Thermodynamic and Kinetic Foundations of the Micellization Theory: 5. Hierarchy of Kinetic Times

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Received September 7, 2000

Abstract—The characteristic kinetic times of micellization in the solution of a nonionic surfactant: the times of establishment of quasi-equilibrium concentrations of molecular aggregates in micellar, subcritical, and overcritical regions, times of establishment of quasi-equilibrium concentrations of molecular aggregates in the near-critical region of their sizes, the average time between two successive acts of emission of surfactant monomers by a micelle, the average value of micelle lifetime, the time of establishment of quasi-stationary mode of matter exchange between the solution and molecular aggregate, as well as the times of fast and slow relaxation in a solution were analyzed. The hierarchy of these times disclosing complex multistage kinetic process of micelle formation and decomposition and the establishment of equilibrium in the micellar solution was revealed. It was shown that this hierarchy is provided by the small parameters of the kinetic theory. The inverse problem of micellization kinetics was discussed; this problem allows us to find the characteristics of the formation work for micellar aggregate from the experimental data on the relaxation time of micellar solution.

INTRODUCTION

We continue the study of micellization in a solution of colloidal surfactant initiated in [1–4]. The elucidation of the hierarchy of the characteristic times of micellization is the major aim of this work. The existence of hierarchy proves reliably that the quasi-equilibrium concentrations of molecular aggregates in subcritical and overcritical regions of their sizes and the quasi-steady-state concentration of molecular aggregates in the near-critical region of their sizes that were qualitatively substantiated in [2] are actually established. Remember that the establishment of the aforementioned concentrations plays a key role in the analytical theory of the relaxation of micellar solution developed in [2–4]. The hierarchy also gives a clear indication of the relative values of the times of the formation and decomposition of micelles and of the complex multistage process of approaching micellar solution to the final state of equilibrium. As in [1–4], we consider the colloidal surfactant as a nonionic substance and the mixture of molecular aggregates in a solution as an ideal mixture.

1. CHARACTERISTIC KINETIC TIMES OF MICELLIZATION

The aggregation number of a molecular aggregate of a surfactant in a micellar solution is denoted by n. At $n = 1$, the aggregates are none other than surfactant monomers, which are identical in the considered case of one nonionic surfactant. The monomer concentration is denoted by c_1. The work formation of an aggregate in the solution containing initially only surfactant monomers is expressed in thermal units kT (k is Boltzmann's

constant and T is the solution temperature) and denoted by W_n. The aggregation numbers of critical and stable molecular aggregates corresponding to the positions of maximum and minimum work W_n at the n-axis we denote by n_c and n_s, respectively; these maximum and minimum works, i.e., the height of a potential barrier and the depth of a potential well are denoted by $W_c \equiv W_n|_{n = n_c}$ and $W_s \equiv W_n|_{n = n_s}$, respectively. The half-widths of potential barrier and potential well, which are defined by equalities (1.1) in [2], we denote by Δn_c and Δn_s, respectively. The regions $n \lesssim n_c - \Delta n_c$, $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$, and $n \gtrsim n_c + \Delta n_c$ we call subcritical, near-critical, and overcritical regions, respectively. Micelles are mainly concentrated in the $n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s$ region. We call this region micellar. It is located inside the overcritical region. The total micelle concentration (their total concentration in the micellar region) we denote by c_M.

The study performed in [2–4] concerns an interesting practical situation where the concentration of surfactant monomers exceeds the critical micellization concentration, but is lower than the concentration corresponding to the onset of the formation of macroscopic phase (crystalline hydrate or liquid crystal of a surfactant). Then, the conditions of the applicability of the macroscopic description of the micellization kinetics employed in [2–4] are:

$$\Delta n_c \gg 1, \quad \Delta n_c/n_c \ll 1, \quad \Delta n_c/(n_s - n_c) \ll 1, \quad (1.1)$$

$$\Delta n_s \gg 1, \quad \Delta n_s/(n_s - n_c) \ll 1 \quad (1.2)$$

(conditions (1.2) and (1.3) in [2]). The first conditions of (1.1) and (1.2) allow us to assume that the value of

n is continuous in the important (for the micellization kinetics) regions of the potential barrier and the potential well of work W_n. The remaining conditions of (1.1) and (1.2) imply that the potential barrier and potential well of work W_n are most clearly pronounced: they are divided from the initial point $n = 1$ at the n-axis and separated from each other at this axis. This circumstance is expressed by the inequalities

$$\exp(W_c) \gg 1, \quad \exp(W_c) \gg \exp(W_s) \qquad (1.3)$$

followed from conditions (1.1) and (1.2) [inequalities (1.4) in [2]].

According to relations (2.14)–(2.17) in [4], it is true that

$$\partial W_c/\partial c_1 = -(n_c - 1)/c_1, \quad \partial W_c/\partial c_1 < 0, \qquad (1.4)$$

$$\partial W_s/\partial c_1 = -(n_s - 1)/c_1, \quad \partial W_s/\partial c_1 < 0. \qquad (1.5)$$

From Eqs. (1.4) and (1.5), it follows that

$$\partial \exp(W_c - W_s)/\partial c_1 > 0. \qquad (1.6)$$

In view of Eq. (1.4), the first inequality of (1.3) becomes weaker with an increase in surfactant monomer concentration c_1. However, the first inequality of (1.3) remains extremely strong due to its exponential character, in spite of the fact that the monomer concentration in the region, which is of interest to us, does not exceed the intensity of the formation of the surfactant macroscopic phase. Inequality (1.6) demonstrates that the second inequality of (1.3) becomes stronger, as surfactant monomer concentration c_1 increases. This is contributed by the possible, in view of (1.5), passage of minimum work W_s to the region of its negative values.

The fact that the fulfillment of conditions (1.1) and (1.2) provides the existence of the hierarchy of characteristic kinetic times of micellization, which is needed for the validity of the analytical theory of the relaxation of micellar solution developed in [2–4], is yet to be proved.

Let us collect the data on the characteristic kinetic times obtained in [3, 4]. We deal, above all, with the times t_s and t' of the establishment of quasi-steady-state concentrations of molecular aggregates in micellar and subcritical regions, respectively; time t'' of the establishment of quasi-steady-state concentration of molecular aggregates in the part of overcritical region located to the left of micellar region at the n-axis; and with the time t_c of the establishment of quasi-steady-state concentration of molecular aggregates in the near-critical region. For the times listed above, we have (formulas (1.16)–(1.18) and (2.13) in [3])

$$t_s = (\Delta n_s)^2/2j_s^+, \qquad (1.7)$$

$$t' \approx n_c \Delta n_c/j_c^+, \qquad (1.8)$$

$$t'' \approx (n_s - n_c)\Delta n_c/j_c^+, \qquad (1.9)$$

$$t_c = (\Delta n_c)^2/2j_c^+. \qquad (1.10)$$

Here, j_s^+ $(j_s^+ > 0)$ is the number of surfactant monomers absorbed by the stable molecular aggregate from the solution per unit time $(n = n_s)$; and j_c^+ $(j_c^+ > 0)$ is the number of surfactant monomers absorbed by the critical molecular aggregate from the solution per unit time $(n = n_c)$.

At the final stage of micellization, the $(c_1 - \tilde{c}_1)/\tilde{c}_1$ value (wavy bar denotes the values in the final state of solution equilibrium) is changed, according to estimate (5.3) in [4], by less than $1/\tilde{n}_s$. Within the interval of times shorter than the duration of final stage, the $(c_1 - \tilde{c}_1)/\tilde{c}_1$ value varies still much less. In view of (1.5) and (1.4) and $n_s > n_c$, this readily proves the assumption (used in [3]) on the constancy of concentration c_1 during determining the times t_s and t_c.

If times t_s, t', t'', and t_c give an idea of the evolution of the ensemble of molecular aggregates within the characteristic ranges of aggregation numbers, the average time τ_1 between the successive acts of emission of surfactant monomers by a micelle and the average value of micelle lifetime τ_M characterize a single micelle. For these times, we have

$$\tau_1 = 1/j_s^+, \qquad (1.11)$$

$$\tau_M = \pi \Delta n_c \Delta n_s \exp(W_c - W_s)/j_c^+ \qquad (1.12)$$

(expressions (3.4) and (3.7) in [3]). The shorter the time τ_1, the greater the ability of a micelle to change the composition of constituting molecules. The longer time τ_M, the more stable the micelle is as an aggregative molecular formation.

We assume, as in [5], that the velocity $\dot{n}$ of the variation (with time) of aggregation number n of molecular aggregate is given by the relation

$$\dot{n} = 4\pi D \frac{v R^2(c_1 - c_{1n})}{D + vR}. \qquad (1.13)$$

Here, D is the diffusion coefficient of monomers in micellar solution; v is the parameter characterizing the velocity of monomer absorption from the solution at the surface of molecular aggregate; R is the radius of aggregate (for simplicity, assumed to be spherical); c_{1n} is the concentration of monomers in an imaginary micellar solution, which is at material equilibrium (at the same temperature and pressure as the micellar solution being considered) with an aggregate of n molecules.

According to formula (3.20) in [2], the relation

$$\dot{n} = j_n^+(1 - c_{1n}/c_1) \qquad (1.14)$$

is valid, where j_n^+ ($j_n^+ > 0$) is the number of surfactant monomers absorbed from solution by the aggregate of n molecules per unit time. It follows from Eqs. (1.13) and (1.14) that

$$j_n^+ = 4\pi D c_1 \frac{vR^2}{D + vR} \qquad (1.15)$$

and in particular, for the critical and stable molecular aggregates

$$j_c^+ = 4\pi D c_1 \frac{vR_c^2}{D + vR_c},$$
$$\qquad\qquad (1.16)$$
$$j_s^+ = 4\pi D c_1 \frac{vR_s^2}{D + vR_s},$$

respectively, where R_c and R_s are the radii of these aggregates.

Formula (1.13) as well as formulas (1.15) and (1.16) refer to the steady-state regime of the matter exchange between solution and molecular aggregate. In the realistic (for micellar solution) situation, where the radius of molecular aggregate R is so small that $vR/D \ll 1$, the establishment of this regime occurs during time t_j, for which relation

$$t_j \approx 10^2 R^2/D \quad (vR/D \ll 1) \qquad (1.17)$$

was derived in [5]. Time t_j given by expression (1.17) supplements the set of the characteristic kinetic times of micellization.

Finally, for time t_r of the relaxation of micellar solution at the final stage of micellization, i.e., the time of the establishment of the final (at this stage) equilibrium state at the material isolation of a solution we have

$$t_r = \frac{\pi^{1/2}\tilde{c}_M\Delta\tilde{n}_c\exp(\tilde{W}_c)}{\tilde{c}_1 j_c^+}\left(1 + \frac{\tilde{n}_s^2\tilde{c}_M}{\tilde{c}_1}\right)^{-1} \qquad (1.18)$$

[expression (4.8) in [4]].

The manner in which concentrations $\tilde{c}_1$ and $\tilde{c}_M$ of surfactant monomers and micelles at the final equilibrium state of micellar solution at a given overall surfactant concentration can be determined, was demonstrated in [4]. In this case, concentrations $\tilde{c}_1$ and $\tilde{c}_M$ are interrelated by the equality

$$\tilde{c}_M/\tilde{c}_1 = \pi^{1/2}\Delta\tilde{n}_s\exp(-\tilde{W}_s) \qquad (1.19)$$

(equality (4.13) in [4]).

The $\tilde{n}_s\tilde{c}_M/\tilde{c}_1$ value represents the ratio of the amount of substance accumulated by micelles in the final equilibrium state of solution to the amount of substance remained in the form of monomers. Two representative limiting cases are of interest.

In the first of these case, the inequality

$$\tilde{n}_s^2\tilde{c}_M/\tilde{c}_1 \gg 1 \qquad (1.20)$$

is fulfilled; in view of inequality $\tilde{n}_s \gg 1$ followed from Eq. (1.2), this situation actually takes place when $\tilde{n}_s\tilde{c}_M/\tilde{c}_1 \gtrsim 1$; i.e., when micelles in the final state of solution equilibrium accumulate noticeable or even the major part of all amount of surfactant containing in solution. Then, according to Eq. (1.18), relation

$$t_r = \frac{\pi^{1/2}\Delta\tilde{n}_c\exp(\tilde{W}_c)}{\tilde{n}_s^2 j_c^+} \quad (\tilde{n}_s^2\tilde{c}_M/\tilde{c}_1 \gg 1) \qquad (1.21)$$

is valid (expression (4.10) in [4]).

In the second representative case, inequality

$$\tilde{n}_s^2\tilde{c}_M/\tilde{c}_1 \ll 1 \qquad (1.22)$$

is fulfilled. Furthermore, in view of $\tilde{n}_s \gg 1$, inequality $\tilde{n}_s\tilde{c}_M/\tilde{c}_1 \ll 1$ is also fulfilled; hence, micelles in the final state of solution equilibrium absorb only small part of the entire amount of surfactant containing in solution. Then, according to Eq. (1.18), relation

$$t_r = \frac{\pi^{1/2}\tilde{c}_M\Delta\tilde{n}_c\exp(\tilde{W}_c)}{\tilde{c}_1 j_c^+} \quad (\tilde{n}_s^2\tilde{c}_M/\tilde{c}_1 \ll 1) \qquad (1.23)$$

is true (expression (4.12) in [4]).

2. HIERARCHY OF THE CHARACTERISTIC KINETIC TIMES OF MICELLIZATION

Let us disclose the hierarchy of the characteristic times of micellization. According to relations (1.8)–(1.10), we have

$$t'/t_c \approx 2n_c/\Delta n_c,$$
$$\qquad\qquad (2.1)$$
$$t''/t_c \approx 2(n_s - n_c)/\Delta n_c.$$

Taking conditions (1.1) into account and using estimate $n_s - n_c \gtrsim n_c$ (which allows for the equality of the orders of magnitude for $n_s - n_c$ and n_c), we obtain from Eq. (2.1)

$$t''/t_c \gtrsim t'/t_c \gg 1. \qquad (2.2)$$

According to Eqs. (1.7) and (1.10), we have

$$t_c/t_s = (\Delta n_c/\Delta n_s)^2(j_s^+/j_c^+). \qquad (2.3)$$

Analytical models [6, 7] for the formation work W_n of molecular aggregate in surfactant solution do not result in large differences between the values of Δn_c and Δn_s. Assuming, as in [8], that the great difference in the j_c^+ and j_s^+ values is also improbable, we can see from Eq. (2.3) that

$$t_c/t_s \sim 1. \qquad (2.4)$$

According to Eqs. (1.7) and (1.11), we have

$$t_s/\tau_1 = (\Delta n_s)^2/2. \tag{2.5}$$

Substituting the first condition of (1.2) into Eq. (2.5), we obtain

$$t_s/\tau_1 \gg 1. \tag{2.6}$$

According to Eqs. (1.15) and (1.17), at $vR/D \ll 1$, we have

$$t_j j_n^+ \approx 4\pi \times 10^2 c_1 R^3 (vR/D) \quad (vR/D \ll 1). \tag{2.7}$$

Strong inequality $c_1 R^3 \ll 1$ is true: the number of monomers per solution volume that is equal (by the order of magnitude) to the volume of molecular aggregate ($\sim R^3$) is quite small due to a relatively small size of an aggregate and the dilution of a micellar solution. Then, from Eq. (2.7) with allowance for $vR/D \ll 1$, it follows that

$$t_j j_n^+ \ll 1. \tag{2.8}$$

According to Eq. (1.17), time t_j increases with R. Hence, it is the longest time in the micellar region of aggregate sizes. Applying inequality (2.8) to this region, using Eq. (1.11) we obtain

$$t_j/\tau_1 \ll 1, \tag{2.9}$$

that is true at any sizes of molecular aggregates (including those in a micellar region).

Further we consider the representative case where inequality (1.20) or reverse inequality (1.22) are true.

According to Eqs. (1.21) and (1.9), in the first representative case we have

$$t_r/t'' \approx \pi^{1/2} \exp(\tilde{W}_c)/(\tilde{n}_s - \tilde{n}_c)\tilde{n}_s^2 \quad (\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \gg 1) \tag{2.10}$$

[we used the estimate (1.9) as applied to the final stage of micellization]. Taking into account that the first inequality of (1.3) is extremely strong due to its exponential character, we readily obtain from Eq. (2.10)

$$t_r/t'' \gg 1 \quad (\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \gg 1). \tag{2.11}$$

Further, in the same representative case, according to Eqs. (1.12) and (1.21) with allowance for Eq. (1.19), we have

$$\tau_M/t_r = \tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \quad (\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \gg 1) \tag{2.12}$$

[we used expression (1.12) as applied to the final stage of micellization]. From Eq. (2.12) with the fulfillment of inequality (1.20), directly follows

$$\tau_M/t_r \gg 1 \quad (\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \gg 1). \tag{2.13}$$

In general, the set of relations (2.2), (2.4), (2.6), (2.9), (2.11), and (2.13) discloses the following hierarchy of the times of micellization kinetics:

$$\tau_M \gg t_r \gg t'' \gtrsim t' \gg t_c \sim t_s \gg \tau_1 \gg t_j$$
$$(\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \gg 1). \tag{2.14}$$

The last five relation in the hierarchical sequence (2.14) are not related with the limit (1.20).

In the case when the inequality (1.20) is fulfilled, the final stage of micellization is preceded by the stage of its build-up. According to [4], the duration t_0 of this stage is not longer than time t_r by factor of 1.5–2.5. This allows us to easily find out the place of time t_0 in the hierarchy of the kinetic times of micellization.

Let us now pass to the second representative case where the inequality (1.22) is fulfilled. According to Eqs. (1.23) and (1.9), we have

$$t_r/t'' \approx \pi^{1/2} \exp(\tilde{W}_c)\tilde{c}_M/(\tilde{n}_s - \tilde{n}_c)\tilde{c}_1$$
$$(\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \ll 1) \tag{2.15}$$

[we used estimate (1.9) as applied to the final stage of micellization]. Substituting the first of inequalities (1.3), we readily obtain from Eq. (2.15)

$$t_r/t'' \gg 1 \quad (\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \ll 1). \tag{2.16}$$

Further, in the same representative case, according to Eqs. (1.12) and (1.23) with allowance for Eq. (1.19), we have

$$\tau_M/t_r = 1 \quad (\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \ll 1) \tag{2.17}$$

[we used expression (1.12) as applied to the final stage of micellization].

In total, the set of relations (2.2), (2.4), (2.6), (2.9), (2.16), and (2.17) discloses the following hierarchy of the kinetic times of micellization:

$$\tau_M = t_r \gg t'' \gtrsim t' \gg t_c \sim t_s \gg \tau_1 \gg t_j$$
$$(\tilde{n}_s^2 \tilde{c}_M/\tilde{c}_1 \ll 1). \tag{2.18}$$

The last five relations in the hierarchical sequence (2.18) are not related with the limit (1.22).

According to Eqs. (2.14) and (2.18), times t_s, t', t'', and t_c are much shorter than time t_r. This is easily proved by the fact that quasi-steady-state concentrations of molecular aggregates in subcritical and overcritical regions and quasi-steady-state concentration of molecular aggregates in the near-critical region that were qualitatively substantiated in [2] are actually established. As is seen from the proportionality between time t_r and exponent $\exp(\tilde{W}_c^+)$, the statement of the smallness of times t_s, t', t'', and t_c (compared with time t_r) is valid, as well as in the general case that is not related with inequalities (1.20) and (1.22), since, in the final analysis, it is the sequence of an extremely strong inequality (1.3).

It follows from Eqs. (2.14) and (2.18) that time t_j is the shortest time of all characteristic times of micellization. This indicates that the kinetic process of micellization begins with the formation of quasi-steady-state absorption intensities j_n^+, j_c^+, and j_s^+.

Time τ_M ranks first and time τ_1 is the second-smallest among the characteristic times of the micellization kinetics in the hierarchical sequences (2.14) and (2.18). This demonstrates that the micelles are stable molecular formations, which are quite capable of renewing the composition of constituting molecules.

As was mentioned in [3], time τ_1 determines (via $n_s\tau_1$) the average value of the resident time of a surfactant monomer specified (labeled) in a micelle. Denoting this time by τ_2, we thus arrive at

$$\tau_2 = n_s\tau_1. \tag{2.19}$$

It follows from Eqs. (2.5) and (2.19) that

$$t_s/\tau_2 = (\Delta n_s)^2/2n_s. \tag{2.20}$$

According to [6, 7], the value in the right-hand side of Eq. (2.20) is close (by the order of magnitude) to unity. Then, we have

$$\tau_2 \sim t_s. \tag{2.21}$$

Estimate (2.21) allows us to easily establish the place occupied by time τ_2 in the hierarchy of kinetic times.

3. TIME OF THE FAST RELAXATION OF MICELLAR SOLUTION

Let us elucidate the interrelation between time t_s and the time of fast relaxation of solution that was found in [8]. This makes it possible to clarify the concepts of fast and slow relaxations of micellar solution introduced in [8] and widely used in literature as the concepts corresponding to the process of local rearrangement of micelles without changing their numbers in a micellar region and to the process of the establishment of final equilibrium in the entire micellar system.

We denote the values corresponding to the end of fast relaxation of micellar solution by superscript zero. Denote via

$$\xi_n = (c_n - c_n^0)/c_n^0 \tag{3.1}$$

the relative deviation of current concentration c_n of aggregates from concentration c_n^0. Assuming that the fast relaxation is implemented via the emission and absorption of monomers only in a micellar region, we take into account in Eq. (3.1) only the aggregates in a micellar region and (at $n = 1$) the monomers. Together with the aggregation number n, we use also variable

$$u = (n - n_s^0)/\Delta n_s^0, \tag{3.2}$$

varying within $-1 \le u \le 1$ range to describe the aggregates in micellar region.

The total micelle concentration c_M is evidently determined by the equality

$$c_M = \int\limits_{n_s^0 - \Delta n_s^0}^{n_s^0 + \Delta n_s^0} c_n dn, \tag{3.3}$$

where the integration is performed over the micellar region. Suggesting that micelle concentration c_n^0 after the termination of fast relaxation satisfies Boltzmann's principle; i.e., it is proportional to $\exp(-W_n)$, using relation

$$W_n = W_s + \left(\frac{n - n_s}{\Delta n_s}\right)^2 \tag{3.4}$$

(relation (1.6) in [2]), and allowing for Eqs. (3.2) and (3.3), we obtain

$$c_n^0 = \frac{c_M^0}{\pi^{1/2}\Delta n_s^0}e^{-u^2} \quad (-1 \le u \le 1). \tag{3.5}$$

The solution of the kinetic equation for the micellar region at the material isolation of a solution was constructed in [8] on the basis of expansion

$$\xi_n(t) = \sum_{i=0}^{\infty}\alpha_i(t)H_i(u) \quad (-1 \le u \le 1) \tag{3.6}$$

according to the full-length system of Hermitian polynomials $H_i(u)$, where $\alpha_i(t)$ are u-independent coefficients of expansion, which are desired functions of time t.

It was shown [8] that $d\alpha_0(t)/dt = 0$, and, hence, coefficient $\alpha_0(t)$ is time-invariant. We then assume

$$\alpha_0(t) = 0 \tag{3.7}$$

(it was not unambiguously mentioned in [8]). Equality (3.7) makes it possible to prove that final concentrations c_n^0 in Eq. (4.1) are not achieved at the end of fast relaxation of a micellar solution.

According to [8], relations

$$\alpha_1(t) = \alpha_1(0)e^{-t/t_1}, \tag{3.8}$$

$$\alpha_i(t) = \alpha_i(0)e^{-it/t_s} \quad (i = 2, 3, \ldots) \tag{3.9}$$

are true provided that equality (3.7) is fulfilled. Here, $\alpha_1(0)$, $\alpha_2(0)$, ... are the values of coefficients $\alpha_1(t)$, $\alpha_2(t)$, ... at the initial (for fast relaxation) time $t = 0$. Times t_1 and t_s are defined by equalities

$$t_1 = 1/(\bar{j}_s)^0[2/(\Delta n_s^0)^2 + c_M^0/c_1^0], \tag{3.10}$$

$$t_s = (\Delta n_s^0)^2/2(\bar{j}_s)^0, \tag{3.11}$$

where $(\bar{j}_s)^0$ is the number of monomers emitted into solution by the stable molecular aggregate per unit time after the end of fast relaxation of solution. Evidently, this number coincides with the number of monomers

$(j_s^+)^0$ absorbed from solution by the stable molecular aggregate per unit time at the end of fast relaxation of solution. Hence, equality (3.11) is consistent with equality (1.7).

According to [8], relation

$$\xi_1(t) = -\frac{c_M^0 \Delta n_s^0}{c_1^0} \alpha_1(t), \qquad (3.12)$$

where $\alpha_1(t)$ is given by relation (3.8), is also true, provided that equality (3.7) is fulfilled.

It follows from Eq. (3.3) with allowance for Eqs. (3.1), (3.2), and (3.5)–(3.7) and the relations of orthogonality and normalization of Hermitian polynomials that

$$c_M(t) = c_M^0. \qquad (3.13)$$

Upon the bimodal approximation of the total amount of substance in a solution (the fulfillment of equality (1.5) in [4]) and the material isolation of a solution, we have

$$c_1^0 + n_s^0 c_M^0 = c, \qquad (3.14)$$

where c is a given overall surfactant concentration (the total number of surfactant molecules per solution unit volume). Relation (3.14) determines the proportion of concentrations c_1^0 and c_M^0 at the end of fast relaxation of solution, but not these concentration as such.

According to Eqs. (3.10) and (3.11), we have

$$t_1 < t_s, \qquad (3.15)$$

$$t_1 = t_s \quad (c_M^0/c_1^0 \ll 2/(\Delta n_s^0)^2). \qquad (3.16)$$

Relations (3.1), (3.6)–(3.9), and (3.12) yield

$$c_n(t)|_{t \gg t_s} = c_n^0 \quad \text{(micellar region)}, \qquad (3.17)$$

where relations (3.15) and

$$c_1(t)|_{t \gg t_1} = c_1^0 \qquad (3.18)$$

are taken into account.

Relations (3.17) and (3.18) indicate that the time-independent aggregate concentrations c_n^0 in a micellar region and monomer concentration c_1^0 are actually established with time. If contributions from the higher terms of expansion (3.6) with $i = 2, 3, \ldots$ are ignored, the condition of applicability $t \gg t_s$ of relation (3.17) can be substituted by a weaker [in view of Eq. (3.15)] condition $t \gg t_1$. Then, it is evident that time t_1 defined by equality (3.10) is the time of fast relaxation of a micellar solution. The place occupied by this time in the hierarchy of the kinetic times of micellization is readily established by relations (3.15) and (3.16).

Fast relaxation of a micellar solution described using [8] is observable in an experiment. This relax-ation can be caused by the instantaneous external disturbance (for example, by temperature or pressure jumps) of equilibrium micellar solution at the instant $t = 0$. The external disturbance of solution was not considered in our theory [1–4], where the evolution of solution was caused exclusively by the internal processes beginning with the time when only monomers were present in a solution.

According to equalities (3.1), (3.8), and (3.12), monomer concentration $c_1(t)$ varies over the period of fast relaxation of a solution: increases at $\alpha_1(0) > 0$, and, on the contrary, decreases at $\alpha_1(0) < 0$. The greater the initial solution disturbance, the greater is the variation of concentration $c_1(t)$.

In view of equality (3.13), the total micelle concentration $c_M(t)$ does not vary in the course of fast relaxation of a micellar solution. However, micelle concentration varies at the slower (final) stage of micellization as well as at the stage preceding to its establishment. As was shown in [4], this variation is caused by the existence of direct J' ($J' > 0$) and reverse J'' ($J'' < 0$) fluxes of molecular aggregates over the potential barrier of aggregation work.

If it turns out that inequality $c_1^0 > \tilde{c}_1$ becomes valid as a result of the external disturbance of a solution, the monomer concentration will lower and the micelle concentration will increase after the fast relaxation is ended. However, if inequality $c_1^0 < \tilde{c}_1$ turns out to be valid, the monomer concentration increases and the micelle concentration lowers after the fast relaxation of a solution is ended. During the evolution of solution considered in [1–4], when the original solution contained only monomers and was not subjected to the external disturbance, the monomer concentration decreases and the micelle concentration increases over the entire evolution of a solution.

Let us explain how the study of the final stage of micellization and the stage of its establishment performed in [4] is generalized to the case of the external disturbance of a solution. The values of c_1^0 and c_M^0 of monomer and micelle concentrations, respectively, achieved at the end of fast relaxation of a solution serve as the initial values. If it turns out that $c_1^0 > \tilde{c}_1$, for the generalization we should only substitute, at the final stage, the initial monomer concentration c by the value c_1^0 retaining the previous final value $(1 + 1/\tilde{n}_s)\tilde{c}_1$ of this concentration. If it turns out that $c_1^0 < \tilde{c}_1$, for the generalization we should only substitute, at the establishment of a final stage, c_1^0 and $(1 - 1/\tilde{n}_s)\tilde{c}_1$ for the initial and final values of monomer concentration, respectively. We also should take into account that dominating, at this stage, is the reverse J' rather than direct J'' flux of molecular aggregates over the potential

barrier of the aggregation work. This can be easily done using expressions derived in [4] for the J' and J'' fluxes.

Both at $c_1^0 > \tilde{c}_1$ and $c_1^0 < \tilde{c}_1$, the relaxation time t_r of a solution at the final stage is determined in the same manner as in [4]. It can be proved that this time almost (even more exactly than in [4]) coincides with the duration t_0 of the establishment of the final stage.

Time t_r serves (in accordance with terminology of [8]) as the time of slow relaxation of a micellar solution. The place of this time in the hierarchy of the characteristic times of the micellization kinetics was established by the sequences in relations (2.14) and (2.18). Inequality $t_r \gg t_1$ followed from Eqs. (2.14), (2.18), and (3.15) is responsible for the possibility of the division of relaxation of micellar solution into the fast and slow processes [8]. Note that, according to formulas (2.13) and (2.17), the $t_r \gg t_1$ inequality also follows from inequality $\tau_M \gg t_1$ that was implied in [8] during the discussion of the stage of fast relaxation.

4. INVERSE PROBLEM OF THE MICELLIZATION KINETICS

By now, there are relatively reliable published data on the position of the potential well of the formation work of surfactant molecular aggregate at the aggregation number axis (on the average micelle size) [6], as well as on the half-width of this well (the scatter of micelle sizes) [9, 10] and even on its depth, i.e., on minimum work (by data on micelle concentration). Even less reliable data are available on the position and the half-width of the potential barrier of a work. Still less reliable are the data on the height of potential barrier (maximum work). The significance of the knowledge of the maximum formation work of surfactant molecular aggregate is explained by the fact that, according to formulas (1.12), (1.18), (1.21), and (1.23) it affects the kinetics of micellization. Because this effect is exponential, it turns out to be extremely strong.

Formulas (1.18), (1.21), and (1.23) make it possible to find the value of $\exp(\tilde{W}_c)$, which is extremely large and quite sensitive to the surfactant monomer concentration [in view of relations (1.3) and (1.4) and inequality $\tilde{n}_c \gg 1$], from the experimental data on the relaxation time of micellar solution. Although data on maximum work are, in this case, obtained by the velocity of the establishment of the equilibrium state of micellar solution, they are also true for its arbitrary state. Indeed, as was shown in [1], the formation work of molecular aggregate and, hence, its maximal value, are not related by their physical meaning to the fact whether micellar solution is at equilibrium or not.

Let us consider the proposed inverse problem of micellization using as an example the representative case when inequalities (1.20) and $vR_c/D \ll 1$ are fulfilled.

Solving Eq. (1.21) with respect to $\exp(\tilde{W}_c)$, we obtain

$$\exp(\tilde{W}_c) = \frac{\tilde{n}_s^2 \tilde{j}_c^+}{\pi^{1/2} \Delta \tilde{n}_c} t_r \quad (\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 \gg 1). \quad (4.1)$$

From Eq. (4.1) with allowance for relation

$$j_c^+ \approx 4\pi c_1 v R_c^2 \quad (vR_c/D \ll 1), \quad (4.2)$$

followed from (1.16) at $vR_c/D \ll 1$, we have

$$\exp(\tilde{W}_c) \approx (4\pi^{1/2} \tilde{n}_s^2 \tilde{c}_1 v \tilde{R}_c^2 / \Delta \tilde{n}_c) t_r$$
$$(v\tilde{R}_c/D \ll 1, \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 \gg 1). \quad (4.3)$$

Relation (4.2) depends on the parameter v characterizing the rate of monomer absorption from solution at the surface of molecular aggregate; however, it does not depend on the diffusion coefficient D of monomers in a solution. This demonstrates that, essentially, relation (4.2) is not connected with the equation of diffusion of monomers in a solution, which can be even inapplicable in the vicinity of molecular aggregate with small sizes [suggested in (4.2)]. All what have been said above is confirmed by inequality (2.8). Indeed, according to Eq. (2.8), time t_j of the establishment of quasi-steady-state regime of matter exchange between solution and molecular aggregate is much shorter than time $1/j_n^+$ between two successive acts of absorption of a monomer from solution by a molecular aggregate in this regime; this would be impossible, if t_j and j_n^+ had determined by the diffusion process of monomers in a solution up to the vicinity of molecular aggregate.

Formula (4.3) allows us to directly find $\exp(\tilde{W}_c)$ from the experimental data on the relaxation time t_r of micellar solution. In view of extremely large value of exponent $\exp(\tilde{W}_c)$ and its quite high sensitivity to the concentration of surfactant monomers, it is sufficient to monitor in Eq. (4.3) only the order of magnitude. Note that, in accordance with what has been said in Section 1, the relaxation time t_r almost coincides with the total time of the establishment of equilibrium in a materially isolated micellar solution.

According to formulas (4.3) and (1.4), it should be expected that time t_r decreases with an increase in concentration $\tilde{c}_1$ of surfactant monomers. This conclusion of the theory is supported by the experimental data reported in [9, 10].

We underline that only the kinetic approach to the micellization problem developed by us in [1–4] made it possible to relate the maximum formation work of surfactant molecular aggregate with the experimental data. This maximum is not generally included into the formulas of the theory of equilibrium micellization. These formulas contain, according to Eq. (1.19), only the min-

imum formation work of surfactant molecular aggregate.

Let us assume, in accordance with [6,7], the following values of parameters that are realistic by the order of magnitude:

$$\tilde{n}_s \sim 10^2, \quad \Delta\tilde{n}_c \sim 10, \quad \tilde{c}_1 \sim 10^{17}\ \text{cm}^{-3},$$
$$\tilde{R}_c \sim 10^{-7}\ \text{cm}, \quad v \sim 1\ \text{cm s}^{-1}. \tag{4.4}$$

The value for v was chosen in (4.4) such that it secures the fulfillment of inequality $v\tilde{R}_c/D \ll 1$ employed in Eqs. (4.2) and (4.3).

Let us consider two micellar solutions where monomer concentrations at the final state of equilibrium are almost identical and given by the estimate shown in (4.4). Denoting corresponding values for these solutions by superscripts 1 and 2, we have $\tilde{c}_1^{(1)}/\tilde{c}_1^{(2)} \approx 1$. According to inequalities (2.20), (2.21), and (4.14) in [4], we also have

$$\tilde{c}_M^{(1)}/\tilde{c}_M^{(2)} = (\tilde{c}_1^{(1)}/\tilde{c}_1^{(2)})^{\tilde{n}_s}, \tag{4.5}$$

$$\exp(\tilde{W}_c^{(1)})/\exp(\tilde{W}_c^{(2)}) = (\tilde{c}_M^{(2)}/\tilde{c}_M^{(1)})^{(\tilde{n}_c-1)/\tilde{n}_s}, \tag{4.6}$$

$$t_r^{(1)}/t_r^{(2)} = (\tilde{c}_M^{(2)}/\tilde{c}_M^{(1)})^{\tilde{n}_c/\tilde{n}_s}. \tag{4.7}$$

Because, according to (4.4), $\tilde{n}_s \sim 10^2$, Eq. (4.5) demonstrates that, at almost identical monomer concentrations in the final states of solution equilibrium, micelle concentrations in these states can be quite different. Then it is convenient [at the accepted in (4.4) order of magnitudes of concentration $\tilde{c}_1$] to characterize the final states of equilibrium by the concentrations of micelles that are just entered into the right-hand sides of equalities (4.6) and (4.7). Furthermore, these concentrations can be relatively easy observed in the experiment.

From Eq. (4.3) with allowance for (4.4), we obtain

$$\exp(\tilde{W}_c^{(1)}) \sim 10^7 t_r^{(1)}, \quad \exp(\tilde{W}_c^{(2)}) \sim 10^7 t_r^{(2)}, \tag{4.8}$$

where times $t_r^{(1)}$ and $t_r^{(2)}$ are expressed in seconds. Let us assume that

$$\tilde{c}_M^{(1)} \sim 10^{15}\ \text{cm}^{-3}, \quad \tilde{c}_M^{(2)} \sim 10^{18}\ \text{cm}^{-3}. \tag{4.9}$$

According to Eqs. (4.9) and (4.4), we have $\tilde{n}_s\tilde{c}_M^{(1)}/\tilde{c}_1 \sim 1$, $\tilde{n}_s\tilde{c}_M^{(2)}/\tilde{c}_1 \sim 10^3$ that are quite realistic estimates. Note that estimates (4.9) and (4.4) and realistic estimate $\Delta\tilde{n}_s \sim 10$ [7] lead, according to formula (1.19), to $\exp(\tilde{W}_s^{(1)}) \sim 10^3$ and $\exp(W_s^{(2)}) \sim 1$ that are also quite true values.

Accepted estimates (4.9) and (4.4) readily secure the fulfillment of inequality (1.20) used in Eqs. (4.1)

and (4.3) and, in view of Eq. (4.5), also the fulfillment of suggested approximate equality of concentrations $\tilde{c}_1^{(1)}$ and $\tilde{c}_1^{(2)}$.

It follows from (4.7) and (4.9) that

$$t_r^{(1)}/t_r^{(2)} \sim 10, \tag{4.10}$$

where the realistic estimate $\tilde{n}_c \sim 30$ [7] was used and it was taken into account that $\tilde{n}_s \sim 10^2$ [in accordance with (4.4)]. The fact that, according to relation (4.10), times $t_r^{(1)}$ and $t_r^{(2)}$ can differ substantially (by an order of magnitude), makes it possible to experimentally verify the relation (4.7). Experimental verification of relation (4.7) could be an important argument in favor the micellization theory developed by us and, hence, in favor of the validity of relation (4.3) that allows us to find exponent $\exp(\tilde{W}_c)$ from the experimental data on the relaxation time t_r of micellar solution.

If the values of exponents $\exp(\tilde{W}_c^{(1)})$ and $\exp(\tilde{W}_c^{(2)})$ determined with the aid of relations of (4.8) type and experimental data on times $t_r^{(1)}$ and $t_r^{(2)}$ would agree with the equality (4.6), this could be yet another confirmation of the validity of the developed kinetic theory of micellization.

ACKNOWLEDGMENTS

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