

# Thermodynamic and Kinetic Foundations of the Micellization Theory: 4. Kinetics of Establishment of Equilibrium in a Micellar Solution

F. M. Kuni, A. P. Grinin, A. K. Shchekin, and A. I. Rusanov

Research Institute of Physics, St. Petersburg State University (Petrodvorets Branch),  
ul. Ul'yanovskaya 1, Petrodvorets, 198904 Russia

Received December 22, 1999

**Abstract**—A system of the kinetic equations of the material balance for the concentrations of surfactant monomers and micelles in a micellar nonionic surfactant solution was formulated. The equilibrium state of a materially isolated micellar solution was analyzed. The system of the kinetic equations of the material balance of a micellar solution was solved. The total time of the establishment of equilibrium in a micellar solution was determined. It was shown that this time increases or (typically) decreases with an increase in micelle concentration, depending on the degree of micellization.

## INTRODUCTION

A large number of theoretical works was devoted to the kinetics of micellization in surfactant solutions. These works were initially stimulated by the existence of two experimentally observed relaxation times of a micellar solution. The understanding of the nature of these times was reported already in [1–4]. The approach proposed in [1] on the basis of the step-by-step growth of micelles gained wide acceptance and then was applied for describing more complex systems (for example, see [5, 6]). However, being based on the idea of the barrier character of a micellization process, this approach did not use to the full extent the potentialities of the theory of nucleation in the establishment of the correlation between the basic characteristics of the micellization process, individual properties of molecular aggregates, and the parameters of the initial and final states of micellar solution. Recently, the interest to the micellization kinetics has been rekindled. The works have been published [7, 8] where the starting (for [1]) step-by-step scheme of the micellization kinetics has been analyzed with respect to the solution stability, and the procedure of shorter description, which allows to optimize the algorithms of the numerical solution of a system of kinetic equations, has been suggested.

The goal of a series of studies started in [9–11] and continued in this work is to analytically describe the micellization process basing on such fundamental ideas and notions of the theory of nucleation as the activation barrier of micellization, quasi-equilibrium and quasi-steady states of the ensembles of molecular aggregates within various ranges of aggregation numbers, direct and reverse quasi-steady-state fluxes of the molecular aggregates over the activation barrier of micellization, and the hierarchy of the scaling times in the evolution of micellar solution. The proposed theory formulates at

a quantitative level the conditions of the applicability of kinetic description, takes these conditions into account, and reveals complex multistage character of the micellization process rather than just treats differently the micellization kinetics.

In this work, we present physically transparent substantiation of the solution (discussed in [1–4]) of the problem of the micellar solution relaxation at a final stage of micellization, near the complete equilibrium of a solution, and find analytically the time required to establish this final stage. In [1], the equation for defining this time, which could be analyzed numerically, was only derived. In this work, we determined the total time of the establishment of an equilibrium in a solution.

## 1. THE SYSTEM OF KINETIC EQUATIONS OF THE MATERIAL BALANCE OF MICELLAR SOLUTION

As in [9–11], we consider the colloidal surfactant in a micellar solution as a nonionic substance and the solution is assumed to be ideal. The aggregation number of the surfactant micellar aggregate in a micellar solution we denote by  $n$ . The work of the aggregate formation in the solution containing initially only surfactant monomers is expressed in thermal units  $kT$  ( $k$  is Boltzmann's constant, and  $T$  is the solution temperature) and is denoted by  $W_n$ . The concentration of molecular aggregates with the aggregation number  $n$  is denoted by  $c_n$ . At  $n = 1$ , the aggregates are none other than surfactant monomers, which, in our case of one nonionic surfactant, are considered to be identical. At  $n \gg 1$ , the value of  $n$  is assumed to be continuous. Positions of maximum and minimum of work  $W_n$  at the  $n$ -axis, i.e., the aggregation numbers of critical and stable

molecular aggregates, are denoted by  $n_c$  and  $n_s$ , respectively; these maximum and minimum, i.e., the height and the depth of the potential barrier and the potential well of work  $W_n$ , are denoted by  $W_c \equiv W_n|_{n=n_c}$  and  $W_s \equiv W_n|_{n=n_s}$ , respectively. The half-widths of potential barrier and potential well are denoted by  $\Delta n_c \equiv [2/|\partial^2 W_n/\partial n^2|_{n=n_c}]^{1/2}$  and  $\Delta n_s \equiv [2/(\partial^2 W_n/\partial n^2)_{n=n_s}]^{1/2}$ , respectively. The  $n \leq n_c - \Delta n_c$  and  $n \geq n_c + \Delta n_c$  regions we call subcritical and supercritical regions, respectively. Micelles are mainly concentrated in the  $n_s - \Delta n_s \leq n \leq n_s + \Delta n_s$  region. We call this region micellar. It is located inside the supercritical region. The part of the supercritical region, where  $n \geq n_s + \Delta n_s$  is of no interest to us, because the concentration of micellar aggregates is quite low in this region. The total concentration of micelles (their total concentration in a micellar region) we denote by  $c_M$ .

Direct  $J'$  and reverse  $J''$  fluxes of molecular aggregates overcoming (by fluctuation) the potential barrier of the work of their formation from the side of the subcritical and supercritical regions, respectively, have been introduced in [10]. According to formulas (5.8) and (5.10) [10], we have:

$$J' = c_1 j_c^+ \exp(-W_c)/\pi^{1/2} \Delta n_c, \quad (1.1)$$

$$J'' = -c_M j_c^+ \exp[-(W_c - W_s)]/\pi \Delta n_c \Delta n_s, \quad (1.2)$$

where  $j_c^+$  ( $j_c^+ > 0$ ) is the number of surfactant monomers absorbed from micellar solution by the critical molecular aggregate with  $n = n_c$  per unit time.

The  $J'$  and  $J''$  fluxes result in the fluctuation transfer of the  $J' + J''$  ( $J'' < 0$ ) number of molecular aggregates from subcritical to micellar regions in a unit volume of micellar solution per unit time. As a result, we have the equation:

$$\partial c_M / \partial t = J' + J''. \quad (1.3)$$

In the case, which is of interest for practice and forthcoming study, where the surfactant concentration is high enough to exceed the critical micellization concentration (CMC), strong inequalities:

$$\Delta n_s \gg 1, \quad \Delta n_s / (n_s - n_c) \ll 1 \quad (1.4)$$

[see [10], inequalities (1.3)] and  $\exp(W_c) \gg 1$ ,  $\exp(W_c) \gg \exp(W_s)$  [see [10], inequalities (1.4)] are valid.

According to the second of inequalities (1.4), the scatter  $\Delta n_s$  of the micellar aggregation numbers with respect to their average value  $n_s$  is quite small. Therefore, the number of surfactant monomers absorbed by micelles in a unit volume of a micellar solution is equal to  $n_s c_M$  at a high degree of accuracy. Then, due to the condition  $\exp(W_c) \gg 1$  and the resultant steep slope of the potential barrier of the aggregation work (at not too large values of  $n_c$ ), the inequality  $\sum_{n=2}^{n_c + \Delta n_c} n c_n \ll c_1$  is

valid. As a result, for the amount of surfactant in solution, we have the following equation:

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

where  $c$  is the overall surfactant concentration (total number of surfactant molecules per unit volume of a solution). The  $n_s c_M$  term is significant in (1.5) when  $\exp(W_s)$  does not exceed too much the  $n_s \Delta n_s$  value, which is large in view of (1.4) (total micelle concentration  $c_M$  is approximately by  $\Delta n_s$  times larger than the concentration  $c_n$  of micellar aggregates with  $n = n_s$ ). The stronger inequality  $\exp(W_c) \gg \exp(W_s)$ , the more noticeable the role of the  $n_s c_M$  term. The possibility that the law of the conservation of the amount of surfactant can be expressed by the bimodal approximation (1.5) was also discussed in [2] basing on the analysis of experimental data. Possible deviations from the bimodal approximation can be taken into account in the theory being developed.

In the considered case of the materially isolated micellar solution, the overall concentration  $c$  is the preset value succeeding the CMC. Let us monitor the temporal evolution of such a solution, assuming that, in the initial moment when the surfactant is added to the solvent and mixed throughout its volume, almost the whole amount of dissolved surfactant is none other than the monomers only. Hence, at the initial moment, conditions  $c_1 = c$ ,  $c_M = 0$ , and  $J'' = 0$  (only the direct flux  $J'$  exists out of two fluxes  $J'$  and  $J''$ ) are valid. The concentration  $c_1$  decreases with time (at a given overall concentration  $c$ ), while the micelle concentration  $c_M$  becomes different from zero and gradually increases. Correspondingly, the reverse flux  $J''$  of molecular aggregates arises, which progressively compete with their direct flux  $J'$ . At fairly long times, the reverse flux  $J''$  begins to fully compensate the direct flux  $J'$ . Then the materially isolated micellar solution comes to equilibrium.

As follows from (1.5) and explicit expressions (1.1) and (1.2) for the  $J'$  and  $J''$  fluxes at the known dependence of the aggregation work  $W_n$  on  $n$  and, hence, at the known dependences of  $n_c$ ,  $n_s$ ,  $\Delta n_c$ ,  $\Delta n_s$ ,  $W_c$ ,  $W_s$ , and  $j_c^+$  on concentration  $c_1$ , Eq. (1.3), at the material isolation of a solution, can be reduced to the nonlinear differential first-order equation for the  $c_1(t)$  function whose right-hand side is independent of  $t$ . The solution of this equation can be written in a general form in quadratures immediately over the entire time interval. However, the dependence of  $W_n$  on  $n$  is known only in some particular cases for the specific models of micelles [12–14]. Therefore, it is of interest to analytically solve the problem of the relaxation of the micellar solution at the final stage of micellization near the state of the complete equilibrium of a solution as well as the problem of the determination of the time of the establishment of this final stage, using only the most representative general characteristics of the aggregation work  $W_n$  but not the

whole dependence of  $W_n$  on  $n$ . This will be performed precisely in the next sections of this work.

## 2. RELATIONSHIP BETWEEN THE MONOMER CONCENTRATION, MICELLE CONCENTRATION, AND THE OVERALL SURFACTANT CONCENTRATION AT THE FINAL EQUILIBRIUM STATE OF MICELLAR SOLUTION

Denoting the values characterizing the equilibrium state of the materially isolated micellar solution by the wavy bar, we have

$$\tilde{J}' + \tilde{J}'' = 0. \quad (2.1)$$

Substituting (1.1) and (1.2) into (2.1), we obtain

$$\tilde{c}_M = \pi^{1/2} \tilde{c}_1 \tilde{\Delta n}_s \exp(-\tilde{W}_s). \quad (2.2)$$

From (2.2) and expressions

$$c_n^{(e)} = c_1 \exp(-W_n) \quad (n \leq n_c - \Delta n_c), \quad (2.3)$$

$$c_n^{(e)} = (c_M / \pi^{1/2} \Delta n_s) \exp[-(W_n - W_s)] \quad (n \geq n_c + \Delta n_c) \quad (2.4)$$

set by formulas (2.4) and (2.8) in [2], for the concentrations  $c_n^{(e)}$  of molecular aggregates in the subcritical and supercritical regions of their sizes it follows that the complete equilibrium between all molecular aggregates of a micellar solution is established at the final stage. According to (2.2)–(2.4), this state is characterized by the concentration of molecular aggregates

$$\tilde{c}_n^{(e)} = \tilde{c}_1 \exp(-\tilde{W}_n), \quad (2.5)$$

thus corresponding to formula (1.10) in [1].

Allowing for (2.2) in (1.5), we have

$$\tilde{c}_1 + \pi^{1/2} \tilde{c}_1 \tilde{n}_s \tilde{\Delta n}_s \exp(-\tilde{W}_s) = c. \quad (2.6)$$

At a given overall concentration  $c$  and the known dependences of  $n_s$ ,  $\Delta n_s$ , and  $W_s$  on monomer concentration  $c_1$ , relation (2.6) results in the equation for the determination of the equilibrium concentration  $\tilde{c}_1$ . Once the equilibrium concentration  $\tilde{c}_1$  of surfactant monomers is found, the equilibrium concentration  $\tilde{c}_M$  can be determined using the relation

$$\tilde{c}_M = (c - \tilde{c}_1) / \tilde{n}_s, \quad (2.7)$$

which follows from (1.5).

If the equilibrium concentration  $\tilde{c}_1$  of surfactant monomers is known from the experiment, the concentration  $c$  and equilibrium concentration  $\tilde{c}_M$  are determined by relations (2.6) and (2.7). If the equilibrium micelle concentration  $\tilde{c}_M$  is known experimentally, the equilibrium concentration  $\tilde{c}_1$  can be calculated solving

Eq. (2.2) with respect to  $\tilde{c}_1$  and concentration  $c$  can be determined using relation (2.7).

Hence, for the nonequilibrium micellar solution, two concentrations (out of three characteristic concentrations  $c_1$ ,  $c_M$ , and  $c$ ) were independent parameters [due to Eq. (1.5)], while for the equilibrium solution, only one concentration will be an independent parameter [because of supplementary equation (2.1)].

According to the mass action law, we have

$$\tilde{c}_n^{(e)} = K_n \tilde{c}_1^n, \quad (2.8)$$

where coefficients  $K_n$  are independent of concentration  $\tilde{c}_1$  at the assumed ideality of micellar solution. From (2.5), (2.6), and (2.8), it follows that

$$\tilde{c}_1 + \pi^{1/2} \tilde{n}_s \tilde{\Delta n}_s K_{\tilde{n}_s} \tilde{c}_1^{\tilde{n}_s} = c. \quad (2.9)$$

According to (1.4), the inequality  $\tilde{n}_s \gg 1$  is valid. In this case, the dependence of the second term in the left-hand side of (2.9) on  $\tilde{c}_1$  is quite strong due to factor  $\tilde{c}_1^{\tilde{n}_s}$ . However, the dependence of this term on  $\tilde{c}_1$  appears to be much weaker because of factors  $\tilde{n}_s$  and  $\tilde{\Delta n}_s$ . Then in full agreement with [12] and basing on (2.9), we can make the following conclusion. As the overall concentration  $c$  exceeds the CMC, the monomer concentration  $\tilde{c}_1$  also begins to exceed gradually (albeit rather slow) the CMC, still remaining near the CMC.

Comparing (2.5) and (2.8), we obtain

$$\tilde{W}_n = -\ln K_n - (n-1) \ln \tilde{c}_1. \quad (2.10)$$

Since, as was shown in [9], the work  $W_n$  of the molecular aggregate formation is not related by its physical meaning with the fact whether micellar solution is at equilibrium or not, we can also specify Eq. (2.10) as

$$W_n = -\ln K_n - (n-1) \ln c_1. \quad (2.11)$$

The relation (2.11) is equivalent to relation (1.12) in [9].

It follows from (2.11):

$$\partial W_n / \partial c_1 = -(n-1) / c_1. \quad (2.12)$$

Taking into account the definition  $W_s \equiv W_n|_{n=n_s}$  of the minimum  $W_s$  of work  $W_n$ , we evidently have

$$\frac{\partial W_s}{\partial c_1} = \left. \frac{\partial W_n}{\partial c_1} \right|_{n=n_s} + \left. \frac{\partial W_n}{\partial n} \right|_{n=n_s} \frac{\partial n_s}{\partial c_1}. \quad (2.13)$$

Because the work  $W_n$  is minimal at  $n = n_s$ , in view of necessary condition  $(\partial W_n / \partial n)|_{n=n_s} = 0$ , from (2.13) with allowance for (2.12), we obtain

$$\partial W_s / \partial c_1 = -(n_s - 1) / c_1, \quad (2.14)$$

and, hence

$$\partial W_s / \partial c_1 < 0. \quad (2.15)$$

The same speculations, which were used for the derivation of (2.14) and (2.15), can be applied to the maximum  $W_c \equiv W_n|_{n=n_c}$  of work  $W_n$ . Then, together with (2.14) and (2.15), we have

$$\partial W_c / \partial c_1 = -(n_c - 1) / c_1, \quad (2.16)$$

$$\partial W_c / \partial c_1 < 0. \quad (2.17)$$

According to (2.15), the value in the left-hand side of Eq. (2.6) monotonically increases with concentration  $\tilde{c}_1$ . This indicates that the solution of Eq. (2.6) with respect to concentration  $\tilde{c}_1$  at a given concentration  $c$  is the unique solution. According to (2.15), the unique solution will also be the solution of Eq. (2.2) with respect to concentration  $\tilde{c}_1$  at a given concentration  $\tilde{c}_M$ .

Let us consider two micellar solutions, where monomer concentrations are almost identical at the equilibrium state so that  $\tilde{n}_s$ ,  $\tilde{n}_c$ , and  $\tilde{\Delta n}_s$  virtually coincide. Denoting the values for these solutions by superscripts 1 and 2, we then have  $\tilde{c}_1^{(1)} / \tilde{c}_1^{(2)} \approx 1$ , and, in view of (2.14) and (2.16), we also have

$$\exp(\tilde{W}_s^{(1)}) / \exp(\tilde{W}_s^{(2)}) = (\tilde{c}_1^{(2)} / \tilde{c}_1^{(1)})^{\tilde{n}_s - 1}, \quad (2.18)$$

$$\exp(\tilde{W}_c^{(1)}) / \exp(\tilde{W}_c^{(2)}) = (\tilde{c}_1^{(2)} / \tilde{c}_1^{(1)})^{\tilde{n}_c - 1}. \quad (2.19)$$

From (2.2) and (2.18), it follows that

$$\tilde{c}_M^{(1)} / \tilde{c}_M^{(2)} = (\tilde{c}_1^{(1)} / \tilde{c}_1^{(2)})^{\tilde{n}_s}. \quad (2.20)$$

Because  $\tilde{n}_s \gg 1$ , Eq. (2.20) demonstrates that, at almost identical monomer concentrations in equilibrium solutions, micelle concentrations can be quite different. According to (2.19) and (2.20), we have

$$\exp(\tilde{W}_c^{(1)}) / \exp(\tilde{W}_c^{(2)}) = (\tilde{c}_M^{(2)} / \tilde{c}_M^{(1)})^{(\tilde{n}_c - 1) / \tilde{n}_s}. \quad (2.21)$$

### 3. LINEARIZATION OF THE SYSTEM OF KINETIC EQUATIONS OF THE MATERIAL BALANCE OF A MICELLAR SOLUTION

The solution of the system of kinetic equations of the material balance of a micellar solution derived in Section 1 at all times after the initial addition of surfactant to the solvent and mixing throughout the entire volume we begin with the times, when concentrations  $c_1$  and  $c_M$  are already close to their values  $\tilde{c}_1$  and  $\tilde{c}_M$  at the equilibrium state of a solution and the reverse flux  $J''$  almost completely compensates the direct flux  $J'$ . These times correspond to the final stage of micellization.

The smallness of the deviations of the solution characteristics from their equilibrium values at a final stage allows us to linearize the system of kinetic equations of the material balance at this stage and hereby to signifi-

cantly simplify this system. This linearization will be our next task.

Let us denote the deviations of the parameters from their values at the equilibrium state of micellar solution by symbol  $\delta$ . Then, we have

$$c_1 = \tilde{c}_1 + \delta c_1, \quad (3.1)$$

$$c_M = \tilde{c}_M + \delta c_M. \quad (3.2)$$

The procedure for the determination of concentrations  $\tilde{c}_1$  and  $\tilde{c}_M$  of surfactant monomers and micelles at the final stage of the solution equilibrium using the overall surfactant concentration was described in Section 2.

Linearizing Eqs. (1.3) and (1.5) and expressions (1.1) and (1.2) discarding Eq. (1.3) with respect to  $\delta c_1$  and  $\delta c_M$  and taking into account Eq. (2.1) and the constancy of the overall concentration  $c$  in the materially isolated solution, we obtain

$$\frac{\partial \delta c_M}{\partial t} = \tilde{J}' \left( \frac{1 + \gamma + \eta}{\tilde{c}_1} \delta c_1 - \frac{1}{\tilde{c}_M} \delta c_M \right), \quad (3.3)$$

$$(1 + \lambda) \delta c_1 + \tilde{n}_s \delta c_M = 0. \quad (3.4)$$

Here,  $\gamma$ ,  $\eta$ , and  $\lambda$  are the dimensionless parameters defined by the equalities

$$\gamma = -\tilde{c}_1 (\partial W_s / \partial c_1) |_{c_1 = \tilde{c}_1}, \quad (3.5)$$

$$\eta = \tilde{c}_1 (\partial \ln \Delta n_s / \partial c_1) |_{c_1 = \tilde{c}_1}, \quad (3.6)$$

$$\lambda = \tilde{c}_M (\partial n_s / \partial c_1) |_{c_1 = \tilde{c}_1}. \quad (3.7)$$

These parameters characterize the influence of monomer concentration  $c_1$  in the vicinity of its equilibrium value  $\tilde{c}_1$  on the values of  $W_s$ ,  $\Delta n_s$ , and  $n_s$ . Similar effect of the concentration  $c_1$  on the values of  $J_c^+$ ,  $W_c$ , and  $\Delta n_c$  in expressions (1.1) and (1.2) was not taken into account in Eq. (3.3) because the dependences on  $J_c^+$ ,  $W_c$ , and  $\Delta n_c$  in expressions (1.1) and (1.2) are identical. From (3.5) and (2.14), it follows:

$$\gamma = \tilde{n}_s - 1. \quad (3.8)$$

According to (1.1), for the flux  $\tilde{J}'$  in (3.3) we have

$$\tilde{J}' = \tilde{c}_1 \tilde{J}_c^+ \exp(-\tilde{W}_c) / \pi^{1/2} \tilde{\Delta n}_c. \quad (3.9)$$

In view of (2.1), the reverse flux  $\tilde{J}''$  differs from  $\tilde{J}'$  only in the sign.

Equations (3.3) and (3.4) form the closed system of kinetic equations of the material balance for micellar solution linearized near the final state of the solution equilibrium. The functions of  $\delta c_1$  and  $\delta c_M$  on time  $t$  are the desired functions.

#### 4. RELAXATION TIME OF MICELLAR SOLUTION

The solution of the system of Eqs. (3.3) and (3.4) makes no problem. We have

$$\delta c_1 = -\frac{\tilde{n}_s}{1+\lambda} \delta c_M, \quad (4.1)$$

$$\delta c_M = \text{const} \exp(-t/t_r), \quad (4.2)$$

where time  $t_r$  is defined by the equality:

$$\frac{1}{t_r} = \tilde{J} \left[ \frac{\tilde{n}_s(1+\gamma+\eta)}{\tilde{c}_1(1+\lambda)} + \frac{1}{\tilde{c}_M} \right]. \quad (4.3)$$

Let us estimate the role of parameters  $\eta$  and  $\lambda$  in (4.3). We begin with parameter  $\eta$ .

From (3.6) and (3.8), we have:

$$\frac{\eta}{1+\gamma} = \frac{\tilde{c}_1}{\tilde{n}_s} (\partial \ln \Delta n_s / \partial c_1) |_{c_1 = \tilde{c}_1}. \quad (4.4)$$

The  $\Delta n_s$  value varies quite slowly with the variation in  $c_1$ : the scatter  $\Delta n_s$  of the micelle aggregation numbers is rather stable. In view of the first of inequalities (1.4), the logarithmic value  $\ln \Delta n_s$  varies with concentration  $c_1$  even more slowly than  $\ln \Delta n_s$ . Further, in view of inequalities (1.4),  $n_s \gg 1$  is readily valid. Then, from (4.4) it follows:

$$|\eta/(1+\gamma)| \ll 1. \quad (4.5)$$

According to (4.5), parameter  $\eta$  in (4.3) can be ignored.

Likewise, in view of the weak dependence of the average micelle aggregation number  $n_s$  on concentration  $c_1$ , from (3.7) it follows

$$|\lambda| \ll 1. \quad (4.6)$$

According to (4.6), parameter  $\lambda$  in (4.3) can also be ignored.

Omitting parameters  $\eta$  and  $\lambda$  in (4.3) and taking into account (3.8), we have

$$\frac{1}{t_r} = \tilde{J} \left( \frac{\tilde{n}_s^2}{\tilde{c}_1} + \frac{1}{\tilde{c}_M} \right). \quad (4.7)$$

Using (3.9) in (4.7), we obtain

$$t_r = \frac{\pi^{1/2} \tilde{c}_M \tilde{\Delta n}_c \exp(\tilde{W}_c)}{\tilde{c}_1 \tilde{j}_c^+} \left( 1 + \frac{\tilde{n}_s \tilde{c}_M}{\tilde{c}_1} \right)^{-1}. \quad (4.8)$$

Within the framework of approximations included in (1.5), time  $t_r$  given by relation (4.7) coincides with the time of "slow relaxation" of micellar solution determined in [1]. However, this coincidence takes place only while allowing for the fact that the  $1/R$  value introduced in [1] has the physical meaning of the direct flux of molecular aggregates overcoming (by fluctuations) the potential barrier of the work of their formation from the side of the subcritical region. The quasi-steady state of this flux was not substantiated in [1].

According to (4.8), time  $t_r$  is positive. Thus, expressions (4.1) and (4.2) correspond to the irreversible tendency of the materially isolated micellar solution to equilibrium. These same expressions indicate that time  $t_r$  given by equality (4.8) is the relaxation time of a solution at the final stage of micellization. For the constant in expression (4.2), we have inequality  $\text{const} < 0$ . Indeed, it is this inequality that, according to (4.2), ensures an increase in micelle concentration  $c_M$  with time mentioned at the end of section 1, whereas, according to (4.1) and (4.6), it provides for a decrease in concentration  $c_1$  with time also mentioned at the end of section 1.

Expressions (4.1) and (4.2) describe the temporal behavior of concentrations  $c_1$  and  $c_M$  at the final stage of micellization.

According to (4.8), the relaxation time of micellar solution does not depend on its volume. Note that the irreversible tendency of micellar solution to its final state of complete equilibrium has been substantiated in a general form in [9].

As is seen from (1.5), the  $\tilde{n}_s \tilde{c}_M / \tilde{c}_1$  value is the ratio of the amount of substance accumulated by the micelles at the final state of solution equilibrium to that of substance remaining in the form of monomers. In terms of the degree of micellization  $\alpha$  [12], this value is equal to  $\alpha/(1-\alpha)$ . Taking into account that, in a typical case, even the critical degree of micellization (corresponding to the CMC) is the value of the order of 0.1 [12] (in our case, it should be much greater); most likely that, at  $\tilde{n}_s \gg 1$ , the condition

$$\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 \gg 1 \quad (4.9)$$

is fulfilled.

Since  $\tilde{n}_s \gg 1$ , this case surely takes place when  $\tilde{n}_s \tilde{c}_M / \tilde{c}_1 \geq 1$ , i.e., when micelles in the final state of solution equilibrium accumulate noticeable or even the main part of the whole amount of a surfactant containing in a solution. In the case considered, term  $n_s c_M$  in (1.5) is significant. From (4.8), we obtain

$$t_r = \frac{\pi^{1/2} \tilde{\Delta n}_c \exp(\tilde{W}_c)}{\tilde{n}_s \tilde{j}_c^+} \quad (\tilde{n}_s \tilde{c}_M / \tilde{c}_1 \gg 1). \quad (4.10)$$

For completeness, we also consider the opposite representative (although highly improbable for non-ionic surfactants) case, where

$$\tilde{n}_s \tilde{c}_M / \tilde{c}_1 \ll 1. \quad (4.11)$$

Because  $\tilde{n}_s \gg 1$ , moreover  $\tilde{n}_s \tilde{c}_M / \tilde{c}_1 \ll 1$ , and, hence, at the final state of solution equilibrium, micelles accumulate only the small part of the whole amount of surfactant remained in a solution. Then term  $n_s c_M$  in (1.5) is a small value. From (4.8), we obtain

$$t_r = \frac{\pi^{1/2} \tilde{c}_M \tilde{\Delta n}_c \exp(\tilde{W}_c)}{\tilde{c}_1 \tilde{j}_c^+} \quad (\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 \ll 1). \quad (4.12)$$

For the  $\tilde{c}_M / \tilde{c}_1$  ratio, under conditions (4.9) and (4.11), we have expression

$$\tilde{c}_M / \tilde{c}_1 = \pi^{1/2} \tilde{\Delta n}_s \exp(-W_s) \quad (4.13)$$

followed from (2.2).

Let us establish the interrelation between time  $t_r$  and micelle concentration in an equilibrium solution at a slow variation of the monomer concentration when  $\tilde{n}_s$ ,  $\tilde{n}_c$ ,  $\tilde{\Delta n}_s$ , and  $\tilde{\Delta n}_c$  remain practically constant. Then, taking into account (2.20) and (2.21) and the fact that the intensity  $\tilde{j}_c^+$  of monomer absorption by critical molecular aggregate is proportional to monomer concentration in a solution, we have from (4.10) and (4.12)

$$t_r^{(1)} / t_r^{(2)} = (\tilde{c}_M^{(2)} / \tilde{c}_M^{(1)})^{\tilde{n}_c / \tilde{n}_s} \quad (4.14)$$

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

$$t_r^{(1)} / t_r^{(2)} = (\tilde{c}_M^{(1)} / \tilde{c}_M^{(2)})^{(\tilde{n}_s - \tilde{n}_c - 1) / \tilde{n}_s} \quad (4.15)$$

$$(\tilde{n}_s^2 \tilde{c}_M^{(1)} / \tilde{c}_1^{(1)} \ll 1, \quad \tilde{n}_s^2 \tilde{c}_M^{(2)} / \tilde{c}_1^{(2)} \ll 1).$$

Superscripts 1 and 2 denote the values at two final states of solution equilibrium, where the monomer concentrations are quite the same but micelle concentrations are probably fairly different.

According to (4.14), i.e., when the degree of micellization at the final state of solution equilibrium is notable, the relaxation time  $t_r$  of a solution to this state decreases with an increase in micelle concentration  $\tilde{c}_M$  in proportion to  $\tilde{c}_M^{\tilde{n}_c / \tilde{n}_s}$ . However, according to (4.15), i.e., when the degree of micellization at the final state of solution equilibrium is small, the relaxation time  $t_r$  to this state increases (because of  $\tilde{n}_s - \tilde{n}_c - 1 > 0$ ) with the micelle concentration  $\tilde{c}_M$  in proportion to  $\tilde{c}_M^{-(\tilde{n}_s - \tilde{n}_c - 1) / \tilde{n}_s}$ . As was already noted, this case is quite improbable.

The higher the micelle concentration at the final state of solution equilibrium, the higher the overall surfactant concentration of this solution. Then from (4.14) and (4.15) follows that, at rather large degree of micellization at the final state of solution equilibrium, the relaxation time of a solution decreases with an increase in the overall surfactant concentration of this solution. On the contrary, if the degree of micellization is low, the relaxation time increases.

## 5. TIME OF THE ESTABLISHMENT OF THE FINAL STAGE OF MICELLIZATION

Let us turn to the solution of the system of kinetic equations of the material balance of a micellar solution at the times preceding to the final stage of micellization derived in Section 1.

Assuming the equality  $n_s = \tilde{n}_s$ , which will be justified somewhat later, from (1.5) and (1.3) we have at a given overall concentration  $c$  of a solution:

$$c_1 + \tilde{n}_s c_M = c, \quad (5.1)$$

$$\partial c_1 / \partial t = -\tilde{n}_s (J' + J''). \quad (5.2)$$

In Eq. (3.3), we used the linearization of exponent  $\exp(W_s)$  with respect to deviation  $\delta c_1$ . Expanding  $\exp(W_s)$  in Taylor's series in powers of  $\delta c_1$  and taking (2.14) into account, we see that this linearization is practically valid at

$$\delta c_1 / \tilde{c}_1 \leq 1 / \tilde{n}_s. \quad (5.3)$$

Condition (5.3) specifies the region at the  $c_1$ -axis, where the final stage of micellization occurs. Although this region is quite narrow at  $\tilde{n}_s \gg 1$ , the relative variation of exponent  $\exp(W_s)$  can be, in view of (2.14), rather significant.

Assuming equality  $\Delta n_s = \tilde{\Delta n}_s$ , which will be substantiated somewhat later, from (1.1) and (1.2) with allowance for (2.1), we have:

$$J' = \tilde{j} \frac{c_1 \tilde{j}_c^+ \tilde{\Delta n}_c}{\tilde{c}_1 \tilde{j}_c^+ \tilde{\Delta n}_c} e^{-W_c + \tilde{W}_c}. \quad (5.4)$$

Using (5.4), we obtain

$$\frac{|J''|}{J'} = \frac{c_M \tilde{c}_1}{\tilde{c}_M c_1} e^{W_s - \tilde{W}_s}. \quad (5.5)$$

At the assumed equality  $n_s = \tilde{n}_s$ , according to (2.14), we have:

$$e^{W_s - \tilde{W}_s} = (\tilde{c}_1 / c_1)^{\tilde{n}_s - 1}. \quad (5.6)$$

Using (5.6) and the evident inequality  $c_M \leq \tilde{c}_M$ , we obtain from (5.5) with allowance for (3.1)

$$|J''| / J' \leq e^{-\tilde{n}_s \ln(1 + \delta c_1 / \tilde{c}_1)}. \quad (5.7)$$

According to (5.7), the inequality

$$|J''| / J' \ll 1 \quad (5.8)$$

will be actually valid at

$$\delta c_1 / \tilde{c}_1 \geq 1 / \tilde{n}_s. \quad (5.9)$$

Taking (5.8) into account, we reduce (5.2) to:

$$\partial c_1 / \partial t = -\tilde{n}_s J' \quad (\delta c_1 / \tilde{c}_1 \geq 1 / \tilde{n}_s). \quad (5.10)$$

Let us emphasize the different relative role of the reverse flux  $J''$  compared with the direct flux  $J'$  while passing from the concentration range  $c_1$  admitted by condition (5.9) to the concentration range  $c_1$  admitted by condition (5.3). In the concentration range  $c_1$  admitted by condition (5.9), the reverse flux  $J''$  does not play, according to inequality (5.8), any significant role. However, in the  $c_1$  concentration range admitted by condition (5.3), the reverse flux  $J''$  is already quite noticeable. According to expression (1.2), which includes exponent  $\exp(\tilde{W}_s)$ , it is this flux that determines the condition (5.3).

We assume equalities  $\Delta n_c = \tilde{\Delta n}_c$  and  $n_c = \tilde{n}_c$ , which will be substantiated below. Then, from (1.1) and (2.16), we have, respectively

$$J' = \tilde{J}' \frac{c_1 \tilde{J}_c^+}{\tilde{c}_1 \tilde{J}_c^+} e^{-w_c + \tilde{w}_c}, \quad (5.11)$$

$$e^{w_c - \tilde{w}_c} = (\tilde{c}_1/c_1)^{\tilde{n}_c - 1} \quad (5.12)$$

[Eq. (5.11) could be derived from (5.4) at  $\Delta n_c = \tilde{\Delta n}_c$ ].

The number of monomers  $J_c^+$  absorbed by the critical molecular aggregate from a solution per unit time is proportional to the monomer concentration  $c_1$  in solution. Taking this fact into account and substituting (5.12) into (5.11), we arrive at

$$J' = \tilde{J}' (c_1/\tilde{c}_1)^{\tilde{n}_c + 1}. \quad (5.13)$$

Substituting (5.13) into (5.10), we obtain:

$$\partial c_1 / \partial t = -\tilde{n}_s \tilde{J}' (c_1/\tilde{c}_1)^{\tilde{n}_c + 1} \quad (\delta c_1/\tilde{c}_1 \approx 1/\tilde{n}_s). \quad (5.14)$$

Condition (5.9), which is opposite to condition (5.3), specifies the region at the  $c_1$ -axis preceding the final stage of micellization. For this region to exist, it is necessary that the monomer concentration  $(1 + 1/\tilde{n}_s) \tilde{c}_1$  corresponding, according to (3.1) and (5.3), to the onset of the final stage of micellization be lower than the monomer concentration  $c$  corresponding to the onset of the whole process of micellization. Thus, we should have:

$$(1 + 1/\tilde{n}_s) \tilde{c}_1 / c < 1. \quad (5.15)$$

Otherwise, condition (5.3) should be valid within the entire region  $c \geq c_1 \geq \tilde{c}_1$  of the micellization process. Then the final stage would occur from the very beginning of this process, and the relaxation time  $t_r$  at this stage would determine the total time of the establishment of the equilibrium in a micellar solution.

Therefore, we assume hereafter that condition (5.15) is true. As is shown by the equality

$$\frac{(1 + 1/\tilde{n}_s) \tilde{c}_1}{c} = \frac{\tilde{n}_s + 1}{\tilde{n}_s + \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1}, \quad (5.16)$$

resulted from (5.1), this is possible only at  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 > 1$ .

The fact that, at  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 < 1$ , inequality (5.15), according to (5.16), is invalid, excludes in advance the case of strong inequality (4.11) from consideration. This can explain the important meaning of the  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1$  value.

Integrating Eq. (5.14) over  $c_1$  from  $c_1 = (1 + 1/\tilde{n}_s) \tilde{c}_1$  to  $c_1 = c$ , for the desired time  $t_0$  of the establishment of the final stage of micellization, we obtain

$$t_0 = \frac{\tilde{c}_1}{\tilde{n}_s \tilde{n}_c \tilde{J}' (1 + 1/\tilde{n}_s)^{\tilde{n}_c}} \left\{ 1 - \left[ \frac{(1 + 1/\tilde{n}_s) \tilde{c}_1}{c} \right]^{\tilde{n}_c} \right\} \quad (5.17)$$

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

or, in view of (3.9)

$$t_0 = \frac{\pi^{1/2} \tilde{\Delta n}_c \exp(\tilde{W}_c)}{\tilde{n}_s \tilde{n}_c \tilde{J}' (1 + 1/\tilde{n}_s)^{\tilde{n}_c}} \left\{ 1 - \left[ \frac{(1 + 1/\tilde{n}_s) \tilde{c}_1}{c} \right]^{\tilde{n}_c} \right\} \quad (5.18)$$

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

The accumulation of substance in micelles occurs precisely during the time  $t_0$  (accumulation at the final stage is negligible).

Let us establish the interrelation between the time  $t_0$  and the micelle concentration at the final state of the solution equilibrium at a small variation in the equilibrium monomer concentration at which  $\tilde{n}_s$ ,  $\tilde{n}_c$ ,  $\tilde{\Delta n}_s$ , and  $\tilde{\Delta n}_c$  remain virtually constant. Ignoring in (5.18) small, in view of (5.15) and  $\tilde{n}_c \gg 1$ , value  $[(1 + 1/\tilde{n}_s) \tilde{c}_1 / c]^{\tilde{n}_c}$ , taking (2.20) and (2.21) and the fact that  $\tilde{J}_c^+$  is proportional to concentration  $\tilde{c}_1$  into account, in complete analogy with (4.14), we have:

$$t_0^{(1)} / t_0^{(2)} = (\tilde{c}_M^{(2)} / \tilde{c}_M^{(1)})^{\tilde{n}_c / \tilde{n}_s} \quad (5.19)$$

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

According to (5.19), at the final state of solution equilibrium, time  $t_0$  decreases with an increase in micelle concentration  $\tilde{c}_M$  in the inverse proportion to  $\tilde{c}_M^{\tilde{n}_c / \tilde{n}_s}$ .

Evidently, the  $(t_0 + t_r)$  sum determines the total time of the establishment of solution equilibrium. If the degree of micellization at this state is quite large, (4.9) and, hence, (4.14), (5.15), and (5.19) are valid. According to (4.14) and (5.19), the  $(t_0 + t_r)$  time decreases with an increase in micelle concentration  $\tilde{c}_M$  in the equilibrium solution in proportion to  $\tilde{c}_M^{\tilde{n}_c / \tilde{n}_s}$ . However, if the degree of micellization is low, relations (4.11) and (4.15) are valid; however, inequality (5.15) is already invalid. In this case, as was mentioned earlier, the  $(t_0 + t_r)$  time coincides with time  $t_r$ . According to (4.15), the  $(t_0 + t_r)$

time increases with the micelle concentration  $\tilde{c}_M$  in proportion to  $\tilde{c}_M^{(\tilde{n}_s - \tilde{n}_c - 1)/\tilde{n}_s}$ .

Integrating Eqs. (5.14) over  $c_1$  at times preceding the  $t_0$  time, we could easily reveal the behavior of the concentration  $c_1$  at these times, whereas integrating (5.1), that of concentration  $c_M$ .

From (5.14) and  $\tilde{n}_c \gg 1$ , it follows that the rate of a decrease in concentration  $c_1$  with time is relatively high in the region where  $c_1$  succeeds (at least negligibly)  $\tilde{c}_1$ , i.e., in the region where  $(c_1/\tilde{c}_1)^{\tilde{n}_c} \gg 1$ . Consequently, this region does not actually appear during the integration of Eq. (5.14). All what have been said above justifies the equalities  $n_s = \tilde{n}_s$ ,  $\Delta n_s = \tilde{\Delta n}_s$ ,  $\Delta n_c = \tilde{\Delta n}_c$ , and  $n_c = \tilde{n}_c$  suggested above. In view of (5.12), this also justifies the suggested practical independence of exponent  $\exp(W_c)$  of time.

Let us consider the representative case, where condition (4.9) is fulfilled. Then, according to (5.16), inequality (5.15) is readily satisfied; hence, expression (5.18) for time  $t_0$  is also valid. Comparing this expression with expression (4.10) derived in the same representative case for time  $t_r$ , and taking (5.16) into account, we obtain

$$\frac{t_0}{t_r} = \frac{\tilde{n}_s}{\tilde{n}_c(1 + 1/\tilde{n}_s)^{\tilde{n}_c}} \left[ 1 - \left( \frac{\tilde{n}_s + 1}{\tilde{n}_s + \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1} \right)^{\tilde{n}_c} \right] \quad (5.20)$$

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

Let us assume in the estimates  $\tilde{n}_s \sim 10^2$  and  $\tilde{n}_c \sim 3 \times 10$ ; these values are quite real. At  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 = 3$ , when (4.9) is virtually fulfilled, from (5.20) we have  $t_0/t_r \approx 1.5$ . As the  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1$  ratio becomes larger than three, and correspondingly, inequality (4.9) becomes stronger, according to (5.20), the  $t_0/t_r$  ratio slightly increases but still remains smaller than 2.5.

As was mentioned above,  $t_0 + t_r$  is responsible for the total time of the establishment of equilibrium in micellar solution. Times  $t_0$  and  $t_r$ , being proportional [according to (5.18) and (4.10)] to exponent  $\exp(\tilde{W}_c)$ , are quite sensitive, together with this exponent, to the

monomer concentration  $\tilde{c}_1$ . Then, it is almost impossible to notice experimentally the slight difference between time  $t_0$  and even the  $(t_0 + t_r)$  time from time  $t_r$ , that was revealed above. Hence, it is clear that time  $t_r$  is responsible for the relaxation time of a solution at the final stage of micellization and also estimates rather exactly the total time of the establishment of equilibrium in a micellar solution.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 98-03-32009a.

## REFERENCES

1. Aniansson, E.A.G. and Wall, S.N., *J. Phys. Chem.*, 1974, vol. 78, p. 1024.
2. Almgren, M., Aniansson, E.A.G., and Holmaker, K., *Chem. Phys.*, 1977, vol. 19, p. 1.
3. Aniansson, E.A.G., *Ber. Bunsenges. Phys. Chem.*, 1978, vol. 82, p. 981.
4. Hoffmann, H., *Prog. Colloid Polym. Sci.*, 1978, vol. 65, p. 148.
5. Aniansson, E.A.G., in *Techniques and Applications of Fast Reactions in Solution*, Gettins, W.J. and Wyn-Jones, E., Eds., Dordrecht: D. Reidel, 1979, pp. 249–258.
6. Wall, S. and Elvingson, C., *J. Phys. Chem.*, 1985, vol. 89, p. 2695.
7. Billingham, J. and Coveney, P.V., *J. Chem. Soc., Faraday Trans.*, 1994, vol. 90, p. 1953.
8. Coveney, P.V. and Wattis, J.A.D., *Proc. Roy. Soc. London, Ser. A*, 1996, vol. 452, p. 2079.
9. Rusanov, A.I., Kuni, F.M., and Shchekin, A.K., *Kolloidn. Zh.*, 2000, vol. 62, no. 2, p. 199.
10. Kuni, F.M., Shchekin, A.K., Grinin, A.P., and Rusanov, A.I., *Kolloidn. Zh.*, 2000, vol. 62, no. 2, p. 204.
11. Kuni, F.M., Grinin, A.P., Shchekin, A.K., and Rusanov, A.I., *Kolloidn. Zh.*, 2000, vol. 62, no. 4, p. 505.
12. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh pov-erkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
13. Grinin, A.P., *Vest. St. Petersburg Univ., Ser. 4: Fiz., Khim.*, 1996, no. 4, p. 3.
14. Nagarajan, R., *Structure-Performance Relationships in Surfactants*, in *Surfactant Science Series*, vol. 70: Usimi, K. and Uena, N., Eds., New York: Dekker, 1997, p. 1.