

Thermodynamic and Kinetic Foundations of the Micellization Theory. 3. Initial Stages of Micellization

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Abstract—The kinetics of the initial stages of micellization was considered for the solution of a nonionic colloidal surfactant. Quasi-equilibrium concentrations of molecular surfactant aggregates in subcritical and overcritical regions of their sizes, as well as the quasi-steady-state concentration of molecular surfactant aggregates in the near-critical region of their sizes, are established at these stages. The average time between two successive acts of emission of a surfactant monomer by a micelle, the average resident time of a monomer in a micelle, and the average micelle lifetime were treated from a statistical point of view.

INTRODUCTION

We continue the study of the micellization kinetics in a surfactant solution, which was initiated in [1, 2]. The aim of this work is to consider the initial stages of micellization. At these stages, quasi-equilibrium concentrations of surfactant molecular aggregates in subcritical and overcritical regions of their sizes, as well as the quasi-steady-state concentration of molecular surfactant aggregates in the near-critical region of their sizes, are being established.

The necessity of isolating the initial stages of micellization in subcritical and overcritical regions of the aggregate sizes, and the role of these stages in the relaxation in micellar systems, were first discussed in [3–7]. However, the quantitative description was only given [3] to establish the quasi-equilibrium concentration in overcritical region of molecular aggregate sizes. It was assumed that it is this process that is responsible for one (smaller) of two observed relaxation times of the micellar solution. The establishment of a quasi-equilibrium concentration in a subcritical region of sizes [3–7] was deliberately considered to be a faster process, and the regularities of the establishment of quasi-steady-state concentration in the near-critical region of sizes were not discussed at all.

In this work, the initial stages of micellization in all size regions of molecular aggregates will be described from a unified viewpoint. Furthermore, as will be seen from the expressions given below, the time of establishing quasi-equilibrium concentration in the overcritical region of the sizes of molecular aggregates cannot be regarded as the largest value and, hence, cannot serve as an estimate of the duration of the initial stages as a whole.

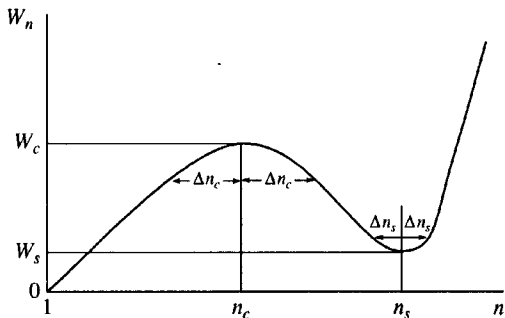
The set of notions used in this work appears also to be convenient for the introduction, together with the solution of main problem, of the important parameters characterizing a micelle as a dynamic object being in

material contact with the solution of monomeric surfactant. Among these parameters are the time between two successive acts of emission, the resident time of a surfactant monomer in a micelle, and the lifetime of a micelle.

As in [1, 2], we consider the colloidal surfactant as a nonionic substance and the solution as an ideal mixture of molecular surfactant aggregates of different sizes in a solvent.

1. TIMES OF ESTABLISHMENT OF QUASI-EQUILIBRIUM CONCENTRATIONS OF MOLECULAR AGGREGATES IN SUBCRITICAL AND OVERCRITICAL REGIONS OF THEIR SIZES

Let us denote the aggregation number of a surfactant in a micellar solution by n . The formation work of a molecular aggregate (the work of aggregation) we express in thermal units kT (k is Boltzmann's constant, and T is the solution temperature) and denote by W_n . The concentration of molecular aggregates with the aggregation number n we denote by c_n . At $n = 1$, 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 work W_n at the n -axis, i.e., the aggregation numbers of critical and stable molecular aggregates, we denote by n_c and n_s , respectively; these maximum and minimum works, i.e., the height and the depth of a potential barrier and potential well of work W_n we denote by $W_c \equiv W_n|_{n=n_c}$ and $W_s \equiv W_n|_{n=n_s}$, respectively. The half-widths of potential barrier and potential well, which are defined by equalities (1.1) in [2], we denote by Δn_c and Δn_s , respectively. The regions $n \leq n_c - \Delta n_c$, $n_c - \Delta n_c \leq n \leq n_c + \Delta n_c$, and $n \geq n_c + \Delta n_c$ we call subcritical, near-



Typical behavior of the formation work W_n of the molecular aggregate as a function of the aggregation number n .

critical, and overcritical 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 overcritical region. The part of the overcritical 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. These notions just introduced are clearly illustrated by the figure.

To construct the theory of micellization, the assumption of quasi-equilibrium concentrations of molecular aggregates in subcritical and overcritical regions of their sizes are important. This assumption was discussed in [3–7] and qualitatively substantiated in [2].

Let us analyze how establishing these quasi-equilibrium concentrations occurs with time. It will be shown in our forthcoming publications that quasi-equilibrium state actually has time to be established, and the quantitative criterion for the quasi-equilibrium aggregate concentration in the subcritical and overcritical regions of aggregate sizes will be defined.

Let us first consider (in accordance with [3]) how the quasi-equilibrium concentration of aggregates is established in the micellar region.

The variations in concentrations c_n of molecular aggregates with time t is defined by the equation of continuity

$$\partial c_n(t)/\partial t = -\partial J_n(t)/\partial n \quad (1.1)$$

[equation (3.3) in [2]]. Here, $J_n(t)$ is the flux of molecular aggregates. Argument t indicates the dependence of c_n and J_n on time.

According to relation (3.10) in [2], for the flux $J_n(t)$ in the micellar region we have:

$$J_n(t) = -j_s^+ [2(n - n_s)/(\Delta n_s)^2 + \partial/\partial n] c_n(t) \quad (1.2)$$

$$(n_s - \Delta n_s \leq n \leq n_s + \Delta n_s),$$

where j_s^+ ($j_s^+ > 0$) represents the number of surfactant monomers absorbed by a stable molecular aggregate (with $n = n_s$) from a solution per unit time.

Boundary conditions to the kinetic equation formed by relations (1.1) and (1.2) in a micellar region have the following forms:

$$c_n(t) \approx 0 \quad (n = n_s \mp \Delta n_s). \quad (1.3)$$

Approximate equality (1.3) should be understood as if the micelle concentration at the boundaries $n \approx n_s \mp \Delta n_s$ of the micellar region is negligible compared to the concentration at $n = n_s$.

For quasi-equilibrium aggregate concentration, which is established with time in the micellar region, according to Boltzmann's fluctuation principle, we have

$$c_n^{(e)} = \text{const} \exp[-(W_n - W_s)] \quad (1.4)$$

$$(n_s - \Delta n_s \leq n \leq n_s + \Delta n_s).$$

Taking into account approximation

$$W_n = W_s + \left(\frac{n - n_s}{\Delta n_s}\right)^2 \quad (1.5)$$

$$(n_s - \Delta n_s \leq n \leq n_s + \Delta n_s)$$

[approximation (1.6) in [2]], we can see from (1.4) that the quasi-equilibrium concentration rather rapidly decreases as n approaches the boundaries $n \approx n_s \mp \Delta n_s$ of the micellar region, thus satisfying the boundary conditions (1.3).

Let us pass in the micellar region from variable n to the variable

$$u \equiv (n - n_s)/\Delta n_s \quad (-1 \leq u \leq 1). \quad (1.6)$$

Assuming that

$$c(u, t) \equiv c_n(t), \quad c^{(e)}(u) \equiv c_n^{(e)} \quad (-1 \leq u \leq 1), \quad (1.7)$$

from (1.1) and (1.2), we derive the kinetic equation

$$\frac{\partial c(u, t)}{\partial t} = \frac{j_s^+}{(\Delta n_s)^2} \frac{\partial}{\partial u} \left(2u + \frac{\partial}{\partial u} \right) c(u, t) \quad (1.8)$$

$$(-1 \leq u \leq 1)$$

(differential operator $\partial/\partial u$ acts on the entire expression to the right-hand side). In this case, equation (1.3) yields boundary conditions

$$c(u, t) \approx 0 \quad (u \approx \mp 1) \quad (1.9)$$

to equation (1.8). According to (1.4)–(1.7), we also have

$$c^{(e)}(u) = \text{const} \exp(-u^2) \quad (-1 \leq u \leq 1). \quad (1.10)$$

Preparatory to solving equation (1.8), we introduce Hermitian polynomials $H_i(\xi)$ ($i = 0, 1, \dots$): $H_0(\xi) = 1$,

$H_1(\xi) = 2x, H_2(\xi) = 4\xi^2 - 2, \dots$ They satisfy recurrent relations

$$\frac{\partial}{\partial \xi} H_i(\xi) = 2iH_{i-1}(\xi), \tag{1.11}$$

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

and orthogonality and normalization relations

$$\pi^{-1/2} \int_{-\infty}^{\infty} \exp(-\xi^2) H_i(\xi) H_{i'}(\xi) d\xi = i! 2^i \delta_{ii'} \tag{1.12}$$

$$(i, i' = 0, 1, \dots),$$

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

In view of (1.11), we obtain

$$\frac{\partial}{\partial \xi} \left(2\xi + \frac{\partial}{\partial \xi}\right) \exp(-\xi^2) H_i(\xi) = -2i \exp(-\xi^2) H_i(\xi) \tag{1.13}$$

$$(i = 0, 1, \dots).$$

Further, according to (1.10), the quasi-equilibrium concentration $c^{(e)}(u)$ satisfies kinetic equation (1.8) and relevant boundary conditions (1.9). Taking into account all that has been said above, we can see that the general solution of equation (1.8) at boundary conditions (1.9) has the following form:

$$c(u, t) = c^{(e)}(u) + \sum_{i=1}^{\infty} k_i \exp[-2ij_s^+ t / (\Delta n_s)^2] \times \exp(-u^2) H_i(u) \quad (-1 \leq u \leq 1). \tag{1.14}$$

Here, coefficients k_i that are independent of u and t are expressed with the aid of (1.12) via the initial concentration $c(u, t)|_{t=0}$ in the micellar region. Quasi-equilibrium concentration $c^{(e)}(u)$ could be included into (1.14) in the sum over i , adding the term with $i = 0$ to the sum. This indicates that the obtained solution (1.14) is indeed the general solution: it represents the expansion in complete function system $\exp(-u^2) H_i(u)$ ($i = 0, 1, \dots$).

Expression (1.14) describes the establishment of the quasi-equilibrium concentration of molecular aggregates in the micellar region. It is seen from (1.14) that $t_s^{(i)}$ values given by equalities

$$t_s^{(i)} = (\Delta n_s)^2 / 2ij_s^+ \quad (i = 1, 2, \dots), \tag{1.15}$$

represent the spectrum of times required to establish this concentration. For the largest of these times, the principal and, hence, the characteristic time, which is denoted by t_s , we have

$$t_s = (\Delta n_s)^2 / 2j_s^+. \tag{1.16}$$

According to (1.16), the larger Δn_s and the smaller j_s^+ , the larger is time t_s . Relation (1.16) for time t_s coincides with the Anianson and Wall formula [3] for the time of

“fast” relaxation of a micellar solution at a relatively low amount of a substance in micelles.

Now let us find out how the quasi-equilibrium concentration of molecular aggregates is established with time in the subcritical region $n \leq n_c - \Delta n_c$. We conclude that, since the same subcritical region also exists in the case of common nucleation, the quasi-equilibrium concentration of molecular aggregates will be established in the subcritical region in the same manner as in the course of common nucleation. As was shown in [8, 9], it occurs due to the tendency of molecular aggregates with the initial aggregation number equal to unity to overcome (by fluctuations) the potential barrier of the work of their formation. Then, according to [8, 9], we can estimate the characteristic time of establishing the quasi-equilibrium concentration of molecular aggregates in the subcritical region $n \leq n_c - \Delta n_c$, denoted by t' , as

$$t' \approx n_c \Delta n_c / j_c^+, \tag{1.17}$$

where j_c^+ ($j_c^+ > 0$) is the number of surfactant monomers absorbed by critical molecular aggregate (with $n = n_c$) from a solution per unit time. According to estimate (1.17), the larger n_c and Δn_c and the lower j_c^+ , the larger is time t' .

Finally, it remains to be explained how the quasi-equilibrium concentration of molecular aggregates is established with time in the part $n_c + \Delta n_c \leq n \leq n_s - \Delta n_s$ of the overcritical region, which is located at the n -axis to the left-hand side of the micellar region just considered. Evidently, it occurs due to the tendency of molecular aggregates, which were originally located in the micellar region, to overcome (by fluctuations) the potential barrier of the work of their formation. Hence, there is a complete analogy between the establishment of the quasi-equilibrium concentration of molecular aggregates in the $n_c + \Delta n_c \leq n \leq n_s - \Delta n_s$ and $n \leq n_c - \Delta n_c$ regions. The only difference is the fact that the role of n_c variable is now played by $(n_s - n_c)$ difference. Taking these facts into account, we estimate, by analogy with (1.17), the characteristic time of establishing a quasi-equilibrium concentration of molecular aggregates in the $n_c + \Delta n_c \leq n \leq n_s - \Delta n_s$ region, denoted by t'' , as

$$t'' \approx (n_s - n_c) \Delta n_c / j_c^+. \tag{1.18}$$

The larger n_s and Δn_c and the smaller n_c and j_c^+ , then, according to (1.18), the larger is time t'' .

2. TIME OF THE ESTABLISHMENT OF QUASI-STEADY-STATE CONCENTRATION OF MOLECULAR AGGREGATES IN THE NEAR-CRITICAL REGION OF THEIR SIZES

To construct the theory of micellization, the assumption of the quasi-steady-state concentration of molecular aggregates in the near-critical region of their

sizes is important. Let us consider how it is established with time. The possibility of the establishment of the quasi-steady state was qualitatively substantiated in [2]. A quantitative criterion of the quasi-steady-state concentration of aggregates in the near-critical region of their sizes will be reported in our forthcoming publications. It will be also shown that this concentration actually has time to be established. In this case, we will proceed from a similar treatment carried out in the kinetic theory of nucleation [10, 11].

The variation in concentrations c_n of molecular aggregates with time is still determined by the continuity equation (1.1). However, according to relation (3.9) in [2], for the $J_n(t)$ flux of molecular aggregates in the near-critical region we have

$$J_n(t) = j_c^+ [2(n - n_c) / (\Delta n_c)^2 - \partial / \partial n] c_n(t) \quad (2.1)$$

$$(n_c - \Delta n_c \leq n \leq n_c + \Delta n_c).$$

According to formulae (4.9) in [2], in the near-critical region, the boundary conditions to the kinetic equation formed by relations (1.1) and (2.1) are:

$$c_n(t) / c_n^{(e)} \approx 1 \quad (n \approx n_c \mp \Delta n_c). \quad (2.2)$$

For the quasi-equilibrium concentration $c_n^{(e)}$ of aggregates in (2.2), according to Boltzmann's fluctuation principle, we have

$$c_n^{(e)} = \text{const exp}[-(W_n - W_c)] \quad (2.3)$$

$$(n_c - \Delta n_c \leq n \leq n_c + \Delta n_c).$$

Let us pass in the near-critical region from the variable n to variable v , using relation:

$$v \equiv (n - n_c) / \Delta n_c \quad (-1 \leq v \leq 1). \quad (2.4)$$

Assuming

$$c(v, t) \equiv c_n(t), \quad c^{(e)}(v) \equiv c_n^{(e)} \quad (-1 \leq v \leq 1), \quad (2.5)$$

we obtain from (1.1) and (2.1) the following kinetic equation:

$$\frac{\partial c(v, t)}{\partial t} = -\frac{j_c^+}{(\Delta n_c)^2} \frac{\partial}{\partial v} \left(2v - \frac{\partial}{\partial v} \right) c(v, t) \quad (2.6)$$

$$(-1 \leq v \leq 1)$$

(differential operator $\partial / \partial v$ acts on the entire expression to the right-hand side). Then, from (2.2) we arrive at the boundary conditions:

$$c(v, t) / c^{(e)}(v) \approx 1 \quad (v \approx \mp 1). \quad (2.7)$$

Allowing for the approximation

$$W_n = W_c - \left(\frac{n - n_c}{\Delta n_c} \right)^2 \quad (n_c - \Delta n_c \leq n \leq n_c + \Delta n_c) \quad (2.8)$$

[approximation (1.5) in [2]], from (2.3)–(2.5) and (2.8), we also have:

$$c^{(e)}(v) = \text{const exp}(v^2) \quad (-1 \leq v \leq 1). \quad (2.9)$$

To find the solution of equation (2.6) with boundary condition (2.7), we cannot directly use results obtained in Section 1, because equations (2.6) and (2.7) differ from equations (1.8) and (1.9).

The quasi-steady-state concentration of molecular aggregates, which is established with time in the near-critical region, we denote by $c^{(s)}(v)$. This concentration satisfies kinetic equation (2.6) with boundary conditions (2.7). Taking this fact into account, and in view of (1.11)

$$\frac{\partial}{\partial \xi} \left(2\xi - \frac{\partial}{\partial \xi} \right) H_i(\xi) = 2(i + 1) H_i(\xi) \quad (2.10)$$

$$(i = 0, 1, \dots),$$

and also allowing for the fact that, according to (2.9), the quasi-steady-state concentration $c^{(e)}(v)$ increases with $|v|$ quite rapidly within boundary conditions (2.7), we represent the general solution of equation (2.6) with boundary conditions (2.7) in the following form:

$$c(v, t) = c^{(s)}(v)$$

$$+ \sum_{i=0}^{\infty} p_i \text{exp}[-2(i + 1) j_c^+ t / (\Delta n_c)^2] H_i(v) \quad (2.11)$$

$$(-1 \leq v \leq 1).$$

Here, coefficients p_i , which are independent of v and t , are expressed via the initial concentration $c(v, t)|_{t=0}$ in the near-critical region with the aid of equation (1.12). The solution obtained is indeed the general solution: it represents the expansion in the complete function system of Hermitian polynomials $H_i(v)$ ($i = 0, 1, \dots$). Note that the rapid increase in the quasi-equilibrium concentration $c^{(e)}(v)$ with $|v|$ provides for the smallness of the contribution from the polynomial sum over i in (2.11) to the boundary conditions (2.7), and, hence, provides for the fulfillment of boundary conditions (2.7).

Expression (2.11) describes the establishment of the quasi-steady-state concentration of molecular aggregates in the near-critical region. As is seen from (2.11), the values of $t_c^{(i)}$, given by equalities

$$t_c^{(i)} = (\Delta n_c)^2 / 2(i + 1) j_c^+ \quad (i = 0, 1, \dots), \quad (2.12)$$

represent the spectrum of times required to establish this concentration. For the largest of these times, the principal and, hence, the characteristic time, which we denote by t_c , we have

$$t_c = (\Delta n_c)^2 / 2 j_c^+. \quad (2.13)$$

According to formula (2.13), the larger Δn_c and the smaller j_c^+ , the larger is time t_c .

Comparing times t_s , t' , t'' , and t_c in (1.16)–(1.18) and (2.13), taking inequalities $n_c < n_s$, $\Delta n_c \ll n_c$, and

$\Delta n_c + \Delta n_s \ll n_s - n_c$ into account, and assuming that $\Delta n_c \sim \Delta n_s$, we conclude that inequalities

$$t_s \ll t_c < t' \quad \text{and} \quad t_s \ll t_c < t'' \quad (2.14)$$

take place.

We cannot determine in advance the interrelation between times t' and t'' . The longest of these times determines the duration of the initial stages of micellization.

3. AVERAGE TIME BETWEEN TWO SUCCESSIVE ACTS OF EMISSION OF SURFACTANT MONOMER BY A MICELLE, THE AVERAGE VALUE OF THE RESIDENT TIME OF A SURFACTANT MONOMER IN A MICELLE, AND THE AVERAGE VALUE OF MICELLE LIFETIME

The average time between two successive acts of emission of a surfactant monomer by a micelle is an important parameter in the micellization. Let us denote this time by τ_1 and find a statistical expression for this value.

Using formula (2.6) in [1], at $n \gg 1$, we have

$$j_n^- = j_n^+ \exp(W_{n+1} - W_n), \quad (3.1)$$

where j_n^- ($j_n^- > 0$) is the number of surfactant monomers emitted by the aggregate containing n molecules into the micellar solution per unit time; and j_n^+ ($j_n^+ > 0$) is the number of surfactant monomers absorbed by the aggregate containing n molecules from the micellar solution per unit time. As is seen from (1.5), in the micellar region, the relation

$$W_{n+1} - W_n = \frac{2(n - n_s)}{(\Delta n_s)^2} \quad (3.2)$$

$$(n_s - \Delta n_s \leq n \leq n_s + \Delta n_s)$$

is true. Allowing for condition $\Delta n_s \gg 1$ of the applicability of the macroscopic description of the micellization kinetics (required by conditions (1.3) in [2]), from (3.1) and (3.2) with a high degree of accuracy we obtain:

$$j_n^- = j_s^+ (n_s - \Delta n_s \leq n \leq n_s + \Delta n_s). \quad (3.3)$$

(j_s^+ is the number of surfactant monomers absorbed by the stable molecular aggregate from the solution per unit time).

According to statistical notions, the average time between two successive acts of emission of surfactant monomer by the aggregate containing n molecules is determined by time $1/j_n^-$. Taking this fact and relation (3.3) into account, for the average time τ_1 between

two successive acts of emission of the surfactant monomer by a micelle we obtain the following expression:

$$\tau_1 = 1/j_s^+. \quad (3.4)$$

It is evident that, simultaneously, τ_1 is the average time of emission of any of n_s surfactant monomers, containing in a micelle, from a micelle. Because the probability of the emission of some of these monomers from a micelle is larger by n_s times than that of the isolated (labeled) surfactant monomer, the $n_s \tau_1$ product determines the average time when the labeled surfactant monomer could emit from a micelle, i.e., the average value of the resident time of a surfactant monomer in a micelle.

The most important parameter in micellization is also the average value of a micelle lifetime. Let us consider this time.

In [2], we found the direct flux J of molecular aggregates overcoming by fluctuations the potential barrier of the work of their formation from the side of the subcritical region and the reverse flux J'' of molecular aggregates overcoming by fluctuations the potential barrier of the work of their formation from the side of the overcritical region. The existence of reverse flux J'' results in the fluctuation transfer of the $-J''$ ($J'' < 0$) number of molecular aggregates from the micellar to subcritical region in the unit volume of the micellar solution per unit time (the outflow of molecular aggregates from the micellar region to the region $n \approx n_s + \Delta n_s$ is virtually not observed due to a rather rapid increase in the formation work of a molecular aggregate with an increase in n in this region.)

The fluctuation transfer of molecular aggregates from the micellar to subcritical region signifies "the decomposition" of micelles. This decomposition occurs by the multistage mechanism of the exchange of surfactant monomers between the molecular aggregates and the micellar solution rather than by a single act of decay. The derivation of the kinetic equation of the formation of molecular aggregates was based on precisely such a mechanism [1].

During time τ_M given by the equality

$$\tau_M = c_M / |J''|, \quad (3.5)$$

where c_M is the total concentration of micelles (with allowance for $J'' < 0$), the micellar region would be left by all the micelles due to their fluctuation transfer to the subcritical region. Hence, it is the time τ_M given by equation (3.5) that represents the average value of a micelle lifetime. Of course, the reverse process of the fluctuation formation of micelles exists, together with the fluctuation decomposition of micelles. This process is caused by the J' flux.

Using formula (5.10) in [2] for the J'' flux

$$J'' = -c_M j_c^+ \exp[-(W_c - W_s)] / \pi \Delta n_c \Delta n_s, \quad (3.6)$$

we represent (3.5) in the form:

$$\tau_M = \tau \Delta n_c \Delta n_s \exp(W_c - W_s) / j_s^+ \quad (3.7)$$

According to (3.7), time τ_M is independent of c_M and the volume of the micellar solution.

Let us emphasize that the statistical substantiation of the notions of the average time between two successive acts of the emission of a surfactant monomer from a micelle, the average resident time of a surfactant monomer in a micelle, and the average value of a micelle lifetime proved to be possible only on the basis of the kinetic approach to the micellization problem that we are developing.

The emission of surfactant monomers by molecular aggregates into the micellar solution and the fluctuation transfer of molecular aggregates from the micellar to subcritical regions do not occur only at the initial stages of micellization. These processes also take place when the final equilibrium of a micellar solution is being established and even after this equilibrium is reached. Hence, characteristic kinetic times τ_1 and τ_M refer to both the initial stages of micellization and the subsequent development of this process as a whole. However, times τ_1 and τ_M are already physically meaningful at the initial stages of micellization where fluxes j_s^+ and J'' are formed.

The shorter the time τ_1 , the greater the ability of micelles to change their entire molecular composition. However, the longer the time τ_M , the stabler the micelles are as aggregative molecular formations.

The hierarchy of times τ_1 , τ_M , t_s , t' , t'' , and t_c in the set of all characteristic kinetic times of micellization will be elucidated in our forthcoming publications.

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