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Thermodynamic and Kinetic Foundations of the Theory of Micellization: 2. Direct and Reverse Fluxes of Molecular Aggregates over the Activation Barrier of Micellization

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Abstract—The conditions of the applicability of a macroscopic description of the kinetics of micellization in a solution of a nonionic surfactant are revealed. Quasi-equilibrium concentrations of molecular aggregates in precritical and supercritical ranges of their sizes are determined. The kinetic equation of the formation of molecular aggregates in the near-critical and micellar ranges of their sizes is derived. Boundary conditions for the equation are formulated. Direct and reverse overcoming of the activation barrier of micellization by the aggregates is described. Quasi-stationary aggregates fluxes over the activation barrier of micellization are found.

INTRODUCTION

The construction of the kinetic theory of micellization in surfactant solutions requires the knowledge of the thermodynamics of the work of formation of surfactant molecular aggregate (the aggregation work). In a practically important situation when the surfactant concentration exceeds the critical micellization concentration (CMC), albeit is lower than the concentration at which macroscopic phase of a surfactant arises, this work, as a function of the aggregation number, is characterized [1] by both the potential barrier and the potential well located to the right-hand side of this barrier at the aggregation number axis. After the well, the work increases infinitely.

The existence of the potential barrier and well on the dependence between the aggregation work and the aggregation number makes the kinetic theory of micellization more complicated than the kinetic theory of nucleation that is based on the fact that the work of the formation of a nucleus of arising phase is characterized (as a function of the number of its molecules) only by a potential barrier, after which it monotonically falls.

The following circumstances seriously complicate the kinetic theory of micellization. As in the kinetic theory of nucleation, the flux of molecular aggregates overcoming (by fluctuations) the potential barrier of the work of their formation from its left-hand side is also of importance in the theory of micellization. However, since in a micellar solution, the potential well follows the potential barrier rather than the monotonic fall of the aggregation work, the flux of molecular aggregates overcoming (by fluctuations) the potential barrier of the work of their formation from the side of the potential well is also of importance.

The determination of direct and reverse fluxes of molecular aggregates over the activation barrier of micellization created by the potential barrier of the aggregation work is the main goal of this paper.

We consider the case of a colloidal nonionic surfactant. It is assumed that a micellar solution is the ideal mixture of a surfactant molecular aggregates of various sizes in a solvent. In other words, the interactions between molecular aggregates are not taken into account, whereas interactions of aggregates with solvent molecules are strictly taken into account via the aggregation work. This assumption is usually well satisfied in experiments.

1. THERMODYNAMIC CHARACTERISTICS OF THE MICELLIZATION KINETICS

The aggregation number (the number of surfactant molecules in an aggregate) is denoted by n. The work of the aggregate formation in a solution containing originally only surfactant monomers is expressed in thermal units kT, where k is Boltzmann's constant, and T is the solution temperature, is denoted by W_n. The concentration of molecular aggregates with the aggregation number n we denote by c_n. At $n = 1$, the aggregates represent surfactant monomers, which in the case under consideration are all identical. Correspondingly, $c_1 \equiv c_n|_{n=1}$ is the concentration of such monomers. At $n \gg 1$, the value n is assumed to be continuous. Then, concentration c_n implies that $c_n dn$ determines the total concentration of aggregates for which n varies within an infinitely narrow range $(n, n + dn)$.

The aggregation work W_n is set by the monomer concentration c_1 by means of term $-(n-1)\ln c_1$ [2]. The behavior of work W_n as a function of n at variable concentration c_1 is shown in the figure. Curve *1* corresponds to the case when the surfactant concentration is below the CMC. Curve *2* corresponds to the case when

the surfactant concentration is near the CMC. Curve *3* corresponds to practically important case when the surfactant concentration exceeds the CMC, but is lower than the concentration that gives rise to the formation of the macroscopic surfactant phase. It is this curve that will be used in our further analysis. Positions of maximum and minimum work at the n-axis, i.e., the aggregation numbers of critical and stable molecular aggregates, are denoted by n_c and n_s, respectively; maximum and minimum per se, i.e., the barrier height and the well depth of this work, are denoted by $W_c \equiv W_n|_{n = n_c}$ and $W_s \equiv W_n|_{n = n_s}$, respectively. The potential barrier gives rise to the activation barrier of micellization. The half-widths of the potential barrier and potential well of the aggregation work are denoted by Δn_c and Δn_s, respectively. They are determined by equalities

$$\Delta n_c = [2/|\partial^2 W_n/\partial n^2|_{n = n_c}]^{1/2},$$
$$\Delta n_s = [2/(\partial^2 W_n/\partial n^2)|_{n = n_s}]^{1/2}. \quad (1.1)$$

Physical meaning of the Δn_c and Δn_s half-widths introduced by (1.1) will be disclosed below. The figure takes into account the equality $W_n|_{n = 1} = 0$. It implies that the formation of surfactant monomers presenting originally in a micellar solution does not require any work [2]. For definiteness, curve *3* in the figure refers to the case when $W_s > 0$ (when concentration c_1 is not too high).

Values n_c, n_s, W_c, W_s, Δn_c, and Δn_s (as well as the work W_n itself) depend on surfactant monomer concentration c_1. All these values are needed in the kinetic theory of micellization as functions of c_1. They themselves represent thermodynamic characteristics of the micellization kinetics.

Further, we consider conditions

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

$$\Delta n_s \gg 1, \quad \Delta n_s/(n_s - n_c) \ll 1 \quad (1.3)$$

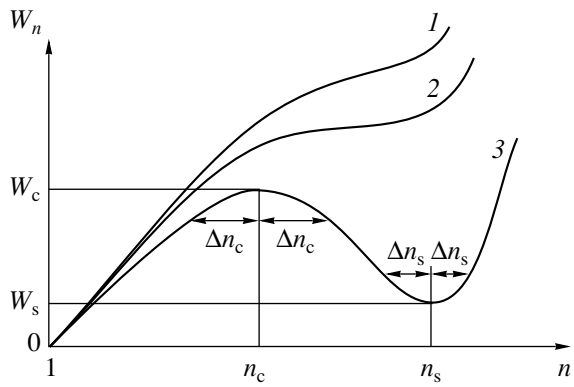
to be fulfilled.

The first conditions in (1.2) and (1.3) allow us to consider value n to be continuous magnitude in the regions of potential barrier and potential well of work W_n, which are the most important for micellization kinetics. The rest of conditions (1.2) and (1.3) imply that potential barrier and potential well of work W_n are fully exhibited. As it is qualitatively shown in the figure, they are separated from the initial point $n = 1$at the n-axis and from each other. This circumstance is expressed by inequalities

$$\exp(W_c) \gg 1, \text{ and } \exp(W_c) \gg \exp(W_s), \quad (1.4)$$

which resulted from conditions (1.2) and (1.3).

Conditions (1.2) and (1.3) are fulfilled when a surfactant concentration sufficiently (in practice, negligibly) exceeds the CMC [possibly, the second condition in (1.2) is valid as a limit]. In particular, conditions (1.2) and (1.3) imply that the aggregation numbers n_c and n_s are much larger than unity.



Behavior of work W_n of the formation of surfactant molecular aggregate as a function of the aggregation number n at the variation of concentration c_1 of surfactant monomers. See text for explanation.

Conditions (1.2) and (1.3) make it possible, together with definitions (1.1), to derive for work W_n in the regions of its potential barrier and well the following quadratic approximations:

$$W_n = W_c - \left(\frac{n - n_c}{\Delta n_c}\right)^2 \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (1.5)$$

$$W_n = W_s + \left(\frac{n - n_s}{\Delta n_s}\right)^2 \quad (n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s). \quad (1.6)$$

According to (1.5), work W_n decreases by a thermal unit when variable n deviates from value n_c by Δn_c. However, in accordance with (1.6), work W_n increases by a thermal unit when variable n deviates from n_s by Δn_s. These facts disclose the physical meaning of introduced values Δn_c and Δn_s.

Conditions (1.2) and (1.3) and inequality (1.4) resulted from these conditions allow us to use a macroscopic description of the micellization kinetics. They generalize the conditions of the macroscopic description revealed previously [3] in the kinetic theory of nucleation.

Regions $n \lesssim n_c - \Delta n_c$, $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$, and $n \gtrsim n_c + \Delta n_c$ are called precritical, near-critical, and supercritical regions, respectively. Micelles are accumulated mainly in the region $n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s$. This region is called micellar. It is located inside the supercritical region. Values n_s and Δn_s have the meaning of the average aggregation number of micelles and the scatter of the aggregation number of micelles around this average value, respectively. As for the regions of potential barrier and potential well of work W_n, we imply (and will imply hereafter) that these regions are near-critical and micellar regions, respectively.

2. QUASI-EQUILIBRIUM CONCENTRATIONS OF MOLECULAR AGGREGATES IN PRECRITICAL AND SUPERCRITICAL REGIONS OF THEIR SIZES

The majority of the number of surfactant molecular aggregates are naturally located in the regions of their sizes, where the work of aggregate formation is minimal. These regions are located to the left- and right-hand sides of the potential barrier of work, i.e., they are precritical and supercritical regions. We are not concerned about the part of supercritical region where $n \gtrsim n_s + \Delta n_s$, because the concentration of molecular aggregates in this region is rather low.

The large supply of molecular aggregates in precritical and supercritical regions may be assumed to be varied by its relative value so slowly that the aggregate concentration in each of these separate regions is maintained as quasi-equilibrium irrespective of permanent decrease or increase in the number of aggregates by their fluxes over the potential barrier of the work of the aggregate formation. However, the mutual quasi-equilibrium between molecular aggregates in precritical and supercritical regions is absent due to these fluxes. Mutual quasi-equilibrium is only reached as the final equilibrium of micellar solution is established when quasi-equilibrium concentrations of molecular aggregates in precritical and supercritical regions, as well as the concentration of molecular aggregates within the entire range of their sizes come to complete equilibrium.

Physical assumptions of quasi-equilibrium state of molecular aggregates in precritical and supercritical regions, which we substantiated in this work, essentially simplify the subsequent discussion. Let us put aside the strict confirmation of this assumption until the hierarchy of the scales of characteristic kinetic times of micellization will be disclosed in our subsequent publications.

Denoting the quasi-equilibrium concentration of molecular aggregates by $c_n^{(e)}$ we, hence, have in precritical and supercritical regions

$$c_n = c_n^{(e)} \quad (n \lesssim n_c - \Delta n_c), \tag{2.1}$$

$$c_n = c_n^{(e)} \quad (n \gtrsim n_c + \Delta n_c). \tag{2.2}$$

In accordance with Boltzmann's fluctuation principle

$$c_n^{(e)} = \text{const}\exp(-W_n). \tag{2.3}$$

We have in precritical and supercritical regions:

$$c_n^{(e)} = c_1\exp(-W_n) \quad (n \lesssim n_c - \Delta n_c), \tag{2.4}$$

$$c_n^{(e)} = c_s\exp[-(W_n - W_s)] \quad (n \gtrsim n_c + \Delta n_c), \tag{2.5}$$

where $c_s \equiv c_n|_{n = n_s}$ is the concentration of molecular aggregates at the point of minimal work of their formation. The fact that pre-exponential factor in (2.4) is equal to c_1 results from $c_1 \equiv c_n|_{n=1}$ and equality $W_n|_{n=1} = 0$ already mentioned in Section 1. The fact that pre-exponential factor in (2.5) is equal to c_s results from the just made definition of concentration c_s and evident equality $(W_n - W_s)|_{n = n_s} = 0$. Note that (2.4) coincides with formula (1.10) derived thermodynamically [2] for the equilibrium aggregate concentration.

Because micelles are accumulated in a micellar region, for their total concentration c_M we have

$$c_M = \int_{n_s - \Delta n_s}^{n_s + \Delta n_s} c_n dn. \tag{2.6}$$

Using formulas (2.2) and (2.5) in (2.6) (micellar region is located inside the supercritical region), allowing for quadratic approximation (1.6), substituting with a high degree of accuracy the integration limits by $-\infty$ and ∞, and calculating integral, we arrive at

$$c_M = \pi^{1/2} c_s \Delta n_s. \tag{2.7}$$

Using (2.7), we express (2.5) as

$$c_n^{(e)} = (c_M/\pi^{1/2}\Delta n_s)\exp[-(W_n - W_s)] \quad (n \gtrsim n_c + \Delta n_c). \tag{2.8}$$

3. KINETIC EQUATION OF THE FORMATION OF MOLECULAR AGGREGATES IN NEAR-CRITICAL AND MICELLAR REGIONS OF THEIR SIZES

Evolution of concentration c_n of molecular aggregates with $n \geq 2$ in time t is determined by the kinetic equation

$$\partial c_n/\partial t = J_{n-1} - J_n \quad (n = 2, 3, \ldots) \tag{3.1}$$

[equation (2.3) in [2]]. Here, J_n is the flux of molecular aggregates in the space of aggregation numbers. It is given by relation

$$J_n = j_n^+[c_n - c_{n+1}\exp(W_{n+1} - W_n)] \quad (n = 1, 2, \ldots) \tag{3.2}$$

[equation (2.7) in [2]]. Value $j_n^+ > 0$ is the number of surfactant monomers absorbing from the solution per unit time by a molecular aggregate composed of n molecules.

According to the first conditions of (1.2) and (1.3), the aggregation number n may be considered to be continuously variable in near-critical and micellar regions of the sizes of molecular aggregates. In these regions, equation (3.1) may, hence, be written as the equation of continuity

$$\partial c_n(t)/\partial t = -\partial J_n(t)/\partial n, \tag{3.3}$$

where we denoted the dependence of values c_n and J_n on time by argument t.

Taking into account that $W_{n+1} - W_n = \partial W_n/\partial n$, from (1.5) and (1.6) we obtain

$$W_{n+1} - W_n = -\frac{2(n-n_c)}{(\Delta n_c)^2} \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{3.4}$$

$$W_{n+1} - W_n = \frac{2(n-n_s)}{(\Delta n_s)^2} \quad (n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s). \tag{3.5}$$

As is shown by the first conditions of (1.2) and (1.3), the values in the right-hand sides of (3.4) and (3.5) are much smaller (by the absolute value) than unity in near-critical and micellar regions of aggregate sizes. Then, from (3.4) and (3.5), with a high degree of accuracy, we have in these regions

$$\exp(W_{n+1} - W_n) = 1 - \frac{2(n-n_c)}{(\Delta n_c)^2} \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{3.6}$$

$$\exp(W_{n+1} - W_n) = 1 + \frac{2(n-n_s)}{(\Delta n_s)^2} \quad (n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s). \tag{3.7}$$

Let us take into account the differential relation

$$c_{n+1} = c_n + \partial c_n/\partial n \tag{3.8}$$

which is true when variable n is continuous.

From (3.2) and (3.6)–(3.8), ignoring the products of small values $\partial c_n/\partial n$, $2(n - n_c)/(\Delta n_c)^2$, and $2(n - n_s)/(\Delta n_s)^2$, we obtain

$$J_n(t) = j_c^+[2(n-n_c)/(\Delta n_c)^2 - \partial/\partial n]c_n(t) \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{3.9}$$

$$J_n(t) = -j_s^+[2(n-n_s)/(\Delta n_s)^2 + \partial/\partial n]c_n(t) \quad (n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s), \tag{3.10}$$

where $j_c^+ \equiv j_n^+\big|_{n=n_c}$ and $j_s^+ \equiv j_n^+\big|_{n=n_s}$ are the intensities of monomer absorption by critical and stable aggregates, respectively.

Relations (3.9) and (3.10), together with the equation of continuity (3.3), result in the kinetic equation of the formation of molecular aggregates in near-critical and micellar regions of their sizes.

Let us demonstrate another way of deriving relations (3.9) and (3.10). We denote the variation rate of the aggregation number $\dot{n}$ of the molecular aggregate in time (derivative of n over time) by n. Evidently, the equality

$$\dot{n} = j_n^+ - j_n^- \tag{3.11}$$

is valid, where $j_n^- > 0$ is the number of surfactant monomers emitted into a solution per unit time by molecular aggregate composed of n molecules. According to relation (2.6) in [2], we have

$$j_{n+1}^- = j_n^+ \exp(W_{n+1} - W_n), \tag{3.12}$$

hence, assuming variable n to be continuous, we have approximately

$$j_n^- = j_n^+ \exp(\partial W_n/\partial n). \tag{3.13}$$

As was already mentioned during the derivation of formulas (3.6) and (3.7), the power of exponent $\exp(\partial W_n/\partial n)$ is small in near-critical and micellar regions of aggregate sizes. Then, from (3.11) and (3.13) with a high degree of accuracy we have in these regions

$$\dot{n} = -j_n^+ \partial W_n/\partial n. \tag{3.14}$$

Let us represent the flux of molecular aggregates $J_n(t)$ as

$$J_n(t) = (\dot{n} + \beta\partial/\partial n)c_n(t). \tag{3.15}$$

Term with $\dot{n}$ describes the regular evolution of a single molecular aggregate. The term with differentiation operator $\partial/\partial n$ describes the fluctuation evolution of the ensemble of molecular aggregates. This evolution smears the regular evolution. The unknown coefficient β at term with operator $\partial/\partial n$ we determine a little bit later.

In the near-critical and micellar regions, we substitute (3.14) into (3.15). Determining the then unknown coefficient β from the condition of vanishing of the flux of molecular aggregates at their equilibrium concentration given by expression (2.3), we obtain

$$J_n(t) = -j_n^+(\partial W_n/\partial n + \partial/\partial n)c_n(t). \tag{3.16}$$

Opening derivative $\partial W_n/\partial n$ in (3.16) in near-critical and micellar regions by means of (1.5) and (1.6), we arrive at previous relations (3.9) and (3.10).

In addition, let us make a number of important statements.

Let us denote the chemical potential of surfactant molecules in a molecular aggregate with the aggregation number n by μ_{1n}, and the chemical potential of surfactant monomers in micellar solution, by μ_1. Under the thermal and mechanical equilibrium of a molecular aggregate with a micellar solution [4], the relation

$$kT\partial W_n/\partial n = \mu_{1n} - \mu_1 \tag{3.17}$$

is valid.

It is evident that μ_{1n} coincides with the chemical potential of surfactant monomers in the imaginary micellar solution, which is under the material equilibrium with molecular aggregate having aggregation number n at the same temperature and pressure as the considered micellar solution. Denoting the concentration of surfactant monomers in such an imaginary micellar solution by c_{1n} and assuming imaginary and considered solutions to be the ideal mixture of aggregates in a solvent, we have by the known formula of the theory of ideal solutions:

$$\mu_{1n} - \mu_1 = kT\ln(c_{1n}/c_1), \tag{3.18}$$

where c_1 is the concentration of surfactant monomers in the considered micellar solution.

Using (3.17) and (3.18) in (3.13), we obtain

$$j_n^- = j_n^+ c_{1n}/c_1. \tag{3.19}$$

Substituting (3.19) into (3.13), we have

$$\dot{n} = j_n^+(1 - c_{1n}/c_1). \tag{3.20}$$

Note that formulas (3.19) and (3.20) are not connected to whether the molecular aggregate is located in near-critical or micellar regions or not.

Usually, the known values are not j_n^+ and j_n^-, separately, but value $\dot{n}$ comprising, according to (3.11), the total flux of monomers absorbing or emitting by the aggregate. Moreover, formula (3.20) allows us to easily determine direct flux j_n^+, which in (3.16) plays the role of the diffusion coefficient of molecular aggregates in the space of aggregation numbers by the total flux $\dot{n}$.

Total flux $\dot{n}$ is proportional to the $(c_1 - c_{1n})$ difference, hence, acting as the driving force for the variation of the size of a single molecular aggregate. It is seen from (3.20) that j_n^+ is always larger than zero, even at $c_1 = c_{1n}$, when the total flux $\dot{n}$ vanishes. Simultaneously, according to (3.19), inequality $j_n^- > 0$ be also always fulfilled. Naturally, these conclusions should be expected.

The intensities of absorption of surfactant monomers j_c^+ and j_s^+ by critical and stable molecular aggregates are to be important in the kinetic theory of micellization. As the thermodynamic characteristics of micellization mentioned in Section 1, in the forthcoming consideration values j_c^+ and j_s^+ are assumed to be the known functions of monomer concentration c_1.

4. DIRECT AND REVERSE OVERCOMING OF THE ACTIVATION BARRIER OF MICELLIZATION BY MOLECULAR AGGREGATES

As was already mentioned above, at micellization, we observe both the direct flux of molecular aggregates overcoming (by fluctuation) the activation barrier of micellization from the side of precritical region and the reverse flux of molecular aggregates overcoming (by fluctuation) the activation barrier of micellization from the side of the supercritical region.

Let us denote direct and reverse fluxes of molecular aggregates in the region of potential barrier of the work of their formation, i.e., in the near-critical region, by $J_n'(t)$ and $J_n''(t)$, respectively. We denote the concentrations of molecular aggregates participating in these fluxes in near-critical region by $c_n'(t)$ and $c_n''(t)$, respectively. In this case, for the total flux $J_n(t)$ of molecular aggregates and their total concentration $c_n(t)$ in the near-critical region, we have

$$J_n(t) = J_n'(t) + J_n''(t) \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{4.1}$$

$$c_n(t) = c_n'(t) + c_n''(t) \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c). \tag{4.2}$$

Considerations underlying the kinetic equation of micellization derived in Section 3 are also valid separately for each of the molecular aggregates transferring (by fluctuation) from precritical to supercritical regions and for molecular aggregates transferring (by fluctuation) from supercritical to precritical regions. Therefore, together with (3.3) and (3.9), we have in near-critical region

$$\partial c_n'(t)/\partial t = -\partial J_n'(t)/\partial n \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{4.3}$$

$$J_n'(t) = j_c^+[2(n - n_c)/(\Delta n_c)^2 - \partial/\partial n]c_n'(t) \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{4.4}$$

as well as

$$\partial c_n''(t)/\partial t = -\partial J_n''(t)/\partial n \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \tag{4.5}$$

$$J_n''(t) = j_c^+[2(n - n_c)/(\Delta n_c)^2 - \partial/\partial n]c_n''(t) \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c). \tag{4.6}$$

It is natural that (4.1)–(4.6) be consistent with (3.3) and (3.9).

Let us formulate the boundary conditions to kinetic equations. Resting on the ideas of the kinetic theory of nucleation and taking into account relations (2.1) and (2.2), we conclude that the boundary conditions to

equations (4.3) and (4.4) for concentration $c'_n(t)$ in the near-critical region are:

$$c'_n(t)/c_n^{(e)} \cong \begin{cases} 1 & (n \cong n_c - \Delta n_c) \\ 0 & (n \cong n_c + \Delta n_c), \end{cases} \quad (4.7)$$

and the boundary conditions to equations (4.5) and (4.6) for concentration $c''_n(t)$ in near-critical region are the following:

$$c''_n(t)/c_n^{(e)} \cong \begin{cases} 0 & (n \cong n_c - \Delta n_c) \\ 1 & (n \cong n_c + \Delta n_c). \end{cases} \quad (4.8)$$

Quasi-equilibrium concentration $c_n^{(e)}$ at the boundary conditions (4.7) and (4.8) is determined by expressions (2.4) and (2.8).

According to (4.2), (4.7), and (4.8), the boundary conditions to equations (3.3) and (3.9) for the total concentration $c_n(t)$ of molecular aggregates in the near-critical region are:

$$c_n(t)/c_n^{(e)} \cong 1 \quad (n \cong n_c \mp \Delta n_c), \quad (4.9)$$

where quasi-equilibrium concentration $c_n^{(e)}$ is still given by expressions (2.4) and (2.8). Boundary conditions (4.9) seem to be quite natural at the conclusion made in Section 2 that the concentrations of molecular aggregates in precritical and supercritical regions are quasi-equilibrium values.

5. QUASI-STATIONARY FLUXES OF MOLECULAR AGGREGATES OVER THE ACTIVATION BARRIER OF MICELLIZATION

At quasi-equilibrium concentrations of molecular aggregates in precritical and supercritical regions, the concentration of molecular aggregates in the near critical region will be quasi-stationary. This statement will be rigorously confirmed after the disclosure of the hierarchy of the scales of characteristic kinetic times of micellization in our forthcoming publications. The "quasi" prefix to the words "equilibrium" and "stationary" stresses the absence of the time dependence within the large time intervals, during which concentrations c_1 and c_M have no time to noticeably vary in the course of the slow tendency of the micellar solution to its final state of complete equilibrium.

Let us study the quasi-stationary state of molecular aggregates in the near-critical region. In this state, concentrations $c'_n(t)$, $c''_n(t)$, and $c_n(t)$ of aggregates are independent of time t, whereas the aggregate fluxes $J'_n(t)$, $J''_n(t)$, and $J_n(t)$ are also independent of the aggregation number n, as it clearly follows from the equations of continuity (4.3), (4.5), and (3.3). Let us denote concentrations $c'_n(t)$, $c''_n(t)$, and $c_n(t)$ in a quasi-stationary state, by $c_n'^{(s)}$, $c_n''^{(s)}$, and $c_n^{(s)}$, and fluxes $J'_n(t)$, $J''_n(t)$, and $J_n(t)$ in this state by J', J'', and J (for simplicity of notations, quasi-stationary state of fluxes is indicated by the absence of index n and argument t). Then, in the near-critical region we have

$$c'_n(t) = c_n'^{(s)} \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.1)$$

$$c''_n(t) = c_n''^{(s)} \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.2)$$

$$c_n(t) = c_n^{(s)} \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.3)$$

as well as

$$J'_n(t) = J' \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.4)$$

$$J''_n(t) = J'' \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.5)$$

$$J_n(t) = J \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c). \quad (5.6)$$

Let us take into account that the right-hand sides of equations of continuity (4.3) and (4.5) in the quasi-stationary state of molecular aggregates are equal to zero. We use expressions (4.4) and (4.6) for the fluxes of molecular aggregates and the boundary conditions (4.7) and (4.8) to the concentrations of molecular aggregates where quasi-equilibrium concentration $c_n^{(e)}$ is given by expressions (2.4) and (2.8) and quadratic approximation (1.5). Then, we obtain in the near-critical region:

$$c_n'^{(s)} = \frac{c_1 \exp(-W_c)}{\pi^{1/2}\Delta n_c} \exp\left[\left(\frac{n - n_c}{\Delta n_c}\right)^2\right] \times \int_n^\infty \exp\left[-\left(\frac{n' - n_c}{\Delta n_c}\right)^2\right] dn' \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.7)$$

$$J' = c_1 j_c^+ \exp(-W_c)/\pi^{1/2}\Delta n_c, \quad (5.8)$$

$$c_n''^{(s)} = \frac{c_M \exp[-(W_c - W_s)]}{\pi \Delta n_c \Delta n_s} \exp\left[\left(\frac{n - n_c}{\Delta n_c}\right)^2\right] \times \int_{-\infty}^n \exp\left[-\left(\frac{n' - n_c}{\Delta n_c}\right)^2\right] dn' \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.9)$$

$$J'' = -c_M j_c^+ \exp[-(W_c - W_s)]/\pi \Delta n_c \Delta n_s. \quad (5.10)$$

For the total concentration of molecular aggregates and their total flux in quasi-stationary state in the near-critical region, according to (4.2) and (4.1), we have

$$c_n^{(s)} = c_n'^{(s)} + c_n''^{(s)} \quad (n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c), \quad (5.11)$$

$$J = J' + J''. \quad (5.12)$$

Direct J' and reverse J'' fluxes given by formulas (5.8) and (5.10) are, naturally, positive and negative, respectively. In accordance with (5.8), direct flux J' the larger, the higher are values of c_1 and j_c^+ and the lower are values of W_c and Δn_c. According to (5.10), the larger the absolute value of the reverse flux J'', the higher c_M and j_c^+ are and the lower $(W_c - W_s)$, Δn_c, and Δn_s are.

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