

Kinetic Description of the Relaxation of Surfactant Solutions in the Absence of Activation Barrier between Spherical and Cylindrical Micelles

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Abstract—The realistic situation, where there is no potential barrier of aggregation work between the spherical and cylindrical micelles, is analyzed within the framework of the kinetic description of the relaxation of non-ionic surfactant solution containing spherical and cylindrical micelles. The variations in the sum of the total concentrations of spherical and cylindrical micelles caused by the total flux of molecular aggregates over the potential barrier of aggregation work between the monomers and spherical micelles is taken into account; it is also accounted for that, in the absence of the potential barrier of aggregation work between the spherical and cylindrical micelles, they are present in the mutual quasi-equilibrium. The closed linearized relaxation equation determining the variations (with time) in the total concentrations of spherical and cylindrical micelles in a materially isolated surfactant solution is derived and solved. The variations (with time) of the total concentrations of spherical and cylindrical micelles, the concentration of surfactant monomers, as well as the total amount of surfactant in cylindrical micelles, in the process of approach of a materially isolated micellar solution to the final equilibrium state are described analytically. It is disclosed that, at the mutual quasi-equilibrium of spherical and cylindrical micelles, the opposite-sign deviations of the total amount of substance in cylindrical micelles and the total amount of cylindrical micelles from their values in the final equilibrium state of a materially isolated solution is attributed to the relatively large cylindrical micelles. The agreement between the results obtained and analogous results of the description of micellar relaxation in the presence of the potential barrier of aggregation work between spherical and cylindrical micelles whose relative height is at least slightly lower than that between monomers and spherical micelles is demonstrated. Comparison is performed for the cases of the absence of either spherical or cylindrical micelles. Analytical expressions, which are accessible for experimental verification, for the ratios of relaxation times of surfactant solutions containing spherical and cylindrical micelles to those of surfactant solutions containing either spherical or cylindrical micelles alone are derived.

INTRODUCTION

We continue the study of thermodynamics and kinetics of aggregation in nonionic surfactant solutions containing spherical and cylindrical micelles above the second critical micellization concentration (CMC₂) that was initiated in [1–3]. In [1, 2] and in the general section of [3], we considered complex situation where the aggregation work done during the micellization was characterized by two potential barriers. The first barrier is the activation barrier for the transition to spherical micelles; the second barrier is the activation barrier for the transition to cylindrical micelles. A simpler (albeit realistic) situation [4, 5], where the height of the second potential barrier of aggregation work is lower than that of the first potential barrier, was also considered in [3]. To be more exact, for the study in [3], it was sufficient for the relative height of the second potential barrier to be at least slightly lower than that of the first potential barrier.

As was demonstrated by recent studies [6], it is possible that the second potential barrier of aggregation work is almost unnoticeable or even absent at all. Then,

the transition from spherical to cylindrical micelles occurs without overcoming the activation barrier, and quasi-equilibrium exists between spherical and cylindrical micelles; however, there is no equilibrium between these micelles and subcritical molecular aggregates located on the aggregation number axis to the left of the first potential barrier of aggregation work. According to [6], the analytical extension of the results of the description (done in [3]) of the micellar relaxation to the realistic situation is impossible, because it was assumed in [3] that the second potential barrier is still expressed noticeably on the dependence of the aggregation work on the aggregation number, even if its height is small. Thus, the situation arising in the absence of the second potential barrier requires special study. This consideration is the one of main goals of this work.

The variations in the sum of the total concentrations of spherical and cylindrical micelles caused by total flux of molecular aggregates over the first potential barrier of aggregation work will be taken into account, as well as the fact that, in the absence of the second poten-

tial barrier of the aggregation work, spherical and cylindrical micelles are in mutual quasi-equilibrium but not in the equilibrium with subcritical molecular aggregates. Closed linearized relaxation equation determining the variations (with time) in the total concentration of spherical micelles and the total concentration of cylindrical micelles in a materially isolated surfactant solution will be derived and solved. On this basis, we will describe analytically the variations (with time) in the total concentrations of spherical and cylindrical micelles, the concentration of surfactant monomers and total amount of surfactant in cylindrical micelles in the approach of a materially isolated micellar solution to the final equilibrium state. We disclose that, at the mutual quasi-equilibrium of spherical and cylindrical micelles, the opposite-sign deviations of the total amount of substance in cylindrical micelles and the total number of cylindrical micelles from their values in the final equilibrium state of a materially isolated solution is explained by the presence of relatively large cylindrical micelles. We will demonstrate the agreement between the obtained results and analogous results [3] obtained upon the description of micellar relaxation in the presence of the second potential barrier of aggregation work whose relative height is at least slightly lower than that of the first potential barrier. We compare the case of the absence of spherical micelles with that of the absence of micellar micelles studied previously [7]. We derive accessible for experimental verification analytical expressions for the ratios of relaxation times of surfactant solutions containing spherical and cylindrical micelles and solutions containing either spherical or cylindrical micelles alone.

1. THE ACCOUNT OF MUTUAL QUASI-EQUILIBRIUM BETWEEN SPHERICAL AND CYLINDRICAL MICELLES IN THE ABSENCE OF ACTIVATION BARRIER BETWEEN THEM

We will use the same system of notations as in [1–3]. 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) is denoted by c_n . At $n = 1$, the aggregates are nothing other than surfactant monomers. Correspondingly, c_1 is the monomer concentration. Overall surfactant concentration (the total number of surfactant molecules per solution unit volume) is denoted by c ; total concentrations of spherical and cylindrical micelles, by c_M and g , respectively. The W_n is understood as the aggregation work of molecular aggregate with aggregation number n expressed in thermal units kT (k is Boltzmann's constant and T is the absolute temperature).

The dependence of work W_n on aggregation number n in the absence of potential barrier between spherical and cylindrical micelles at the overall surfactant concentration in solution above the CMC2 generalizing

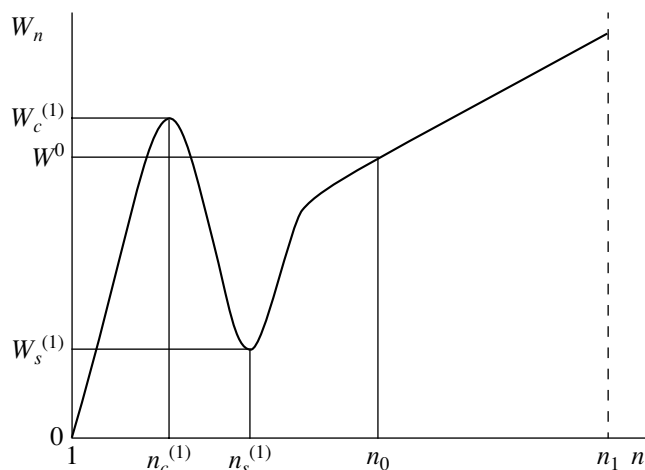


Fig. 1. The work of aggregation W_n as a function of aggregation number n in the absence of the potential barrier between spherical and cylindrical micelles in the solution at the overall surfactant concentration above the CMC2.

known experimental and theoretical data [4–6] is shown in Fig. 1. The value of aggregation work $W_c^{(1)}$ in point $n = n_c^{(1)}$ of its first maximum on the aggregation number axis (the second maximum is absent) determines the height of activation barrier for the formation of spherical and cylindrical micelles. Hence, we can state the aggregates in the region $1 \leq n < n_c^{(1)} - \Delta n_c^{(1)}$ on the aggregation number axis, where $\Delta n_c^{(1)}$ is the half-width of the only potential barrier of aggregation work, as subcritical aggregates. The value of aggregation work $W_s^{(1)}$ in point $n = n_s^{(1)}$ of its first (and the only one) minimum characterizes the depth of potential well where spherical micelles are accumulated. The half-width of this potential well on the aggregation number axis is denoted by $\Delta n_s^{(1)}$. According to constraints (1.3) and (1.4) in [2], we assume $\Delta n_c^{(1)} \gg 1$, $\Delta n_c^{(1)}/n_c^{(1)} \ll 1$, $\Delta n_c^{(1)}/(n_s^{(1)} - n_c^{(1)}) \ll 1$, and $\Delta n_s^{(1)} \gg 1$, $\Delta n_s^{(1)}/(n_s^{(1)} - n_c^{(1)}) \ll 1$. These constraints mean that the potential barrier and potential well of aggregation work are noticeably exhibited on the dependence of work W_n on n . To the right of point $n_s^{(1)} + \Delta n_s^{(1)}$ on the aggregation number axis, the micelles exist already in a cylindrical modification [6]. The value of aggregation work W^0 is taken in point $n = n_0$ corresponding to the left-hand boundary of the region of aggregation numbers, where the length of cylindrical micelle is already such that the dependence of aggregation work W_n on n is linear. In this case, it is assumed that $\Delta n_s^{(1)}/(n_0 - n_s^{(1)}) \ll 1$. The right-hand boundary of the region of the linear depen-

dence of W_n on n is set by point $n = n_1$; as one approaches this point, the equilibrium distribution of cylindrical micelles over aggregation numbers (proportional to $\exp(-W_n)$) decays rapidly. Thus, the region of aggregation numbers $n > n_1$ is no longer of interest.

As in [1–3], we assume for $n_s^{(1)}$, n_0 , and n_1 values the estimates that are typical for many surfactants

$$n_s^{(1)} \sim 10^2, \quad n_0 \sim 10^3, \quad n_1 \sim 10^6. \quad (1.1)$$

Note that, according to [1, 2], estimates $W_s^{(1)} \sim 4$ and $W_0 \sim 14$, as well as, according to [8], estimate $W_c^{(1)} \sim 16$ –18 are valid.

The $n_0 < n < n_1$ region of the linear dependence of aggregation work W_n on n contributes mainly to the total number N of surfactant molecules (the total amount of substance) in cylindrical micelles per solution unit volume and to the total concentration of cylindrical micelles g . Indeed, in the absence of the second barrier, work W_n increases with aggregation number n from the $n_s^{(1)} + \Delta n_s^{(1)}$ value (above which the micelles exist already in cylindrical modification); moreover, this value first increases very fast [6] approaching value W^0 (qualitatively, this is shown in Fig. 1). Provided that $n_0 \gg n_s^{(1)} + \Delta n_s^{(1)}$ in the main part of $n_s^{(1)} + \Delta n_s^{(1)} < n < n_0$ region is fulfilled, work W_n is approximately equal to W^0 and, according to Boltzmann's principle, the distribution of cylindrical micelles over the aggregation numbers is approximately equal to $c_1 \exp(-W^0)$. To estimate contributions of ΔN and Δg from the $n_s^{(1)} + \Delta n_s^{(1)} < n < n_0$ region to values N and g , one can use relations $\Delta N \sim \frac{1}{2} c_1 [n_0^2 - (n_s^{(1)} + \Delta n_s^{(1)})^2] \exp(-W^0)$ and $\Delta g \sim c_1 [n_0 - (n_s^{(1)} + \Delta n_s^{(1)})] \exp(-W^0)$. Taking into account these relations, as well as estimates (1.1) and $W^0 \sim 14$, we have $\Delta N \sim c_1$ and $\Delta g \sim 10^{-3} c_1$. It is seen that $\Delta N \ll N$ and $\Delta g \ll g$, because in the experimentally important range (which is of interest to us) of overall concentration c of surfactant solution, where the predominant contribution to this concentration is introduced by cylindrical micelles, $N \approx c \sim 10^4 c_1$ and $g \sim 10^{-1} c_1$ are valid [2].

Let us introduce direct $J^{(1)}$ and reverse $J''^{(1)}$ fluxes of molecular aggregates over the potential barrier of aggregation work. These fluxes determine the numbers of molecular aggregates, which pass (by fluctuations) over the potential barrier per unit time in micellar solution unit volume from the $n < n_c^{(1)} - \Delta n_c^{(1)}$ region to the $n > n_c^{(1)} + \Delta n_c^{(1)}$ region (direct flux) and from the $n > n_c^{(1)} + \Delta n_c^{(1)}$ region to the $n < n_c^{(1)} - \Delta n_c^{(1)}$ region (reverse flux). Evidently, $J^{(1)} + J''^{(1)}$ is the total flux of

molecular aggregates passing (by fluctuations) from the $n < n_c^{(1)} - \Delta n_c^{(1)}$ region to the $n > n_c^{(1)} + \Delta n_c^{(1)}$ region.

In accordance with the meaning of introduced fluxes, we have

$$\frac{d}{dt}(c_M + g) = J^{(1)} + J''^{(1)}, \quad (1.2)$$

where t is the time. Remind that c_M is the total concentration (the total number per solution unit volume) of spherical micelles that are present in the $n_s^{(1)} - \Delta n_s^{(1)} < n < n_s^{(1)} + \Delta n_s^{(1)}$, region and g is the total concentration (the total number per solution unit volume) of cylindrical micelles that are present in the $n_0 < n < n_1$ region.

With the fulfillment of aforementioned constraints imposed on $\Delta n_c^{(1)}$ and $\Delta n_s^{(1)}$, we have

$$J^{(1)} = c_1 j_c^{+(1)} \exp(-W_c^{(1)}) / \pi^{1/2} \Delta n_c^{(1)}, \quad (1.3)$$

$$J''^{(1)} = -c_M j_c^{+(1)} \exp[-(W_c^{(1)} - W_s^{(1)})] / \pi \Delta n_c^{(1)} \Delta n_s^{(1)} \quad (1.4)$$

(expressions (1.8) and (1.9) in [2]) where $j_c^{+(1)}$ is the number of surfactant monomers absorbed ($j_c^{+(1)} > 0$) from solution per unit time by the molecular aggregate composed of $n_c^{(1)}$ molecules.

The values in the final state of complete aggregation equilibrium are denoted by the tilde over symbols. Hereafter, direct flux $\tilde{J}^{(1)}$ will be often encountered. Denoting, for brevity, this flux as J_1 , as was already done in [3], we have from Eq. (1.3)

$$J_1 = \tilde{c}_1 \tilde{j}_c^{+(1)} \exp(-\tilde{W}_c^{(1)}) / \pi^{1/2} \Delta \tilde{n}_c^{(1)}. \quad (1.5)$$

We denote the deviations of values from their magnitudes in the final equilibrium state of a materially isolated solution by symbol δ to the left of these values. In the process of solution relaxation, relative values of these deviations become small; then, one can perform the linearization using these values, thus significantly simplifying the study.

In this case, relation (1.2) is expressed as

$$d(\delta c_M + \delta g) / dt = \delta(J^{(1)} + J''^{(1)}). \quad (1.6)$$

According to [2], provided that condition $|\delta c_1 / \tilde{c}_1| \ll 2 / \tilde{n}_s^{(1)}$ is fulfilled, we have

$$\delta(J^{(1)} + J''^{(1)}) = J_1 \left(\frac{\tilde{n}_s^{(1)}}{\tilde{c}_1} \delta c_1 - \frac{1}{\tilde{c}_M} \delta c_M \right) \quad (1.7)$$

(relation (2.4) in [2]). Definition $J_1 \equiv \tilde{J}^{(1)}$ is accounted for in Eq. (1.7).

In the absence of the second potential barrier of aggregation work, there is no equation supplemented to

Eq. (1.6) that is analogous to Eq. (2.2) in [2]. This manifests the originality of the situation studied in this work compared to the situation treated in [2, 3]. We consider in the near future how Eq. (1.6) can be supplemented to make it mathematically closed equation.

Using definition

$$c_s^{(1)} \equiv c_n|_{n=n_s^{(1)}} \quad (1.8)$$

let us introduce the concentration of spherical micelles $c_s^{(1)}$ in point $n = n_s^{(1)}$ at the bottom of potential well of aggregation work W_n . At $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$, concentration $c_s^{(1)}$ is related to concentration c_M by the expression

$$c_s^{(1)} = c_M/\pi^{1/2} \Delta n_s^{(1)}. \quad (1.9)$$

Then, using definition

$$c_s \equiv c_n|_{n=n_0} \quad (1.10)$$

we introduce the concentration of cylindrical micelles c_s in point $n = n_0$ corresponding to the left-hand side of the boundary of the region of aggregation numbers where the dependence of aggregation work W_n on n is already linear.

In the absence of the second potential barrier of aggregation work, the transformation of spherical micelles into cylindrical ones occurs without overcoming the activation barrier. Therefore, spherical and cylindrical micelles are in mutual quasi-equilibrium (but not in equilibrium with subcritical molecular aggregates). Accounting for Eqs. (1.8) and (1.10), according to Boltzmann's principle, we arrive at

$$c_s^{(1)}/c_s = e^{W^0}/e^{W_s^{(1)}}. \quad (1.11)$$

From Eqs. (1.9) and (1.11), we obtain

$$\ln c_M - \ln c_s - (W^0 - W_s^{(1)}) - \ln(\pi^{1/2} \Delta n_s^{(1)}) = 0. \quad (1.12)$$

Let us use relations

$$\partial W_s^{(1)}/\partial c_1 = -(n_s^{(1)} - 1)/c_1, \quad (1.13)$$

$$\partial W^0/\partial c_1 = -(n_0 - 1)/c_1$$

(the second and the third of relations (1.2) in [1]). Linearizing (with the aid of Eq. (1.13)) equality (1.12) with respect to deviations δc_M , δc_s , and δc_1 and accounting for fairly weak sensitivity of the $\Delta n_s^{(1)}$ value (the more so, its logarithm) to concentration c_1 shown in [8], we obtain

$$\frac{1}{\tilde{c}_M} \delta c_M - \frac{1}{\tilde{c}_s} \delta c_s + \frac{1}{\tilde{c}_1} (n_0 - \tilde{n}_s^{(1)}) \delta c_1 = 0. \quad (1.14)$$

As in [1–3], we are interested in experimentally significant region of the overall concentration \tilde{c} of surfactant solution where the predominant contribution to the

total amount of surfactant in solution is made by cylindrical micelles. In this case, we have

$$b - \tilde{a} = (4/n_1) \ln 10 \quad (1.15)$$

(relation (3.1) in [2]) and

$$e^{-\tilde{W}^0} = 16(\ln 10)^2 \frac{\tilde{c}}{\tilde{c}_1} \frac{1}{n_1^2} \quad (1.16)$$

(relation (3.2) in [2]). Here, $b - \tilde{a}$ is the coefficient of the linear dependence of work \tilde{W}_n on n in the $n_0 < n < n_1$ region. From Eqs. (1.15) and (1.16), we obtain

$$e^{\tilde{W}^0} (b - \tilde{a}) = \frac{1}{4 \ln 10} \frac{\tilde{c}_1}{\tilde{c}} n_1, \quad (1.17)$$

$$e^{\tilde{W}^0} (b - \tilde{a})^2 = \frac{\tilde{c}_1}{\tilde{c}}, \quad (1.18)$$

$$e^{\tilde{W}^0} (b - \tilde{a})^3 = \frac{\tilde{c}_1 4 \ln 10}{\tilde{c} n_1}. \quad (1.19)$$

At the overall concentration \tilde{c} , at which the predominant contribution to the total amount of surfactant in solution is introduced by cylindrical micelles, for a materially isolated surfactant solution, we have

$$\delta c_1 = -e^{\tilde{W}^0} \tilde{n}_s^{(1)} (b - \tilde{a})^3 \delta c_M - e^{\tilde{W}^0} (b - \tilde{a})^2 \delta g, \quad (1.20)$$

$$\delta c_s = \tilde{n}_s^{(1)} (b - \tilde{a})^2 \delta c_M + 2(b - \tilde{a}) \delta g \quad (1.21)$$

(relations (8.10) and (8.11) in [1]). The condition of the applicability of linearized expressions (1.20) and (1.21) is

$$|\delta c_1/\tilde{c}_1| \ll (8/3n_1) \ln 10 \quad (1.22)$$

(condition (8.5) in [1]). As is seen from estimates (1.1), condition (1.22) is much stronger than aforementioned condition $|\delta c_1/\tilde{c}_1| \ll 2/\tilde{n}_s^{(1)}$ of the applicability of linearized expression (1.7). Condition (1.22) is the condition that determines the closeness of a materially isolated solution to its final equilibrium state accessible for the relaxation theory.

Substituting relations (1.20) and (1.21) into Eq. (1.14) and taking into account Eqs. (1.17)–(1.19), as well as equality $\tilde{c}_s = \tilde{c} \exp(-\tilde{W}_0)$ (equality (2.5) in [1]) that is valid at the solution equilibrium, we obtain

$$\left[\frac{\tilde{c}_1}{\tilde{c}_M} - \tilde{n}_s^{(1)} \frac{\tilde{c}_1}{\tilde{c}} - \frac{4 \ln 10}{n_1} (n_0 - \tilde{n}_s^{(1)}) \tilde{n}_s^{(1)} \frac{\tilde{c}_1}{\tilde{c}} \right] \delta c_M - \left[\frac{n_1}{2 \ln 10} \frac{\tilde{c}_1}{\tilde{c}} + (n_0 - \tilde{n}_s^{(1)}) \frac{\tilde{c}_1}{\tilde{c}} \right] \delta g = 0. \quad (1.23)$$

In relation (1.11), the mutual quasi-equilibrium of spherical and cylindrical micelles was required only for relatively small cylindrical micelles for which $n \leq n_0$. Meanwhile, in relation (1.23), the mutual quasi-equilibrium of spherical and cylindrical micelles is required

already throughout the $n_0 < n < n_1$ region where cylindrical micelles are mainly accumulated. This is associated with the fact that relations (1.20) and (1.21) used in Eq. (1.23) were derived [1] under the assumption that quasi-equilibrium state of cylindrical micelles is true throughout the $n_0 < n < n_1$ region.

As is [2, 3], we take estimates

$$\tilde{c}/\tilde{c}_1 \sim 10^4, \quad (1.24)$$

$$\tilde{c}_M/\tilde{c}_1 \sim (0.1-1), \quad (1.25)$$

where according to [2], it is assumed that $\tilde{c}_M/\tilde{c}_1 \sim 0.1$, 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 already becomes noticeable; $\tilde{c}_M/\tilde{c}_1 \sim 1$, if the CMC2 exceeds the CMC1 by two orders of magnitude.

Let us combine Eqs. (1.1), (1.24), and (1.25) to estimate the relative values of the contributions of summands at the coefficients at δc_M and δg in Eq. (1.23). Then, we have

$$\tilde{n}_s^{(1)} \frac{\tilde{c}_M}{\tilde{c}} \sim (10^{-3} - 10^{-2}), \quad (1.26)$$

$$\frac{4 \ln 10}{n_1} (n_0 - \tilde{n}_s^{(1)}) \tilde{n}_s^{(1)} \frac{\tilde{c}_M}{\tilde{c}} \sim (10^{-5} - 10^{-4}), \quad (1.27)$$

$$\frac{2 \ln 10}{n_1} (n_0 - \tilde{n}_s^{(1)}) \sim 10^{-2}. \quad (1.28)$$

Estimates (1.26)–(1.28) demonstrate that the predominant contribution to the coefficients at δc_M and δg in Eq. (1.23) is introduced by the first summands in these coefficients. Then, from Eq. (1.23) with relatively high accuracy of the order of 10^{-2} , we obtain

$$\delta g = \frac{2 \ln 10}{n_1} \frac{\tilde{c}}{\tilde{c}_M} \delta c_M. \quad (1.29)$$

This is equality (1.29) that serves as the desired supplement to Eq. (1.6).

2. RELAXATION OF A MATERIALLY ISOLATED MICELLAR SOLUTION IN THE ABSENCE OF THE ACTIVATION BARRIER BETWEEN SPHERICAL AND CYLINDRICAL MICELLES

According to [3], let us introduce parameters

$$u \equiv \tilde{n}_s^{(1)} \frac{\tilde{c}_1}{\tilde{c}}, \quad v \equiv \frac{n_1}{2 \ln 10} \frac{\tilde{c}_1}{\tilde{c}}, \quad w \equiv \frac{\tilde{c}_1}{\tilde{c}_M}, \quad (2.1)$$

related to experimentally measurable characteristics of equilibrium surfactant solution. In view of Eqs. (1.1), (1.24), and (1.25), these parameters satisfy the estimates

$$u \sim 10^{-2}, \quad v \sim 10, \quad w \sim (1-10). \quad (2.2)$$

With the aid of Eq. (2.1), relation (1.29) is expressed as

$$\delta g = \frac{w}{v} \delta c_M. \quad (2.3)$$

Substituting Eqs. (1.18) and (1.19) into Eq. (1.20), we arrive at

$$\delta c_1 = -\frac{4 \ln 10}{n_1} \tilde{n}_s^{(1)} \frac{\tilde{c}_1}{\tilde{c}} \delta c_M - \frac{\tilde{c}_1}{\tilde{c}} \delta g. \quad (2.4)$$

From Eq. (2.4) with the aid of Eq. (2.3) and definitions (2.1), we find

$$\delta c_1 = -\frac{w + 2u\tilde{c}_1}{v} \delta c_M \quad (2.5)$$

or, what is equivalent,

$$\delta c_1 = -\frac{w + 2u\tilde{c}_1}{w} \delta g. \quad (2.6)$$

Let us substitute Eq. (2.5) into Eq. (1.7). Accounting for definitions (2.1), we obtain

$$\delta(J^{(1)} + J^{m(1)}) = -\frac{1}{\tilde{c}_1} J_1 w \left(1 + \frac{u}{v}\right) \delta c_M, \quad (2.7)$$

where the $2u^2/vw$ term, which is in view of estimates (2.2) has the second order of smallness, is ignored compared to the u/v term.

From Eqs. (1.6), (2.3), and (2.7), we derive linearized relaxation equation

$$\left(1 + \frac{w}{v}\right) \frac{d(\delta c_M)}{dt} = -\frac{1}{\tilde{c}_1} J_1 w \left(1 + \frac{u}{v}\right) \delta c_M, \quad (2.8)$$

describing the variations (with time) in the total concentration of spherical micelles in a materially isolated surfactant solution. The same equation, in view of linear relation (2.3) between δg and δc_M , describes variations (with time) in the total concentration of cylindrical micelles in a materially isolated surfactant solution.

Common solution to Eq. (2.8) has the following form:

$$\delta c_M = A e^{-\theta t}, \quad (2.9)$$

where A is the arbitrary constant of integration, and positive value θ is given by equality

$$\theta = \frac{1}{\tilde{c}_1} \frac{w(v+u)}{w+v} J_1. \quad (2.10)$$

From Eqs. (2.3) and (2.9), it also follows

$$\delta g = A \frac{w}{v} e^{-\theta t}. \quad (2.11)$$

The θ value plays in Eqs. (2.9) and (2.11) the role of the rate of relaxation of a materially isolated micellar solution. Inverse value t_r , which, according to Eq. (2.10), is set by the analytical expression

$$t_r = \tilde{c}_1 \frac{w + v}{w(v + u)} \frac{1}{J_1}, \quad (2.12)$$

has the meaning of the relaxation time of micellar solution.

Let us take into account relation

$$\delta N = -\tilde{n}_s^{(1)} \delta c_M \quad (2.13)$$

(relation (8.12) in [1]), which is true for a materially isolated micellar solution. Remind that N is the total number of surfactant molecules in cylindrical micelles per solution unit volume. Formulas (2.3), (2.5), (2.6), and (2.9)–(2.13) provide the complete analytical description of the relaxation stage of a materially isolated surfactant solution containing spherical and cylindrical micelles. Note that the n_0 value, which by its meaning can be determined only with some allowance, is not entered into these formulas.

Let us clarify the sign of arbitrary constant A of integration in formulas (2.9) and (2.11). We consider the situation when total concentrations of spherical (c_M) and cylindrical (g) micelles increase with time at the relaxation stage so that deviations δc_M and δg also increase approaching zero from the lower limit. Then

$$d(\delta c_M)/dt > 0, \quad d(\delta g)/dt > 0. \quad (2.14)$$

The mutual consistency of inequalities is secured by equality (2.3); i.e., by the fact that spherical and cylindrical micelles are in mutual quasi-equilibrium. Relations (2.9), (2.11), and (2.14) yield

$$A < 0. \quad (2.15)$$

According to Eqs. (2.5), (2.6), and (2.13), together with inequalities (2.14), inequalities

$$d(\delta c_1)/dt < 0, \quad d(\delta N)/dt < 0 \quad (2.16)$$

are also valid.

According to inequalities (2.16), the tendency of deviations δc_1 and δN to zero with time takes place at the stage of relaxation from the side of positive δc_1 and δN values.

In the situation opposite to that described above when total concentrations c_M and g of spherical and cylindrical micelles decrease with time at the stage of relaxation, inequalities (2.14)–(2.16) would be also opposite. Such a situation can be observed experimentally during the relaxation of a materially isolated micellar solution to the new equilibrium state after external distortion of the previous equilibrium state of solution by the instantaneous changes of its pressure or temperature.

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 (1.22) determining the accessible for relaxation theory the degree of closeness of the state of a materially isolated micellar solution to its final equilibrium.

From Eqs. (1.22) and (2.5) with account of definitions (2.1) and estimates (2.2), we obtain

$$|\delta c_M|/\tilde{c}_M \ll 4/3. \quad (2.17)$$

Further, according to [2], we have

$$\frac{\tilde{g}}{\tilde{c}_1} = 4 \frac{\tilde{c}}{\tilde{c}_1} \frac{\ln 10}{n_1} \quad (2.18)$$

(relation (4.15) in [2]). From Eqs. (1.22), (2.6), and (2.18) with account of estimates (2.2), we find

$$|\delta g|/\tilde{g} \ll 2/3. \quad (2.19)$$

Finally, from Eqs. (1.22), (2.5), (2.13), and equality

$$\tilde{N} \approx \tilde{c}, \quad (2.20)$$

that is valid with high accuracy in the experimentally significant range of the overall surfactant concentration \tilde{c} , where the predominant fraction of the total amount of surfactant in solution is contained in cylindrical micelles, with account of estimates (1.1) and (1.2), we obtain

$$|\delta N|/\tilde{N} \ll (10^{-2} - 10^{-3}). \quad (2.21)$$

Constraints (2.17) and (2.19), which are much weaker than extremely strong (in view of estimate $n_1 \sim 10^6$ in Eq. (1.1)) constraint (1.22), 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 kinetics deviations of the total concentrations of spherical and cylindrical micelles from their values in the final equilibrium state of a materially isolated surfactant solution can be actually measured in experiment. In this case, the relaxation time of solution given by equality (2.12) can also be measured experimentally and the validity of relation (2.3) can be verified as well.

Although constraint (2.21) is much weaker than extremely strong constraint (1.22), it is still strong enough. This is explained by the fact that, in a materially isolated solution with the overall surfactant concentration significantly exceeding the CMC2, the total amount of substance in cylindrical micelles per solution unit volume, in practice, coincides with a given overall surfactant concentration and, hence, slightly changes at the stage of solution relaxation. Thus, the deviation of the total amount of substance in cylindrical micelles from its value in the final equilibrium state of a materially isolated surfactant solution predicted by the relaxation kinetics is rather difficult to be measured in experiment.

According to Eq. (2.13), the sign of deviation δN is opposite to that of deviation δc_M . At the mutual quasi-equilibrium of spherical and cylindrical micelles when Eq. (2.3) is true, the sign of deviation δN is opposite also to that of deviation δg ; at first glance, this seems to be strange. Let us disclose the reason for this fact.

For the distribution of cylindrical micelle concentration c_n over the aggregation numbers, on the basis of formula (2.3) in [1], we have

$$c_n = c_s e^{-(b-a)(n-n_0)} \quad (n_0 < n < n_1). \quad (2.22)$$

Formula (2.22) suggests the quasi-equilibrium state of cylindrical micelles (but not their equilibrium with subcritical molecular aggregates and spherical micelles). Taking into account that the a value, by its definition (2.4) in [1], depends on monomer concentration c_1 via term $\ln c_1$ and the b value, according to its meaning established in [1], is independent of c_1 , we find, using Eq. (2.22), deviation δc_n

$$\delta c_n = \tilde{c}_n \left[\frac{\delta c_s}{\tilde{c}_s} + (n - n_0) \frac{\delta c_1}{\tilde{c}_1} \right] \quad (n_0 < n < n_1). \quad (2.23)$$

Condition of linearization of Eq. (2.23) with respect to δc_1 (the disregard for quadratic and higher-order corrections to deviation δc_1) is $|\delta c_1 / \tilde{c}_1| \ll 2/(n - n_0)$ that is fulfilled throughout the $n_0 < n < n_1$ region, provided that condition (1.22) is fulfilled.

From Eq. (1.21) with account of Eqs. (1.15) and (2.3) and definitions (2.1), for a materially isolated surfactant solution at the mutual quasi-equilibrium of spherical and cylindrical micelles, we obtain

$$\delta c_s = 4 \frac{\tilde{c}_1 w + u}{\tilde{c}} \frac{\delta c_M}{v^2}. \quad (2.24)$$

Substituting Eqs. (2.5) and (2.24) into Eq. (2.23), we have for a materially isolated surfactant solution at the mutual quasi-equilibrium of spherical and cylindrical micelles

$$\delta c_n = \tilde{c}_n \left[\frac{4\tilde{c}_1 w + u}{\tilde{c}\tilde{c}_s} \frac{w + u}{v^2} - \frac{(n - n_0)w + 2u}{\tilde{c}} \frac{w + 2u}{v} \right] \delta c_M \quad (2.25)$$

$$(n_0 < n < n_1).$$

The first term in square brackets of Eq. (2.25) is positive; the second one is negative. These terms become identical by the absolute values in point $n_1/2 \ln 10$ on the number aggregation axis. This is seen from formula $\tilde{c}_s = \tilde{c}_1 \exp(-\tilde{W}^0)$ [formula (2.5) in [1] with account of Eqs. (1.16) and (2.1)] that is valid in the state of solution equilibrium, as well as from inequality $n_1 \gg n_0$ and the smallness (in view of estimates (2.2)) of parameter u compared to parameter w .

As was already mentioned, the $n_0 < n < n_1$ region of the linear dependence of aggregation work of cylindrical micelle on n mainly contributes to the total amount N of substance in cylindrical micelles and the total concentration g of cylindrical micelles. Then, with a high accuracy, we have

$$N = \int_{n_0}^{n_1} n c_n dn, \quad g = \int_{n_0}^{n_1} c_n dn, \quad (2.26)$$

$$\delta N = \int_{n_0}^{n_1} n (\delta c_n) dn, \quad \delta g = \int_{n_0}^{n_1} (\delta c_n) dn. \quad (2.27)$$

Using Eqs. (2.25) and (2.27), let us elucidate the contributions of the first and second terms in square brackets of Eq. (2.25) to δN and δg . These contributions are from relatively small and relatively large cylindrical micelles, respectively. It can be expected that, due to factor n under the sign of the first of integrals in Eq. (2.27), the role of relatively large cylindrical micelles in the integral for δN will be larger than in the integral for δg .

Let us take advantage of formulas (4.14), (7.1), (7.4), and (7.6) in [1]

$$\int_{n_0}^{n_1} \tilde{c}_n dn = \tilde{g} = \frac{\tilde{c}_s}{b - \tilde{a}}, \quad (2.28)$$

$$\int_{n_0}^{n_1} n \tilde{c}_n dn = \tilde{N} = \frac{\tilde{c}_s}{(b - \tilde{a})^2}, \quad \int_{n_0}^{n_1} n^2 \tilde{c}_n dn = \tilde{Q} = \frac{2\tilde{c}_s}{(b - \tilde{a})^3},$$

as well as of relation (1.15) and inequality $(b - \tilde{a})n_0 \ll 1$ that, in this case, is fulfilled in view of $n_1 \gg n_0$. To find the $\tilde{c}_s / \tilde{c}_1$ value, we use formula $\tilde{c}_s = \tilde{c}_1 \exp(-\tilde{W}^0)$ (formula (2.5) in [1]) that is valid in the state of solution equilibrium and relation (1.16). Taking into account definitions (2.1), we represent contributions to δN and δg from the first and second terms in square brackets of Eq. (2.25) (that are of interest to us) with the aid of relations

$$\delta N = \frac{n_1}{2 \ln 10} \left(\frac{w + u}{v} - \frac{w + 2u}{v} \right) \delta c_M, \quad (2.29)$$

$$\delta g = \left(2 \frac{w + u}{v} - \frac{w + 2u}{v} \right) \delta c_M. \quad (2.30)$$

The first and second terms in parentheses in Eqs. (2.29) and (2.30) just correspond to contributions to δN and δg we are interested in. For brevity, we call them the first and the second contributions to δN and δg .

It follows from Eqs. (2.29) and (2.30) that the first contributions to δN and δg are identical by the sign to deviation δc_M ; the second contributions are opposite by the sign to deviation δc_M . According to Eq. (2.29), in the principal order set by estimates (2.2), i.e., with account of term w/v , the first and the second contributions to δN are mutually compensated. As for the corrections, i.e., with account of term u/v , the second contribution is twice as large as the first one. This explains why the sign of deviation δN is opposite to the sign of

deviation δc_M . The conclusion drawn for a materially isolated surfactant solution at the mutual quasi-equilibrium of spherical and cylindrical micelles owes to a relatively large cylindrical micelles for which the second term in square brackets in Eq. (2.25) is quite significant. As would be expected, after mutual cancellations, relation (2.29) is exactly transformed, due to definitions (2.1), into relation (2.13).

According to Eq. (2.30), the first and the second contributions to δg are not mutually cancelled in the principal order set by estimates (2.2), i.e., with account of term w/v . In this order, the first contribution is twice as large as the second one so that the signs of deviations δg and δc_M are identical. It is seen that, in a materially isolated surfactant solution at the mutual quasi-equilibrium of spherical and cylindrical micelles, deviation δg of the total concentration of cylindrical micelles is caused mainly by relatively small cylindrical micelles, for which the first term in square brackets in Eq. (2.25) is relatively more significant. As for the corrections, i.e., with account of term u/v , the first and second contributions to deviation δg are mutually compensated. As would be expected, after cancellations, relation (2.30) is exactly transformed into relation (2.3).

Using Eq. (2.3), we represent Eq. (2.29) as

$$\delta N = \frac{n_1}{2 \ln 10} \left(\frac{w+u}{w} - \frac{w+2u}{w} \right) \delta g. \quad (2.31)$$

This relation demonstrates that opposite signs of deviations δN and δg in a materially isolated surfactant solution at the mutual quasi-equilibrium of spherical and cylindrical micelles are associated with relatively large cylindrical micelles and explains the fact that deviation δN appears only in the correction order set by estimates (2.2).

Let us emphasize the significant role played by the ability of cylindrical micelles to be distributed, in accordance with inequality $n_1 \gg n_0$, within a rather wide range of aggregation numbers. This ability is not inherent to spherical micelles, which, on the contrary, are accumulated within a rather narrow range of aggregation numbers due to inequality $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$.

Let us compare these data with the results obtained in [3] under the existence of the second potential barrier of aggregation work between spherical and cylindrical micelles whose relative height is at least slightly lower than that of the first potential barrier of aggregation work between monomers and spherical micelles. Let us make the following tentative remark. The consideration of the second potential barrier in [3] suggested the fulfillment of constraints $\Delta n_c^{(2)} \gg 1$, $\Delta n_c^{(2)}/(n_c^{(2)} - n_s^{(1)}) \ll 1$, and $\Delta n_c^{(2)}/(n_0 - n_c^{(2)}) \ll 1$ (constraints (1.5) in [2]), where $\Delta n_c^{(2)}$ is the half-width of the second barrier and $n_c^{(2)}$ is the position of its vertex on the aggregation number axis. By the meaning of half-width $\Delta n_c^{(2)}$, work W_n

(expressed in thermal units kT) decreases by unity when variable n deviates from $n_c^{(2)}$ value by $\Delta n_c^{(2)}$. Consequently, these constraints imply that the potential barrier should be distinctly marked on the dependence of work W_n on n , even when its height is low. Therefore, one cannot be assured for the coincidence of results obtained in [3] when the relative height of the second potential barrier is at least slightly lower than that of the first potential barrier and the results reported in this communication for the complete absence of the second potential barrier of aggregation work.

Nevertheless, as can be easily seen from this comparison, these results appeared to be completely coinciding. It is clear that the θ , t_r , and A values should be understood as the θ_2 , t_{r2} , and A_2 values in [3] related to the higher (of two) relaxation time (the least of two relaxation rates). However, the θ_1 , t_{r1} values found in [3] correspond to times at which the mutual quasi-equilibrium between spherical and cylindrical micelles is attained relatively fast, beginning with relatively small cylindrical micelles, and equality (1.11) becomes valid.

All what have been said above makes it possible to state the following. The dependence of the relaxation time of solution on the overall surfactant concentration disclosed in [3] by formulas (2.31) and (2.32) and derived in [3] expression (3.10) for characteristic time τ of the establishment of the quasi-equilibrium state of cylindrical micelles throughout the $n_0 < n < n_1$ region where cylindrical micelles are mainly accumulated, as well as constraint (3.17) on the lower limit of the height of the first potential barrier of aggregation work remain also valid in the situation studied in this work. However, the reason for the opposite signs of deviations δN and δg in a materially isolated surfactant solution at the mutual quasi-equilibrium between spherical and cylindrical micelles disclosed by formulas (2.22)–(2.31) in this communication will be also valid in the situation studied in [3].

3. COMPARISON WITH THE CASE OF THE ABSENCE OF SPHERICAL MICELLES AND THE CASE OF THE ABSENCE OF CYLINDRICAL MICELLES

Relations discussed in Section 2 (and relevant relations in [3]) refer to the most complicated case when the spherical and cylindrical micelles coexist simultaneously above the CMC2. However, in practice, more simple case is encountered when the spherical shape of a micelle becomes unrealizable due to the structure and packing conditions of surfactant molecules and the micellization starts just from the formation of cylindrical micelles. Thus, there is only the CMC2 and the CMC1 is absent. We start the consideration in this section with this case.

The dependence of the work of molecular aggregate formation in a surfactant solution on the aggregation number in the case of the absence of spherical micelles

at the overall surfactant concentration above the CMC2 was qualitatively shown in the figure to [2]. For the uniformity of notations employed in this work with the those used in [2], we assume $W_c = W_c^{(1)}$, $n_c = n_c^{(1)}$, and $\Delta n_c = \Delta n_c^{(1)}$. The $W_c^{(1)}$ value of the aggregation work in point $n = n_c^{(1)}$ of its first maximum on the aggregation number axis (the second maximum is absent) determines the height of the activation barrier needed only for the formation of cylindrical micelles. The W^0 value of the aggregation work is still taken in point $n = n_0$ corresponding to the left-hand boundary of the aggregation number region where the dependence of W_n on n is already linear. The right-hand boundary of this region is still set by point $n = n_1$; as one approaches this point, the equilibrium distribution of cylindrical micelles over aggregation numbers decays rapidly so that the region of aggregation numbers $n > n_1$ is no longer of interest. We assume also that estimates for values n_0 and n_1 in Eq. (1.1), as well as estimates $W^0 \sim 14$ and $W_c^{(1)} \sim 16-18$, are still valid.

Considering the case of the absence of spherical micelles as a specific case of the study performed in Section 2, we should take into account that now we have

$$\tilde{n}_s^{(1)} = 0, \quad \tilde{c}_M = 0, \quad \delta c_M = 0. \quad (3.1)$$

In this case, definitions (2.1) look like

$$u \equiv 0, \quad v \equiv \frac{n_1 \tilde{c}_1}{2 \ln 10 \tilde{c}}, \quad w \equiv \infty, \quad (3.2)$$

and estimates (2.2) are reduced to:

$$v \sim 10. \quad (3.3)$$

From Eq. (2.6) with allowance for Eq. (3.2), we have

$$\delta c_1 = -\frac{\tilde{c}_1}{\tilde{c}} \delta g, \quad (3.4)$$

that coincides with relation (4.14) in [2].

It was mentioned in Section 2 that the total concentration of cylindrical micelles in a materially isolated surfactant solution varies with time by the same equation as Eq. (2.8). Accounting for this fact, as well as for Eq. (3.2), we obtain from Eq. (2.8)

$$\frac{1}{v} \frac{d(\delta g)}{dt} = -\frac{1}{\tilde{c}_1} J_1 \delta g, \quad (3.5)$$

where J_1 is given by the same expression (1.5). Common solution to Eq. (3.5) has the following form:

$$\delta g = B e^{-\theta t}, \quad (3.6)$$

where B is the arbitrary constant of integration and positive value θ is determined by the equality

$$\theta = \frac{v}{\tilde{c}_1} J_1. \quad (3.7)$$

The θ value acts as the rate of relaxation of a materially isolated surfactant solution in the absence of spherical micelles. Inverse value t_r given, according to Eq. (3.7), by the analytical expression

$$t_r = \frac{\tilde{c}_1}{v J_1}, \quad (3.8)$$

has the meaning of relaxation time of this solution.

In [3] (prior to the derivation of relations (2.31) and (2.32)), it was shown that, upon the variations in overall concentration \tilde{c} within the limits admissible by estimate (1.24), values \tilde{c}_1 and J_1 are independent of concentration \tilde{c} with rather high accuracy. Then it is seen from Eqs. (3.2) and (3.8) that time t_r is proportional to the overall concentration of the solution.

For a materially isolated surfactant solution in the absence of spherical micelles, equality $\delta N = -\delta c_1$ is strictly valid that refines relation followed from Eq. (2.13) at $\delta c_M = 0$. Then, accounting for Eq. (3.4), we have

$$\delta N = \frac{\tilde{c}_1}{\tilde{c}} \delta g. \quad (3.9)$$

Relation (3.9) indicates that, in the absence of spherical micelles in a materially isolated surfactant solution, the signs of deviations δN and δg are identical.

In the case under consideration, if Eq. (2.14) is fulfilled, the relation

$$d(\delta g)/dt > 0 \quad (3.10)$$

is also fulfilled that, according to Eq. (3.6), leads to the inequality

$$B < 0 \quad (3.11)$$

for the constant of integration B in formula (3.6). According to Eq. (3.4), together with inequality (3.10), the inequality

$$d(\delta c_1)/dt < 0 \quad (3.12)$$

is also valid. If the inequality opposite to inequality (3.10) is fulfilled, it is possible that, after the instantaneous distortion of solution equilibrium state, inequalities (3.11) and (3.12) will be opposite.

In the considered case, condition (1.22) determining the degree of closeness of a materially isolated micellar solution to its final equilibrium accessible for the relaxation theory is still true. From Eqs. (1.22), (2.18), and (3.4) with account of estimate (3.3) follow aforementioned constraint (2.19) that coincides with constraint (4.16) in [2].

Let us now consider the case of the absence of cylindrical micelles. We make the following tentative remark. The theory proposed above was developed for the experimentally significant region of the overall surfactant concentrations in a solution where the predom-

inant contribution to the total amount of surfactant is introduced by the cylindrical micelles. Thus, one cannot pass in this theory to the situation where cylindrical micelles are virtually absent. The kinetic theory of the relaxation of a materially isolated surfactant solution was developed in [7] for the case of the absence of cylindrical micelles and the presence of only spherical micelles.

We summarize briefly the main formulas and conclusions made in [7] at the overall surfactant concentration in solution above the CMC1 but below the CMC2 when the main contribution to the total amount of surfactant is introduced by the spherical micelles. In this case, the dependence of work W_n on the aggregation number is shown in Fig. 2 (we adhere to notations accepted in this work but not in [7]). The $W_c^{(1)}$ value of aggregation work in point $n = n_c^{(1)}$ of its maximum on the aggregation number axis determines the height of activation barrier needed for the formation of spherical micelles. Unlimited increase of work W_n on the n axis to the right of the potential well of work with the minimum in point $n = n_s^{(1)}$ and depth $W_s^{(1)}$ corresponds to the fact that, at the overall surfactant concentration in solution below the CMC2, no cylindrical micelles are yet appeared. For the $n_s^{(1)}$ value, we take the same estimate $\tilde{n}_s^{(1)} \sim 10^2$ as in relation (1.1).

The direct flux of molecular aggregates over the potential barrier for the formation work, which is denoted by J_1 , is given by expression (1.5). In the case of a materially isolated surfactant solution, the surfactant balance equation

$$c_1 + n_s^{(1)} c_M = c \quad (3.13)$$

(Eq. (1.5) in [7]), after its linearization in the vicinity of the final equilibrium state of solution, leads to relation

$$\delta c_1 = -\tilde{n}_s^{(1)} \delta c_M, \quad (3.14)$$

where a rather weak sensitivity of $n_s^{(1)}$ value (demonstrated in [8]) to concentration c_1 is accounted for.

Further, the linearized sum of direct and reverse fluxes of molecular aggregates over the potential barrier of the aggregation work is given by expression (1.7). As was already mentioned, the condition of the applicability of this equation is

$$|\delta c_1 / \bar{c}_1| \ll 2 / \tilde{n}_s^{(1)}. \quad (3.15)$$

Condition (3.15) justifies with large excess the disregard for the dependence of the $n_s^{(1)}$ value on concentration c_1 made while deriving relation (3.14). It is seen that, in the case of a materially isolated surfactant solution containing spherical micelles, the domain of the applicability of analytical theory is limited by the domain of the applicability of the linearization of the

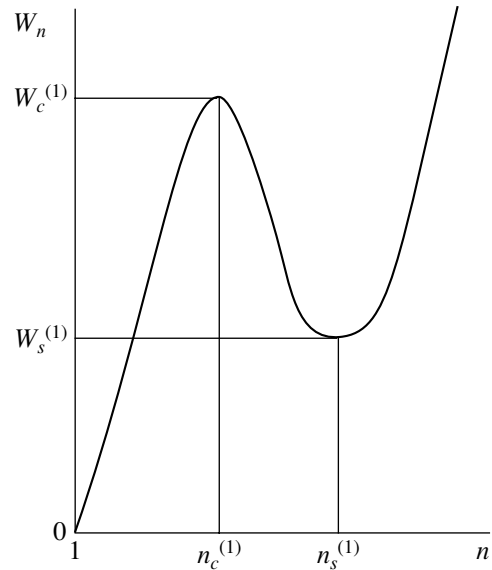


Fig. 2. The work of aggregation W_n as a function of aggregation number n in the presence of only spherical micelles in the solution at the overall surfactant concentration above the CMC1 (but below the CMC2).

sum of direct and reverse fluxes of molecular aggregates over the potential barrier for the aggregation work but not by the linearization of the surfactant balance equation for the solution. However, in the case of a materially isolated surfactant solution containing spherical and cylindrical micelles, as well as only cylindrical micelles, the situation, as was disclosed in [2], turned out to be just opposite.

According to substance balance equation (3.13), we have

$$N^{(s)} = n_s^{(1)} c_M, \quad (3.16)$$

where the total number of surfactant molecules in spherical micelles per solution unit volume is denoted by $N^{(s)}$. From Eq. (3.16) and already mentioned rather exact relation $n_s^{(1)} \approx \tilde{n}_s^{(1)}$, it follows

$$\delta N^{(s)} = \tilde{n}_s^{(1)} \delta c_M. \quad (3.17)$$

It is seen that expression (3.17) for the solution containing only spherical micelles is opposite by the sign to analogous expression (2.13) for the number of molecules in cylindrical micelles in solution containing spherical and cylindrical micelles. The reason for this difference was elucidated in Section 2.

In the considered case of a materially isolated surfactant solution containing spherical micelles, we have inequality $d(\delta c_M)/dt > 0$, provided that relation (2.14) is fulfilled. Then, in view of Eq. (3.14), inequality $d(\delta c_1)/dt < 0$ is true and, in view of Eq. (3.17), the inequality

$$d(\delta N^{(s)})/dt > 0 \quad (3.18)$$

is also true.

Inequality (3.18) is opposite by the sign to the second of inequalities (2.16), i.e., to its analogue of a materially isolated surfactant solution containing spherical and cylindrical micelles. The noted discrepancy would also exist at $d(\delta c_M)/dt < 0$ that is possible only after the instantaneous external distortion of the state of solution equilibrium. The reason for these discrepancies was disclosed in Section 2.

In accordance with balance equation (3.13), at the overall surfactant concentration in solution twice or more exceeding the CMC1, inequality $\tilde{n}_s^{(1)}\tilde{c}_M/\tilde{c}_1 > 1$ is fulfilled. In view of $\tilde{n}_s^{(1)} \gg 1$, strong inequality $(\tilde{n}_s^{(1)})^2\tilde{c}_M/\tilde{c}_1 \gg 1$ is fulfilled with large excess. In this case, from relation (4.7) in [7] for relaxation time $t_r^{(s)}$ of a materially isolated surfactant solution containing spherical micelles, we have

$$t_r^{(s)} = \frac{\tilde{c}_1}{(\tilde{n}_s^{(1)})^2 J_1} \quad (3.19)$$

(direct flux J_1 is given by expression (1.5)).

From Eqs. (3.14)–(3.17) with account of estimate $\tilde{c}_M/\tilde{c}_1 \sim 10^{-1}$ that is valid at the overall surfactant concentration in solution significantly higher than the CMC1 (but lower than the CMC2), we have

$$\begin{aligned} |\delta c_M/\tilde{c}_M| &\ll 20/(\tilde{n}_s^{(1)})^2, \\ |\delta N^{(s)}/\tilde{N}^{(s)}| &\ll 20/(\tilde{n}_s^{(1)})^2. \end{aligned} \quad (3.20)$$

In view of $\tilde{n}_s^{(1)} \sim 10^2$, constraints (3.20) are much stronger than constraints (3.15) which is itself rather strong. Thus, predicted by the theory deviations of the total concentration of spherical micelles and the total amount of substance in these micelles from their values in the final equilibrium state of a materially isolated solution containing spherical micelles are rather difficult to be measured in experiment at the stage of relaxation.

The fact that time $t_r^{(s)}$ is still experimentally significant is seen from the following explanation. An increase in the total concentration of spherical micelles and the total amount of substance in these micelles in a materially isolated solution occurs prior to the attainment of the stage of relaxation of surfactant solution, which is the final stage of micellization. The expression for the time of the attainment of the final stage of micellization from the beginning of this process in a materially isolated surfactant solution containing spherical micelles was derived in [7]. As was shown in [7], this time exceeds the time of solution relaxation by no more

than 2.5 times. Hence, it is seen that time $t_r^{(s)}$ given by expression (3.19) determines not only the relaxation time of a solution at the final stage of micellization but also rather exactly estimates experimentally measurable total time of the establishment of equilibrium from the onset of the micellization process in a materially isolated surfactant solution containing spherical micelles.

4. COMPARISON OF RELAXATION TIMES OF SURFACTANT SOLUTIONS CONTAINING SIMULTANEOUSLY SPHERICAL AND CYLINDRICAL MICELLES, ONLY CYLINDRICAL AND ONLY SPHERICAL MICELLES

The cases where spherical and cylindrical micelles simultaneously and only cylindrical and only spherical micelles are present in the surfactant solution we denote by superscripts (sc), (c), and (s), respectively, in the designation of relaxation time t_r of a materially isolated surfactant solution. Let us compare times $t_r^{(sc)}$, $t_r^{(c)}$, and $t_r^{(s)}$.

According to Eqs. (2.12), (3.8), and (3.19), we have the following analytical expressions:

$$t_r^{(sc)} = \tilde{c}_1 \frac{w + v}{w(v + u)J_1}, \quad (4.1)$$

$$t_r^{(c)} = \frac{\tilde{c}_1}{v J_1}, \quad (4.2)$$

$$t_r^{(s)} = \frac{\tilde{c}_1}{(\tilde{n}_s^{(1)})^2 J_1}. \quad (4.3)$$

Direct flux J_1 of molecular aggregates over the potential barrier of aggregation work in the equilibrium state of surfactant solution is given in all three formulas (4.1)–(4.3) by the united analytical expression (1.5). Parameters u , v , and w are expressed by definitions (2.1) via experimentally measurable characteristics of equilibrium surfactant solution. These parameters satisfy estimates (2.2). Estimate $w \sim 1$ shown in Eq. (2.2) is valid, if the CMC2 exceeds the CMC1 by two orders of magnitude; estimate $w \sim 10$ is true, if the CMC2 exceeds the CMC1 by the order of magnitude.

It is natural to assume that the solvent and the dissolved surfactant, as well as the pressure and temperature remain the same in all three cases under consideration. Expressions (4.1) and (4.2) refer to experimentally significant region of the values of overall concentration \tilde{c} of surfactant solution where the predominant contribution to the total amount of surfactant in solution is introduced by the cylindrical micelles. This region is located much above the CMC2. We will use expression (4.3) in experimentally accessible

region of the values of overall concentration \tilde{c} of surfactant solution located in the vicinity of the CMC2. In this region, the main contribution to the total amount of surfactant in solution is introduced by the spherical micelles (cylindrical micelles do not play a significant role yet); hence, expression (4.3) is valid. As was shown in [1], throughout the region of the values of overall concentration \tilde{c} above the CMC2, monomer concentration \tilde{c}_1 will be identical with a rather high accuracy (irrespective of vary large variations in overall concentration \tilde{c} in this region). In this case, the value of exponent $\exp(-\tilde{W}_c^{(1)})$ dependent on \tilde{c}_1 and, according to Eq. (1.5), the value of flux J_1 will be practically invariable throughout the region above the CMC2. Using expression (4.3) in the region of the values of overall concentration \tilde{c} located in the vicinity of the CMC2, we thus secure practical equality of the \tilde{c}_1/J_1 value (for the solutions with the same solvents and dissolved surfactant, as well as the pressure and temperature) in all three expression (4.1)–(4.3). When finding ratios $t_r^{(sc)}/t_r^{(c)}$ and $t_r^{(c)}/t_r^{(s)}$ (which are of interest to us), factor \tilde{c}_1/J_1 is eliminated. This fact markedly simplifies the problem.

Let us ignore parameter u in Eq. (4.1); according to Eq. (2.2), this parameter is by three orders of magnitude smaller than parameter v . According to Eq. (2.1), only parameter v (out of parameters v and w) depends on overall concentration \tilde{c} . Referring expressions (4.1) and (4.2) to the identical values of overall concentration \tilde{c} located, as was already mentioned, much above the CMC2, we secure the identical values of parameter v in these expressions. Then, canceling (when finding $t_r^{(sc)}/t_r^{(c)}$) factor v , as well as factor \tilde{c}_1/J_1 , we finally obtain with high accuracy from Eqs. (4.1) and (4.2)

$$\frac{t_r^{(sc)}}{t_r^{(c)}} = \frac{w + v}{w}. \quad (4.4)$$

Because v , according to Eq. (2.1), is inversely proportional to overall concentration \tilde{c} and w is independent of \tilde{c} , Eq. (4.4) agrees with the fact (followed from Section 3) that $t_r^{(c)}$ is proportional to \tilde{c} , as well as with the fact (reported in [3]) that $t_r^{(sc)}$ is approximately proportional to \tilde{c} at $v \ll w$ and practically is independent of \tilde{c} at $v \gg w$. Accounting in Eq. (4.4) for estimates of v and w in Eq. (2.2), we find

$$\frac{t_r^{(sc)}}{t_r^{(c)}} \sim \begin{cases} 2 & (\text{CMC2/CMC1} \sim 10) \\ 10 & (\text{CMC2/CMC1} \sim 10^2). \end{cases} \quad (4.5)$$

From Eqs. (4.2) and (4.3), it follows (after the cancellation by factor \tilde{c}_1/J_1):

$$\frac{t_r^{(c)}}{t_r^{(s)}} = \frac{(\tilde{n}_s^{(1)})^2}{v}. \quad (4.6)$$

Using in Eq. (4.6) estimate for v in Eq. (2.2), we obtain

$$\frac{t_r^{(c)}}{t_r^{(s)}} \sim \frac{(\tilde{n}_s^{(1)})^2}{10}. \quad (4.7)$$

We would like to emphasize an extreme simplicity of analytical expressions (4.4) and (4.6). Knowing at least one of the relaxation times $t_r^{(s)}$, $t_r^{(c)}$, and $t_r^{(sc)}$, one can easily find other times, using Eqs. (4.4) and (4.6).

According to Eq. (4.5), time $t_r^{(sc)}$ cannot too noticeably exceed time $t_r^{(c)}$. According to relation (4.7), time $t_r^{(c)}$ exceeds time $t_r^{(s)}$ quite largely (by 10^3 times at $\tilde{n}_s^{(1)} \sim 10^2$). Note that time $t_r^{(s)}$ used in relations (4.6) and (4.7) at overall concentration \tilde{c} in the vicinity of the CMC2, according to [7], will be by $(\text{CMC2}/\tilde{c})^{\tilde{n}_c^{(1)}/\tilde{n}_s^{(1)}}$ times shorter than analogous time $t_r^{(s)}$ referred to overall concentration \tilde{c} between the CMC1 and the CMC2. According to [9], for typical nonionic surfactants above the CMC1, experimental estimates of time $t_r^{(s)}$ lie within the range from 1 to 100 s. In view of the preceding, time $t_r^{(c)}$ should fit the 10^3 – 10^5 s range; time $t_r^{(sc)}$, the 10^3 – 10^6 s range.

From what have been said above at the end of Section 2 follows that expression (4.1) is exactly valid also in the situation where, in addition to the first potential barrier of aggregation work between the monomers and spherical micelles, there is still the second potential barrier of aggregation work between the spherical and cylindrical micelles whose height at least slightly lower (by the relative value) than the height of the first potential barrier. Consequently, in this, more complex, situation, equality (4.4) and approximate relation (4.5) are still valid.

Comparing the values of times $t_r^{(sc)}$, $t_r^{(c)}$, and $t_r^{(s)}$ calculated by formulas (4.1)–(4.3) and experimental data on the relaxation times of surfactant solution at various values of its overall concentrations, one can see, even with no other information on the micellar structure of a solution, whether these values of overall concentration lie above the CMC1, between the CMC1 and the CMC2, or above the CMC2.

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