approx -\tilde{n}_c + \frac{\tilde{\alpha}\tilde{n}_s\Delta\tilde{n}_s^2}{2\tilde{n}_s + \tilde{\alpha}\Delta\tilde{n}_s^2} + \frac{\tilde{n}_s}{1 + \tilde{\alpha}(\tilde{n}_s - \tilde{n}_c)}. \quad (4.13)$$

Formulas (4.11)–(4.13) are valid for concentrations both slightly below and above CMC₁, however, only up to CMC₂. At overall concentrations well above CMC₁, when $\tilde{\alpha}\Delta\tilde{n}_s^2/\tilde{n}_s \gg 1$ and, consequently, $\tilde{\alpha} \gg 1$, in the right-hand parts of relations (4.11)–(4.13), the sum of the first and second terms tends to the difference $\tilde{n}_s - \tilde{n}_c$, while the latter terms may be ignored. Thus, markedly above CMC₁, the same simple power law follows from relations (4.11)–(4.13) for the dependences of times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ on the final equilibrium concentration \tilde{c}_1 of surfactant monomers:

$$t_r \propto t_r^{(u)} \propto t_r^{(b)} \propto \tilde{c}_1^{\tilde{n}_s - \tilde{n}_c} \quad (\tilde{\alpha}\Delta\tilde{n}_s^2/\tilde{n}_s \gg 1). \quad (4.14)$$

This law is valid up to CMC₂.

Since always $\tilde{n}_s > \tilde{n}_c$ (the minimum of the aggregation work is attained at larger aggregation numbers than the maximum), it follows from formula (4.14) that, as the final concentration of surfactant monomers diminishes in the region of overall concentrations well above CMC₁, times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ monotonically decrease. As is seen from relations (4.11)–(4.13), this decrease may be upset in the vicinity of and below CMC₁.

Equating the right-hand parts of relations (4.11)–(4.13) to zero, we derive equations for extrema in the dependences of times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ on surfactant overall concentration. Taking into account strong inequalities $\Delta\tilde{n}_s^2 \ll \tilde{n}_s\tilde{n}_c$ and $\Delta\tilde{n}_s^2 \ll \tilde{n}_c(\tilde{n}_s - \tilde{n}_c)$ (the latter inequality is valid, may be barely, at the lower boundary of surfactant overall concentrations accessible for the theory), we have

$$\alpha_r^2 \Delta\tilde{n}_s^2 (\tilde{n}_s - \tilde{n}_c) - 2\alpha_r \tilde{n}_s \tilde{n}_c + 2(\tilde{n}_s - \tilde{n}_c) = 0, \quad (4.15)$$

$$\alpha_{ru}\Delta\tilde{n}_s^2(\tilde{n}_s - \tilde{n}_c) - 2\tilde{n}_s\tilde{n}_c = 0, \quad (4.16)$$

$$\alpha_{rb}^2\Delta\tilde{n}_s^2(\tilde{n}_s - \tilde{n}_c) - 2\alpha_{rb}\tilde{n}_s\tilde{n}_c + 2\tilde{n}_s = 0, \quad (4.17)$$

where symbols α_r , α_{ru} and α_{rb} have been introduced to denote $\tilde{\alpha}$, values at which extrema t_r , $t_r^{(u)}$, and $t_r^{(b)}$, respectively, are attained. At surfactant overall concentrations in a narrow vicinity of CMC_1 , the final concentration \tilde{c}_1 of surfactant monomers in a solution may be with a sufficient accuracy believed to coincide with its value c_{1m} at CMC_1 . Then, the \tilde{n}_s , \tilde{n}_c , and $\Delta\tilde{n}_s$ values in relations (4.15)–(4.17) may be considered as equal to their values n_{sm} , n_{cm} , and Δn_{sm} at CMC_1 . This makes it possible to easily solve these relations with respect to α_r , α_{ru} , and α_{rb} . As follows from relations (4.15)–(4.17), in the vicinity of CMC_1 , each of equations (4.15) and (4.17) can have two real roots α_r^{\max} , α_r^{\min} , and α_{rb}^{\max} , α_{rb}^{\min} , while equation (4.16) has one root α_{ru}^{\min} (superscripts denote the types of the extrema of corresponding characteristic times, which are attained at aforementioned $\tilde{\alpha}$ values). As is seen from relations (4.15) and (4.17), real roots α_r^{\max} and α_r^{\min} exist provided that the condition $n_{sm}^2 n_{cm}^2 \geq 2\Delta n_{sm}^2 (n_{sm} - n_{cm})^2$, is satisfied, while roots α_{rb}^{\max} and α_{rb}^{\min} take place, when stronger condition $n_{sm} n_{cm}^2 \geq 2\Delta n_{sm}^2 (n_{sm} - n_{cm})$ is fulfilled. As follows from relation (4.16), the minimum of time $t_r^{(u)}$ at

$$\alpha_{ru}^{\min} = \frac{2}{\Delta n_{sm}^2 (1/n_{cm} - 1/n_{sm})} \quad (4.18)$$

occurs in the vicinity of CMC_1 without any conditions. When the strong inequality

$$\frac{2\Delta n_{sm}^2 (n_{sm} - n_{cm})}{n_{sm}^2 n_{cm}^2} \ll 1 \quad (4.19)$$

is satisfied, we, from relations (4.15) and (4.17), obtain the following approximate and simple expressions for α_r^{\max} , α_r^{\min} , α_{rb}^{\max} , and α_{rb}^{\min} :

$$\alpha_r^{\max} \approx \frac{1}{n_{cm}} - \frac{1}{n_{sm}}, \quad (4.20)$$

$$\alpha_r^{\min} \approx \frac{2}{\Delta n_{sm}^2 (1/n_{cm} - 1/n_{sm})}, \quad \alpha_r^{\max} < \alpha_r^{\min},$$

$$\alpha_{rb}^{\max} \approx \frac{1}{n_{cm}}, \quad \alpha_{rb}^{\min} \approx \frac{2}{\Delta n_{sm}^2 (1/n_{cm} - 1/n_{sm})}, \quad (4.21)$$

$$\alpha_{rb}^{\max} < \alpha_{rb}^{\min}.$$

From relations (4.18), (4.20) and (4.21), it is seen that the minima of characteristic times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ almost coincide with each other provided that inequality (4.19) is fulfilled. At reasonable estimates $n_{sm} = 10^2$, $n_{sm}/n_{cm} = 3$, and $\Delta n_{sm}/n_{sm} = 0.1$ [10], strong inequality (4.19) is satisfied and, from relations (4.18), (4.20), and (4.21), we obtain $\alpha_r^{\max} = 0.02$, $\alpha_{rb}^{\max} = 0.03$, and $\alpha_r^{\min} = \alpha_{rb}^{\min} = \alpha_{ru}^{\min} = 1$. As the $\tilde{\alpha}_m = 0.1$ value corresponds to CMC_1 , the obtained values $\alpha_r^{\max} = 0.02$ and $\alpha_{rb}^{\max} = 0.03$ are slightly below CMC_1 , that is, in the region where the above-considered analytical theory may be, although possibly barely, still applicable.

Note that the existence of a maximum and minimum in the dependence of time t_r on surfactant overall concentration in a solution in the vicinity of CMC_1 was predicted quite long ago in [3] on the basis of somewhat different ideas (as the reciprocal time of exponent-law relaxation was considered in [3], the minimum and maximum of t_r^{-1} were discussed there). However, neither relations for the positions of the maxima and minima of the characteristic times of slow relaxation nor expressions for the maximum and minimum values of these times were previously considered.

Simple relations (4.18), (4.20), and (4.21) enable us to reliably determine important parameters of the theory, such as n_{cm} , n_{sm} , and Δn_{sm} , from experimental data on the characteristic times of slow relaxation. In combination with relation (4.14), they also make it possible to verify the self-consistency of experimental data and thermodynamic models of micelles.

5. NUMERICAL SOLUTION OF EQUATIONS FOR SLOW RELAXATION IN TERMS OF DROPLET AND QUASI-DROPLET MODELS

Let us illustrate the general formulas derived in the above sections irrespective of a thermodynamic model of a micelle by the direct numerical calculation of slow relaxation via Eqs. (1.5) and (1.6) at W_c , W_s , n_c , n_s , Δn_c , Δn_s , and j_c^+ values specified as functions of c_1 in terms of the droplet [6, 8] and quasi-droplet [6, 9] models of the work of surfactant spherical aggregate formation. In the droplet model of surfactant molecular aggregates, the dependence of the aggregation work on the aggregation number n at $n \gg 1$ has the following form [6, 8]:

$$W_n^{(d)} = b_1 n^{4/3} - \left[\ln(c_1/c_{10}^{(d)}) + \frac{4}{3}(2b_1 b_3)^{1/2} \right] n + b_3 n^{2/3}. \quad (5.1)$$

Similarly, in the quasi-droplet model of surfactant molecular aggregates, at $n \gg 1$ [6, 9], we have

$$W_n^{(q)} = a_1 n^2 - a_3 n^{3/2} - \left[\ln(c_1/c_{10}^{(q)}) - \frac{9a_3^2}{32a_1} \right] n. \quad (5.2)$$

Hereafter, superscripts (d) and (q) denote the droplet and quasi-droplet models, respectively. Parameters b_1 , b_3 , $c_{10}^{(d)}$, a_1 , a_3 , and $c_{10}^{(q)}$ in the models are positive and independent of n and c_1 . The physical meaning of these parameters reported in [6, 8, 9], which enables us to determine them, though rather approximately, from rough quantitative data on micellization published in the literature by now, will be of no importance below. Note that parameter c_{10} in both models represents monomer concentrations corresponding to the potential barrier and well of work W_n .

As was shown in [10], parameters b_1 , b_3 , $c_{10}^{(d)}$, a_1 , a_3 , and $c_{10}^{(q)}$ may be expressed via the position and half-width of the potential well of aggregation work and the minimum of the latter as determined at CMC_1 . The following values of these parameters were accepted for both models as accessible for experimental determination:

$$\begin{aligned} n_{sm}^{(d)} = n_{sm}^{(q)} = 70, \quad \Delta n_{sm}^{(d)} = \Delta n_{sm}^{(q)} = 10, \\ W_{sm}^{(d)} = W_{sm}^{(q)} = 9.4 \end{aligned} \quad (5.3)$$

(as was mentioned above, additional subscript m denotes that the values were determined at CMC_1). At these $n_{sm}^{(d)}$, $n_{sm}^{(q)}$, $\Delta n_{sm}^{(d)}$, $\Delta n_{sm}^{(q)}$, $W_{sm}^{(d)}$, and $W_{sm}^{(q)}$, values, parameters of the models themselves turn out to be as follows:

$$b_1 = 1.6255, \quad b_3 = 29.256, \quad c_{10}^{(d)} = 4.2483 \times 10^{14} \text{ cm}^{-3}, \quad (5.4)$$

$$a_1 = 0.0457, \quad a_3 = 0.79656, \quad c_{10}^{(q)} = 3.7956 \times 10^{21} \text{ cm}^{-3}, \quad (5.5)$$

while maxima of aggregation work $W_n^{(d)}$ and $W_n^{(q)}$ at a surfactant monomer concentration corresponding to CMC_1 are $W_{cm}^{(d)} = 34.2$ ($n_{cm}^{(d)} = 10.4$) and $W_{cm}^{(q)} = 19.1$ ($n_{cm}^{(q)} = 22.1$). The dependence of aggregation work W_n on aggregation number n for the droplet and quasi-droplet models at the aforementioned values (5.4) and (5.5) of the parameters and at $c_1/c_{10} = c_{1m}/c_{10}$ is presented in Fig. 1.

It is known [8] that the absorption intensity $j_c^{+(d)}$ of a critical molecular aggregate in the droplet model linearly depends on monomer concentration c_1 and aggregate surface area at $n = n_c$ as $j_c^{+(d)} = \tilde{j}_c^{+(d)} \frac{c_1 n_c^{2/3}}{\tilde{c}_1 \tilde{n}_c^{2/3}}$. In the quasi-droplet model, $j_c^{+(q)}$ is independent of aggregate

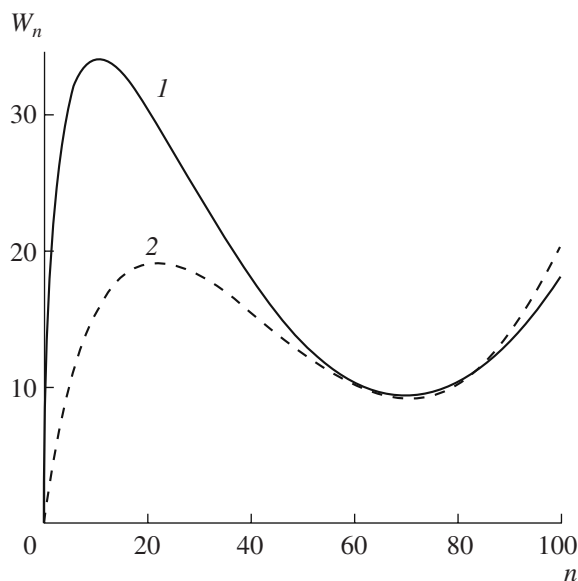


Fig. 1. Aggregation work W_n as a function of aggregation number n for the (1) droplet and (2) quasi-droplet models at CMC_1 .

surface area [9]; $j_c^{+(q)} = \tilde{j}_c^{+(q)} \frac{c_1}{\tilde{c}_1}$. When performing calculations through formula (1.6) in terms of the droplet and quasi-droplet models, it is reasonable to express time t in $1/\tilde{j}_c^{+(d)}$ and $1/\tilde{j}_c^{+(q)}$ units, respectively. The $\tilde{j}_c^{+(d)}$ and $\tilde{j}_c^{+(q)}$ values per se are difficult to theoretically calculate; however, as follows from relations (1.10) and (1.2), reciprocal values $1/\tilde{j}_c^{+(d)}$ and $1/\tilde{j}_c^{+(q)}$ are introduced into the expression for characteristic time t_r as coefficients. Therefore, it is convenient to further express different time moments in the course of relaxation in t_r units.

Figures 2 and 3 illustrate the time dependences of surfactant monomer concentration in a micellar solution for the droplet and quasi-droplet models at model parameters (5.4) and (5.5), initial conditions $\beta_u = 17.9$ ($|\delta c_1^{(u)}(0)|/\tilde{c}_1 = 0.25$) and $\beta_b = 7.16$ ($|\delta c_1^{(b)}(0)|/\tilde{c}_1 = 0.1$), and an overall concentration $c = 2\text{CMC}_1$. These initial conditions were selected in order to diminish their influence in accordance with relations (3.11) and (3.13). The effect of the initial conditions will be considered in more detail when discussing Fig. 7.

Heavy solid lines 1 and 1' in Figs. 2 and 3 refer to dependences $c_1^{(u)}(t/t_r)/\tilde{c}_1$ and $c_1^{(b)}(t/t_r)/\tilde{c}_1$, calculated by relations (1.5), (1.6), (1.10) and (1.2). Thin solid lines 2 and 2' show exponential approximations (1.9) of monomer concentration at $\delta c_1^{(u)}(0) > 0$ and $\delta c_1^{(b)}(0) < 0$, respectively, in which pre-exponential factors and the characteristic time t_r of exponential decay were deter-

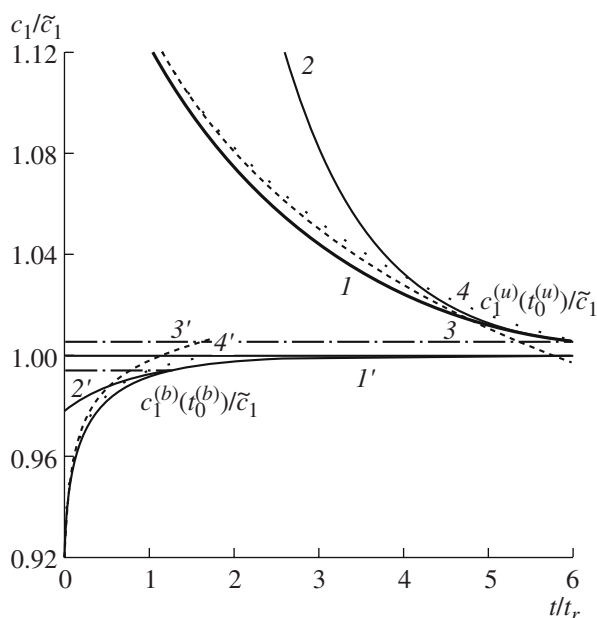


Fig. 2. Dependences of monomer concentration c_1/\tilde{c}_1 on time t/t_r for the droplet model. See text for explanations.

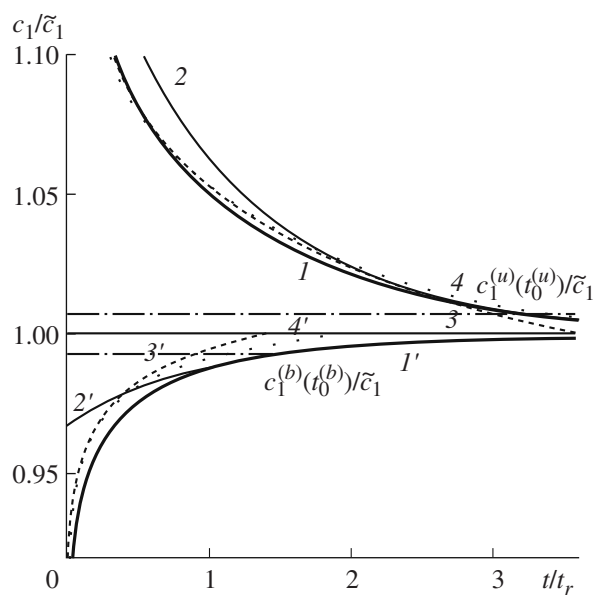


Fig. 3. Dependences of monomer concentration c_1/\tilde{c}_1 on time t/t_r for the quasi-droplet model. See text for explanations.

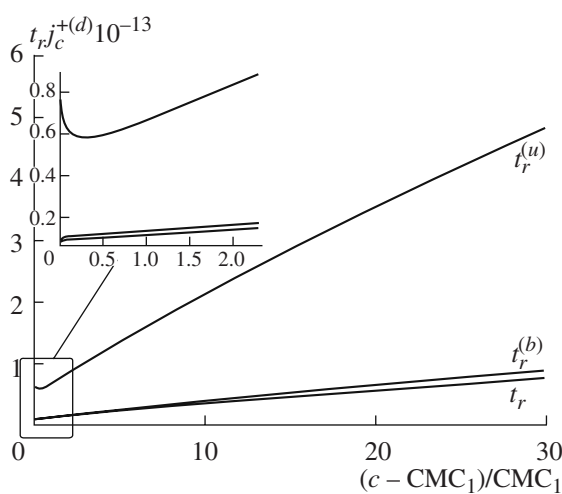


Fig. 4. Dependences of characteristic times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ on overall concentration $(c - \text{CMC}_1)/\text{CMC}_1$ for the droplet model.

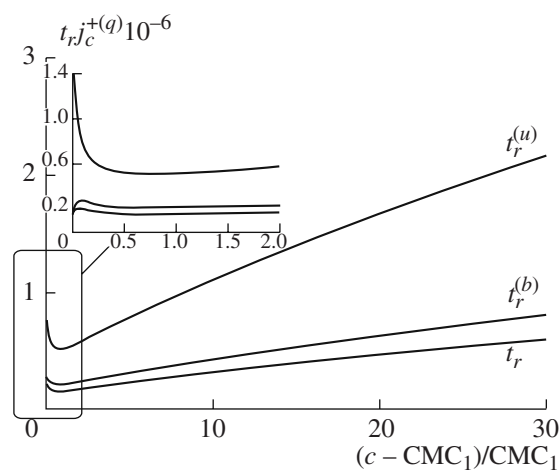


Fig. 5. Dependences of characteristic times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ on overall concentration $(c - \text{CMC}_1)/\text{CMC}_1$ for the quasi-droplet model.

mined from the final parts of curves I and I' at $c_1^{(u)}(t/t_r)/\tilde{c}_1 \rightarrow 1$ and $c_1^{(b)}(t/t_r)/\tilde{c}_1 \rightarrow 1$. Dashed lines 3 and $3'$ demonstrate the basic power-law approximations of monomer concentration as calculated through relations (4.1) and (4.2). Dotted lines 4 and $4'$ illustrate curves plotted employing more correct relations (3.8) and (3.9). The horizontal thin solid line denotes the final monomer concentration. Two thin dot-and-dash lines denote the $c_1^{(u)}(t_0^{(u)})/\tilde{c}_1$ and $c_1^{(b)}(t_0^{(b)})/\tilde{c}_1$,

values that are attained according to conditions (2.7) by the onset of the exponent-law relaxation stage.

As is seen from Figs. 2 and 3, even basic approximation relations (4.1) and (4.2) adequately approximate calculated curves I and I' for the droplet and quasi-droplet models. The comparison of curves 4 and $4'$ with curves I and I' indicates that times $t_0^{(u)}$ and $t_0^{(b)}$, determined from these curves are slightly shifted, with the shift being larger for $t_0^{(b)}$. This is explained by the fact

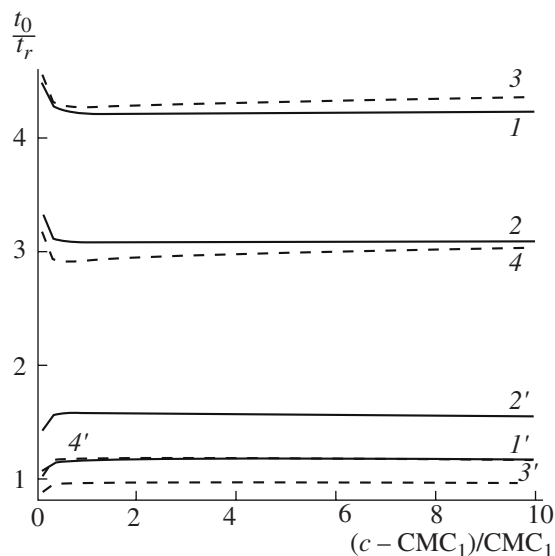


Fig. 6. Dependences of $t_0^{(u)}/t_r$ and $t_0^{(b)}/t_r$ ratios at the power-law stage of relaxation on overall concentration $(c - \text{CMC}_1)/\text{CMC}_1$ for the droplet and quasi-droplet models. See text for explanations.

that, when deriving formulas (3.8) and (3.9), we used accurate initial values of $\delta c_1^{(u)}(0)$ and $\delta c_1^{(b)}(0)$. However, it is the values $\delta c_1 = \delta c_1^{(u)}(0)$ and $\delta c_1 = \delta c_1^{(b)}(0)$ at which the errors in relations (3.5)–(3.7) are largest. Note that, upon the relaxation from above, in the droplet model, each subsequent approximation describes the curvature of curve *I* more adequately; however, the deviation from this curve also increases. This is associated with the fact that, in the droplet model, the first of formulas (3.1) and, accordingly, relations (3.7) and (3.8) exhibit insufficiently adequate approximation because \tilde{n}_c is equal to ten at the accepted parameter values.

Now, let us consider the dependences of characteristic times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ on the relative overall concentration $(c - \text{CMC}_1)/\text{CMC}_1$ of a solution in terms of the droplet and quasi-droplet model. These dependences plotted using formulas (1.17), (4.3), and (4.4) with allowance for relations (1.2) and (1.14)–(1.16) may be experimentally determined from different parts of relaxation curves measured for a micellar solution in the course of a gradual variation in its concentration. Thus, important parameters \tilde{W}_c , $\Delta\tilde{n}_c$, and \tilde{j}_c^+ , employed in the theory can be determined with a high accuracy as functions of solution overall concentration. Curves in Figs. 4 and 5 comprise both maxima and minima (they are more pronounced in Fig. 5), which were predicted by the general analysis of expressions for times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ at the end of Section 4. In view of

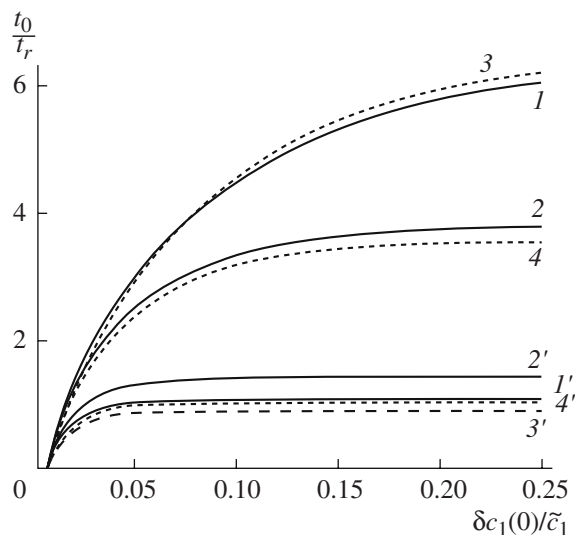


Fig. 7. Dependences of $t_0^{(u)}/t_r$ and $t_0^{(b)}/t_r$ ratios at the power-law stage of relaxation on the initial $|\delta c_1(0)|/\tilde{c}_1$ value of monomer concentration for the droplet and quasi-droplet models. See text for explanations.

approximate equality $\tilde{\alpha} \approx (c - \text{CMC}_1)/\text{CMC}_1$, the positions of the maxima and minima in the relative overall concentration axis may be directly superposed with α_{ru}^{\min} , α_r^{\max} , α_r^{\min} , α_{rb}^{\max} , and α_{rb}^{\min} using relations (4.18), (4.20), and (4.21). There is an agreement for the droplet and quasi-droplet models of micelles with respect to α_{ru}^{\min} , and this might be expected, because formula (4.18) did not required additional constraints with respect to model parameters. The absence and the presence of maxima and minima in the curves for t_r and $t_r^{(b)}$ plotted in terms of the droplet and quasi-droplet models, respectively, reflect the fact that, in the quasi-droplet model, the n_{cm} value appears to be approximately twofold larger than that in the droplet model. Therefore, in the case of the droplet model, the conditions for the reality of α_r^{\max} , α_r^{\min} , α_{rb}^{\max} , and α_{rb}^{\min} , values are not fulfilled at the selected parameters, and we see inflection points rather than extrema in the curves for t_r and $t_r^{(b)}$. In the case of the quasi-droplet model, inequality (4.19) is satisfied; therefore, the maxima and minima are pronounced in the curves for t_r and $t_r^{(b)}$. The behavior of times t_r , $t_r^{(u)}$, and $t_r^{(b)}$ (Figs. 4, 5) almost agrees with the experimental data on the slow relaxation time reported in [3], with the quasi-droplet model demonstrating better agreement.

In Fig. 6, heavy solid lines show the dependences of $t_0^{(u)}/t_r$ (curves *I* and *2* refer to the droplet and quasi-

droplet models, respectively) and $t_0^{(b)}/t_r$ (curves 1' and 2' refer to the droplet and quasi-droplet models, respectively) on the solution relative overall concentration $(c - \text{CMC}_1)/\text{CMC}_1$, which were calculated by relations (1.5), (1.6), (1.8), (1.10), and (1.2); conditions (2.7); and models (5.1) and (5.2) with parameters (5.4) and (5.5). Dashed lines in Fig. 6 illustrate the dependences of $t_0^{(u)}/t_r$ plotted using relations (3.8) (curve 3 and 4 refer to the droplet and quasi-droplet models, respectively) and (3.9) (curves 3' and 4' refer to the droplet and quasi-droplet models, respectively) at $t = t_0^{(u)}$ and $t = t_0^{(b)}$. Initial conditions were specified in the form $|\delta c_1^{(u)}(0)|/\tilde{c}_1 = 0.25$ and $|\delta c_1^{(b)}(0)|/\tilde{c}_1 = 0.2$ in order to maximally weaken their influence. As is seen from Fig. 6, for both micelle models, relation (3.8) adequately predicts the behavior of $t_0^{(u)}/t_r$. Formula (3.9) is somewhat less adequate, seemingly because the power-law relaxation at $\delta c_1^{(b)}(t) < 0$ proceeds noticeably faster than at $\delta c_1^{(u)}(t) > 0$. The fact that $t_0^{(b)}/t_r$ initially rises at overall concentrations close to CMC_1 (in contrast to $t_0^{(u)}/t_r$ value, which decreases at these concentrations) is explained by a marked reduction in micelle concentration at $\delta c_1^{(b)}(t) < 0$ in the vicinity of CMC_1 .

Let us return to the quantitative description of the effect of an initial disturbance. In Fig. 7, solid heavy lines demonstrate the dependences of $t_0^{(u)}/t_r$ (curves 1 and 2 refer to the droplet and quasi-droplet models, respectively) and $t_0^{(b)}/t_r$ (curves 1' and 2' refer to the droplet and quasi-droplet models, respectively) on initial condition $|\delta c_1(0)|/\tilde{c}_1$, which were calculated employing relations (1.5), (1.6), (1.10), and (1.2); conditions (2.7), and models (5.1) and (5.2) with parameters (5.4) and (5.5) at $c = 2\text{CMC}_1$. Dashed lines in Fig. 7 illustrate dependences of $t_0^{(u)}/t_r$ on the initial conditions plotted using relations (3.8) (curves 3 and 4 refer to the

droplet and quasi-droplet models, respectively) and (3.9) (curves 3' and 4' refer to the droplet and quasi-droplet models, respectively) at $t = t_0^{(u)}$ and $t = t_0^{(b)}$. Similar to Fig. 6, it is seen that relation (3.8) is somewhat more adequate for predicting the behavior of $t_0^{(u)}/t_r$ than relation (3.9). At the same time, Fig. 7 suggests that, at $\delta c_1^{(b)}(t) < 0$, we may ignore the initial condition in relation (3.9) already beginning with small deviations at $\delta c_1^{(b)}(0)$. At $\delta c_1^{(u)}(t) > 0$, we cannot do this in formula (3.8) until the almost maximum possible deviation of $|\delta c_1^{(u)}(0)|/\tilde{c}_1$ is reached.

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