

Kinetic Description of the Relaxation of Surfactant Solutions Containing Spherical and Cylindrical Micelles

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Abstract—Monotonically decaying relaxation of a materially isolated nonionic surfactant solution containing spherical and cylindrical micelles at the arbitrary heights of the first and second potential barriers of aggregation work is kinetically substantiated. The realistic situation, where the height of second potential barrier is at least slightly higher (by the relative value) than that of the first barrier, is studied. Analytical expressions for two relaxation times of materially isolated surfactant solution are calculated. The shortest of these times corresponds to the relatively fast establishment of the mutual quasi-equilibrium of spherical and cylindrical micelles, beginning with relatively small cylindrical micelles. The longest of relaxation times corresponds to the relatively slow establishment of the total equilibrium of surfactant solution. It is shown that this time (the only significant for the establishment of the final equilibrium of materially isolated surfactant solution) is determined by the height of the first potential barrier of aggregation work and is by no means dependent on the height of the second potential barrier about which not much is known. Variations (with time) of the total concentrations of spherical and cylindrical micelles, surfactant monomer concentration, and the total amount of the substance in cylindrical micelles in the approach of solution to the final equilibrium state are described analytically. It is shown that theoretically admitted small relative deviations of the concentrations of spherical and cylindrical micelles from their values in the final equilibrium state are fully measurable in experiment. Calculated relaxation time of surfactant solution can also be measured experimentally together with the aforementioned values. It is elucidated that this time is approximately proportional to the overall solution concentration, if the second critical micellization concentration (CMC2) by the order of magnitude exceeds the first critical micellization concentration (CMC1), and is virtually independent of the overall solution concentration, if the CMC2 exceeds the CMC1 by two orders of magnitude. The characteristic time of the establishment of quasi-equilibrium distribution of cylindrical micelles throughout the region of their sizes is estimated, thus allowing us to establish the lower limit of the height of the first barrier of aggregation work.

INTRODUCTION

Earlier [1], we developed the theory of nonionic surfactant solutions containing spherical and cylindrical micelles above the second critical micellization concentration (CMC2) in the experimentally significant region of overall surfactant concentrations where the overwhelming part of the total amount of surfactant in solution was accumulated in cylindrical micelles. Although the equilibrium states of surfactant solution were mainly considered in [1], we performed the linearization of the balance equation of the surfactant amount in the vicinity of the final equilibrium state of materially isolated solution where the state of solution is not at equilibrium. Further, in [2], we derived the closed system of two linearized relaxation equations determining in the materially isolated surfactant solution the variations (with time) of the total concentrations of spherical and cylindrical micelles in the vicinity of the final equilibrium state of solution in a complex situation, where the first and second potential barriers of aggregation work are present. The kinetic description of the relaxation of nonionic surfactant solution containing spherical and cylindrical micelles

on the basis of these equations is the main aim of this communication. Data on such a description are not available in the published literature.

In this paper, we present the kinetic substantiation of the monotonically decaying character of the relaxation of the materially isolated nonionic surfactant solution containing spherical and cylindrical micelles at the arbitrary heights of the first and second potential barriers of aggregation work at the values of overall solution concentration above the CMC2 but below the values of overall concentration at which crosslinked micellar structures begin to be formed [3] or the transition to liquid-crystal state takes place [4]. We will study the realistic situation [5–7] when the height of second potential barrier is lower than that of the first potential barrier. In fact, for this study it is sufficient for the height of the second potential barrier to be at least relatively slightly lower than the height of the first potential barrier. We will derive analytical expressions for two relaxation times of the materially isolated surfactant solution. The shortest of these times corresponds to a relatively fast establishment (beginning with comparatively small cylindrical micelles) of the mutual quasi-equilibrium of

spherical and cylindrical micelles at the absence of their equilibrium with subcritical molecular aggregates located on the aggregation number axis to the left of the first potential barrier of aggregation work. The longest of these times corresponds to a relatively slow establishment of the total equilibrium of surfactant solution. It will be demonstrated that this time (the only significant time for the establishment of the final equilibrium of the materially isolated surfactant solution) is determined by the height of the first potential barrier of aggregation work and is by no means dependent on a scarcely known height of the second potential barrier. We will analytically describe the variations (with time) of the total concentrations of spherical and cylindrical micelles, surfactant monomer concentration, and total amount of substance in cylindrical micelles when the materially isolated surfactant solution approaches its final equilibrium state. It will be shown that, at the small relative deviations of the total concentrations of spherical and cylindrical micelles from their values in the final equilibrium state admitted by the proposed relaxation theory, these deviations can actually be measured in the experiment. The relaxation time of surfactant solution found in this communication can also be measured experimentally. It will be disclosed that this time is approximately proportional to the overall solution concentration, if the CMC2 exceeds (by the order of magnitude) the first critical micellization concentration (CMC1) equal to the overall solution concentration at which the amount of surfactant in spherical micelles becomes already noticeable and is actually independent of the overall solution concentration, if the CMC2 exceeds the CMC1 by two orders of magnitude. Characteristic time needed to establish the quasi-equilibrium distribution of cylindrical micelles throughout the region of their sizes will be estimated. Based on this time, we determine the lower limit of the height of the first potential barrier of aggregation work.

1. MONOTONICALLY DECAYING CHARACTER OF THE RELAXATION OF SURFACTANT SOLUTION AT THE ARBITRARY HEIGHTS OF THE FIRST AND SECOND BARRIERS OF AGGREGATION WORK

We will use the same system of notations as in [1, 2]. The aggregation number (the number of surfactant molecules in an aggregate) is denoted by n . The concentration of molecular aggregates (the number of aggregates per solution unit volume) with aggregation number n is denoted by c_n . At $n = 1$, aggregates represent surfactant monomers. Correspondingly, c_1 gives the monomer concentration. Overall surfactant concentration (the total number of surfactant molecules per solution unit volume) is denoted by c ; the total concentration of spherical and cylindrical micelles, by c_M and g , respectively. The formation work of molecular aggregate with aggregation number n is expressed in thermal units kT (k is Boltzmann's constant and T is the absolute temper-

ature) and denoted by W_n . Following to [1, 2], we obtain

$$\begin{aligned} W_c^{(1)} &\equiv W_n|_{n=n_c^{(1)}}, & W_s^{(1)} &\equiv W_n|_{n=n_s^{(1)}}, \\ W_c^{(2)} &\equiv W_n|_{n=n_c^{(2)}}, & W^0 &\equiv W_n|_{n=n_0}. \end{aligned} \quad (1.1)$$

The value of $W_c^{(1)}$ of aggregation work in point $n = n_c^{(1)}$ of its first maximum on the aggregation number axis determines the height of activation barrier for the formation of spherical micelles. Therefore, aggregates in the $1 \leq n < n_c^{(1)} - \Delta n_c^{(1)}$ region on the aggregation number axis, where $\Delta n_c^{(1)}$ is the half-width of the first potential barrier of aggregation work, are considered as subcritical aggregates. The value of aggregation work $W_s^{(1)}$ in point $n = n_s^{(1)}$ of its first minimum characterizes the depth of potential well where spherical micelles are accumulated. The value of aggregation work $W_c^{(2)}$ in point $n = n_c^{(2)}$ of its second maximum determines the height of activation barrier for the formation of cylindrical micelles. The value of aggregation work W^0 is taken in point $n = n_0$ corresponding to the left boundary of the region of aggregation numbers where the dependence of W_n on n is already linear. The right-hand boundary of this region is set by the $n = n_1$ point; as one approaches this point, the equilibrium concentration of cylindrical micelles (proportional to $\exp(-W_n)$) rapidly decays. Thus, the region of aggregation numbers $n > n_1$ is no longer of interest. The dependence of work W_n on aggregation number n at the simultaneous existence of spherical and cylindrical micelles and at the overall surfactant concentration in solution above the CMC2 that generalizes known experimental and theoretical data [5–7] was demonstrated in the figure reported in [1].

Evidently, $n_c^{(1)} < n_s^{(1)}$ and $n_s^{(1)} < n_c^{(2)} < n_0$. As in [1, 2], we assume for values $n_s^{(1)}$, n_0 , and n_1 the following estimates:

$$n_s^{(1)} \sim 10^2, \quad n_0 \sim 10^3, \quad n_1 \sim 10^6. \quad (1.2)$$

that are typical of many surfactants. Note that, according to [1, 2], $W_s^{(1)} \sim 4$, $W^0 \sim 14$ and, according to [8], $W_c^{(1)} \sim (16-18)$ are valid.

We denote the half-width of the first potential well of aggregation work and the half-width of the second potential barrier of aggregation work on the n axis by $\Delta n_s^{(1)}$ and $\Delta n_c^{(2)}$, respectively. We assume that $\Delta n_s^{(1)}$, $\Delta n_c^{(1)}$, and $\Delta n_c^{(2)}$ satisfy constraints (1.3)–(1.5) in [2]. These constraints imply that the potential well and

potential barriers of aggregation work are noticeably manifested on the dependence of work W_n on n .

The state of total aggregation equilibrium in a materially isolated micellar surfactant solution is attained due to relaxation. The parameter values in this final equilibrium state we mark by the tilde over symbols. Resultant formulas derived in [2] include direct fluxes $\tilde{J}^{(1)}$ and $\tilde{J}^{(2)}$ of molecular aggregates over the first and second potential barriers of aggregation work referred only to the final equilibrium state of a solution. Denoting (for brevity) these fluxes by J_1 and J_2 , we have (provided that aforementioned constraints (1.3)–(1.5) in [2] are satisfied) the following analytical expressions:

$$J_1 = \tilde{c}_1 \tilde{j}_c^{+(1)} \exp(-\tilde{W}_c^{(1)}) / \pi^{1/2} \Delta \tilde{n}_c^{(1)}, \quad (1.3)$$

$$J_1 = \tilde{c}_M \tilde{j}_c^{+(1)} \exp[-(\tilde{W}_c^{(1)} - \tilde{W}_s^{(1)})] / \pi \Delta \tilde{n}_c^{(1)} \Delta \tilde{n}_s^{(1)}, \quad (1.4)$$

$$J_2 = \tilde{c}_M \tilde{j}_c^{+(2)} \exp[-(\tilde{W}_c^{(2)} - \tilde{W}_s^{(1)})] / \pi \Delta \tilde{n}_c^{(2)} \Delta \tilde{n}_s^{(1)} \quad (1.5)$$

([2], expressions (1.17)–(1.19)). Here, $\tilde{j}_c^{+(1)}$ is the number of surfactant monomers absorbed ($\tilde{j}_c^{+(1)} > 0$) per unit time from solution by the spherical molecular aggregate composed of $\tilde{n}_c^{(1)}$ molecules; $\tilde{j}_c^{+(2)}$ is the number of surfactant monomers absorbed ($\tilde{j}_c^{+(2)} > 0$) per unit time from solution by the aspherical molecular aggregate composed of $\tilde{n}_c^{(2)}$ molecules. The equivalency of expressions (1.3) and (1.4) is seen from relation $\tilde{c}_M = \pi^{1/2} \tilde{c}_1 \Delta \tilde{n}_s^{(1)} \exp(-\tilde{W}_s^{(1)})$ derived in [2].

As is [1, 2], we are interested in the experimentally important range of the values of overall surfactant concentration \tilde{c} where the overwhelming contribution to the total amount of surfactant in solution is made by cylindrical micelles. As is [2], we assume the following estimates:

$$\tilde{c}/\tilde{c}_1 \sim 10^4, \quad (1.6)$$

$$\tilde{c}_M/\tilde{c}_1 \sim (0.1-1). \quad (1.7)$$

Estimate (1.6) agrees with the existence of a certain upper boundary of the range of overall concentrations of micellar states admitted at a given temperature by the phase diagram of a specific nonionic surfactant solution. Estimate (1.7) corresponds to $\tilde{c}_M/\tilde{c}_1 \sim 0.1$, if the CMC2 exceeds the CMC1 by the order of magnitude, and to $\tilde{c}_M/\tilde{c}_1 \sim 1$, if the CMC2 exceeds the CMC1 by two orders of magnitude.

Denoting the values of deviations from their values in final equilibrium state to the left of these values by symbol δ , we arrive at (provided that Eqs. (1.2), (1.6), and (1.7) are fulfilled) the closed set of two linearized relaxation equations determining the evolution (with

time t) of deviations δc_M and δg of the total concentrations of spherical and cylindrical micelles in a materially isolated solution

$$d(\delta c_M)/dt = -\alpha_{11} \delta c_M - \alpha_{12} \delta g, \quad (1.8)$$

$$d(\delta g)/dt = -\alpha_{21} \delta c_M - \alpha_{22} \delta g, \quad (1.9)$$

where

$$\alpha_{11} = (J_1 + J_2)/\tilde{c}_M, \quad \alpha_{12} = J_1 \frac{\tilde{n}_s^{(1)}}{\tilde{c}} - J_2 \frac{1}{2 \ln 10} \frac{n_1}{\tilde{c}}, \quad (1.10)$$

$$\alpha_{21} = -J_2/\tilde{c}_M, \quad \alpha_{22} = J_2 \frac{1}{2 \ln 10} \frac{n_1}{\tilde{c}}$$

(Eqs. (2.10) and (2.11) and expressions (3.11) and (3.15)–(3.17) in [2]). The condition of linearization of the system of equations (1.8) and (1.9) is the inequality

$$|\delta c_1/\tilde{c}_1| \ll (8/3n_1) \ln 10 \quad (1.11)$$

(condition (2.9) in [2]).

Let us introduce parameters

$$u \equiv \tilde{n}_s^{(1)} \frac{\tilde{c}_1}{\tilde{c}}, \quad v \equiv \frac{n_1}{2 \ln 10} \frac{\tilde{c}_1}{\tilde{c}}, \quad w \equiv \frac{\tilde{c}_1}{\tilde{c}_M}, \quad (1.12)$$

related to the experimentally measurable characteristics of equilibrium surfactant solution. In view of Eqs. (1.2), (1.6), and (1.7), these parameters satisfy the estimates

$$u \sim 10^{-2}, \quad v \sim 10, \quad w \sim (1-10). \quad (1.13)$$

Definitions (1.12) make it possible to more shortly express relation (1.10) as

$$\alpha_{11} = \frac{w}{\tilde{c}_1} (J_1 + J_2), \quad \alpha_{12} = \frac{1}{\tilde{c}_1} (uJ_1 - vJ_2), \quad (1.14)$$

$$\alpha_{21} = -\frac{w}{\tilde{c}_1} J_2, \quad \alpha_{22} = \frac{v}{\tilde{c}_1} J_2.$$

Common solution to the system of two equations (1.8) and (1.9) is given by equalities

$$\delta c_M = A_1 e^{-\theta_1 t} + A_2 e^{-\theta_2 t}, \quad (1.15)$$

$$\delta g = B_1 e^{-\theta_1 t} + B_2 e^{-\theta_2 t}. \quad (1.16)$$

Here, A_1 and A_2 are two arbitrary constants of integration. Constants B_1 and B_2 are interrelated with A_1 and A_2 by equalities

$$\frac{B_1}{A_1} = \frac{1}{\alpha_{12}} (\theta_1 - \alpha_{11}), \quad \frac{B_2}{A_2} = \frac{1}{\alpha_{12}} (\theta_2 - \alpha_{11}). \quad (1.17)$$

Further, values θ_1 and θ_2 are defined by equalities which can be written as a single formula

$$\theta_{1,2} = \frac{\alpha_{11} + \alpha_{22}}{2} \pm \left[\left(\frac{\alpha_{11} - \alpha_{22}}{2} \right)^2 + \alpha_{12} \alpha_{21} \right]^{1/2} \quad (1.18)$$

(the plus sign before the square bracket corresponds to value θ_1 ; the minus sign, to θ_2). It is evident that constants of integration A_1 and A_2 are interrelated with initial deviations $\delta c_M|_{t=0}$ and $\delta g|_{t=0}$.

Let us demonstrate that, whatever positive values J_1 and J_2 may be; i.e., whatever heights $\tilde{W}_c^{(1)}$ and $\tilde{W}_c^{(2)}$ of the first and second potential barriers of aggregation may be according to Eqs. (1.3)–(1.5), formulas (1.14) and (1.18) ensure the real and positive values θ_1 and θ_2 . Let us, using Eq. (1.14), rewrite Eq. (1.18) in the following form:

$$\theta_{1,2} = \frac{1}{2\tilde{c}_1} [wJ_1 + (w + v)J_2 \pm D^{1/2}], \quad (1.19)$$

where

$$D \equiv w^2 J_1^2 + 2w(w - v - 2u)J_1 J_2 + (w + v)^2 J_2^2. \quad (1.20)$$

Let us first prove the inequality

$$D > 0, \quad (1.21)$$

i.e., that θ_1 and θ_2 values, according to Eq. (1.19), are real quantities. Using Eq. (1.20), we make certain that, at any real J_1 and J_2 values (that do not vanish simultaneously), inequality (1.21) is reduced to condition

$$(w + v)^2 - (w - v - 2u)^2 > 0, \quad (1.22)$$

which (as can be easily assured) is strongly equivalent to condition

$$(v + u)(w - u) > 0. \quad (1.23)$$

It is evident from inequality (1.23) that proof of inequality (1.21) is valid at

$$w > u, \quad (1.24)$$

in view of estimates (1.13), this inequality is satisfied with large excess.

Let us now demonstrate that

$$\theta_1 > 0, \quad \theta_2 > 0. \quad (1.25)$$

Evidently, it is sufficient to prove only inequality $\theta_2 > 0$. As is seen from Eq. (1.19), this inequality requires

$$[wJ_1 + (w + v)J_2]^2 > D. \quad (1.26)$$

Using expression (1.20), we obtain the identity

$$[wJ_1 + (w + v)J_2]^2 - D \equiv 4w(v + u)J_1 J_2, \quad (1.27)$$

and see that inequality (1.26) is valid irrespective of positive J_1 and J_2 values. According to Eq. (1.19), inequality $\theta_2 > 0$ (what is more, inequality $\theta_1 > 0$) is also fulfilled.

Inequalities (1.25), together with solutions (1.15) and (1.16), give the kinetic substantiation of monotonically (with no oscillations) decaying approach of materially isolated solution containing spherical and cylindrical micelles to the state of final equilibrium. Although the fact of this approach is natural, its kinetic

substantiation acts as an important argument in favor of the validity of the proposed theory.

Inequalities (1.25) demonstrate that θ_1 and θ_2 values in solutions (1.15) and (1.16) have the meaning of relaxation rates. In this case, values t_{r1} and t_{r2} that are determined according to

$$t_{r1} \equiv 1/\theta_1, \quad t_{r2} \equiv 1/\theta_2 \quad (1.28)$$

will have the meaning of relaxation times.

Multiplying θ_1 and θ_2 values given by formula (1.19) and accounting for identity (1.27), we arrive at the inequality

$$\theta_1 \theta_2 = \frac{1}{\tilde{c}_1^2} w(v + u)J_1 J_2. \quad (1.29)$$

2. KINETICS OF THE RELAXATION OF A MATERIALLY ISOLATED SURFACTANT SOLUTION AT THE HEIGHT OF THE SECOND POTENTIAL BARRIER OF AGGREGATION WORK BELOW THE HEIGHT OF ITS FIRST POTENTIAL BARRIER

The procedure for finding the height of the first potential barrier of aggregation work in the droplet and quasi-droplet models of spherical molecular surfactant aggregate [9, 10] from the experimental data on $n_s^{(1)}$ and $\Delta n_s^{(1)}$ was proposed in [8]. Using this procedure, at $n_s^{(1)} \approx 10^2$ (consistent with Eq. (1.2)) and $\Delta n_s^{(1)} \approx 10$, in [8] we obtain

$$W_c^{(1)} \sim (16-18). \quad (2.1)$$

Reliable data on the height of the second potential barrier of aggregation work are not available at present. It is only known [7] that this height is slightly lower than that of the first potential barrier. Then it is acceptable, for example

$$\tilde{W}_c^{(1)} - \tilde{W}_c^{(2)} > 3. \quad (2.2)$$

As is seen from (2.1), to fulfill constraint (2.2), it is sufficient just to have the relative height of the second potential barrier of aggregation work at least slightly lower than that of the first potential barrier of aggregation work.

From Eqs. (1.4) and (1.5), we have

$$J_2/J_1 = (\tilde{j}_c^{+(2)}/\tilde{j}_c^{+(1)}) (\Delta \tilde{n}_c^{(1)}/\Delta \tilde{n}_c^{(2)}) \times \exp(\tilde{W}_c^{(1)} - \tilde{W}_c^{(2)}). \quad (2.3)$$

It is seen that, with the fulfillment of expression (2.2), the third multiplier in the right-hand side of Eq. (2.3) is already large: its value exceeds 20. Then, the first multiplier in the right-hand side of Eq. (2.3) is proportional to the ratio between surface areas of the aggregates composed of $\tilde{n}_c^{(2)}$ and $\tilde{n}_c^{(1)}$ molecules; i.e., by the order

of magnitude, this ratio is equal to $(\tilde{n}_c^{(2)}/\tilde{n}_c^{(1)})^{2/3}$. Assuming, in accordance with [8], $\tilde{n}_c^{(1)} \sim 30$ and $\tilde{n}_c^{(2)} \sim 3 \times 10^2$ (according to estimates (1.2) and evident inequality $n_s^{(1)} < n_c^{(2)} < n_0$), we can see that the first multiplier in the right-hand side of Eq. (2.3) is also large: its value exceeds 4.6 (it will be even still slightly larger with the account of the deviation of the shape of aggregate composed of $\tilde{n}_c^{(2)}$ from the spherical form). Assuming with excess that the second multiplier in the right-hand side of Eq. (2.3) is at least not as small as unity (provided that constraints (1.3)–(1.5) in [2] are fulfilled), we conclude from Eq. (2.3) that, with the fulfillment of constraint (2.2), we have

$$J_2/J_1 \gg 1. \quad (2.4)$$

Realistic situation, where constraint (2.2) is valid and, hence, strong inequality (2.4) is also valid, will be studied thereafter.

Using in identity (1.20) the expansion in powers of small (in view of (2.4)) J_1/J_2 value and ignoring various corrections to this value, we obtain

$$D^{1/2} = (w + v)J_2 \left[1 + \frac{w(w - v - 2u)J_1}{(w + v)^2 J_2} \right]. \quad (2.5)$$

It follows from Eqs. (1.19) and (2.5)

$$\theta_1 = \frac{1}{\tilde{c}_1} (w + v)J_2, \quad (2.6)$$

$$\theta_2 = \frac{1}{\tilde{c}_1} \frac{w(v + u)}{(w + v)} J_1, \quad (2.7)$$

that agrees with common equality (1.29). Equalities (2.6) and (2.7) give

$$\frac{\theta_2}{\theta_1} = \frac{w(v + u)J_1}{(w + v)^2 J_2} \quad (2.8)$$

and, in view of expressions (1.13) and (2.4), indicate that

$$\theta_2/\theta_1 \ll 1. \quad (2.9)$$

From Eqs. (1.14), (1.17), (2.6), and (2.7) with account of Eqs. (1.13) and (2.4), we obtain

$$B_1/A_1 = -1, \quad B_2/A_2 = w/v. \quad (2.10)$$

Because of a relatively large, according to (2.4), value of flux J_2 , the direct and reverse fluxes of molecular aggregates over the second potential barrier of aggregation work start to balance each other at relatively short (in view of (2.9)) times $t \gtrsim 1/\theta_1$ determined, according to Eq. (2.6), by flux J_2 . Then, mutual quasi-equilibrium is established between spherical and cylindrical micelles (beginning with relatively small cylindrical micelles); however, this time is not sufficient to establish their equilibrium with subcritical molecular

surfactant aggregates. Total equilibrium in surfactant solution is attained at relatively much longer (in view of (2.9)) times

$$t \gtrsim 1/\theta_2, \quad (2.11)$$

that are determined, according to (2.7), by flux J_1 . At such times, first terms in the right-hand sides of Eqs. (1.15) and (1.16), in view of strong inequality (2.9), are negligible compared to the second terms. Then, under condition (2.11), according to Eqs. (1.15), (1.16), and the second of equalities (2.10), we have

$$\delta c_M = A_2 e^{-\theta_2 t}, \quad (2.12)$$

$$\delta g = A_2 \frac{w}{v} e^{\theta_2 t}, \quad (2.13)$$

and, hence

$$\delta g = \frac{w}{v} \delta c_M. \quad (2.14)$$

For the validity of relation (2.14), it is now required that the mutual quasi-equilibrium between spherical and cylindrical micelles be established, without their equilibrium with subcritical surfactant molecular aggregates, throughout the region of cylindrical micelle sizes. The time of establishment of such quasi-equilibrium will be found in Section 3.

According to relations (1.28), relaxation rate θ_1 (the largest (in view of (2.9)) of θ_2 and θ_2 values) corresponds to the shortest (of t_{r1} and t_{r2}) relaxation time t_{r1} describing a relatively fast establishment (beginning with relatively small cylindrical micelles) of mutual quasi-equilibrium between spherical and cylindrical micelles without their equilibrium with subcritical surfactant molecular aggregates. The smallest (of θ_1 and θ_2 , in view of (2.9)) relaxation rate θ_2 corresponds, according to (1.28), the longest (of t_{r1} and t_{r2}) relaxation time t_{r2} describing a relatively slow establishment of the total equilibrium of surfactant solution. This time (which is the most significant in the establishment of the final equilibrium of materially isolated surfactant solution) will be of interest to us hereafter. For this time, according to Eqs. (2.7) and (1.28), we have the analytical expression

$$t_{r2} = \tilde{c}_1 \frac{(w + v)}{w(v + u)} \frac{1}{J_1}. \quad (2.15)$$

Assuming that important formulas (2.7) and (2.12)–(2.15) do not contain at all the J_2 flux, which cannot be found using expression (1.5) because of scarce data on the $\tilde{W}_c^{(2)}$ height of the second potential barrier of aggregation work. Flux J_1 entering into these formulas can be determined using expression (1.3), because, as was already mentioned, the $\tilde{W}_c^{(1)}$ height of the first potential barrier of aggregation work is accessible for determination.

Let us use

$$\delta c_1 = -e^{\tilde{w}^0} \tilde{n}_s^{(1)} (b - \tilde{a})^3 \delta c_M - e^{\tilde{w}^0} (b - \tilde{a})^2 \delta g, \quad (2.16)$$

$$e^{\tilde{w}^0} (b - \tilde{a})^2 = \frac{\tilde{c}_1}{\tilde{c}}, \quad (2.17)$$

$$e^{\tilde{w}^0} (b - \tilde{a})^3 = \frac{\tilde{c}_1 4 \ln 10}{\tilde{c} n_1} \quad (2.18)$$

(relations (2.7), (3.6) and (3.7) in [2]), where $b - \tilde{a}$ presents the coefficient of the linear dependence of work \tilde{W}_n on n in the $n_0 < n < n_1$ region. Let us open relation (2.16), using Eqs. (2.17) and (2.18), and make allowance for determination (1.12) and equality (2.14). Then we obtain

$$\delta c_1 = -\frac{\tilde{c}_1 w + 2u}{\tilde{c} v} \delta c_M \quad (2.19)$$

or (that is equivalent)

$$\delta c_1 = -\frac{\tilde{c}_1 w + 2u}{\tilde{c} w} \delta g. \quad (2.20)$$

We take into account relation

$$\delta N = -\tilde{n}_s^{(1)} \delta c_M \quad (2.21)$$

(relation (8.12) in [1]), which is valid for materially isolated surfactant solution; in this relation, N is the total number of surfactant molecules (the total amount of substance) in cylindrical micelles per solution unit volume. Using inequality (2.14), we can also rewrite relation (2.21) as

$$\delta N = -\tilde{n}_s^{(1)} \frac{V}{w} \delta g. \quad (2.22)$$

Formulas (2.7), (2.12)–(2.15), and (2.19)–(2.22) give the total analytical description of the relaxation of materially isolated surfactant solution containing spherical and cylindrical micelles. Flux J_1 is given by expression (1.3). Parameters u , v , and w are expressed by definitions (1.12) via the characteristics of equilibrium surfactant solution that are accessible for experimental measurement. The n_0 value, which, due to its meaning, can be determined only on some assumption, falls out of an answer.

Let us clarify the sign of the constant of integration A_2 in formulas (2.12) and (2.13). Let us consider the situation when total concentrations c_M and g of spherical and cylindrical micelles increase with time at the stage of relaxation so that deviations δc_M and δg also increase approaching zero from the side of negative values. Then

$$d(\delta c_M)/dt > 0, \quad d(\delta g)/dt > 0. \quad (2.23)$$

The mutual consistency of inequalities (2.23) is ensured by equality (2.14); i.e., by the fact that spheri-

cal and cylindrical micelles are in mutual quasi-equilibrium. Relations (2.12), (2.13), and (2.23) yield

$$A_2 < 0. \quad (2.24)$$

According to Eqs. (2.19)–(2.22) and inequalities (2.23), inequalities

$$d(\delta c_1)/dt < 0, \quad d(\delta N)/dt < 0 \quad (2.25)$$

are also valid. The first of inequalities (2.25) is evident, while the second one should be clarified. As was already mentioned in Section 1, we are interested in experimentally important region of the values of overall concentration \tilde{c} of surfactant solution, where the overwhelming contribution to the total amount of surfactant in solution is made by cylindrical micelles. In this region, approximate equality

$$N \approx c \quad (2.26)$$

is fulfilled with a high accuracy near the final equilibrium state of solution.

Because, by definition, the overall surfactant concentration in a materially isolated solution retains with time and, hence, strictly coincides with its value \tilde{c} in the final state of solution equilibrium, the N value will still vary with time, being close to its final equilibrium value \tilde{N} even at a high accuracy of approximate equality (2.26). The second of inequalities (2.25) shows that the tendency of deviation δN to zero with time takes place at the stage of relaxation from the side of positive values of deviation δN : $\delta N > 0$. The tendency of deviation δc_1 to zero with time takes place according to the first of inequalities (2.25) also at the stage of relaxation from the side of positive values of this deviation. On the contrary, the tendency of deviations δc_M and δg to zero with time occurs, according to inequalities (2.23), at the stage of relaxation from the side of negative values of these deviations.

In the situation opposite to that considered above when total concentrations c_M and g of spherical and cylindrical micelles decrease, inequalities (2.23)–(2.25) would also be opposite. Such a situation could be observed experimentally during the relaxation of a materially isolated surfactant solution to the new equilibrium state after the external distortion of previous equilibrium state of a solution by the instantaneous changes of its pressure or temperature.

Note now that ratio N/g determines the average value \bar{n} of the aggregation number of cylindrical micelles. Taking this into account, from Eqs. (1.12), (2.22), (2.26) and relation

$$\frac{\tilde{g}}{\tilde{c}_1} = 4 \frac{\tilde{c}}{\tilde{c}_1} \frac{\ln 10}{n_1} \quad (2.27)$$

(relation (4.15) in [2]), we obtain $\delta \bar{n}/\bar{n} = -(1 + 2u/w)\delta g/\tilde{g}$. This equality demonstrates the opposite signs of deviations $\delta \bar{n}$ and δg . Using estimates (1.13),

we can rewrite this equality with a high accuracy as $\delta\bar{n}/\bar{n} = -\delta g/\tilde{g}$. Note that, from $\bar{n} = N/g$ with account of relations (2.26) and (2.27) and estimate $n_1 \sim 10^6$ in (1.2), follows $\tilde{n} \sim 10^5$. The ability of cylindrical micelles to be distributed in accordance with strong inequality $n_1 \gg n_0$ over rather wide range of aggregation numbers is responsible for the fact that $n_1 \gg \tilde{n} \gg n_0$. Such an ability is not inherent to spherical micelles, which, due to strong inequality $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$, are accumulated within a rather narrow range of aggregation numbers so that their average size with a high accuracy coincides with $n_s^{(1)}$, i.e., with the position of the bottom of the first potential well of aggregation work.

Let us elucidate what constraints on the values of relative deviations $|\delta c_M/\tilde{c}_M|$, $|\delta g/\tilde{g}|$, and $|\delta N/\tilde{N}|$ follow from condition (1.11) determining the accessible for relaxation theory degree of closeness of the state of materially isolated solution to its final equilibrium. From Eqs. (1.11) and (2.19) with account of definitions (1.12) and estimates (1.13), we obtain

$$|\delta c_M/\tilde{c}_M| \ll 4/3. \quad (2.28)$$

Further, from Eqs. (1.11), (2.20), and (2.27) with account of estimates (1.13), we find

$$|\delta g/\tilde{g}| \ll 2/3 \quad (2.29)$$

(note that inequality (2.29) coincides with similar inequality (4.16) in [2]). Finally, from Eqs. (1.11), (2.19), (2.21), and (2.26) with account of estimates (1.2) and (1.13), we obtain

$$|\delta N/\tilde{N}| \ll (10^{-2} - 10^{-3}). \quad (2.30)$$

Constraints (2.28) and (2.29), which are much weaker than extremely strong (in view of estimate $n_1 \sim 10^6$ in (1.2)) constraint (1.11), admit noticeable (not too small compared to unity) relative deviations $|\delta c_M/\tilde{c}_M|$ and $|\delta g/\tilde{g}|$ of the total concentrations of spherical and cylindrical micelles. Hence, predicted by the relaxation theory deviations of the total concentrations of spherical and cylindrical micelles from their values in the final equilibrium state of materially isolated surfactant solution can actually be measured in experiment. In this case, the relaxation time of a solution (set by equality (2.15)) can also be measured in experiment and the validity of relation (2.14) can also be verified.

Although constraint (2.30) is much weaker than extremely strong constraint (1.11), it is still strong enough. This is explained by the fact that, in a materially isolated solution with the overall concentration above the CMC2, the total amount of substance in cylindrical micelles per solution unit volume, in practice, coincides with a given overall surfactant concen-

tration near the equilibrium, and, hence, as was mentioned above, slightly changes at the stage of relaxation. The deviation of the total amount of substance in cylindrical micelles from its value in the final equilibrium state of materially isolated solution is thus rather difficult to be measured in experiment.

Let us compare relaxation times $t_{r2}^{(1)}$ and $t_{r2}^{(2)}$ in surfactant solutions with different overall concentrations $\tilde{c}^{(1)}$ and $\tilde{c}^{(2)}$ falling within the limits of estimate (1.6). As shown in [1], in spite of possible significant difference between overall concentrations $\tilde{c}^{(1)}$ and $\tilde{c}^{(2)}$, corresponding monomer concentrations $\tilde{c}_1^{(1)}$ and $\tilde{c}_1^{(2)}$ will coincide with extremely high accuracy, provided that estimate (1.6) is fulfilled. In this case, according to formula (1.3), fluxes $J_1^{(1)}$ and $J_1^{(2)}$ and corresponding overall concentrations $\tilde{c}^{(1)}$ and $\tilde{c}^{(2)}$ will also coincide even with a rather high accuracy (in contrast to Section 1, superscripts at flux J_1 refer to different overall concentrations). Taking what have been said above into account, from Eq. (2.15), we have

$$\frac{t_{r2}^{(1)}}{t_{r2}^{(2)}} = \frac{w + v^{(1)} v^{(2)}}{w + v^{(2)} v^{(1)}}, \quad (2.31)$$

where, in view of estimates (1.13), correction term u is neglected compared to v and, according to definitions (1.12), it is assumed that

$$v^{(1)} \equiv \frac{n_1 \tilde{c}_1}{2 \ln 10 \tilde{c}^{(1)}}, \quad v^{(2)} \equiv \frac{n_1 \tilde{c}_1}{2 \ln 10 \tilde{c}^{(2)}} \quad (2.32)$$

in addition, it is taken into account that w is independent of overall concentration \tilde{c} .

Formulas (2.31) and (2.32) allow us to compare the times of solution relaxation to its final equilibrium state with different overall concentrations in this state. If the CMC2 exceeds the CMC1 by the order of magnitude, then in accordance with Eqs. (1.7) and (1.12), $w \sim 10$. According to estimates (1.13), it is quite real that inequalities $v^{(1)} \ll w$ and $v^{(2)} \ll w$ are fulfilled (let it be not quite strong). In this case, it follows from Eqs. (2.31) and (2.32) that $t_{r2}^{(1)}/t_{r2}^{(2)} \approx \tilde{c}^{(1)}/\tilde{c}^{(2)}$, so that time t_{r2} of the solution relaxation to final equilibrium state increases with the overall surfactant concentration in solution approximately in proportion to the overall concentration.

However, if the CMC2 exceeds the CMC1 by two orders of magnitude, then, in accordance with Eqs. (1.7) and (1.12), $w \sim 1$. Then, according to estimates (1.13), the fulfillment of inequalities $v^{(1)} \gg w$ and $v^{(2)} \gg w$ is typical. In this case, it is evident from Eqs. (2.31) and (2.32) that time t_{r2} of solution relaxation to final equi-

librium state is practically independent of the overall concentration in this state.

Similarly, we can disclose the dependence of shortest (out of t_{r1} and t_{r2}) relaxation time t_{r1} on overall concentration c given, according to Eqs. (2.6) and (1.28), by the following analytical expression

$$t_{r1} = \tilde{c}_1 \frac{1}{w + v} \frac{1}{J_2}. \quad (2.33)$$

Let us again take into account that, upon the variations of overall concentration \tilde{c} within the limits admitted by estimate (1.6), monomer concentration \tilde{c}_1 is independent of concentration \tilde{c} with extremely high accuracy, as was shown in [1]. In this case, values $\tilde{W}_s^{(1)}$ and $\tilde{W}_c^{(2)}$ in formula (1.5) and, hence, value J_2 will also be independent of concentration c (no specific expression for $\tilde{W}_c^{(2)}$ is required). Using the same considerations for finding $w + v$, it is evident from Eq. (2.33) that relaxation time t_{r1} is almost independent of the overall solution concentration (provided that the CMC2 exceeds the CMC1 by the order of magnitude) and is approximately proportional to the overall solution concentration if the CMC2 exceeds the CMC1 by two orders of magnitude.

Conclusions drawn above are different than those made in [11] that the relaxation time of surfactant solution at the overall surfactant concentration below the CMC2 (when practically there are no cylindrical micelles in solution) decreases with an increase in the total concentration of spherical micelles, that is, with an increase in the overall concentration in the final equilibrium state of materially isolated solution. This is explained by the fact that, at the overall surfactant concentration below the CMC2, the direct flux of molecular aggregates over the potential barrier of aggregation work depends, according to [11], on the overall concentration, namely, increases with the overall concentration in proportion to $\tilde{c}^{\tilde{n}_c^{(1)}/\tilde{n}_s^{(1)}}$.

The established in this section behavior of the relaxation times of molecular solution at the overall surfactant concentration above the CMC2 but below the values of overall concentration, at which crosslinked micellar structures begin to be formed or the transition to liquid-crystal state is observed, well agrees with experimental results discussed in [12, 13]. It was revealed in these works that, at the overall surfactant concentration above the CMC2, new relaxation mode have been arisen with the characteristic relaxation time differing from the relaxation time below the CMC2. For some surfactants, this time increases linearly with the overall solution concentration, while for others, remains almost constant.

3. THE LOWER LIMIT OF THE HEIGHT OF THE FIRST POTENTIAL BARRIER OF AGGREGATION WORK IN THE RELAXATION KINETICS OF SOLUTIONS CONTAINING SPHERICAL AND CYLINDRICAL MICELLES

Let us estimate characteristic time τ needed to establish the quasi-equilibrium distribution of cylindrical micelle concentration c_n over the entire region of aggregation numbers $n_0 < n < n_1$ where, according to [1], cylindrical micelles are mainly accumulated.

As was mentioned in [2], relation $b - \tilde{a} = (4/n_1)\ln 10$ (relation (3.1) in [2]) is valid for coefficient $b - \tilde{a}$ of the linear dependence of aggregation work \tilde{W}_n on n in the $n_0 < n < n_1$ region. In view of the last of estimates in (1.2), we then have $b - \tilde{a} \ll 1$. Therefore, to vary concentration c_n with time, in estimating considerations, we can use the diffusion equation

$$\frac{\partial c_n}{\partial t} = \frac{\partial}{\partial n} \left(\tilde{j}_n^+ \frac{\partial c_n}{\partial n} \right) \quad (n_0 < n < n_1), \quad (3.1)$$

which accounts for a purely fluctuation evolution of the ensemble of molecular aggregates with diffusion coefficient \tilde{j}_n^+ of molecular aggregates in the space of aggregation numbers defined as the number of surfactant monomers absorbed ($\tilde{j}_n^+ > 0$) from solution with monomer concentration \tilde{c}_1 per unit time by the aggregate composed of n molecules. In Eq. (3.1), we used relation $\tilde{j}_n^+ = \tilde{j}_n^+$, which is valid, in view of Eq. (1.11), with high relative accuracy of $\sim (8/3n_1)\ln 10$. If we had taken into account that $b - \tilde{a} \equiv \partial \tilde{W}_n / \partial n = (4/n_1)\ln 10$, then term $(\partial \tilde{W}_n / \partial n)c_n$ accounting for the regular evolution of the ensemble of molecular aggregates would be added in Eq. (3.1) to derivative $\partial c_n / \partial n$. This would diminish the role of molecular aggregates near the upper limit of the $n_0 < n < n_1$ region and, as a result, would slightly diminish the desired time τ and weaken the desired lower limit of the height of the first potential barrier of aggregation work.

We set the following boundary conditions to Eq. (3.1):

$$\left(\partial c_n / \partial n \right) \Big|_{n=n_0} = 0, \quad \left(\partial c_n / \partial n \right) \Big|_{n=n_1} = 0, \quad (3.2)$$

suggesting the conservation of the total concentration of cylindrical micelles in the $n_0 < n < n_1$ region. These conditions will be proved somewhat later.

The \tilde{j}_n^+ value is proportional to the surface area of a cylindrical micelle, which, in turn, is proportional to aggregation number n . Therefore, we have

$$\tilde{j}_n^+ = \alpha n \quad (n_0 < n < n_1), \quad (3.3)$$

where α is a positive constant. We assume

$$n \equiv r^2/4, \quad n_0 \equiv r_0^2/4, \quad n_1 \equiv R^2/4, \quad c_n(t) \equiv \varphi(r, t). \quad (3.4)$$

Using Eqs. (3.3) and (3.4), we reduce Eq. (3.1) to

$$\frac{\partial \varphi}{\partial t} = \alpha \left(\frac{\partial^2 \varphi}{\partial r^2} + \frac{1}{r} \frac{\partial \varphi}{\partial r} \right) \quad (r_0 < r < R) \quad (3.5)$$

and, using (3.4), we reduce boundary conditions (3.2) to

$$(\partial \varphi / \partial r)|_{r=r_0} = 0, \quad (3.6)$$

$$(\partial \varphi / \partial r)|_{r=R} = 0. \quad (3.7)$$

Strong inequality $n_0 \ll n_1$ resulted from estimates (1.2) allows us, in view of Eq. (3.4), to consider that $r_0 = 0$. In this case, boundary condition (3.6) can be replaced by the condition of boundedness

$$|\varphi|_{r=0} \neq \infty. \quad (3.8)$$

Solving Eq. (3.5) at boundary conditions (3.7) and (3.8), for characteristic time τ needed to establish quasi-equilibrium distribution of the concentrations of cylindrical micelles, we have (e.g., see [14])

$$\tau = R^2 / \alpha \mu_1^2, \quad (3.9)$$

where $\mu_1 \approx 3.8$ is the least of positive roots of transcendental equation $J_1(\mu) = 0$ where $J_1(\mu)$ is the Bessel function of the first kind (with subscript equal to unity). Returning in Eq. (3.9) to the initial designations with the use of equalities $\alpha = \tilde{j}_{n_1}^+ / n_1$ and $R^2 = 4n_1$ followed from Eqs. (3.3) and (3.4) and taking into account that, in this case, $\mu_1 \approx 3.8$, we obtain

$$\tau \approx 0.28 n_1^2 / \tilde{j}_{n_1}^+. \quad (3.10)$$

Seemingly, the condition of the maintenance of the quasi-equilibrium distribution of the concentrations of cylindrical micelles over the entire region of their sizes at the slow establishment of the total equilibrium of materially isolated surfactant solution is

$$t_{r2} / \tau \gg 1. \quad (3.11)$$

Indeed, according to Eqs. (2.13) and (1.28), deviation δg of the total concentration of cylindrical micelles from its final equilibrium state has no time to be changed by the relative value during time $\Delta t \leq \tau$, given that condition (3.11) is fulfilled. This explains condition (3.11) and, at the same time, justifies boundary conditions (3.2).

According to the meaning of time τ and the meaning of time t_{r1} disclosed in Section 2, the largest of τ and t_{r1} value is responsible for the time of the establishment of mutual quasi-equilibrium of spherical and cylindrical micelles without their equilibrium with subcritical surfactant molecular aggregates over the entire region of the sizes of cylindrical micelles. Only after the elapse of this time (the largest of τ and t_{r1}), relation (2.14) will

be valid. In view of Eq. (3.11) and $t_{r1} \ll t_{r2}$, this time is much shorter than time t_{r2} .

Substitution of Eq. (1.3) into Eq. (2.15) yields

$$t_{r2} = \pi^{1/2} \frac{w + v}{wv} \frac{\Delta \tilde{n}_c^{(1)}}{\tilde{j}_c^{+(1)}} e^{\tilde{w}_c^{(1)}}, \quad (3.12)$$

where, in view of Eq. (1.13), term u is neglected compared to v . Using Eqs. (3.10) and (3.12), we obtain

$$\frac{t_{r2}}{\tau} \approx 6.3 \frac{w + v}{wv} \frac{\Delta \tilde{n}_c^{(1)}}{n_1^2} \frac{\tilde{j}_{n_1}^+}{\tilde{j}_c^{+(1)}} e^{\tilde{w}_c^{(1)}}. \quad (3.13)$$

Ratio $\tilde{j}_{n_1}^+ / \tilde{j}_c^{+(1)}$ is set equal to ratio $A^{(c)} / A^{(s)}$, where $A^{(c)}$ is the surface area of cylindrical micelle composed of n_1 molecules and $A^{(s)}$ is the surface area of spherical molecular aggregate composed of $\tilde{n}_c^{(1)}$ molecules. Let us find the surface area $A^{(c)}$ using formulas (46.1) in [4] and surface area $A^{(s)}$, using formula (1.1) in [9]; we used also aforementioned estimate $\tilde{n}_c^{(1)} \sim 30$ obtained in [8]. Then, we have

$$\frac{\tilde{j}_{n_1}^+}{\tilde{j}_c^{+(1)}} \sim 1.4 \times 10^{-2} n_1. \quad (3.14)$$

For $\Delta \tilde{n}_c^{(1)}$, we assume estimate $\Delta \tilde{n}_c^{(1)} \sim 10$ calculated in [8]; for n_1 , estimate $n_1 \sim 10^6$ in Eq. (1.2). On this basis, and accounting for Eq. (3.14), from Eq. (3.13) we obtain

$$\frac{t_{r2}}{\tau} \sim 0.9 \times 10^{-6} \frac{w + v}{wv} e^{\tilde{w}_c^{(1)}}, \quad (3.15)$$

where, according to Eq. (1.13), we can use

$$\frac{w + v}{wv} \sim (0.2-1). \quad (3.16)$$

On the basis of Eqs. (3.15) and (3.16), we reduce condition (3.11) to

$$1.8 \times (1-5) \times 10^{-7} e^{\tilde{w}_c^{(1)}} \gg 1. \quad (3.17)$$

Condition (3.17) imposes the desired lower limit on the height of the first potential barrier of aggregation work in the kinetic theory of the relaxation of surfactant solutions containing spherical and cylindrical micelles. If the CMC2 exceeds the CMC1 by the order of magnitude, constraint (3.17) is fulfilled at $\tilde{W}_c^{(1)} > 15.5$. However, if the CMC2 exceeds the CMC1 by two orders of magnitude, constraint (3.17) is fulfilled already at $\tilde{W}_c^{(1)} > 13.9$.

Note that constraint (3.17) derived on the basis of the kinetic theory is consistent with estimate (2.1), which was obtained in [8] from the analysis of solution equilibrium.

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