Russian Journal of Physical Chemistry, Vol. 79, No. 6, 2005, pp. 833–853. Translated from Zhurnal Fizicheskoi Khimii, Vol. 79, No. 6, 2005, pp. 967–990.

ON THE 75th ANNIVERSARY OF THE RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY

Kinetics of Aggregation in Micellar Solutions

F. M. Kuni, A. I. Rusanov, A. K. Shchekin, and A. P. Grinin
Fock Research Institute of Physics, St. Petersburg State University, Ul'yanovskaya ul. 1, Petrodvorets, 198904 Russia
E-mail: Alexander.Shchekin@pobox.spbu.ru

Received July 7, 2004

Abstract—Small parameters were introduced for describing the kinetics of aggregation of nonionic surfactants in solutions in an analytical form. The direct and reverse transition of molecular aggregates over the activation barrier of aggregation at a surfactant concentration between the first and second critical micellation concentrations was described. The kinetics of the initial stages of micellation was considered. Expressions for the characteristic times of attainment of the quasi-equilibrium concentrations of molecular aggregates in the micellar, subcritical, and supercritical regions, as well as the time of attainment of the quasistationary concentration of molecular aggregates in the near-critical size region were derived. The times of rapid and slow relaxation of the solution were examined. The total time it takes to establish the state of complete equilibrium in the solution was determined. It was demonstrated that this time decreases with increasing concentration of micelles. A probabilistic–statistical interpretation of the mean time interval between two consecutive emissions of a surfactant monomer from a micelle, the mean life time of a surfactant monomer in the micelle, and the mean lifetime of a micelle was proposed. The hierarchy of characteristics times of aggregation in micellar solutions, which characterize a complex multistage character of the nucleation and decomposition of micelles and the establishment of equilibrium in micellar solutions, was discussed. It was demonstrated that these hierarchy arise due to the existence of small parameters in the kinetic theory of aggregation.

Only a small fraction of the vast body of publications on surfactant solutions concern the kinetic of aggregation in micellar solutions, a fact that can be explained by the enormous complexity of micellation processes. The pioneering studies of micellation kinetics were motivated by the desire to gain insights into the experimentally observed stages of the slow and rapid relaxation of micellar solutions. An explanation of the nature of these times was given in [1–5]. The concept of the stepwise growth of micelles proposed in [1], by analogy with homogeneous nucleation, became widespread and has been used to describe more complex systems (see, e.g., [5–7]). Based on the concept of aggregation as a process involving the overcoming of a barrier, this approach stopped short of fully using the methodology of the nucleation theory in establishing relationships between the main characteristic of aggregation, properties of molecular aggregates of various sizes, and the parameters of the initial and final states of the micellar solution. Since experimental information on premicellar aggregates, especially critical nuclei of micelles, was limited at that time, the development of the kinetic theory of aggregation slowed down.

In recent years, however, a revival of interest in the kinetics of micellation has been observed. In the studies [8–10], the stepwise aggregation scheme [1] based on the Becker–Döring [11] was examined to find out whether this scheme described irreversible behavior and provided stable solution. As a result, a simplified calculation procedure was proposed, which made it possible to optimize the algorithms for solving the system of kinetic equations of aggregation. Advances in the nucleation theory, in particular, in solving the problems of ion-induced nucleation [12] and heterogeneous nucleation on wettable particles [13, 14] (processes similar to micellation), have also been made.

To construct a kinetic theory of micellation in surfactant solutions, it is necessary to know the thermodynamic characteristics of formation of a molecular surfactant aggregate (work of aggregation). Under conditions important for practice, when the total surfactant concentration exceeds the first critical micellation concentration (CMC) but is lower than the second CMC (beginning with which a considerable fraction of the surfactant forms cylindrical micelles [15–17]), the work of aggregation as a function of the aggregation number has not only a hump but also a well (to the right of the hump) after which the work of aggregation tend to infinity with increasing aggregation number [18–21]. The existence of the hump and well in the aggregation work–aggregation number dependence make the kinetic theory of micellation more complex than the kinetic theory of homogeneous nucleation, in which the work of formation of a nucleus as a function of the number of constituent molecules has only a maximum, monotonically decreasing to either side of it.

As in the kinetic theory of nucleation, an important characteristic of the kinetic theory of micellation is the fluctuation-driven flux of molecular aggregates through the hump from the region located to the left from it. However, since the aggregation work–aggregation number dependence for micellar solution has a well after the hump, the reverse fluctuation-driven flux from the well becomes important. The determination of the direct and reverse fluxes of molecular aggregates through hump (barrier to aggregation) plays a key role in constructing kinetic models of aggregation in analyzing the stages of micellation.

In the present review, the different stages of micellation in surfactant solutions were considered from a single point of view on the basis of the results obtained in [22–26]. The problem of the relaxation of a micellar solution at the final stage of micellation (near the state of complete equilibrium) at concentrations between the first and second CMCs was solved and an analytical expression for the time of attainment of this stage was derived. The overall time of attainment of the final equilibrium state in micellar solutions was obtained.

An important aspect of the review is a discussion of the hierarchy of characteristic times of micellation. This hierarchy gives a graphic representation of the relative values of the characteristic times of formation and decomposition of micelles and of the complex, multistage process of approach of the micellar solution to the state of equilibrium.

1. WORK OF AGGREGATION AND THE LAW OF MASS ACTION

Let us consider a solution of a single-component nonionic surfactant capable of forming molecular aggregates in a polar liquid not participating in the formation of aggregates, for example, water. Let the solution be ideal (infinitely dilute). The aggregates were postulated to be dense formations with the temperature equal to that of the solution. The internal state of an aggregate was characterized by the number of molecules n it comprises (aggregation number). This discrete characteristic is convenient, since it remains an adequate parameter down to $n = 1$, when an aggregate consists of a single surfactant molecule.

Let μ_n and c_n be the chemical potential and concentration of aggregates composed of n molecules (the number of aggregates per unit volume), with μ_1 and c_1 being the chemical potential and concentration of monomers, respectively. For the nonionic surfactant under consideration, all the monomers are identical.

When considering the process of aggregation, it is convenient to present the chemical potential μ_n of a molecular aggregate as

$$\mu_n = G_n^\circ + kT\ln(\Lambda_n^3 c_n f_n), \qquad (1)$$

where G_n° is the Gibbs energy of an aggregate composed of n surfactant molecules with its center of mass at rest in a pure solvent (in the absence of other aggregates), $\Lambda_n = h(2\pi m_n kT)^{-1/2}$ is the contribution from the averaged momentum of the molecular aggregate as a whole (it has a dimensionality of length; h is Planck's constant, and m_n is the mass of the molecular aggregate), and f_n is the activity coefficient of the aggregate. The quantity Λ_n^{-3} is the partition function of the translational motion of the aggregate, with $kT\ln\Lambda_n^3$ being the corresponding contribution to the Gibbs free energy. The quantity $kT\ln f_n$ is the contribution from the interaction of the aggregates with one another.

Let us recast (1) as

$$\mu_n = G_n + kT\ln(c_n/c_{\mathrm{st}}), \qquad (2)$$

where G_n is the chemical potential (Gibbs energy) of a molecular aggregate at a fixed standard concentration c_{st}. Formula (2) is valid in the absence and presence of the interaction between the aggregates in the standard state. Since the solution was postulated to be ideal, we assumed that the standard state at the concentration c_{st} is ideal as well. In other words, we set $f_n = 1$ in formulas (1) and (2).

When the fluctuation-mode nucleation of aggregates with $n = 2, 3, \ldots$ occurs in a solution that initially contained only surfactant monomers, it is convenient to set $c_{\mathrm{st}} = c_1$; thus, (2) yields

$$\mu_n = G_n + kT\ln(c_n/c_1). \qquad (3)$$

The $c_{\mathrm{st}} = c_1$ definition is convenient because a solution containing monomers in a concentration of c_1 is characterized by

$$G_1 = \mu_1, \qquad (4)$$

i.e., the Gibbs energy G_1 coincides with the chemical potential μ_1, an equality that follows from (3).

Let us consider the most important case in practice, i.e., aggregation at constant temperature and pressure. In this case, the Gibbs energy is an appropriate thermodynamic potential (its increment is the work done on the system). If any of c_1 monomers in a unit volume of the solution can grow into a molecular aggregate, the work of aggregation is given by

$$W_n = (G_n - n\mu_1)/kT. \qquad (5)$$

The work W_n is expressed in kT units. The term $n\mu_1$ in (5), the total Gibbs energy of n monomers, suggests that the formation of aggregates occurs in a solution that initially contained only monomers. In this case, the work W_n is independent of the concentrations c_n at $n \geq 2$, being dependent, however, on the concentration of monomers c_1. As follows from (4) and (5),

$$W_1 = 0. \qquad (6)$$

Indeed, no work is required to form monomers from monomers.

Let the Gibbs energy per unit volume of solution be G, then, $G = \sum_{n\geq 1}\mu_n c_n$.

At constant temperature and pressure, we have

$$dG = \sum_{n \geq 1} \mu_n dc_n. \tag{7}$$

If the system is materially isolated, the total concentration of the solution

$$c = c_1 + \sum_{n \geq 2} n c_n \tag{8}$$

is constant.

Differentiating either side of Eq. (8) yields

$$dc_1 = -\sum_{n \geq 2} n dc_n. \tag{9}$$

Substituting Eq. (9) into (7) results in

$$dG = \sum_{n \geq 2} (\mu_n - n\mu_1) dc_n. \tag{10}$$

As can be seen, the aggregative equilibrium for a materially isolated solution at constant temperature and pressure (characterized by $dG = 0$) is attained at

$$\mu_n^{(\mathrm{e})} = n\mu_1, \tag{11}$$

where the superscript e corresponds to the aggregates are at equilibrium with one another.

From Eqs. (3) and (5), it follows that

$$\mu_n - n\mu_1 = kT[W_n + \ln(c_n/c_1)]. \tag{12}$$

Combining Eqs. (11) and (12) yields the expression for the equilibrium concentration of aggregates:

$$c_n^{(\mathrm{e})} = c_1 \exp(-W_n). \tag{13}$$

The equation (13) corresponds to the Boltzmann fluctuation principle. Note that (12) can be obtained immediately from Eqs. (11) and (13), and the expression $\mu_n - \mu_n^{(\mathrm{e})} = kT\ln(c_n/c_n^{(\mathrm{e})})$ for ideal solutions.

Let A_n be the chemical affinity defined as

$$A_n = -(\mu_n - n\mu_1) \quad (n = 1, 2, \ldots). \tag{14}$$

In view of (14), Eq. (10) can be recast as

$$dG = -\sum_{n \geq 2} A_n dc_n. \tag{15}$$

If the aggregates are at equilibrium with one another, combining Eqs. (11) and (14) yields

$$A_n^{(\mathrm{e})} = 0 \quad (n = 1, 2, \ldots). \tag{16}$$

Substituting Eq. (12) into Eq. (14), we obtained

$$A_n = -kT[W_n + \ln(c_n/c_1)] \quad (n = 1, 2, \ldots). \tag{17}$$

Expression (17) shows how the affinity A_n depends on the work of aggregation and the concentration of aggregates. According to (17), the affinity A_n increased with decreasing work W_n and ratio c_n/c_1.

Since the chemical potentials μ_n and μ_1 for an ideal solution depend on the concentrations c_n and c_1 through the terms $kT\ln c_n$ and $kT\ln c_1$, the condition of aggregative equilibrium (11) yields the law of mass action:

$$c_n^{(\mathrm{e})} = K_n c_1^n, \tag{18}$$

where the coefficient K_n is independent of the concentrations c_1 and c_n ($n \geq 2$), being dependent only on the aggregation number n.

From Eqs. (13) and (18), it follows that

$$W_n = -\ln K_n - (n-1)\ln c_1. \tag{19}$$

The term $-(n - 1)\ln c_1$ in Eq. (19) presents an explicit dependence of the work W_n on the concentration of monomers c_1 (W_n is independent of the concentrations c_n with $n \geq 2$). According to the physical meaning of W_n, its value is independent of whether the concentration of aggregates corresponds to the state of equilibrium; therefore, Eq. (19) is valid at an arbitrary concentration of aggregates in an ideal solution.

2. KINETIC EQUATION OF AGGREGATION IN MICELLAR SOLUTIONS

According to the principles of the classical nucleation theory [11, 27], the number of molecules in an aggregates changes only via the addition or removal of a monomer. Let us consider the corresponding pair of forward and reverse transitions of aggregates:

$$\{n\} + \{1\} \rightleftharpoons \{n+1\} \quad (n = 1, 2, \ldots), \tag{20}$$

where $\{n\}$ denotes aggregates containing n molecules. An important parameter in the classical nucleation theory is the flux J_n of aggregates for each pair (20), which reads

$$J_n = j_n^+ c_n - j_{n+1}^- c_{n+1} \quad (n = 1, 2, \ldots). \tag{21}$$

Here, j_n^+ is the number of monomers added to an aggregate $\{n\}$ from the solution per unit time and j_{n+1}^- is the number of monomers removed into the solution over the same period. Clearly, $j_n^+ > 0$ and $j_{n+1}^- > 0$.

The rate of variation of the concentration c_n ($n \geq 2$) is expressed through the flux as

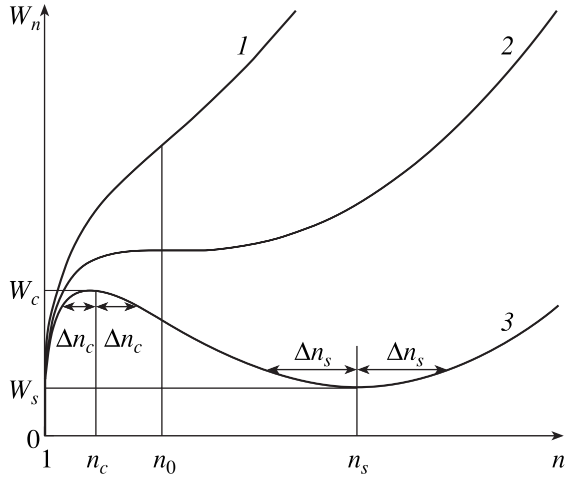
$$\partial c_n/\partial t = J_{n-1} - J_n \quad (n = 2, 3, \ldots). \tag{22}$$

For aggregative equilibrium, when (11) is valid, the condition of detailed equilibrium between aggregates should be fulfilled for each pair of transitions; i.e.,

$$J_n^{(\mathrm{e})} = 0 \quad (n = 1, 2, \ldots), \tag{23}$$

where $J_n^{(\mathrm{e})}$ is given by expression (21) at $c_n = c_n^{(\mathrm{e})}$.

Since the aggregates were postulated to be highly dense, j_n^+ and j_{n+1}^- are independent of whether the solution is in the state of aggregative equilibrium at a



Dependence of the work W_n of formation of a molecular surfactant aggregate on the aggregation number n at various concentrations of surfactant monomers: (*1*) $c <$ CMC1, (*2*) $c \lesssim$ CMC1, and (*3*) CMC1 $< c <$ CMC2; c is the total concentration of the surfactant, while CMC1 and CMC2 are the first and second CMCs, respectively.

given concentration c_1, combining Eqs. (21) and (23) yields

$$j^-_{n+1} = j^+_n c_n^{(e)}/c_{n+1}^{(e)} \quad (n = 1, 2, \ldots). \tag{24}$$

Substituting (13) into (24), we obtain

$$j^-_{n+1} = j^+_n \exp(W_{n+1} - W_n) \quad (n = 1, 2, \ldots). \tag{25}$$

Substituting (25) in (21) results in

$$J_n = j^+_n [c_n - c_{n+1}\exp(W_{n+1} - W_n)] \quad (n = 1, 2, \ldots). \tag{26}$$

Combining Eq. (22) with (26) yields a kinetic equation for the formation of molecular aggregates. This equation is also called the Becker–Döring equation of stepwise evolution; it was first used to describe the kinetic of homogeneous nucleation of vapor [11]. The mathematical aspects of these equations were considered in [28]. Using Eq. (17), it is possible to write (26) as

$$J_n = j^+_n c_n \{1 - \exp[-(A_{n+1} - A_n)/kT]\} \quad (n = 1, 2, \ldots). \tag{27}$$

For aggregative equilibrium, when equality (16) is satisfied, formula (27) confirms detailed equilibrium condition (23).

When performing a detailed description of a nonequilibrium process in a dispersed system within the framework of the kinetic theory, it is natural to decide whether aggregation or disaggregation occurs on the basis of the ratio of the rates of the forward and reverse transitions for each pair (20) as a function of the time. Clearly, for a pair of transitions at a given moment of time, aggregation or disaggregation occurs depending on whether $J_n > 0$ or $J_n < 0$, respectively.

Since $j^+_n > 0$, formula (27) suggests that

$$\left.\begin{array}{l} J_n > 0(\text{aggregation}),\ \text{if}\ A_{n+1} - A_n > 0 \\ J_n < 0(\text{disaggregation}),\ \text{if}\ A_{n+1} - A_n < 0 \end{array}\right\} \tag{28}$$
$$(n = 1, 2, \ldots).$$

Using Eq. (17), we obtained

$$A_{n+1} - A_n = -kT[W_{n+1} - W_n + \ln(c_{n+1}/c_n)] \quad (n = 1, 2, \ldots), \tag{29}$$

which shows that the sign of the difference $A_{n+1} - A_n$ depends not only on $W_{n+1} - W_n$, but also on $\ln(c_{n+1}/c_n)$, i.e., on the random-fluctuation factor. Conditions (28) and relationship (29) are valid when a dispersed system evolves starting from an arbitrary initial state.

If a dispersed system contained only monomers at the initial moment of time, the inequalities $c_1 \gg c_2 \gg c_3 \gg c_4 \ldots$ would be satisfied, at least shortly after this moment, giving rise according to (29) to the inequalities $0 < A_2 - A_1 < A_3 - A_2 < A_4 - A_3 \ldots$ irrespective of whether W_n increases with n from $W_1 = 0$ at $n = 1$. Inequalities (28) suggest that, within a short period after the initial moment, aggregation is prevalent in the dispersed system at any step of the nonequilibrium process. The driving force of this process is the random-fluctuation factor, which, however, can be substantially counterbalanced by the energetic factor.

To demonstrate that, irrespective of the initial state of a materially isolated solution at constant temperature and pressure, the kinetic theory predicts the monotonic decrease in its Gibbs energy with time, we recast Eq. (15) as

$$\partial G/\partial t = -\sum_{n \ge 2} A_n \partial c_n/\partial t. \tag{30}$$

Using Eq. (22), we obtained (after changing the summation index and taking into account that $A_1 = 0$)

$$\partial G/\partial t = -\sum_{n \ge 1} (A_{n+1} - A_n) J_n. \tag{31}$$

According to (28), at $n \ge 1$, the sign of the flux J_n coincides with that of the difference $A_{n+1} - A_n$; then, Eq. (31) yields

$$\partial G/\partial t \le 0. \tag{32}$$

The equality in (32) is fulfilled only if $J_n = 0$ and, hence, $A_{n+1} - A_n = 0$ at $n \ge 1$, i.e., for the aggregative equilibrium state of the solution (according to Eqs. (23) and (27)).

Thus, irrespective of the initial state of a materially isolated solution at constant temperature and pressure, the kinetic theory predicts that its Gibbs energy should monotonically decrease with time (inequality (32)) until the Gibbs energy attains its minimum value at the final state of aggregative equilibrium of the solution. Since the monotonic decrease of the Gibbs energy of a system suggests, according to the principles of thermodynamics, that the system tends irreversibly to the state of complete thermodynamic equilibrium, inequality (32) provides a kinetic substantiation of the irreversible evolution of the solution to the state of aggregative equilibrium.

That a system tends irreversibly to thermodynamic equilibrium is one of the main postulates of thermodynamics. In particular, this postulate underlies the derivation of the conditions of thermodynamic stability of a system in the state of thermodynamic equilibrium. The postulate of a system irreversibly tending to thermodynamic equilibrium can be substantiated only within the framework of a kinetic approach, for example, Boltzmann kinetic equation, irreversible thermodynamics equations, Fokker–Planck equation, and Markovian process equations. The above analysis of the aggregation in micellar solutions was based on the Becker–Döring equations ((22) and (26)).

3. SUBCRITICAL, NEAR-CRITICAL, AND MICELLAR SIZE REGIONS OF AGGREGATES

According to Eq. (19), the work of aggregation W_n depends on the concentration of monomers c_1 through the term $-(n-1)\ln c_1$. A typical dependence of W_n on n at various c_1 is displayed in the figure. Curve *1* corresponds to a total surfactant concentration substantially below the first CMC, curve *2* corresponds to a concentration immediately below the first CMC, and curve *3* was obtained at a concentration above the first CMC but below the second CMC (the case under consideration); the behavior of curve *3* will be considered in detail. The aggregation numbers for the critical and stable aggregates, n_c and n_s, are the positions of the maximum and minimum in the dependence of W_n on n, while $W_c \equiv W_n|_{n=n_c}$ and $W_s \equiv W_n|_{n=n_s}$ are, respectively, the height the maximum and depth of the minimum; n_0 is the position of the inflection point in the aggregation work–aggregation number dependence. The hump in the aggregation work–aggregation number dependence acts as the barrier to micellation. The halfwidths of the hump and well in this dependence read

$$\begin{aligned}\Delta n_c &= [2/|\partial^2 W_n/\partial n^2|_{n=n_c}]^{1/2},\\ \Delta n_s &= [2/(\partial^2 W_n/\partial n^2)|_{n=n_s}]^{1/2}.\end{aligned} \tag{33}$$

The physical meaning of Δn_c and Δn_s will be considered below. The figure was plotted with consideration given to equality (6), which means that the monomers initially present in the solution require no work to be formed. For the sake of certainty, curve *3* in figure was plotted for $W_s > 0$ and not too high c_1.

The parameters n_c, n_s, W_c, W_s, Δn_c, and Δn_s, as the work W_n itself, depend on the concentration c_1 of surfactant monomers; these thermodynamic characteristics are used in the kinetic model of micellation considered below. Let us assume that

$$\Delta n_c \gg 1, \quad \Delta n_c/n_c \ll 1, \quad \Delta n_c/(n_s - n_c) \ll 1, \tag{34}$$

$$\Delta n_s \gg 1, \quad \Delta n_s/(n_s - n_c) \ll 1. \tag{35}$$

The first inequalities in (34) and (35) make it possible to consider n as a continuous parameter in the regions of the hump and well in the aggregation work–aggregation number dependence. The rest of the inequalities in (34) and (35) suggest that the hump and well in the aggregation work–aggregation number dependence are located at n values larger than 1 and do not overlap (figure). This can be expressed by the inequalities

$$\exp W_c \gg 1, \quad \exp W_c \gg \exp W_s, \tag{36}$$

which follow from (34) and (35). Conditions (34) and (35) are satisfied if the total surfactant concentration exceeds, at least slightly, the first CMC (the second of inequalities (34) is probability satisfied with a small margin). The conditions (34) and (35) mean that the aggregation numbers n_c and n_s are much larger than one.

Definitions (33) and inequalities (34) and (35) allowed us to present the aggregation work–aggregation number dependence in the regions of the hump and well in the form

$$W_n = W_c - \left(\frac{n-n_c}{\Delta n_c}\right)^2 \quad \text{at } n_c - \Delta n_c \le n \le n_c + \Delta n_c, \tag{37}$$

$$W_n = W_s + \left(\frac{n-n_s}{\Delta n_s}\right)^2 \quad \text{at } n_s - \Delta n_s \le n \le n_s + \Delta n_s. \tag{38}$$

According to (37) and (38), the work W_n, respectively, decreases and increases by unity when n deviates from n_c by Δn_c and from n_s by Δn_s. This illustrates the physical meaning of Δn_c and Δn_s. Inequalities (34) and (35) and entailing inequalities (36) make it possible to describe kinetics of micellation in macroscopic terms. These inequalities generalize the conditions of macroscopic description suggested in the kinetic theory of homogeneous and heterogeneous nucleation [14].

Let us call the regions $n \le n_c - \Delta n_c$, $n_c - \Delta n_c \le n \le n_c + \Delta n_c$, and $n \ge n_c + \Delta n_c$, respectively, subcritical, near-critical, and supercritical. Most of the micelles are concentrated within $n_s - \Delta n_s \le n \le n_s + \Delta n_s$, the micellar region; it is located inside the supercritical region. The quantities n_s and Δn_s can be considered the mean aggregation number and the variance of the micelle size distribution with respect to this mean. The regions of hump and well in the aggregation work–aggregation number dependence correspond to the near-critical and micellar regions.

The dependence of the concentrations of aggregates on the aggregation number will be considered as the size distribution of molecular aggregates. The majority of the surfactant aggregates occupy size regions with a small work of aggregation, i.e., to the left and right of the hump in the aggregation work–aggregation number dependence (the subcritical and supercritical regions. The part of the supercritical region where $n \ge n_s + \Delta n_s$ is of no interest to us, since it contains only a tail of the size distribution of molecular aggregates.

The concentrations of molecular aggregates in the subcritical and supercritical regions can be assumed to change so slowly (due to their transport through the hump in the aggregation work–aggregation number dependence) that the distribution of aggregates in each of these regions exists in a quasi-equilibrium state. This transport, however, precludes the establishment of quasi-equilibrium between the molecular aggregates in the subcritical and supercritical regions. The quasi-equilibrium between these regions is attained as the micellar solution as a whole attains the state of final equilibrium, i.e., when the quasi-equilibrium concentrations of molecular aggregates in the subcritical and supercritical regions become completely equilibrium, as does the size distribution of aggregates in the entire range of sizes.

Let the quasi-equilibrium and equilibrium concentrations of molecular aggregates with aggregation number n be $c_n^{(e)}$; then, for the subcritical and supercritical regions, we can write

$$c_n = c_n^{(e)} \quad (n \le n_c - \Delta n_c), \tag{39}$$

$$c_n = c_n^{(e)} \quad (n \ge n_c + \Delta n_c). \tag{40}$$

According to the Boltzmann principle, the quasi-equilibrium concentrations read (by analogy with (13))

$$c_n^{(e)} = \text{const} \times \exp(-W_n). \tag{41}$$

For the subcritical and supercritical regions, formula (41) yields

$$c_n^{(e)} = c_1 \exp(-W_n) \quad (n \le n_c - \Delta n_c), \tag{42}$$

$$c_n^{(e)} = c_s \exp[-(W_n - W_s)] \quad (n \ge n_c + \Delta n_c), \tag{43}$$

where $c_s \equiv c_n|_{n = n_s}$ is the concentration of molecular aggregates at the minimum in the aggregation work–aggregation number dependence. That the preexponential factor in (42) equals c_1 follows from the identity $c_1 \equiv c_n|_{n = 1}$ and equality (6). That the preexponential factor in (43) equals c_s follows from the definition of c_s and the obvious equality $(W_n - W_s)|_{n = n_s} = 0$.

Since micelles are accumulated in the micellar region, their total concentration is given by

$$c_{\mathrm{M}} = \int_{n_s - \Delta n_s}^{n_s + \Delta n_s} c_n dn. \tag{44}$$

Substituting (40) and (43) in (44), taking to account approximation (37), replacing (with high accuracy) the integration limits in (44) by $-\infty$ and ∞, and performing integration, we obtained at the quasi-equlibrium in the micellar region

$$c_{\mathrm{M}} = \pi^{1/2} c_s \Delta n_s. \tag{45}$$

Relationship (45) makes it possible to recast (43) as

$$c_n^{(e)} = (c_{\mathrm{M}}/\pi^{1/2}\Delta n_s)\exp[-(W_n - W_s)] \\ (n \ge n_c + \Delta n_c). \tag{46}$$

4. KINETIC EQUATION FOR AGGREGATION IN THE NEAR-CRITICAL AND MICELLAR REGIONS

According to the first of conditions (34) and (35), the aggregation number n can be considered a continuous variable in the near-critical and micellar regions of aggregate sizes. Therefore, Eq. (22) can be written as the equation of continuity,

$$\partial c_n(t)/\partial t = -\partial J_n(t)/\partial n, \tag{47}$$

where argument t indicates the dependence of c_n and y_n on time. Since $W_{n+1} - W_n = \partial W_n/\partial n$, (37) and (38) yield

$$W_{n+1} - W_n = -\frac{2(n - n_c)}{(\Delta n_c)^2} \\ \text{at } n_c - \Delta n_c \le n \le n_c + \Delta n_c, \tag{48}$$

$$W_{n+1} - W_n = \frac{2(n - n_s)}{(\Delta n_s)^2} \\ \text{at } n_s - \Delta n_s \le n \le n_s + \Delta n_s. \tag{49}$$

The first of conditions (34) and (35) show that the moduli of the quantities on the right-hand sides of (48) and (49) are much smaller than unity in the near-critical and micellar ranges of sizes of aggregates; therefore, with high accuracy, Eqs. (48) and (49) for these regions can be rewritten as

$$\exp(W_{n+1} - W_n) = 1 - \frac{2(n - n_c)}{(\Delta n_c)^2} \\ \text{at } n_c - \Delta n_c \le n \le n_c + \Delta n_c, \tag{50}$$

$$\exp(W_{n+1} - W_n) = 1 + \frac{2(n - n_s)}{(\Delta n_s)^2} \\ \text{at } n_s - \Delta n_s \le n \le n_s + \Delta n_s. \tag{51}$$

If n can be considered a continuous variable,

$$c_{n+1} = c_n + \partial c_n/\partial n. \tag{52}$$

Using (26) and (50)–(52) and ignoring the products of the small quantities $\partial c_n/\partial n$, $2(n - n_c)/(\Delta n_c)^2$, and $2(n - n_s)/(\Delta n_s)^2$, we then obtain

$$J_n(t) = j_c^+[2(n-n_c)/(\Delta n_c)^2 + \partial/\partial n]c_n(t) \quad \text{at } n_c - \Delta n_c \le n \le n_c + \Delta n_c, \tag{53}$$

$$J_n(t) = -j_s^+[2(n-n_s)/(\Delta n_s)^2 + \partial/\partial n]c_n(t) \quad \text{at } n_s - \Delta n_s \le n \le n_s + \Delta n_s, \tag{54}$$

where $j_c^+ \equiv j_n^+\big|_{n = n_c}$ and $j_s^+ \equiv j_n^+\big|_{n = n_s}$ are the intensities of the absorption of monomers by critical and stable aggregates. Relationships (53) and (54) in conjunction with equation of continuity (47) yield a kinetic equation of formation of aggregates in the near-critical and micellar regions of their sizes.

Consider another method of derivation of Eqs. (53) and (54). Let $\dot{n}$ be the rate of change of the aggregation number with time (the derivative of n with respect to the time). Clearly,

$$\dot{n} = j_n^+ - j_n^-. \tag{55}$$

Since n was assumed to be continuous, Eq. (25) yields

$$j_n^- \simeq j_n^+\exp(\partial W_n/\partial n). \tag{56}$$

As discussed above, in the near-critical and micellar aggregate size regions, the exponent in the exponential function is small; then, with high accuracy, Eqs. (55) and (56) for these regions yield

$$\dot{n} = -j_n^+\partial W_n/\partial n. \tag{57}$$

The flux $J_n(t)$ of molecular aggregates can be presented as

$$J_n(t) = (\dot{n} + \beta\partial/\partial n)c_n(t). \tag{58}$$

The term containing $\dot{n}$ describes the regular evolution of a single aggregate, while the term containing the differentiation operator $\partial/\partial n$ describes the fluctuation-mode evolution of an ensemble of molecular aggregates, a process that smears aggregate size distribution during the regular evolution. For the near-critical and micellar regions, we used Eqs. (57) and (58). The unknown coefficient β was then determined from the condition of the molecular aggregate flux becoming zero at the equilibrium concentrations of the aggregates (given by (41)); as a result, we obtain

$$J_n(t) = -j_n^+(\partial W_n/\partial n + \partial/\partial n)c_n(t). \tag{59}$$

Rearranging the derivative $\partial W_n/\partial n$ in (59) for the near-critical and micellar regions by using (48) and (49), we obtain expressions identical to (53) and (54).

5. DIRECT AND REVERSE FLUXES OF AGGREGATES THROUGH THE BARRIER TO MICELLATION

As discussed above, during micellation, the aggregates transferred through the barrier to micellation (the hump in the aggregation work–aggregation number dependence) from the subcritical region to the supercritical region and back. Let the direct and reverse fluxes of molecular aggregate near the hump in the micellation work versus aggregate size dependence be $J'_n(t)$ and $J''_n(t)$, respectively, and let the concentrations of molecular aggregates providing these fluxes be $c'_n(t)$ and $c''_n(t)$. The total flux $J_n(t)$ of molecular aggregates and the overall size distribution of aggregates in the near-critical region can be written as

$$J_n(t) = J'_n(t) + J''_n(t) \quad \text{at } n_c - \Delta n_c \le n \le n_c + \Delta n_c, \tag{60}$$

$$c_n(t) = c'_n(t) + c''_n(t) \quad \text{at } n_c - \Delta n_c \le n \le n_c + \Delta n_c. \tag{61}$$

The considerations underlying the kinetic equation for the near-critical region derived in the previous section (formulas (47) and (53)) are also valid separately for molecular aggregates migrating from the subcritical to the supercritical region and those (due to fluctuations) migrating back. Therefore, along with Eqs. (47) and (53), we obtained the following expressions for the near-critical region:

$$\partial c'_n(t)/\partial t = -\partial J'_n(t)/\partial n \quad (n_c - \Delta n_c \le n \le n_c + \Delta n_c), \tag{62}$$

$$J'_n(t) = j_c^+[2(n-n_c)/(\Delta n_c)^2 - \partial/\partial n]c'_n(t) \quad (n_c - \Delta n_c \le n \le n_c + \Delta n_c), \tag{63}$$

and

$$\partial c''_n(t)/\partial t = -\partial J''_n(t)/\partial n \quad (n_c - \Delta n_c \le n \le n_c + \Delta n_c), \tag{64}$$

$$J''_n(t) = j_c^+[2(n-n_c)/(\Delta n_c)^2 - \partial/\partial n]c''_n(t) \quad (n_c - \Delta n_c \le n \le n_c + \Delta n_c). \tag{65}$$

Naturally, formulas (60)–(65) are consistent with (47) and (53).

Let us formulate boundary conditions for the above equations. Based on the kinetic nucleation theory and relationships (42), (43), we obtain the boundary conditions for Eqs (62), (63), which describe the $c'_n(t)$ distribution in the near-critical region, in the form:

$$c'_n(t)/c_n^{(e)} \approx \begin{cases} 1 & (n \approx n_c - \Delta n_c) \\ 0 & (n \approx n_c + \Delta n_c), \end{cases} \tag{66}$$

The boundary conditions for Eqs. (64), (65), which describe the $c''_n(t)$ distribution in the near-critical region, read

$$c''_n(t)/c_n^{(e)} \approx \begin{cases} 0 & (n \approx n_c - \Delta n_c) \\ 1 & (n \approx n_c + \Delta n_c). \end{cases} \tag{67}$$

The quasi-equilibrium concentration $c_n^{(e)}$ in boundary conditions (66) and (67) is given by (42) at $n \approx n_c - \Delta n_c$ and (43) (or (46)) at $n \approx n_c + \Delta n_c$.

According to (61), (66), and (67), the boundary conditions for Eqs. (47) and (53) (involving the total size distribution $c_n(t)$ of molecular aggregates in the near-critical region take the form

$$c_n(t)/c_n^{(e)} \approx 1 \quad (n \approx n_c \mp \Delta n_c), \tag{68}$$

where the quasi-equilibrium concentration $c_n^{(e)}$ is also given by (42) at $n \approx n_c - \Delta n_c$ and (43) (or (46)) at $n \approx n_c + \Delta n_c$. In view of the above conclusion that the concentrations of molecular aggregates in the subcritical and supercritical regions are quasi-equilibrium, boundary conditions (68) seem quite natural.

If the concentrations of molecular aggregates in the subcritical and supercritical regions are quasi-equilibrium, the concentration of molecular aggregates in the near-critical reaction should also be quasistationary. The terms *quasistationary* and *quasi-equilibrium*, introduced in Section 3, signify that the concentration of the aggregates are time-independent over sufficiently long time intervals, which, on the other hand, are too short for the concentrations c_1 and c_M to change markedly during the slow process of equilibration of the micellar solution.

Consider the quasistationary state of molecular aggregates in the near-critical region. In this state, the concentrations $c'_n(t)$, $c''_n(t)$, and $c_n(t)$ of aggregates are time-independent while the fluxes $J'_n(t)$, $J''_n(t)$, and $J_n(t)$ are, in addition, independent as follows from the continuity equations (62), (64), and (47) of n. Let the concentrations $c'_n(t)$, $c''_n(t)$, and $c_n(t)$ in the quasistationary state be denoted as $c_n'^{(s)}$, $c_n''^{(s)}$, and $c_n^{(s)}$ while the corresponding fluxes as $J'_n(t)$, $J''_n(t)$, and $J_n(t)$ as J', J'', and J (for simplicity, these notations in the case of quasistationary fluxes do not include n and t). For the near-critical region $n_c - \Delta n_c \le n \le n_c + \Delta n_c$, we can write

$$c'_n(t) = c_n'^{(s)}, \quad c''_n(t) = c_n''^{(s)}, \quad c_n(t) = c_n^{(s)}, \tag{69}$$

and

$$J'_n(t) = J', \quad J''_n(t) = J'', \quad J_n(t) = J. \tag{70}$$

Under quasistationary conditions, the right-hand sides of equations of continuity (62) and (64) are equal to zero; therefore, using expressions (63) and (65) for the fluxes of molecular aggregates, boundary conditions (66) and (67) for the concentrations of molecular aggregates, and quadratic approximation (37), we obtain the following relationship for the near-critical region ($n_c - \Delta n_c \le n \le n_c + \Delta n_c$):

$$\begin{aligned} c_n'^{(s)} &= \frac{c_1 \exp(-W_c)}{\pi^{1/2}\Delta n_c} \\ &\times \exp\left[\left(\frac{n - n_c}{\Delta n_c}\right)^2\right]\int_n^{\infty} \exp\left[-\left(\frac{n' - n_c}{\Delta n_c}\right)^2\right] dn', \end{aligned} \tag{71}$$

$$J' = c_1 j_c^+ \exp(-W_c)/\pi^{1/2}\Delta n_c, \tag{72}$$

$$\begin{aligned} c_n''^{(s)} &= \frac{c_M \exp[-(W_c - W_s)]}{\pi \Delta n_c \Delta n_s} \\ &\times \exp\left[\left(\frac{n - n_c}{\Delta n_c}\right)^2\right]\int_{-\infty}^{n} \exp\left[-\left(\frac{n' - n_c}{\Delta n_c}\right)^2\right] dn', \end{aligned} \tag{73}$$

$$J'' = -c_M j_c^+ \exp[-(W_c - W_s)]/\pi \Delta n_c \Delta n_s. \tag{74}$$

The total size distribution of molecular aggregates and the total flux of aggregates under quasistationary conditions in the near-critical region ($n_c - \Delta n_c \le n \le n_c + \Delta n_c$) are given by (according to (61), (62))

$$c_n^{(s)} = c_n'^{(s)} + c_n''^{(s)}, \tag{75}$$

$$J = J' + J''. \tag{76}$$

The direct and reverse fluxes (J' and J'') given by formulas (72) and (74) are positive and negative, respectively. According to (72), the direct flux J' increases with increasing c_1 and j_c^+ and decreasing W_c and Δn_c; according to (74), the modulus of the reverse flux J'' c_M increases with increasing c_1 and j_c^+ and decreasing $W_c - W_s$, Δn_c, and Δn_s. Clearly, J' and J'' are determined by the numbers of molecular aggregates migrating through the hump in the micellation work–aggregation number dependence per unit time in unit volume of the micellar solution from the subcritical to supercritical region and back.

6. ESTABLISHMENT OF QUASI-EQUILIBRIUM DISTRIBUTIONS OF MOLECULAR AGGREGATES IN THE SUBCRITICAL AND SUPERCRITICAL REGIONS

Let us now consider the initial stages of micellation. During these stages, the quasi-equilibrium size distributions of the molecular aggregates of surfactant molecules in the subcritical and supercritical regions and the quasistationary size distribution of surfactant aggregates in the near-critical region are established. Let us first consider how the quasi-equilibrium distribution of aggregates in the micellar region (inside the supercritical region; $n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s$) is attained. The time evolution of the concentrations c_n of molecular aggregates is described by the equation of continuity (Eq. (47)). The flux in the micellar region is given by formula (54). For the micellar region, the boundary conditions for the kinetic equation (Eqs. (47) and (54)) read

$$c_n(t) \approx 0 \quad (n \approx n_s \mp \Delta n_s). \tag{77}$$

Approximate equality (77) suggests that the concentration of micelles at the boundaries of the micellar region, $n \approx n_s \mp \Delta n_s$, is much smaller than at $n = n_s$.

The quasi-equilibrium size distribution of aggregates eventually attained in the micellar region is described by formula (46), which was derived based on the Boltzmann fluctuation principle. Substituting approximation (38) for the work W_n into (46), it is easy to show that the quasi-equilibrium distribution rapidly decays as n tends to the boundaries of the micellar region, $n \approx n_s \mp \Delta n_s$, i.e., satisfies boundary conditions (77).

Changing from n to the variable

$$u \equiv (n - n_s)/\Delta n_s \quad (-1 \lesssim u \lesssim 1) \tag{78}$$

in the micellar region and assuming that

$$c(u, t) \equiv c_n(t), \quad c^{(e)}(u) \equiv c_n^{(e)} \quad (-1 \lesssim u \lesssim 1), \tag{79}$$

we obtained, from (47) and (54), the kinetic equation

$$\frac{\partial c(u, t)}{\partial t} = \frac{j_s^+}{(\Delta n_s)^2}\frac{\partial}{\partial u}\left(2u + \frac{\partial}{\partial u}\right)c(u, t) \tag{80}$$
$$(-1 \lesssim u \lesssim 1)$$

(the differentiation operator acts upon the entire expression to the right from it). The boundary conditions for (80) were obtained from (77):

$$c(u, t) \approx 0 \quad (u \approx \mp 1). \tag{81}$$

According to (46), (78), and (79),

$$c^{(e)}(u) = \text{const} \times \exp(-u^2) \quad (-1 \lesssim u \lesssim 1). \tag{82}$$

Equation (80) was solved using Hermite polynomials $H_i(\xi)$ $(i = 0, 1, \ldots)$: $H_0(\xi) = 1$, $H_1(\xi) = 2\xi$, $H_2(\xi) = 4\xi^2 - 2$, …. The Hermite polynomials satisfy the recurrence relationships

$$\frac{\partial}{\partial \xi}H_i(\xi) = 2iH_{i-1}(\xi),$$
$$\left(2\xi - \frac{\partial}{\partial \xi}\right)H_i(\xi) = H_{i+1}(\xi) \tag{83}$$

and the orthogonality and normalization conditions

$$\pi^{-1/2}\int_{-\infty}^{\infty}\exp(-\xi^2)H_i(\xi)H_{i'}(\xi)d\xi = i!2^i\delta_{ii'} \tag{84}$$
$$(i, i' = 0, 1, \ldots),$$

where $\delta_{ii'}$ is the Kronecker symbol and $0! \equiv 1$.

By virtue of (83),

$$\frac{\partial}{\partial \xi}\left(2\xi + \frac{\partial}{\partial \xi}\right)\exp(-\xi^2)H_i(\xi) = -2i\exp(-\xi^2)H_i(\xi) \tag{85}$$
$$(i = 0, 1, \ldots).$$

According to (82), the quasi-equilibrium distribution $c^{(e)}(u)$ satisfies kinetic equation (80) and boundary conditions (81); therefore, the solution to Eq. (80) takes the form

$$c(u, t) = c^{(e)}(u) + \sum_{i=1}^{\infty} k_i \exp[-2ij_s^+ t/(\Delta n_s)^2] \tag{86}$$
$$\times \exp(-u^2)H_i(u) \quad (-1 \lesssim u \lesssim 1).$$

The coefficients k_i, which are independent of u and t, can be expressed by (84) through the initial concentration $c(u, t)|_{t=0}$ in the micellar region. The quasi-equilibrium concentration $c^{(e)}(u)$ could be introduced under the sign of summation by adding a term with $i = 0$. This means that the solution (86) is indeed a general solution, an expansion over a complete system of functions. As can be seen from (44), (78), and (84), solution (86) provides the conservation of the total concentration of micelles.

Solution (86) describes the establishment of a quasi-equilibrium distribution of molecular aggregates in the micellar region. As follows from (86), the set of quantities

$$t_s^{(i)} = (\Delta n_s)^2/2ij_s^+ \quad (i = 1, 2, \ldots), \tag{87}$$

is the spectrum of times of establishment of this distribution. The longest and, hence, characteristic time, denoted as t_s, is given by

$$t_s = (\Delta n_s)^2/2j_s^+. \tag{88}$$

According to (88), t_s increases with increasing Δn_s and decreasing j_s^+.

Let us now examine the establishment of the quasi-equilibrium distribution of molecular aggregates in the subcritical region, at $n \lesssim n_c - \Delta n_c$. Since the same subcritical region is considered in the theory of homogeneous nucleation [29, 30], we conclude that the character of the establishment of the quasi-equilibrium distribution of molecular aggregates in this region should be similar to that predicted by this theory. This distribution is established because of the tendency of molecular aggregates (which initially have an aggregation number of 1) to overcome the hump in the aggregation work–aggregation number dependence. According to the homogeneous nucleation theory [29, 30], the characteristic time t' of establishment of the quasi-equilibrium distribution of molecular aggregates in the subcritical region ($n \lesssim n_c - \Delta n_c$) is given by

$$t' \approx n_c \Delta n_c / j_c^+, \tag{89}$$

where j_c^+ ($j_c^+ > 0$) as in Sections 4, 5 is the number of surfactant monomers absorbed by a critical molecular aggregate ($n = n_c$) from the solution per unit time. As can be seen from (89), t' increases with increasing n_c and Δn_c and decreasing j_c^+.

It remains to understand how the quasi-equilibrium distribution of molecular aggregates is established within the $n_c + \Delta n_c \lesssim n \lesssim n_s - \Delta n_s$ size range, which lies in the supercritical region to the left from the micellar region. Clearly, this process occurs due to the tendency of molecular aggregates (initially located in the micellar region) to overcome the hump in the aggregation work–aggregation number dependence. Thus, there is a complete analogy in the character of the establishment of the quasi-equilibrium distribution of molecular aggregates over the $n_c + \Delta n_c \lesssim n \lesssim \lesssim n_s - \Delta n_s$ and $n \lesssim n_c - \Delta n_c$ ranges. The only difference is that, in the former case, the quantity $n_s - n_c$ plays the role of n_c. Thus, by analogy with (89), the characteristic time t'' of establishment of the quasi-equilibrium distribution of molecular aggregates over the $n_c + \Delta n_c \lesssim n \lesssim n_s - \Delta n_s$ range is given by

$$t'' \approx (n_s - n_c) \Delta n_c / j_c^+. \tag{90}$$

As can be seen from (90), t'' increases with increasing n_s and Δn_c and decreasing n_c and j_c^+.

7. ESTABLISHMENT OF QUASISTATIONARY DISTRIBUTIONS OF MOLECULAR AGGREGATES IN THE SUBCRITICAL AND SUPERCRITICAL REGIONS

The assumption that the distribution of molecular aggregates in the near-critical size range is quasistationary is important for developing a theory of micellation. Let us consider how this distribution is established. The time evolution of the concentrations c_n of molecular aggregates is described by the equation of continuity (Eq. (47)), in which the flux $J_n(t)$ of molecular aggregates in the near-critical region is given by (53). The boundary conditions for the kinetic equation (Eqs. (47) and (53)) in the near-critical region are given by relationships (68). Expressing the quasi-equilibrium concentration $c_n^{(e)}$ of aggregates in (68) by using the Boltzmann fluctuation principle, we obtained

$$\begin{gathered} c_n^{(e)} = \text{const} \times \exp[-(W_n - W_c)] \\ (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c). \end{gathered} \tag{91}$$

Changing from n to the variable

$$\nu \equiv (n - n_c)/\Delta n_c \quad (-1 \lesssim \nu \lesssim 1) \tag{92}$$

in the near-critical region and assuming that

$$c(\nu, t) \equiv c_n(t), \quad c^{(e)}(\nu) \equiv c_n^{(e)} \quad (-1 \lesssim \nu \lesssim 1), \tag{93}$$

we obtain, from (47) and (53), the kinetic equation

$$\begin{gathered} \frac{\partial c(\nu, t)}{\partial t} = -\frac{j_c^+}{(\Delta n_c)^2} \frac{\partial}{\partial \nu}\left(2\nu - \frac{\partial}{\partial \nu}\right) c(\nu, t) \\ (-1 \lesssim \nu \lesssim 1) \end{gathered} \tag{94}$$

(the differentiation operator $\partial/\partial \nu$ acts on the entire expression to the right from it). The boundary conditions for (94) were obtained from (68):

$$c(\nu, t)/c^{(e)}(\nu) \approx 1 \quad (\nu \approx \mp 1). \tag{95}$$

Combining approximation (37) with expressions (91)–(93) yields

$$c^{(e)}(\nu) = \text{const} \times \exp(\nu^2) \quad (-1 \lesssim \nu \lesssim 1). \tag{96}$$

Note that the values of the constant in (96) may differ to the left and right from the near-critical region. Clearly, when solving Eq. (94) with boundary conditions (95), it is impossible to use directly the results obtained in Section 6, since expressions (94) and (95) differ from (80) and (81).

Let $c^{(s)}(\nu)$ be the quasistationary size distribution of molecular aggregates eventually established in the near-critical region; it should satisfy Eq. (94) with boundary conditions (95). Taking into account that (by virtue of (83)),

$$\begin{gathered} \frac{\partial}{\partial \xi}\left(2\xi - \frac{\partial}{\partial \xi}\right) H_i(\xi) = 2(i+1) H_i(\xi) \\ (i = 0, 1, \ldots), \end{gathered} \tag{97}$$

and that the distribution $c^{(e)}(\nu)$ rapidly increases with $|\nu|$ (according to (96)), we present the general solution to Eq. (94) with boundary conditions (95) as

$$\begin{gathered} c(\nu, t) = c^{(s)}(\nu) \\ + \sum_{i=0}^{\infty} p_i \exp[-2(i+1) j_c^+ t/(\Delta n_c)^2] H_i(\nu) \\ (-1 \lesssim \nu \lesssim 1). \end{gathered} \tag{98}$$

Here, the coefficients p_i (independent of ν and t) can be expressed through the initial distribution $c(\nu, t)|_{t=0}$ in the near-critical region. The solution obtained is indeed general, being an expansion of $c(v, t) - c^{(s)}(v)$ in the complete set of Hermite polynomials $H_i(v)$ ($i = 0, 1, \ldots$). The rapid increase of $c^{(e)}(v)$ with $|v|$ is required to make the effect of the sum in (98) on boundary conditions (95) small, so as to ensure their fulfillment.

Solution (98) describes the established of a quasistationary distribution of molecular aggregates in the near-critical region. As can be seen from (98), the set of quantities $t_c^{(i)}$, given by

$$t_c^{(i)} = (\Delta n_c)^2/2(i+1)j_c^+ \quad (i = 0, 1, \ldots), \tag{99}$$

is the spectrum of times of establishment of this distribution. The longest and hence, characteristic time, denoted as t_c, is given by

$$t_c = (\Delta n_c)^2/2j_c^+. \tag{100}$$

According to (100), t_c increases with increasing Δn_c and decreasing j_c^+.

8. STAGE OF THE RAPID RELAXATION OF THE MICELLAR SOLUTION

Let us now examine how the characteristic time t_s is related to the experimentally measured time of the rapid relaxation of a micellar solution in order to refine the concept of rapid relaxation of a micellar solution (introduced by Aniansson [1–3] and used by many authors; see, e.g., [4–6, 31]). According to this concept, the relaxation of a micellar solution can be thought of as a rapid local rearrangement of the size distribution of micelles (without changes in the number of micelles in the micellar region) that occurs after an initial perturbation of the work of aggregation.

Let the superscript 0 denote the quantities after the rapid relaxation of a micellar solution, then the relative deviation of the current concentration c_n of aggregates from $c_n^{(0)}$ is given by

$$\xi_n = (c_n - c_n^{(0)})/c_n^{(0)}. \tag{101}$$

Assuming that the rapid relaxation involves the attachment to and detachment of monomers from aggregates only in the micellar region, we will consider that (101) describes only aggregates belonging to the micellar region and monomers ($n = 1$). Along with the aggregation number n, by analogy with (78) we will describe aggregates in the micellar region by the variable

$$\tilde{u} = (n - n_s^{(0)})/\Delta n_s^{(0)}, \tag{102}$$

changing approximately in the region $-1 < \tilde{u} < 1$. Note that the quantities n_s and Δn_s in (78) describe the states of the system at the current concentration of monomers, which was postulated to be time-independent or only slightly dependent on time, while $n_s^{(0)}$ and $\Delta n_s^{(0)}$ describe the state after rapid relaxation.

Taking into account (46), (38), and (102), the size distribution of micelles after rapid relaxation takes the form

$$c_n^{(0)} = \frac{c_{\mathrm{M}}^{(0)}}{\pi^{1/2}\Delta n_s^{(0)}} e^{-\tilde{u}^2} \quad (-1 < \tilde{u} < 1). \tag{103}$$

In Section 6, we considered the solution of the kinetic equation of aggregation in the micellar region. The kinetic equation (Eq. (80)) was written under the assumption that the concentration of monomers in the solution is constant. At sufficiently high concentration of micelles in the micellar region (at a monomer concentration above the first CMC), the local rearrangement of the size distribution of micelles may result in a marked change in the concentration of monomers. This means that, when describing the process of rapid relaxation, it is incorrect to consider the monomer concentration constant; therefore, the form of the kinetic equation should be modified.

Using (101), monomers and aggregates in the micellar region are described by

$$c_n(t) = c_n^{(0)}(1 + \xi_n(t)), \tag{104}$$

$$j_n^+(c_1(t)) = j_n^{+(0)}(1 + \xi_1(t)), \tag{105}$$

where $j_n^{+(0)} \equiv j_n^+(c_1^{(0)})$. After rapid relaxation, the micellar region is characterized by the equality

$$j_n^{+(0)} c_n^{(0)} = j_{n+1}^- c_{n+1}^{(0)}, \tag{106}$$

where j_{n+1}^- is independent of the concentration of monomers.

Combining definition (21) with Eqs. (104)–(106) yields the expression for the flux J_n in the form

$$\begin{aligned} J_n &= j_n^{+(0)} c_n^{(0)}(\xi_n - \xi_{n+1}) \\ &\quad + j_n^{+(0)} c_n^{(0)} \xi_1 + j_n^{+(0)} c_n^{(0)} \xi_1 \xi_n. \end{aligned} \tag{107}$$

As the system approaches the state that arises after the period of rapid relaxation, ξ_n becomes much smaller than unity. Therefore, we can neglect the product $\xi_1\xi_n$ in comparison with the rest of the terms in (107). For the micellar region (where $n \gg 1$), formula (107) can be rearranged as

$$J_n \simeq -j_n^{+(0)} c_n^{(0)} \frac{\partial \xi_n}{\partial n} + j_n^{+(0)} c_n^{(0)} \xi_1. \tag{108}$$

Combining (47), (104), and (108) makes it possible to present the kinetic equation for the rapid relaxation of the system in the micellar region as

$$c_n^{(0)}\frac{\partial\xi_n(t)}{\partial t} \simeq \frac{\partial}{\partial n}\left(j_n^{+(0)}c_n^{(0)}\frac{\partial\xi_n(t)}{\partial n}\right) - \xi_1(t)\frac{\partial}{\partial n}(j_n^{+(0)}c_n^{(0)}). \tag{109}$$

As when deriving (54), we can set $j_n^{+(0)} \simeq j_s^{+(0)}$ on the right-hand side of (109). One important feature of Eq. (109) is the last term on the right-hand side; as a result, Eq. (109) is nonuniform. At $\xi_1(t) = 0$, Eq. (109) can be transformed into Eq. (80).

To determine the current concentration of monomers, it is necessary to use, in addition to Eq. (109), Eq. (8) of material balance of surfactant for unit volume of a materially isolated solution. Substituting (104) into the right-hand side of (8) and taking into account that, during rapid relaxation, the amount of surfactant in the solution remains unchanged, we can write

$$c_1^{(0)}\xi_1(t) = -\sum_{n=2}^{\infty} nc_n^{(0)}\xi_n(t), \tag{110}$$

where definition (101) is extended to be valid at $n \geq 1$.

Let us search for the solutions to Eqs. (109), (110) in the form of the expansion

$$\xi_n(t) = \sum_{i=0}^{\infty} q_i(t)H_i(\tilde{u}) \quad (-1 < \tilde{u} < 1) \tag{111}$$

over the complete set of Hermite polynomials $H_i(\tilde{u})$. Here, $q_i(t)$ are $\tilde{u}$-independent expansion coefficients. Substituting (111) into (110), assuming the main contribution to the sum on the right-hand side of (110) comes from the micellar region, changing from summation over n to integration over $\tilde{u}$ on the right-hand side of (110), and taking into account (103), (102), and the conditions of orthogonality and normalization of the Hermite polynomials (relationship (84)), we obtain

$$c_1^{(0)}\zeta_1(t) = -c_{\mathrm{M}}^{(0)}\Delta n_s^{(0)}q_1(t) - c_{\mathrm{M}}^{(0)}n_s^{(0)}q_0. \tag{112}$$

Substituting (111) and (112) into Eq. (109), using (103) and (102), making scalar products both sides of (109) with H_i ($i = 0, 1, 2, \ldots$), and taking into account (83) and (84), we arrive at

$$\partial q_0(t)/\partial t = 0, \text{ i.e. } q_0 = \text{const}, \tag{113}$$

$$\frac{\partial q_1(t)}{\partial t} = -\frac{2j_s^{+(0)}}{(\Delta n_s^{(0)})^2}q_1(t) - j_s^{+(0)}\frac{c_{\mathrm{M}}^{(0)}}{c_1^{(0)}}\left[q_1(t) + \frac{n_s^{(0)}}{\Delta n_s^{(0)}}q_0\right], \tag{114}$$

$$\frac{\partial q_i(t)}{\partial t} = -\frac{2j_s^{+(0)}i}{(\Delta n_s^{(0)})^2}q_i(t) \quad (i = 2, 3, \ldots). \tag{115}$$

Let

$$q_0 = 0. \tag{116}$$

From (114) and (115) under condition (116), we have

$$q_1(t) = q_1(0)e^{-t/t_1}, \tag{117}$$

$$q_i(t) = q_i(0)e^{-it/t_s^{(0)}} \quad (i = 2, 3, \ldots). \tag{118}$$

Here, $q_1(0), q_2(0), \ldots$ are the coefficients $q_1(t), q_2(t), \ldots$ at the beginning of the rapid relaxation of the system ($t = 0$). The characteristic times t_1 and $t_s^{(0)}$ are given by

$$t_1 = \frac{1}{j_s^{+(0)}[2/(\Delta n_s^{(0)})^2 + c_{\mathrm{M}}^{(0)}/c_1^{(0)}]}, \tag{119}$$

$$t_s^{(0)} = (\Delta n_s^{(0)})^2/2j_s^{+(0)}. \tag{120}$$

Note that $t_s^{(0)}$ is analogous to the characteristic time t_s given by expression (88). If condition (116) is satisfied, combining (112) and (117) yields

$$\xi_1(t) = -\frac{c_{\mathrm{M}}^{(0)}\Delta n_s^{(0)}}{c_1^{(0)}}q_1(0)e^{-t/t_1}. \tag{121}$$

As can be seen from (104) and (121), the concentration of monomers $c_1(t)$ changes during the period of rapid relaxation, increasing at $q_1(0) > 0$ and decreasing at $q_1(0) < 0$. The higher the amplitude of the initial perturbation of the solution, the larger the change in the concentration $c_1(t)$.

According to (119) and (120),

$$t_1 < t_s^{(0)}, \tag{122}$$

$$t_1 = t_s^{(0)} \quad (c_{\mathrm{M}}^{(0)}/c_1^{(0)} \ll 2/(\Delta n_s^{(0)})^2). \tag{123}$$

The strong inequality $c_{\mathrm{M}}^{(0)}/c_1^{(0)} \ll 2/(\Delta n_s^{(0)})^2$ is satisfied only near the first CMC. As the total concentration of the solution increases still further, the ratio $c_{\mathrm{M}}^{(0)}/c_1^{(0)}$ rises rapidly, and, therefore, the time t_1 may become markedly smaller than the time $t_s^{(0)}$.

Relationships (104), (111), (116)–(118) and (122) yield

$$c_n(t)\big|_{t \gg t_s^{(0)}} = c_n^{(0)} \quad \text{(micellar region)}, \tag{124}$$

By virtue of (121),

$$c_1(t)\big|_{t \gg t_1} = c_1^{(0)}. \tag{125}$$

Relationships (124) and (125) show that the time-independent distribution $c_n^{(0)}$ of aggregates in the micellar region and the monomer concentration $c_1^{(0)}$ are eventually attained. Truncating expansion (111) after $i = 2, 3, \dots$ makes it possible to replace the condition of validity of (124), $t \gg t_s^{(0)}$, by $t \gg t_1$, a weaker condition by virtue of (122). As a result, it becomes clear that the time t_1 (given by (119)) is the characteristic time of rapid relaxation of the micellar solution.

The rapid relaxation of micellar solutions at total concentrations between the first and second CMCs was described in [1–7], observed experimentally in [31–34], and simulated in computer experiments in [35]. Such relaxation can be caused by an instantaneous perturbation of an equilibrium micellar solution (for example, by a jump in its temperature or pressure). We did not considered such an external perturbation in the previous sections, in which the evolution of a surfactant solution was assumed to occur due to internal processes, starting from the moment when only surfactant monomers were present.

Using relationships (102)–(102), (111), and (116) and the orthogonality and normalization conditions of Hermite polynomials (84), we obtain from (44)

$$c_M(t) = c_M^{(0)}, \tag{126}$$

i.e., the total concentration of micelles during the rapid relaxation of the micellar solution remains constant. At longer times, however, the total concentration of micelles will slowly change due to the direct and reverse quasistationary migration of molecular aggregates through the hump in the aggregation work–aggregation number dependence until the overall equilibrium between the aggregates in the micellar solution is established.

9. SYSTEM OF KINETIC EQUATIONS FOR DESCRIBING THE RELAXATION OF A MICELLAR SOLUTION

The quasistationary direct J' and reverse J'' fluxes of molecular aggregates introduced in Section 5 provide the fluctuation migration of $J' + J''$ ($J'' < 0$) molecular aggregates per unit time in unit volume from the subcritical to the micellar region. Therefore, the rate of change of the total concentration c_M of micelles is given by

$$\partial c_M/\partial t = J' + J''. \tag{127}$$

When the total concentration of surfactant exceeds the first CMC, a case important for practice, strong inequalities (35) are valid. According to the second of inequalities (35), the deviation Δn_s of the aggregation number from its mean value is small; therefore, with high accuracy, the number of surfactant monomers absorbed by micelles in unit volume of the solution is given by $n_s c_M$. By virtue of the first of conditions (36) and the ensuing high (at not too high n_c values) steepness of the hump in the aggregation work–aggregation number dependence, we have

$$\sum_{n=2}^{n_c + \Delta n_c} n c_n \ll c_1.$$

As a result, the amount of surfactant in a materially isolated solution at a total surfactant concentration above the first but below the second CMC at an arbitrary moment of time is given in accord with (8) by the equation of bimodal approximation:

$$c_1 + n_s c_M = c. \tag{128}$$

In view of (45) and the definition $c_s \equiv c_n|_{n = n_s}$, the term $n_s c_M$ in (128) is important when $\exp W_s$ moderately exceeds $n_s \Delta n_s$, which, according to (35), is large. The stronger the inequality $\exp W_c \gg \exp W_s$ in (36), the more important the role of the term $n_s c_M$.

Let us examine the evolution of a micellar solution to its final state under the condition that, at the initial moment of time (when the surfactant is introduced and mixed to attain its uniform distribution over the volume of the solution), the surfactant exists in the monomeric form. Therefore, at the initial moment, $c_1 = c$, $c_M = 0$, and $J'' = 0$ (of the two fluxes, only the direct one, J', differs from zero). With time, the concentration c_1 decreases (at a given total concentration c), while the concentration c_M of micelles gradually increases. As a result, the reverse flux J'' of aggregates arises, which increasingly competes with the direct flux J'. After a long period, when the equilibrium state of a materially isolated solution is attained, $J' = J''$.

As follows from (128) and the expressions for J' and J'' ((72) and (74)), when the dependence of the work of aggregation W_n on n and the dependences of n_c, n_s, Δn_c, Δn_s, W_c, W_s, and j_c^+ on the concentration c_1 are known and when the solution is materially isolated, Eq. (127) can be reduced to a nonlinear first-order differential equation with respect to the time for the function $c_1(t)$, with the right-hand side of this equation independent on t. The general solution to this equation at an arbitrary moment of time can be expressed through quadratures. Note, however, that the explicit dependence of W_n on n is known only for a few models of micelles [19–21, 36–40]. Therefore, it is interesting to construct analytical solutions to the kinetic equation of aggregation of a micellar solution at the final stage of micellation by using not the entire aggregation work–aggregation number dependence but only its most representative features.

Let tilde denote the state of equilibrium of a materially isolated micellar solution; then,

$$\tilde{J}' + \tilde{J}'' = 0. \tag{129}$$

Substituting (72) and (74) into (129) yields

$$\tilde{c}_{\mathrm{M}} = \pi^{1/2}\tilde{c}_1\Delta\tilde{n}_s\exp(-\tilde{W}_s). \tag{130}$$

As follows from (130) and formulas (42) and (46) for the quasi-equilibrium distributions $c_n^{(\mathrm{e})}$ of molecular aggregates in the subcritical and supercritical regions of sizes, in the state of complete equilibrium, the global equilibrium between all the molecular aggregates present in the micellar solution is established, not only the local quasi-equilibria between the molecular aggregates in the subcritical and supercritical regions. According to (130), (42), and (46), the distribution corresponding to the complete equilibrium reads

$$\tilde{c}_n^{(\mathrm{e})} = \tilde{c}_1\exp(-\tilde{W}_n). \tag{131}$$

Substituting (130) into (128), we obtain

$$\tilde{c}_1 + \pi^{1/2}\tilde{c}_1\tilde{n}_s\Delta\tilde{n}_s\exp(-\tilde{W}_s) = c. \tag{132}$$

At a fixed total concentration c and the known dependences of n_s, Δn_s, and W_s on the concentration c_1 of monomers, relationship (132) yields an equation for determining the equilibrium concentration $\tilde{c}_1$. Once the equilibrium concentration of surfactant monomers $\tilde{c}_1$ is determined, c_{M} is calculated by

$$\tilde{c}_{\mathrm{M}} = (c - \tilde{c}_1)/\tilde{n}_s, \tag{133}$$

which follows from (128).

If the equilibrium concentration of surfactant monomers $\tilde{c}_1$ was measured, the concentration c and the equilibrium concentration $\tilde{c}_{\mathrm{M}}$ can be determined from (132) and (133). If the equilibrium concentration $\tilde{c}_{\mathrm{M}}$ is measured, the equilibrium concentration $\tilde{c}_1$ can be determined by solving Eq. (130) with respect to $\tilde{c}_1$, after which c is calculated using formula (133). Thus, while a nonequilibrium micellar solution is characterized by two independent concentrations of the three characteristic concentrations (c_1, c_{M}, c), an equilibrium micellar solution is characterized only by one independent concentration (due to additional relationship (129)).

Formula (19) yields

$$\partial W_n/\partial c_1 = -(n-1)/c_1. \tag{134}$$

Using the definition of the minimum of the work W_n, $W_s \equiv W_n|_{n = n_s}$, we obtain

$$\frac{\partial W_s}{\partial c_1} = \left.\frac{\partial W_n}{\partial c_1}\right|_{n = n_s} + \left.\frac{\partial W_n}{\partial n}\right|_{n = n_s}\frac{\partial n_s}{\partial c_1}. \tag{135}$$

Since the work W_n takes its minimum value at $n = n_s$, $(\partial W_n/\partial n)_{n = n_s} = 0$, and, therefore, a combination of (135) and (134) yield

$$\partial W_s/\partial c_1 = -(n_s - 1)/c_1, \tag{136}$$

i.e.,

$$\partial W_s/\partial c_1 < 0. \tag{137}$$

A similar consideration is applicable to the maximum of the work W_n, $W_c \equiv W_n|_{n = n_c}$. In this case,

$$\partial W_c/\partial c_1 = -(n_c - 1)/c_1, \tag{138}$$

$$\partial W_c/\partial c_1 < 0. \tag{139}$$

According to (137), the left-hand side of Eq. (132) increases monotonically with $\tilde{c}_1$, and, hence, Eq. (132) has a unique solution at a given total concentration c. On the strength of (137), there is also only one solution to Eq. (130) with respect to $\tilde{c}_1$ at a given concentration $\tilde{c}_{\mathrm{M}}$. At $\tilde{n}_s \gg 1$, in view of relationship (136), the dependence of the second term on the left-hand side of Eq. (132) on $\tilde{c}_1$ through the factor $\exp(-\tilde{W}_s)$ is rather sharp; the influence of the factors $\tilde{n}_s$ and $\Delta\tilde{n}_s$ as functions of $\tilde{c}_1$ on this dependence is much weaker. An analysis of Eqs. (132), (136), and (137) led us to the following conclusion. As the total concentration c increases above the first CMC, the monomer concentration $\tilde{c}_1$ also begins to rise above the first CMC, but more slowly, without exceeding it significantly.

Let us compare two micellar solutions (marked by the subscripts 1 and 2) with almost identical concentrations of monomers in the equilibrium state; therefore, the quantities $\tilde{n}_s$, $\tilde{n}_c$, and $\Delta\tilde{n}_s$, which are slightly sensitive to the monomer concentration [40], virtually coincide. In this case, $\tilde{c}_1^{(1)}/\tilde{c}_1^{(2)} \approx 1$ and, in addition, by virtue of (136) and (138),

$$\exp\tilde{W}_s^{(1)}/\exp\tilde{W}_s^{(2)} = (\tilde{c}_1^{(2)}/\tilde{c}_1^{(1)})^{\tilde{n}_s - 1}, \tag{140}$$

$$\exp\tilde{W}_c^{(1)}/\exp\tilde{W}_c^{(2)} = (\tilde{c}_1^{(2)}/\tilde{c}_1^{(1)})^{\tilde{n}_c - 1}. \tag{141}$$

Relationships (130) and (140) yield

$$\tilde{c}_{\mathrm{M}}^{(1)}/\tilde{c}_{\mathrm{M}}^{(2)} = (\tilde{c}_1^{(1)}/\tilde{c}_1^{(2)})^{\tilde{n}_s}. \tag{142}$$

Since $\tilde{n}_s \gg 1$, relationship (142) suggests that, at nearly identical concentrations of monomers in equilibrium solutions, the concentrations of micelles in these solutions may differ significantly. According to (141) and (142),

$$\exp\tilde{W}_c^{(1)}/\exp\tilde{W}_c^{(2)} = (\tilde{c}_{\mathrm{M}}^{(2)}/\tilde{c}_{\mathrm{M}}^{(1)})^{(\tilde{n}_c - 1)/\tilde{n}_s}. \tag{143}$$

10. FINAL STAGE OF MICELLATION

Let us solve system of equations (127), (128) (which describes the kinetics of aggregation of a micellar solution after introducing and mixing the surfactant to attain its uniform distribution over the volume of the solution) beginning with a moment of time when the concentrations c_1 and c_{M} are close to their values in the state of complete equilibrium, $\tilde{c}_1$ and $\tilde{c}_{\mathrm{M}}$, while the reverse flux J'' almost completely counterbalances the direct flux J', i.e., a moment of time corresponding to the onset of the final stage of micellation.

Since the characteristics of the solution at its final stage of evolution deviate only slightly from their equilibrium value, the kinetic equation of aggregation can be linearized and, thereby, simplified substantially. Let the symbol δ in front of a parameter denote its deviation from its equilibrium value; thus,

$$c_1 = \tilde{c}_1 + \delta c_1, \quad c_{\mathrm{M}} = \tilde{c}_{\mathrm{M}} + \delta c_{\mathrm{M}}. \tag{144}$$

Linearizing Eqs. (127) and (128) and the expressions for the fluxes J' and J'' (Eqs. (72), (74)) with respect to δc_1 and δc_2 and taking into account equality (129) and the constancy of the total concentration c for a materially isolated solution, we obtain

$$\frac{\partial \delta c_{\mathrm{M}}}{\partial t} = \tilde{J}'\left(\frac{1+\gamma+\eta}{\tilde{c}_1}\delta c_1 - \frac{1}{\tilde{c}_{\mathrm{M}}}\delta c_{\mathrm{M}}\right), \tag{145}$$

$$(1+\lambda)\delta c_1 + \tilde{n}_s \delta c_{\mathrm{M}} = 0. \tag{146}$$

Here, γ, η, and λ are dimensionless parameters given by

$$\gamma = -\tilde{c}_1(\partial W_s/\partial c_1)\big|_{c_1 = \tilde{c}_1}, \quad \eta = \tilde{c}_1(\partial \ln \Delta n_s/\partial c_1)\big|_{c_1 = \tilde{c}_1},$$
$$\lambda = \tilde{c}_{\mathrm{M}}(\partial n_s/\partial c_1)\big|_{c_1 = \tilde{c}_1}. \tag{147}$$

These parameters describe the dependence of W_s, Δn_s, and n_s on the monomer concentration c_1 near its equilibrium value, $\tilde{c}_1$. The analogous dependence of j_c^+, W_c, and Δn_c on c_1 in (72) and (74) disappeared in (145), since the dependences of J' and J'' on j_c^+, W_c, and Δn_c in (72) and (74) are identical. Equation (136) and the first relationship in (147) yield

$$\gamma = \tilde{n}_s - 1. \tag{148}$$

Based on (72), the flux $\tilde{J}'$ in (145) can be presented as

$$\tilde{J}' = \tilde{c}_1 \tilde{j}_c^+ \exp(-\tilde{W}_c)/\pi^{1/2}\Delta\tilde{n}_c. \tag{149}$$

According to (129), the reverse flux $\tilde{J}''$ differs from the direct flux $\tilde{J}'$ only in sign. The solution of system of equations (145), (146) is straightforward:

$$\delta c_1 = -\frac{\tilde{n}_s}{1+\lambda}\delta c_{\mathrm{M}}, \tag{150}$$

$$\delta c_{\mathrm{M}} = \mathrm{const} \times \exp(-t/t_r), \tag{151}$$

where the time t_r is given by

$$\frac{1}{t_r} = \tilde{J}'\left[\frac{\tilde{n}_s(1+\gamma+\eta)}{\tilde{c}_1(1+\lambda)} + \frac{1}{\tilde{c}_{\mathrm{M}}}\right]. \tag{152}$$

Let us examine the role of the parameters η and λ in (152). From (148) and the second relationship in (147), it follows that

$$\frac{\eta}{1+\gamma} = \frac{\tilde{c}_1}{\tilde{n}_s}\left(\frac{\partial \ln \Delta n_s}{\partial c_1}\right)\bigg|_{c_1 = \tilde{c}_1}. \tag{153}$$

The quantity Δn_s depends on c_1 only slightly [40], with the $\ln\Delta n_s$–c_1 dependence as follows from (35) being still weaker; in addition, according to (35), $n_s \gg 1$. Then, as can be seen from (153), $|\eta/(1+\gamma)| \ll 1$, an equality that allows one to drop η in (152).

Analogously, due to the weak dependence of the mean aggregation number n_s on the concentration c_1 [40] and the third relationship in (147), $|\lambda| \ll 1$, an inequality that makes it possible to disregard λ in (152).

Thus, omitting η and λ in (152) and taking into account (148), we obtained

$$\frac{1}{t_r} = \tilde{J}'\left(\frac{\tilde{n}_s^2}{\tilde{c}_1} + \frac{1}{\tilde{c}_{\mathrm{M}}}\right). \tag{154}$$

Substituting (149) into (154) yields

$$t_r = \frac{\pi^{1/2}\tilde{c}_{\mathrm{M}}\Delta\tilde{n}_c \exp\tilde{W}_c}{\tilde{c}_1\tilde{j}_c^+}\left(1 + \frac{\tilde{n}_s^2\tilde{c}_{\mathrm{M}}}{\tilde{c}_1}\right)^{-1}. \tag{155}$$

According to (155), the time t_r is positive; thus, solutions (150) and (151) describe the irreversible tendency of a materially isolated micellar solution to the state of complete equilibrium. As can be seen, the time t_r given by (155) is the characteristic time of relaxation of the solution during the final stage of micellation. The constant in (151) is negative, const < 0. This inequality provides for the increase of the concentration c_{M} of micelles (according to (151)) and the decrease of the monomer concentrations c_1 (according to (150) at $|\lambda| \ll 1$) with time. As follows from (155), the time of relaxation of a micellar solution is independent of its volume.

As can be seen from (128), the quantity $\tilde{n}_s\tilde{c}_{\mathrm{M}}/\tilde{c}_1$ is the ratio of the amount of surfactant in the micelles in the state of complete equilibrium of the solution to the amount of surfactant in the form of monomers. In terms of the degree of micellization α [18],

$$\alpha \equiv n_s c_{\mathrm{M}}/c, \tag{156}$$

this ratio equals $\tilde{\alpha}/(1-\tilde{\alpha})$. Typically, the critical degree of micellization corresponding to the first CMC is ~0.1, being still higher between the first and second CMCs. In this case, at $\tilde{n}_s \gg 1$,

$$\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1. \tag{157}$$

Combining (157) and (155) yields

$$t_r = \frac{\pi^{1/2}\Delta\tilde{n}_c \exp\tilde{W}_c}{\tilde{n}_s^2\tilde{j}_c^+}. \tag{158}$$

Let us now consider how the time t_r depends on the concentration of micelles in the state of complete equilibrium of the solution when the monomers concentration is slightly changed, so that $\tilde{n}_s$, $\tilde{n}_c$, $\Delta\tilde{n}_s$, and $\Delta\tilde{n}_c$ (which are weakly sensitive to the monomer concentration [40]) remain virtually unchanged. Using (142), (143) and (158) and taking into account that the intensity $\tilde{j}_c^+$ of absorption of monomers by a critical molecular aggregate from the solution is proportional to the concentration of monomers in the solution, we obtained

$$t_r^{(1)}/t_r^{(2)} = (\tilde{c}_{\mathrm{M}}^{(2)}/\tilde{c}_{\mathrm{M}}^{(1)})^{\tilde{n}_c/\tilde{n}_s}. \qquad (159)$$

As previously, the superscripts 1 and 2 denote the characteristics of two solutions with very similar monomer concentrations but, possibly, markedly different in the concentration of micelles in the state of complete equilibrium of the solution. According to (159), the time of relaxation of the solution decreases with increasing total concentration of micelles $\tilde{c}_{\mathrm{M}}$ as $\tilde{c}_{\mathrm{M}}^{\tilde{n}_c/\tilde{n}_s}$. The higher the concentration of micelles in the state of complete equilibrium of the solution, the greater the total concentration of surfactant molecules in it. Then, according to (159), the time of relaxation of the solution decreases as the total concentration of surfactant in it increases above the first CMC.

The time t_r was first introduced in [1], where it was termed the time of slow relaxation of a micellar solution.

11. APPROACHING THE FINAL STAGE OF MICELLATION

Let us now solve the system of kinetic equations of aggregation (Eqs. (127) and (128)) for the period preceding the final stage of micellation. Using the equalities $n_s = \tilde{n}_s$, $\Delta n_s = \Delta\tilde{n}_s$, $n_c = \Delta\tilde{n}_c$, and $\Delta n_c = \Delta\tilde{n}_c$, the validity of which will be proven at the end of this section, we rearrange (127) and (128) at a fixed total concentration c of the solution to obtain

$$c_1 + \tilde{n}_s c_{\mathrm{M}} = c, \qquad (160)$$

$$\partial c_1/\partial t = -\tilde{n}_s(J' + J''). \qquad (161)$$

When deriving (145), we linearized the exponential function $\exp W_s$ with respect to δc_1. Expanding $\exp W_s$ in the Taylor series in δc_1 and taking into account (136), it is easy to see that the linearization is valid at

$$\delta c_1/\tilde{c}_1 < 1/\tilde{n}_s. \qquad (162)$$

Condition (162) specifies the region on the axis of concentrations c_1 within which the final stage of micellation occurs. Although this region is relatively narrow at $\tilde{n}_s \gg 1$, in view of (136), the exponential function $\exp W_s$ can change substantially within it.

At $\Delta n_s = \Delta\tilde{n}_s$ and $\Delta n_c = \Delta\tilde{n}_c$, substituting (129) into (72) and (74) yields

$$J' = \tilde{J}'\frac{c_1 j_c^+}{\tilde{c}_1\tilde{j}_c^+}\exp(-W_c + \tilde{W}_c), \qquad (163)$$

$$J'' = -\tilde{J}'\frac{c_{\mathrm{M}} j_c^+}{\tilde{c}_{\mathrm{M}}\tilde{j}_c^+}\exp(W_s - \tilde{W}_s - W_c + \tilde{W}_c). \qquad (164)$$

Using (163) and (164), we obtained

$$\frac{|J''|}{J'} = \frac{c_{\mathrm{M}}\tilde{c}_1}{\tilde{c}_{\mathrm{M}}c_1}\exp(W_s - \tilde{W}_s). \qquad (165)$$

At $n_s = \tilde{n}_s$, integration of Eq. (136) yields

$$\exp(W_s - \tilde{W}_s) = (\tilde{c}_1/c_1)^{\tilde{n}_s - 1}. \qquad (166)$$

Using (166) and the obvious inequality $c_{\mathrm{M}} \le \tilde{c}_{\mathrm{M}}$ and combining (165) with (144), we obtained

$$|J''|/J' \le \exp[-\tilde{n}_s\ln(1 + \delta c_1/\tilde{c}_1)]. \qquad (167)$$

According to (167), at $\delta c_1/\tilde{c}_1 > 1/\tilde{n}_s$,

$$|J''|/J' \ll 1. \qquad (168)$$

Inequality (168) makes it possible to reduce Eq. (161) to the form

$$\partial c_1/\partial t = -\tilde{n}_s J' \quad (\delta c_1/\tilde{c}_1 \gtrsim 1/\tilde{n}_s). \qquad (169)$$

Note that the ratio of the reverse flux J'' to the direct one J' changes in passing from monomer concentrations satisfying the inequality $\delta c_1/\tilde{c}_1 > 1/\tilde{n}_s$ to concentrations satisfying $\delta c_1/\tilde{c}_1 < 1/\tilde{n}_s$. As can be seen from (168), at $\delta c_1/\tilde{c}_1 > 1/\tilde{n}_s$, J'' is negligibly small, but it becomes important at $\delta c_1/\tilde{c}_1 < 1/\tilde{n}_s$. It is the expression for J'' (Eq. (74)) (which contains $\exp W_s$) that leads to condition (162).

At $n_c = \tilde{n}_c$, integration of (138) results in

$$\exp(W_c - \tilde{W}_c) = (\tilde{c}_1/c_1)^{\tilde{n}_c - 1}. \qquad (170)$$

Substituting (170) into (163) and taking into account that j_c^+ is proportional to c_1 yields

$$J' = \tilde{J}'(c_1/\tilde{c}_1)^{\tilde{n}_c + 1}. \qquad (171)$$

Substituting (171) into (169), we obtain

$$\partial c_1/\partial t = -\tilde{n}_s\tilde{J}'(c_1/\tilde{c}_1)^{\tilde{n}_c + 1} \quad (\delta c_1/\tilde{c}_1 \gtrsim 1/\tilde{n}_s). \qquad (172)$$

For the region of concentrations with $\delta c_1/\tilde{c}_1 > 1/\tilde{n}_s$ to exist, it is necessary that the monomer concentration $(1 + 1/\tilde{n}_s)\tilde{c}_1$ (which, according to (144) and (162), is characteristic of the beginning of the final stage of micellation) be lower than the monomer concentration

$c_1 = c$ corresponding to the beginning of the whole process of micellation, i.e.,

$$(1 + 1/\tilde{n}_s)\tilde{c}_1/c < 1. \quad (173)$$

Otherwise, over the entire range of micellation ($c \geq c_1 \geq \tilde{c}_1$), condition (162) would be valid, and, therefore, the process immediately after beginning would enter its final stage. In this case, the time t_r would be identical to the time required to establish the state of complete equilibrium in the micellar solution.

The subsequent analysis is based on the assumption that inequality (173) is valid. The relationship

$$\frac{(1 + 1/\tilde{n}_s)\tilde{c}_1}{c} = \frac{\tilde{n}_s + 1}{\tilde{n}_s + \tilde{n}_s^2\tilde{c}_{\rm M}/\tilde{c}_1}, \quad (174)$$

which follows from (160), shows that this assumption is valid only if $\tilde{n}_s^2\tilde{c}_{\rm M}/\tilde{c}_1 > 1$. This inequality is consistent with condition (157) and is always satisfied at surfactant concentrations above the first CMC.

Integration of Eq. (172) over c_1 from $c_1 = (1 + 1/\tilde{n}_s)\tilde{c}_1$ to $c_1 = c$ gives the time required to reach the final stage of micellation:

$$t_0 = \frac{\tilde{c}_1}{\tilde{n}_s\tilde{n}_c\tilde{J}'(1 + 1/\tilde{n}_s)^{\tilde{n}_c}}\left\{1 - \left[\frac{(1 + 1/\tilde{n}_s)\tilde{c}_1}{c}\right]^{\tilde{n}_c}\right\} \quad (175)$$

$$((1 + 1/\tilde{n}_s)\tilde{c}_1/c < 1),$$

or, with consideration given to (149),

$$t_0 = \frac{\pi^{1/2}\Delta\tilde{n}_c\exp(\tilde{W}_c)}{\tilde{n}_s\tilde{n}_c\tilde{j}_c^+(1 + 1/\tilde{n}_s)^{\tilde{n}_c}}\left\{1 - \left[\frac{(1 + 1/\tilde{n}_s)\tilde{c}_1}{c}\right]^{\tilde{n}_c}\right\} \quad (176)$$

$$((1 + 1/\tilde{n}_s)\tilde{c}_1/c < 1).$$

The period up to t_0 corresponds to the stage of accumulation of substance in the micelles (during the final stage the amount accumulated is negligibly small).

Let us now consider how the time t_0 depends on the concentration of micelles in the state of complete equilibrium of the solution when the monomers concentration is slightly changed, so that $\tilde{n}_s$, $\tilde{n}_c$, $\Delta\tilde{n}_s$, and $\Delta\tilde{n}_c$, which are weakly sensitive to the monomer concentration [40], remain virtually unchanged. Omitting in (176) $[(1 + 1/\tilde{n}_s)\tilde{c}_1/c]^{\tilde{n}_c}$ (in view of (173) and $\tilde{n}_c \gg 1$), using (142) and (143), and taking into account that j_c^+ is proportional to the concentration $\tilde{c}_1$, we obtained

$$t_0^{(1)}/t_0^{(2)} = (\tilde{c}_{\rm M}^{(2)}/\tilde{c}_{\rm M}^{(1)})^{\tilde{n}_c/\tilde{n}_s} \quad (177)$$

$$((1 + 1/\tilde{n}_s)\tilde{c}_1^{(1)}/c^{(1)} < 1, (1 + 1/\tilde{n}_s)\tilde{c}_1^{(2)}/c^{(2)} < 1),$$

which is exactly analogous to (159). According to (177), t_0 decreases with increasing micelle concentration $\tilde{c}_{\rm M}$ in the final state inversely proportionally to $\tilde{c}_{\rm M}^{\tilde{n}_c/\tilde{n}_s}$.

Equation (172) and the inequality $\tilde{n}_c \gg 1$ suggest that the rate of the decrease of the monomer concentration with time is relatively high in a region in which c_1 is at least only slightly higher than $\tilde{c}_1$, i.e., where $(c_1/\tilde{c}_1)^{\tilde{n}_c} \gg 1$. Therefore, this region virtually does not affect the result of integration of Eq. (172). Indeed, in (175) and (176), the total (initial) concentration of monomers c ($c_1^{(i)} > c_1$) enters only in the second term in the braces, which is much less than unity and, hence, only slightly affects t_0, even if c_1 is replaced by $c_1^{(i)}$, which is at least somewhat higher than $(1 + 1/\tilde{n}_s)\tilde{c}_1$. For example, at $\tilde{n}_s \sim 10^2$ and $\tilde{n}_c \sim 30$, it suffices to use $c_1^{(i)} \simeq (1 + 7/\tilde{n}_s)\tilde{c}_1$. The fact that the $(1 + 7/\tilde{n}_s)\tilde{c}_1 > c_1 > (1 + 1/\tilde{n}_s)\tilde{c}_1$ range, though extremely narrow, largely determines the value of t_0 substantiates setting $n_s = \tilde{n}_s$, $\Delta n_s = \Delta\tilde{n}_s$, $n_c = \tilde{n}_c$, and $\Delta n_c = \Delta\tilde{n}_c$ (see above).

12. HIERARCHY OF CHARACTERISTIC TIMES OF MICELLATION

Let us now consider a hierarchy of characteristic times of micellation. The existence of such a hierarchy is required that the quasi-equilibrium concentrations of molecular aggregates in the subcritical and supercritical regions and the quasistationary concentration of molecular aggregates in the near-critical region, qualitatively substantiated in preceeding sections, be established. Such a hierarchy gives a visual representation of the relative values of the characteristic times of formation and decomposition of micelles and of the complex, multistage process of approach of the micellar solution to the state of equilibrium.

Let the mean time interval between two consecutive emissions of a surfactant monomer by a micelle be τ_1. According to probabilistic–statistical concepts, the mean time between two consecutive emissions of a surfactant monomer by an aggregate comprised of n molecules is given by $1/j_n^-$. Since the condition of macroscopic description of micellation kinetics is satisfied in the micellar region, $\Delta n_s \gg 1$, (25) and (49) suggest that, with a high accuracy, $j_n^- = j_s^+$ at $n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s$. Using this equality, we obtain

$$\tau_1 = 1/j_s^+. \quad (178)$$

Since τ_1 is the mean time it takes for n_s-mer micelle to emit an arbitrary surfactant molecule, the probability of emitting a marked molecule (one of n_s) is n_s longer, i.e., $n_s\tau_1$. This quantity can be considered the mean time of residence of a surfactant molecule in such a micelle.

The shorter the time τ_1, the greater the ability of a micelle to change the composition of the constituent molecules.

Let us now determine the mean lifetime of a micelle. In Section 5, we derived the expressions for the direct quasistationary flux J' of molecular aggregates through the hump in the aggregation work–aggregation number dependence from the subcritical to the supercritical region and for the reverse quasistationary flux J''. The existence of the reverse flux means that J'' molecules in unit volume per unit time migrate due to fluctuations from the micellar into the subcritical region (molecular aggregates virtually do not migrate into the $n \gtrsim n_s + \Delta n_s$ region due to the rapid growth of the work of aggregation with increasing n).

The migration of molecular aggregates from the micellar to the subcritical region means that micelles decay. This decay is not a single event but occurs by the multistep mechanism of exchange of surfactant monomers between the molecular aggregates and the micellar solution. This mechanism underlies the derivation of the kinetic equation of aggregation in Section 2.

It would take time

$$\tau_{\mathrm{M}} = c_{\mathrm{M}}/|J''| \tag{179}$$

for all the micelles to pass from the micellar into the subcritical region. Here, c_{M} is the total concentration of micelles; the modulus of J'' is used because it is negative. Thus, τ_{M} is the mean lifetime of a micelle.

Substituting expression (74) for J'' into (179) yields

$$\tau_{\mathrm{M}} = \pi \Delta n_c \Delta n_s \exp(W_c - W_s)/j_c^+. \tag{180}$$

According to (180), τ_{M} is independent of the total concentration of micelles c_{M} and the volume of the micellar solution. The longer the time τ_{M}, the stabler the micelles.

The emission of surfactant monomers by the molecular aggregates into the micellar solutions and the fluctuation-mode migration of aggregates from the micellar to the subcritical region occur not only at the initial stage of micellation but also when the micellar solution approaches its equilibrium state and even afterwards. Therefore, the characteristic times τ_1 and τ_{M} characterize not only the initial stage of micellation but also the subsequent evolution of the micellar solution. Note, however, that, even at the initial stage of micellation, when the quantities j_s^+ and J'' just take nonzero values, τ_1 and τ_{M} become physically sensible parameters.

Consider the entire set of characteristic times governing the kinetics of micellation: τ_1, τ_{M}, t_s, t', t'', t_c, t_1, t_r, and t_0. While the times t_s and t' of attainment of quasi-equilibrium concentrations of molecular aggregates in the micellar and subcritical regions, the time t'' of attainment of the quasi-equilibrium concentrations of the molecular aggregates within the range of the supercritical region to the left from the micellar region at the n axis, and time t_c of attainment of the quasistationary concentrations of the molecular aggregates within the near-critical region characterize the evolution of an ensemble of molecular aggregates within the characteristic ranges of aggregation numbers, the mean time τ_1 between two consecutive emissions of a surfactant monomer by a micelle and the mean lifetime τ_{M} of a micelle characterize individual micelles. On the other hand, the times t_1 and t_r of rapid and slow relaxation and the time t_0 of attainment of the final stage of micellation describe the relaxational behavior of the micellar solution as a whole.

According to (89), (90), and (100),

$$t'/t_c \approx 2n_c/\Delta n_c, \quad t''/t_c \approx 2(n_s - n_c)/\Delta n_c. \tag{181}$$

Taking into account conditions (34) and using the estimate $n_s - n_c \gtrsim n_c$ (which suggest that $n_s - n_c$ and n_c can be comparable), we obtained from (181)

$$t''/t_c \gtrsim t'/t_c \gg 1. \tag{182}$$

Combining (88) and (100) yields

$$t_c/t_s = (\Delta n_c/\Delta n_s)^2 (j_s^+/j_c^+). \tag{183}$$

The available analytical model for describing the work of aggregation W_n for surfactant solutions predict that Δn_c and Δn_s are comparable [40]. Assuming that j_c^+ and j_s^+ are similar, we obtained from (183)

$$t_c/t_s \sim 1. \tag{184}$$

According to (88) and (178),

$$t_s/\tau_1 = (\Delta n_s)^2/2. \tag{185}$$

Applying the first of conditions (35) to (185) results in

$$t_s/\tau_1 \gg 1. \tag{186}$$

Comparing expression (176) for t_0 with expression (158) for t_r, and taking into account that the conditions of validity ((173) and (157)) of these expressions are compatible, we obtain

$$\frac{t_0}{t_r} = \frac{\tilde{n}_s}{\tilde{n}_c (1 + 1/\tilde{n}_s)^{\tilde{n}_c}} \left[1 - \left(\frac{\tilde{n}_s + 1}{\tilde{n}_s + \tilde{n}_s^2 \tilde{c}_{\mathrm{M}}/\tilde{c}_1}\right)^{\tilde{n}_c}\right] \tag{187}$$

$$(\tilde{n}_s^2 \tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1).$$

Let $\tilde{n}_s \sim 10^2$ and $\tilde{n}_c \sim 30$, quite realistic estimates. Above the first CMC, at $\tilde{n}_s^2 \tilde{c}_{\mathrm{M}}/\tilde{c}_1 > 10$, the ratio t_0/t_r increases only slightly with the total concentration (in view of (187)), remaining, nevertheless, below 2.5. Clearly, the sum $t_0 + t_r$ is the overall time of attainment of the equilibrium state of the solution. Being according to (176) and (158) proportional to the exponential function $\exp \tilde{W}_c$, the times t_0 and t_r are highly sensitive, as this function, to the monomer concentration $\tilde{c}_1$. In this case, it is difficult, if not impossible, to observe experimentally a small difference between t_0, or even $t_0 + t_r$, from t_r. Therefore, it is safe to claim that t_r not only determines the time of relaxation of the solution at the final stage of micellation but also provides an estimate of the time it takes to attain the equilibrium state of the micellar solution:

$$t_r/t_0 \sim 1. \tag{188}$$

According to (158) and (90)

$$t_r/t'' \approx \pi^{1/2}\exp\tilde{W}_c/[(\tilde{n}_s - \tilde{n}_c)\tilde{n}_s^2] \quad (\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1) \tag{189}$$

(we applied estimate (90) to the final stage of micellation). Since the first of equalities (36) is very strong due to its exponential character, the condition $\exp\tilde{W}_c/[(\tilde{n}_s - \tilde{n}_c)\tilde{n}_s^2] \gg 1$ is satisfied (according to (130), this means that the second of inequalities (36) is much stronger than inequality (157)), we have

$$t_r/t'' \gg 1 \quad (\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1). \tag{190}$$

Combining (180), (158), and (130),

$$\tau_{\mathrm{M}}/t_r = \tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \quad (\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1) \tag{191}$$

(we applied expression (180) to the final stage of micellation). By virtue of (191),

$$\tau_{\mathrm{M}}/t_r \gg 1 \quad (\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1). \tag{192}$$

In the case when the surfactant in the solution initially exists in the form of monomers, and, hence, its evolution to the equilibrium state is governed only by the internal factors, the set of relationships (182), (184), (186), (188), (190), and (192) gives the following hierarchy of characteristic times:

$$\tau_{\mathrm{M}} \gg t_0 \sim t_r \gg t'' \gtrsim t' \gg t_c \sim t_s \gg \tau_1 \quad (\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1). \tag{193}$$

The last four relationships in (193) are not associated with restriction (157).

According to (193), the times t_s, t', t'', and t_c are much shorter than t_0 and t_r. This rigorously proves that the quasi-equilibrium concentrations of the molecular aggregates in the near-critical region are actually attained. A consequence of strong inequalities (36) (generally not associated with inequality (157)), the claim that the times t_s, t', t'', and t_c are much shorter than the times t_0 and t_r is valid, which follows from the t_0 and t_r times being proportional to $\exp\tilde{W}_c^+$.

Consider the hierarchy of characteristic times when a micellar solution experiences the action of an external perturbation. In this case, an important characteristic of the process is the time of rapid relaxation of the solution (discussed in Section 8). It is this time that characterizes the establishment of the quasi-equilibrium distributions in the subcritical and supercritical regions of molecular aggregate sizes. According to

$$t_1 \lesssim t_c \tag{194}$$

(which follows from (100) and (119) at $j_c^{+(0)} \sim j_s^{+(0)}$), the time t_c remains to be the time of establishment of the quasistationary state in the near-critical region of molecular aggregate sizes in the presence of an external perturbation of the micellar solution. The concentrations of monomers and micelles at the end of the rapid relaxation of the solution, $c_1^{(0)}$ and $c_{\mathrm{M}}^{(0)}$, are the basic characteristics for the subsequent analysis. Clearly, the expressions for the relaxation time of the solution at the final stage of micellation obtained in Section 10 remain valid in the presence of an external perturbation, irrespective of whether $c_1^{(0)} > \tilde{c}_1$ or $c_1^{(0)} < \tilde{c}_1$. In view of (158) and (119),

$$\frac{t_r}{t_1} = \frac{2\pi^{1/2}\tilde{j}_s^+\Delta\tilde{n}_c(1 + \tilde{c}_{\mathrm{M}}(\Delta\tilde{n}_s)^2/2\tilde{c}_1)\exp\tilde{W}_c}{\tilde{j}_c^+(\Delta\tilde{n}_s)^2\tilde{n}_s^2} \quad (\tilde{n}_s^2\tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1) \tag{195}$$

(we applied expression (119) to the final stage of micellation). The inequality

$$t_r \gg t_1 \tag{196}$$

(which follows from (195), strong inequalities (36) (as noted above, the second of inequalities (36) is much stronger than (157)), and the estimates $\tilde{j}_c^+ \sim \tilde{j}_s^+$ and $\tilde{c}_{\mathrm{M}}(\Delta\tilde{n}_s)^2/\tilde{c}_1 \sim 1$) suggests that it is possible to separate the overall process of relaxation of a micellar solution into slow and rapid stages. It is obvious that the times τ_1 and τ_{M} retain their physical meaning in the absence and presence of an external perturbation, with (192) remaining valid. Note that, according to (184), (186), and (194), we have

$$t_1/\tau_1 \gg 1, \tag{197}$$

while, according to (192), inequality (196) yields

$$\tau_{\mathrm{M}} \gg t_1, \tag{198}$$

which was assumed to be valid when rapid relaxation was discussed.

Let us now consider how to extend the expressions for the time of attainment of the final stage of micellation t_0 (obtained in Section 11) to the case of a micellar solution experiencing an external perturbation. To formulate the main conclusions, we will consider not the time t_0 itself but its maximum value ($\max t_0$). If $c_1^{(0)} > \tilde{c}_1$, and, correspondingly, the concentration c_1

decreases while c_{M} decreases, $\max t_0$ is achieved at $c_1^{(0)} > (1 + 7/\tilde{n}_s)\tilde{c}_1$; then,

$$\max t_0/t_r \simeq 2.5 \quad (\tilde{n}_c/\tilde{n}_s \simeq 1/3, c_1^{(0)} > \tilde{c}_1), \qquad (199)$$

with the main contribution to $\max t_0$ coming from a narrow range $(1 + 7/\tilde{n}_s)\tilde{c}_1 > c_1 > (1 + 1/\tilde{n}_s)\tilde{c}_1$ of integration over c_1. Within this range, the equalities $n_s = \tilde{n}_s$, $n_c = \tilde{n}_c$, $\Delta n_s = \Delta\tilde{n}_s$, and $\Delta n_c = \Delta\tilde{n}_c$, which were used to determine $\max t_0$, are fulfilled with a high accuracy. If $c_1^{(0)} < \tilde{c}_1$, and, correspondingly, the concentration c_1 increases while c_{M} decreases, $\max t_0$ is achieved at $c_1^{(0)} < (1 - 4/\tilde{n}_s)\tilde{c}_1$; then,

$$\max t_0/t_r \simeq 0.77 \quad (\tilde{n}_c/\tilde{n}_s \simeq 1/3, c_1^{(0)} < \tilde{c}_1), \qquad (200)$$

with the main contribution to $\max t_0$ coming from a narrow range $(1 - 4/\tilde{n}_s)\tilde{c}_1 < c_1 < (1 - 1/\tilde{n}_s)\tilde{c}_1$ of integration over c_1. Within this range, the equalities $n_s = \tilde{n}_s$, $n_c = \tilde{n}_c$, $\Delta n_s = \Delta\tilde{n}_s$, $\Delta n_c = \Delta\tilde{n}_c$, and $c_{\mathrm{M}}/\tilde{c}_{\mathrm{M}} = 1$, which were used to determine $\max t_0$, are fulfilled with a high accuracy.

Note that, in the integration (over c_1) ranges $c_1^{(0)} > c_1 > (1 + 7/\tilde{n}_s)\tilde{c}_1$ and $c_1^{(0)} < c_1 < (1 - 4/\tilde{n}_s)\tilde{c}_1$ (unimportant for determining $\max t_0$ but not t_0 itself over the entire range of its possible variation), changes in c_1 and even in c_{M} after rapid relaxation completion can be significant if $c_1^{(0)} \gg (1 + 7/\tilde{n}_s)\tilde{c}_1$ and, correspondingly, $c_1^{(0)} \ll (1 - 4/\tilde{n}_s)\tilde{c}_1$.

Thus, relationships (192), (194), (196)–(200) specify the following hierarchy in the characteristic times of micellation in the presence of an external perturbation of the micellar solution

$$\begin{gathered} \tau_{\mathrm{M}} \gg \max t_0 \sim t_r \gg t_c \gtrsim t_1 \gg \tau_1 \\ (\tilde{n}_s^2 \tilde{c}_{\mathrm{M}}/\tilde{c}_1 \gg 1). \end{gathered} \qquad (201)$$

As can be seen, chains of inequalities (201) and (193) begin with τ_{M} and end with τ_1. This suggests that micelles are stable molecular formations and, at the same time, capable of changing the composition of the constituent molecules. As can be seen, the mean lifetime of the micelles considerably exceeds the time of slow relaxation of the micellar solution, to which it is sometimes attributed.

The above hierarchy of the characteristic times of micellation between the first and second CMCs in nonionic surfactant solutions was recently supported [35] by numerically solving system of equations (22), (26) for the kinetics of aggregation within the framework of a quasi-drop model of micelles. Results of a molecular dynamics modeling of the kinetics of spontaneous micellation between the first and second CMCs were reported in [41]. The development of experimental studies of the characteristic times of micellation and the values of these times for various technological processes in surfactant solutions were discussed in [42, 43].

CONCLUSIONS

At present, there are comparatively reliable data on the position of the well in the aggregation work–aggregation number dependence for the formation of molecular surfactant aggregates (the mean micelle size), the halfwidth of this well (the variance of the micelle size) and even the depth of the well, i.e., the minimum of the work of aggregation (from data on the concentration of micelles). Less reliable data have been obtained on the position, halfwidth, and, especially, height of the hump in the aggregation work–aggregation number dependence. Note, however, that the rates of the slowest processes of micellation exponentially depend on the height of this hump (see (158), (176), and (180)), i.e. its influence is extremely strong.

Formula (158) makes it possible to determine $\exp \tilde{W}_c$, which is the extremely large and highly sensitive to the concentrations of surfactant monomers, from the measured time of slow relaxation of the micellar solution. Although the information about the maximum work is obtained from the rate of establishment of the equilibrium state of the solution, it is valid for all of the states of the micellar solution. Indeed the work of formation of a molecular aggregate and, hence, its maximum value is independent of whether the micellar solution exist in the state of complete equilibrium.

Note that the above kinetic approach to describing the process of micellation made it possible to relate the maximum work of formation of a molecular surfactant aggregate to experimental data. The equilibrium micellation theory does not consider this maximum at all—only the minimum of the work of formation of a molecular aggregate enters into the formulas of this theory (as in expression (130) for the total equilibrium concentration of micelles).

Any thermodynamic model of the work of aggregation in micellar solution relates the amplitudes of the maximum and minimum of the work of aggregation and their positions at the aggregation number axis [40]. In this case, experimental data on the characteristic times of aggregation in a micellar solution can be related (using the above formulas for describing the kinetics of aggregation) with its equilibrium characteristics. Thus, the above kinetic approach to the process of micellation can be considered as the basis for systematic tests of the consistency of models of micelles.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-03-32134.

REFERENCES

1. E. A. G. Aniansson and S. N. Wall, J. Phys. Chem. **78** (10), 1024 (1974).
2. M. Almgren, E. A. G. Aniansson, and K. Holmaker, Chem. Phys. **19**, 1 (1977).
3. E. A. G. Aniansson, Ber. Bunsen-Ges. Phys. Chem. **82**, 981 (1978).
4. H. Hoffmann, Prog. Colloid Polym. Sci. **65**, 148 (1978).
5. M. Kahlweit and M. Teubner, Adv. Colloid Interface Sci. **13** (1–2), 1 (1980).
6. E. A. G. Aniansson, in *Techniques and Applications of Fast Reactions in Solution*, Ed. by W. J. Gettins and E. Wyn-Jones (D. Reidel, Dordrecht, 1979), p. 249.
7. S. Wall and C. Elvingson, J. Phys. Chem. **89**, 2695 (1985).
8. J. Billingham and P. V. Coveney, J. Chem. Soc., Faraday Trans. **90**, 1953 (1994).
9. P. V. Coveney and J. A. D. Wattis, Proc. Roy. Soc. A (London) **452**, 2079 (1996).
10. G. Waton, J. Phys. Chem. B **101** (47), 9727 (1997).
11. R. Becker, *Theory of Heat*, 2nd ed. (Springer, Berlin, 1967; Energiya, Moscow, 1974) [in Russian].
12. F. M. Kuni, Kolloidn. Zh. **46**, 674 (1984).
13. F. M. Kuni, A. K. Shchekin, and A. I. Rusanov, Kolloidn. Zh. **55**, 45 (1993).
14. F. M. Kuni, A. K. Shchekin, and A. P. Grinin, Usp. Fiz. Nauk **171** (4), 345 (2001).
15. G. Porte, Y. Poggi, J. Appell, and G. Maret, J. Phys. Chem. **88**, 5713 (1984).
16. A. Bernheim-Groswasser, E. Wachtel, and Y. Talmon, Langmuir **16**, 4131 (2000).
17. S. May and A. Ben-Shaul, J. Phys. Chem. B **105**, 630 (2001).
18. A. I. Rusanov, *Micellization in Solutions of Surfactants* (Khimiya, St. Petersburg, 1992) [in Russian].
19. A. I. Rusanov, F. M. Kuni, A. P. Grinin, and A. K. Shchekin, Kolloidn. Zh. **64**, 670 (2002) [Colloid J. **64**, 605 (2002)].
20. A. I. Rusanov, A. P. Grinin, F. M. Kuni, and A. K. Shchekin, Zh. Obshch. Khim. **72**, 651 (2002) [Russ. J. Gen. Chem. **72**, 607(2002)].
21. A. P. Grinin, A. I. Rusanov, F. M. Kuni, and A. K. Shchekin, Kolloidn. Zh. **65**, 168 (2003) [Colloid J. **65**, 145 (2003)].
22. A. I. Rusanov, F. M. Kuni, and A. K. Shchekin, Kolloidn. Zh. **62**, 199 (2000) [Colloid J. **62**, 167 (1999)].
23. F. M. Kuni, A. K. Shchekin, A. P. Grinin, and A. I. Rusanov, Kolloidn. Zh. **62**, 204 (2000) [Colloid J. **62**, 172 (2000)].
24. F. M. Kuni, A. P. Grinin, A. K. Shchekin, and A. I. Rusanov, Kolloidn. Zh. **62**, 505 (2000) [Colloid J. **62**, 451 (2000)].
25. F. M. Kuni, A. P. Grinin, A. K. Shchekin, and A. I. Rusanov, Kolloidn. Zh. **63**, 220 (2001) [Colloid J. **63**, 197 (2001)].
26. F. M. Kuni, A. K. Shchekin, A. P. Grinin, and A. I. Rusanov, Kolloidn. Zh. **63**, 792 (2001) [Colloid J. **63**, 723 (2001)].
27. M. Volmer, *Kinetik der Phasenbildung* (T. Steinkopff, Dresden, 1939; Nauka, Moscow, 1986) [in Russian].
28. J. M. Ball, J. Carr, and O. Penrose, Commun. Math. Phys. **104**, 657 (1986).
29. K. Binder, Phys. Rev. B: Solid State **15** (19), 4425 (1977).
30. F. M. Kuni and A. P. Grinin, Kolloidn. Zh. **46** (1), 23 (1984).
31. *Molecular Interactions*, Ed. by H. Ratajczak and W. J. Orville-Thomas (Wiley, New York, 1981; Mir, Moscow, 1984), Vol. 2.
32. T. Telgmann and U. Kaatze, J. Phys. Chem. B **101**, 7758 (1997).
33. T. Telgmann and U. Kaatze, J. Phys. Chem. B **101**, 7766 (1997).
34. E. V. Chertkov, A. A. Saidov, and P. K. Khabibullaev, Colloids Surf., A **168**, 185 (2000).
35. A. P. Grinin and D. S. Greben'kov, Kolloidn. Zh. **65**, 603 (2003) [Colloid J. **65**, 552 (2003)].
36. C. Tanford, J. Phys. Chem. **78**, 2469 (1974).
37. J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, J. Chem. Soc., Faraday Trans. 2 **72** (9), 1525 (1976).
38. C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed. (Wiley, Toronto, 1980).
39. R. Nagarajan and E. Ruckenstein, *Equations of State for Fluids and Fluid Mixtures*, Ed. by J. V. Sengers *et al.* (IUPAC, 2000), p. 589.
40. F. M. Kuni, A. K. Shchekin, A. P. Grinin, and A. I. Rusanov, Kolloidn. Zh. **65**, 500 (2003) [Colloid J. **65**, 459 (2003)].
41. S. J. Marrink, D. P. Tieleman, and A. E. Mark, J. Phys. Chem. **104**, 12165 (2000).
42. A. Patist, S. G. Oh, R. Leung, and D. O. Shah, Colloids Surf., A **176**, 3 (2001).
43. A. Patist, J. R. Kanicky, P. K. Shukla, and D. O. Shah, J. Colloid Interface Sci. **245**, 1 (2002).