Boltzmann Distributions and Slow Relaxation in Systems with Spherical and Cylindrical Micelles

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Received August 4, 2005. In Final Form: December 6, 2005

Equilibrium and nonequilibrium distributions of molecular aggregates in a solution of a nonionic surfactant are investigated at the total surfactant concentration above the second critical micelle concentration (CMC_2). The investigation is not limited by the choice of a specific micellar model. Expressions for the direct and reverse fluxes of molecular aggregates over the potential humps of the aggregation work are derived. These aggregation work humps set up activation barriers for the formation of spherical and cylindrical micelles. With the aid of the expressions for molecular aggregate fluxes, a set of two kinetic equations of micellization is derived. This set, along with the material balance equation, describes the molecular mechanism of the slow relaxation of micellar solution above the CMC_2. A realistic situation has been analyzed when the CMC_2 exceeds the first critical micelle concentration, CMC_1, by an order of magnitude, and the total surfactant concentration varies within the range lying markedly above the CMC_2 but not by more than 2 orders of magnitude. For such conditions, an equation relating the parameters of the aggregation work of a cylindrical micelle to the observable ratio of the total surfactant concentration and the monomer concentration is found for an equilibrium solution. For the same conditions, but in the nonequilibrium state of materially isolated surfactant solution, a closed set of linearized relaxation equations for total concentrations of spherical and cylindrical micelles is derived. These equations determine the time development of two modes of slow relaxation in micellar solutions markedly above the CMC_2. Solving the set of equations yields two rates and two times of slow relaxation.

Introduction

The ability of amphiphiles to engage in molecular aggregation and micellization in aqueous solutions excites interest not only because of multiple physicochemical and technological applications,[1,2] but also because of the peculiarity of the micellization mechanism itself.[2−4] In describing this mechanism, the approach based on methods of the nucleation theory[5−7] can be especially useful. This approach relies on the concept of the minimal work of formation of a molecular aggregate and employs the quasi-equilibrium and quasi-steady distributions of molecular aggregates as well as the Becker−Döring equation for the kinetics of step-by-step aggregation. In particular, this approach succeeded in describing the kinetics and thermodynamics of the formation of spherical micelles (within the droplet and quasi-droplet models of surfactant molecular aggregates) and providing a description of the relaxation of a micellar solution at total concentrations of surfactant between the first (CMC_1) and second (CMC_2) critical micelle concentrations.[7−16]

If the CMC_1 corresponds to the beginning of the accumulation of a surfactant in spherical micelles, a further concentration increase above the CMC_1 can result in the appearance of cylindrical micelles,[2−4,17−21] the aggregation numbers of which are considerably larger than those for spherical micelles. This is qualified as a polymorphous transition in a surfactant solution. Experimental and theoretical results[17,21−24] show that cylindrical micelles appear if the work of aggregate formation has, as a function of the aggregation number, two maxima: the minimum between them and the broad, gently sloping part after the second maximum where the work rises linearly. The first maximum and minimum of the work correspond to critical embryos of micelles and stable spherical micelles, respectively, while the second maximum sets up a barrier for the transition from spherical to cylindrical micelles with subsequent accumulation of cylindrical micelles within the broad sloping part of the work. This

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10.1021/la052136m CCC: $33.50

polymorphous transition becomes noticeable when the total surfactant concentration attains the CMC$_2$. It introduces new significant features in the kinetics of micellization compared with the situation below the CMC$_2$ when only the first potential hump and the potential well are present for the formation of spherical micelles. The relaxation processes that involve transitions between premicellar molecular aggregates and spherical micelles are referred to as slow relaxation at micellization.[1,25] The presence of the second maximum and the broad sloping part of the work of aggregate formation above the CMC$_2$ should lead to the appearance of new modes of slow relaxation in micellar solution.

The formulation of kinetic equations of micellization describing slow relaxation in surfactant solution under the coexistence of spherical and cylindrical micelles and finding linearized solutions of the kinetic equations is the main goal of this paper. It involves the study of equilibrium and nonequilibrium distributions of molecular aggregates at the total surfactant concentration above the CMC$_2$. With increasing concentration substantially above the CMC$_2$ and with lengthening cylindrical micelles, the structural phase transitions associated with intermicellar interactions and the effects of excluded volume begin to play an important role in relaxation processes.[22,23,26,27] Below, we confine ourselves to the case of not too high total surfactant concentrations to consider the molecular mechanism of transition from spherical to cylindrical micelles as a mechanism of the step-by-step aggregation due to emission and absorption of surfactant monomers. In a realistic situation with the practical absence of micellar collisions, when CMC$_2$ exceeds CMC$_1$ by an order of magnitude and the total surfactant concentration varies within the range lying markedly above the CMC$_2$ but not by more than 2 orders of magnitude, the approach proposed will allow us to find explicit formulas for two rates and two times of slow relaxation in micellar solution.

1. The Work of Formation of a Molecular Aggregate in Surfactant Solution

We assume a surfactant to be nonionic. The aggregation number (the number of molecules in an aggregate) is denoted as n. The concentration of molecular aggregates (the number of aggregates per unit volume) with the aggregation number n is denoted as c_n. The aggregates with $n = 1$ are monomers. Correspondingly, c_1 is the monomer concentration. The total surfactant concentration (the total number of surfactant molecules in the unit volume of a solution) is denoted as c. For cylindrical micelles, concentration c_n includes contributions from all possible orientations of the axes of micelles with a given aggregation number n. All the orientations are equiprobable.

The known experimental and theoretical results[17,21,24] are summarized in Figure 1, which shows the dependence of the work of formation of a molecular aggregate in a surfactant solution on the aggregation number. Figure 1 refers to the case when the fraction of the surfactant matter accumulated in cylindrical micelles is already significant. W_n is the work of formation of an aggregate with the aggregation number n (below, for the sake of brevity, we call W_n the aggregation work). We express W_n in thermal units kT, where k is the Boltzmann constant and T is the absolute temperature. Other notations are $W_{\mathrm{c}}^{(1)} \equiv W_n|_{n=n_{\mathrm{c}}^{(1)}}$, $W_{\mathrm{s}}^{(1)} \equiv W_n|_{n=n_{\mathrm{s}}^{(1)}}$, $W_{\mathrm{c}}^{(2)} \equiv W_n|_{n=n_{\mathrm{c}}^{(2)}}$, and $W^0 \equiv W_n|_{n=n_0}$. The value $W_{\mathrm{c}}^{(1)}$ of the aggregation work at its first maximum point, $n = n_{\mathrm{c}}^{(1)}$, in the aggregation number axis determines the height of an activation barrier for the formation of spherical micelles. The value $W_{\mathrm{s}}^{(1)}$ corresponds to the first minimum of the work at the point $n = n_{\mathrm{s}}^{(1)}$ and characterizes the depth of the potential well where spherical micelles are accumulated. The difference $W_{\mathrm{c}}^{(2)} - W_{\mathrm{s}}^{(1)}$, where $W_{\mathrm{c}}^{(2)}$ is the second maximum value of the aggregation work at the point $n = n_{\mathrm{c}}^{(2)}$, determines the height of an activation barrier for the formation of cylindrical micelles. The value W^0 is taken at the point $n = n_0$ corresponding to the left boundary of the aggregation number range where the dependence of W_n on n is already linear.

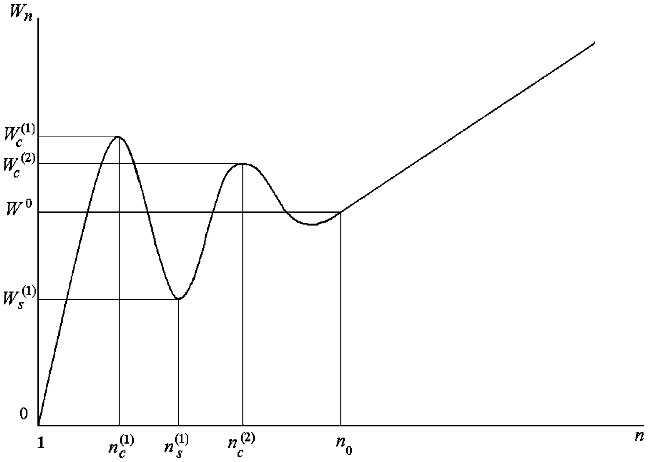

Figure 1. The work of aggregation W_n as a function of the aggregation number n under the coexistence of spherical and cylindrical micelles at a total surfactant concentration above the CMC$_2$.

At $n > n_0$, the micelle core is an elongated cylindrical body with identical ends in the form of a hemispheres or quasi-hemispheres. Such a shape is also called spherocylindrical. Since the limit of the spherical packing of the hydrophobic parts of monomers is already achieved in the hemispherical ends, further adding the monomers to such a micelle does not lead to the reconstruction of the ends and only elongates the cylindrical part of a micelle. As a result, the length, area, and volume of a cylindrical micelle turn to be linearly related to the aggregation number n.

The following contributions to the aggregation work W_n are considered in the droplet and quasi-droplet models of a micelle.[2−4,7,13−15] A hydrophobic contribution is present because of the advantage of the work of the transfer of the hydrophobic parts of a surfactant monomer from a solution to the micelle core. A surface contribution is related to the surface tension of the micelle core. An electrical contribution is caused by the electrical double layer created by the dipole hydrophilic parts of surfactant monomers on the micelle surface. Finally, a concentration contribution appears because of the dependence of the aggregation work on the monomer concentration in solution. In the main order of magnitude, the hydrophobic and concentration contributions to the work of formation of a cylindrical micelle are proportional to the aggregation number n, as in the case of spherical micelles. As was stated above, the dependence of the area of a cylindrical micelle on the aggregation number n is linear. The surface and electrical contributions to the aggregation work W_n of a cylindrical micelle are proportional to the micelle area and, hence, are also linear functions of n. The preceding explains the linear dependence of the total aggregation work W_n on the aggregation number at $n > n_0$, which is shown in Figure 1 and will be used in further discussion. Finding parameters for

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this dependence is possible without the knowledge of the specific properties of surfactant monomers. Below, we just assume that the estimates $n_s^{(1)} \sim 10^2$ and $n_0 \sim 3 \times 10^2$ are valid.

The concentration contribution to the aggregation work is universal and independent of the model of a molecular aggregate or a specific polymorphous form of a micelle in the absence of intermicellar interactions. In the case of a dilute solution, the concentration contribution is known[7,8] to depend on the surfactant monomer concentration c_1 via the term $-(n - 1) \ln c_1$ to give

$$\partial W_n/\partial c_1 = -(n-1)/c_1, \quad \partial W_s^{(1)}/\partial c_1 = -(n_s^{(1)} - 1)/c_1, \quad \partial W^0/\partial c_1 = -(n_0 - 1)/c_1 \quad (1.1)$$

Thermodynamic eqs 1.1, which will be important below as well as the work W_n itself, are determined by the monomer concentration c_1 at every $n > 1$ and are valid at an arbitrary distribution of the aggregate concentrations in a dilute solution.

In view of that stated above about the dependence of work W_n on the monomer concentration c_1 and the aggregation number n, it is convenient to write the expression for W_n at $n > n_0$ as

$$W_n = W^0 + [b - \ln(c_1/c_{1c})](n - n_0), \quad (n > n_0) \quad (1.2)$$

where b and c_{1c} are positive quantities independent of the monomer concentration c_1, $b - \ln(c_1/c_{1c})$ being the coefficient of the linear dependence of W_n on n. Evidently, the sum $b + \ln(c_{1c})$, by means of which the quantities b and c_{1c} enter eq 1.2, can be explicitly expressed and numerically estimated via the parameters of the hydrophobic, surface, and electrical contributions to the aggregation work within the droplet or quasi-droplet model of a micelle. In this sense, the quantity c_{1c} will play a role of a specific concentration of surfactant monomers in solution. In particular, we can choose c_{1c} to be equal to the surfactant monomer concentration at the CMC$_2$. We assume the concentration c_1 to be not too high, so that the condition $b - \ln(c_1/c_{1c}) > 0$ (which was taken into account in Figure 1) fulfills. Under these conditions only, the total number of cylindrical micelles and the total amount of surfactant in them are finite.

With two potential humps in the aggregation work, the main fractions of molecular aggregates are in the regions beyond the first and second hump: $1 \le n < n_c^{(1)} - \Delta n_c^{(1)}$, $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$, and $n > n_c^{(2)} + \Delta n_c^{(2)}$. Here, $\Delta n_c^{(1)}$ and $\Delta n_c^{(2)}$ stand for the half-widths of the potential humps, and the work W_n (expressed in thermal units kT) decreases by unity if the variable n deviates from $n_c^{(1)}$ and $n_c^{(2)}$ by $\Delta n_c^{(1)}$ and $\Delta n_c^{(2)}$, respectively. Aggregates are spherical within the region $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$ and cylindrical within the region $n > n_c^{(2)} + \Delta n_c^{(2)}$. The aggregates within the region $1 \le n < n_c^{(1)} - \Delta n_c^{(1)}$ will be called premicellar.

2. The Boltzmann Distribution of Concentrations of Premicellar Aggregates and Spherical and Cylindrical Micelles

Even in a nonequilibrium state of surfactant solution, a large excess of aggregates in the regions $1 \le n < n_c^{(1)} - \Delta n_c^{(1)}$, $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$, and $n > n_c^{(2)} + \Delta n_c^{(2)}$ provides quasi-equilibrium distributions of aggregate concentrations in each of these regions separately. It fulfills regardless of the variations in the number of aggregates in these regions due to the aggregate fluxes over the humps. With neglecting interaggregate interactions, the quasi-equilibrium distributions of the concentrations of premicellar aggregates and spherical and cylindrical micelles obey the Boltzmann distribution. The aggregation work in the exponent in the distributions depends on the current monomer concentration. The preexponential factor is determined by the value of aggregate concentration taken at a certain chosen aggregation number in the corresponding region. Thus the quasi-equilibrium distributions have the Boltzmann form:

$$c_n = c_1 e^{-W_n} \quad (1 \le n < n_c^{(1)} - \Delta n_c^{(1)})$$

$$c_n = c_s^{(1)} \mathrm{e}^{-(W_n - W_s^{(1)})} \quad (n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)})$$

$$c_n = c^0 \mathrm{e}^{-(W_n - W^0)} \quad (n > n_c^{(2)} + \Delta n_c^{(2)}) \quad (2.1)$$

Here, c_1 is the current value of the monomer concentration (at a current moment of time), $c_s^{(1)} \equiv c_n|_{n=n_s^{(1)}}$ is the current value of the concentration of spherical micelles at $n = n_s^{(1)}$, and $c^0 \equiv c_n|_{n=n_0}$ is the current value of the aggregate concentration at the point $n = n_0$ corresponding to the left boundary of the aggregation number region where the dependence of W_n on n is already linear. We assume $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$, where $\Delta n_s^{(1)}$ is the half-width of the potential well of the work W_n in the vicinity of the point $n = n_s^{(1)}$, and the work W_n increases by unity when n deviates from $n_s^{(1)}$ by $\Delta n_s^{(1)}$. Then, the equality $c_s^{(1)} = c_M/\pi^{1/2}\Delta n_s^{(1)}$ holds,[7,9] where c_M is a current value of the total concentration of spherical micelles (the total number of spherical micelles per unit volume of solution).

When the aggregation work has two potential humps, the transition of subcritical molecular aggregates into spherical micelles and the transition of spherical micelles into cylindrical ones proceed with overcoming activation barriers. Although premicellar aggregates, spherical micelles, and cylindrical micelles taken separately are in quasi-equilibrium, their mutual equilibrium can, however, be absent. The equality[9]

$$c_M = \pi^{1/2} c_1 \Delta n_s^{(1)} \mathrm{e}^{-W_s^{(1)}} \quad (2.2)$$

and the equality

$$c^0 = c_1 \mathrm{e}^{-W^0} \quad (2.3)$$

(following from $c^0 \equiv c_n|_{n=n_0}$ and $W^0 \equiv W_n|_{n=n_0}$, according to the Boltzmann principle) fulfill simultaneously only at the state of complete equilibrium. Evidently, eqs 2.2 and 2.3 together with eqs 2.1 and the equality $c_s^{(1)} = c_M/\pi^{1/2}\Delta n_s^{(1)}$ show that the Boltzmann distribution $c_n = c_1 \exp(-W_n)$ expands over the whole range of aggregation numbers in the state of complete equilibrium.

In view of eq 1.2, the quasi-equilibrium distribution of the concentrations of cylindrical micelles in eqs 2.1 can be written as

$$c_n = c^0 \mathrm{e}^{-(b-a)(n-n_0)} \; (n > n_0) \quad (2.4)$$

where $a \equiv \ln(c_1/c_{1c})$. Let us denote the total concentration of cylindrical micelles (the total number of cylindrical micelles per unit volume) as g and the total number of surfactant molecules in cylindrical micelles per unit volume as N. In view of the estimates $n_s^{(1)} \sim 10^2$ and $n_0 \sim 3 \times 10^2$ and the inequality $n_s^{(1)} < n_c^{(2)} + \Delta n_c^{(2)} < n_0$ (see Figure 1), the contributions to g and N from the region $n_c^{(2)} + \Delta n_c^{(2)} < n < n_0$ can be neglected compared with the contribution from region $n > n_0$. Thus we have

$$g = \int_{n_0}^{\infty} c_n \mathrm{d}n, \quad N = \int_{n_0}^{\infty} n c_n \mathrm{d}n \quad (b - a > 0) \quad (2.5)$$

where the inequality $b - a > 0$ noted at the end of section 1 is taken into account.

As is seen from eq 2.4, the quantity

$$n_* - n_0 \equiv 1/(b - a) \tag{2.6}$$

represents the width of the cylindrical micelle distribution c_n in the aggregation numbers: adding this width to $n - n_0$ decreases the concentration c_n by e times. If $n - n_0$ exceeds $n_* - n_0$ by at least 3−4 times, the contributions to the integrals in eqs 2.5 from the interval (n,∞) become relatively small.

Substituting eq 2.4 in eqs 2.5 and performing integration, we obtain

$$g = \frac{c^0}{b - a}, \quad N = \frac{c^0 n_0}{b - a} + \frac{c^0}{(b - a)^2} \quad (b - a > 0) \tag{2.7}$$

As follows from eqs 2.6 and 2.7, $n_* = N/g$. This shows that n_* is the average aggregation number for cylindrical micelles.

3. The First and Second Critical Micelle Concentrations

The definitions of the CMC$_1$ and CMC$_2$ are rather conditional and are realized in the literature by dozens of methods permitting the estimation of the critical micellization degree for the appearance of spherical and cylindrical micelles. Let us specify what we understand for the CMC$_1$ and CMC$_2$ in this paper. Denoting the total number of surfactant molecules in spherical micelles per unit solution volume as N_s and assuming $\Delta n_\mathrm{s}^{(1)}/n_\mathrm{s}^{(1)} \ll 1$, we have

$$N_\mathrm{s} = n_\mathrm{s}^{(1)} c_\mathrm{M} \tag{3.1}$$

(eq 3.1 requires only the quasi-equilibrium distribution of spherical micelles). Evidently, the balance equation for the total concentration c in a surfactant solution can be written as

$$c = c_1 + N_\mathrm{s} + N \tag{3.2}$$

We define the CMC$_1$ by the numerical specification of the micellization degree[2] (or the amount ratio of the micellar and monomeric surfactant forms) in the state of complete equilibrium of the solution. We assume that the surfactant monomer concentration c_{1m} corresponding to the CMC$_1$ satisfies the condition

$$\left.\frac{N_\mathrm{s}}{c_1}\right|_{c_1 = c_{1m}} \equiv \frac{1}{10} \tag{3.3}$$

In accordance with eq 3.2, eq 3.3 shows that the role of spherical micelles in the balance of surfactant amount is already noticeable at $c_1 = c_{1m}$. Since cylindrical micelles are still absent at $c_1 = c_{1m}$, c_{1m} is seen from eqs 3.2 and 3.3 to coincide nearly with the CMC$_1$:

$$\mathrm{CMC}_1 \simeq c_{1m} \tag{3.4}$$

Let us assign c_{1c} in eq 1.2 as the equilibrium monomer concentration corresponding to the CMC$_2$. We define the CMC$_2$ as the equilibrium total surfactant concentration at which the ratio of the total surfactant amount in cylindrical micelles to the surfactant amount in monomers is 1/10. In view of eq 3.2, the role of cylindrical micelles is already noticeable at $c_1 = c_{1c}$ in the surfactant amount balance. We then have

$$\left.\frac{N}{c_1}\right|_{c_1 = c_{1c}} \equiv \frac{1}{10} \tag{3.5}$$

by analogy with the definition of the CMC$_1$ via c_{1m} in eq 3.3.

We will consider in sections 5−7 a realistic situation with

$$\left.\frac{N_\mathrm{s}}{c_1}\right|_{c_1 = c_{1c}} \sim 10, \quad \left.\frac{c_\mathrm{M}}{c_1}\right|_{c_1 = c_1} \sim \frac{1}{10} \tag{3.6}$$

where eq 3.1 and the estimate $n_\mathrm{s}^{(1)} \sim 10^2$ are taken into account. As is seen from eqs 3.2 and 3.5 and the inequality $(N_\mathrm{s}/c_1)|_{c_1=c_{1c}} \gg 1$, the CMC$_2$ coincides nearly with $N_\mathrm{s}|_{c_1=c_{1c}}$:

$$\mathrm{CMC}_2 \simeq N_\mathrm{s}|_{c_1 = c_{1c}} \tag{3.7}$$

With variation in the total concentration c_M of spherical micelles within wide limits in such a way that the ratio c_M/c_1 changes from values on the order of 10^{-3} to values on the order of 10^{-1}, the surfactant monomer concentration c_1 and the quantities $n_\mathrm{s}^{(1)}$ and $\Delta n_\mathrm{s}^{(1)}$ stay practically constant.[16] Then, as follows from eqs 3.1, 3.3, 3.4, 3.6, and 3.7, we have $c_{1c} \simeq c_{1m}$ and

$$\mathrm{CMC}_2/\mathrm{CMC}_1 \sim 10 \tag{3.8}$$

Evidently, we can take somewhat different estimates in eqs 3.6 and, correspondingly, in eq 3.8. Such a replacement does not change the conclusions obtained in sections 5−7.

4. Kinetic Equations of Micellization in Systems with Spherical and Cylindrical Micelles

We assume the following inequalities to be valid:

$$\begin{gathered}\Delta n_\mathrm{c}^{(1)} \gg 1, \quad \Delta n_\mathrm{c}^{(1)}/n_\mathrm{c}^{(1)} \ll 1, \quad \Delta n_\mathrm{c}^{(1)}/(n_\mathrm{s}^{(1)} - n_\mathrm{c}^{(1)}) \ll 1 \\ \Delta n_\mathrm{s}^{(1)} \gg 1, \quad \Delta n_\mathrm{s}^{(1)}/(n_\mathrm{s}^{(1)} - n_\mathrm{c}^{(1)}) \ll 1, \quad \Delta n_\mathrm{s}^{(1)}/(n_\mathrm{c}^{(2)} - n_\mathrm{s}^{(1)}) \ll 1 \\ \Delta n_\mathrm{c}^{(2)} \gg 1, \quad \Delta n_\mathrm{c}^{(2)}/(n_\mathrm{c}^{(2)} - n_\mathrm{s}^{(1)}) \ll 1, \quad \Delta n_\mathrm{c}^{(2)}/(n_0 - n_\mathrm{c}^{(2)}) \ll 1\end{gathered} \tag{4.1}$$

First, the inequalities found in eqs 4.1 permit us to consider the aggregation number n as a continuous variable in the region of the potential humps and well for the work W_n. Second, these inequalities imply that both the humps and the well of work W_n are pronounced: as is shown in Figure 1, they are distanced from the points $n = 1$ and $n = n_0$, as well as from each other.

Let us introduce the direct, $J'^{(1)}$, and the reverse, $J''^{(1)}$, fluxes of molecular aggregates over the first potential hump of the aggregation work. These fluxes determine the number of molecular aggregates overcoming (by fluctuations) the first potential hump per unit time in the unit volume of micellar solution from the region $n < n_\mathrm{c}^{(1)} - \Delta n_\mathrm{c}^{(1)}$ to the region $n > n_\mathrm{c}^{(1)} + \Delta n_\mathrm{c}^{(1)}$ (the direct flux) and back from the region $n > n_\mathrm{c}^{(1)} + \Delta n_\mathrm{c}^{(1)}$ to the region $n < n_\mathrm{c}^{(1)} - \Delta n_\mathrm{c}^{(1)}$ (the reverse flux). Evidently, $J'^{(1)} - J''^{(1)}$ is the net flux of molecular aggregates passing by fluctuations from the region $n < n_\mathrm{c}^{(1)} - \Delta n_\mathrm{c}^{(1)}$ to the region $n > n_\mathrm{c}^{(1)} + \Delta n_\mathrm{c}^{(1)}$.

We also introduce the direct, $J'^{(2)}$, and the reverse, $J''^{(2)}$, fluxes of molecular aggregates over the second potential hump of the aggregation work. These fluxes determine the number of molecular aggregates overcoming (by fluctuations) the second potential hump per unit time in the unit volume of micellar solution from the region $n < n_\mathrm{c}^{(2)} - \Delta n_\mathrm{c}^{(2)}$ to the region $n > n_\mathrm{c}^{(2)} + \Delta n_\mathrm{c}^{(2)}$ and back from the region $n > n_\mathrm{c}^{(2)} + \Delta n_\mathrm{c}^{(2)}$ to the region $n <$

$n_c^{(2)} - \Delta n_c^{(2)}$. Evidently, $J'^{(2)} - J''^{(2)}$ is the net flux of molecular aggregates passing by fluctuations from the region $n < n_c^{(2)} - \Delta n_c^{(2)}$ to the region $n > n_c^{(2)} + \Delta n_c^{(2)}$.

In accordance with the meaning of the fluxes introduced, the variations of the numbers of spherical and cylindrical micelles in time are determined in the unit solution volume by the equations

$$\mathrm{d}c_M/\mathrm{d}t = J'^{(1)} - J''^{(1)} - (J'^{(2)} - J''^{(2)})$$

$$\mathrm{d}g/\mathrm{d}t = J'^{(2)} - J''^{(2)} \qquad (4.2)$$

where t is the time. Summing eqs 4.2, we arrive at the evident result $\mathrm{d}(c_M + g)/\mathrm{d}t = J'^{(1)} - J''^{(1)}$. Equations 4.2 have the meaning of the kinetic equations of micellization in systems with spherical and cylindrical micelles. These equations can be derived from general kinetic equations of the step-by-step aggregation (the Becker−Döring equations[5−7]) by summing these equations over aggregation numbers in the regions where spherical and, correspondingly, cylindrical micelles are located in the aggregation axis.

As was noted in section 2, the distributions of concentrations of molecular aggregates in the regions $1 \le n < n_c^{(1)} - \Delta n_c^{(1)}$, $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$, and $n > n_c^{(2)} + \Delta n_c^{(2)}$, that is, beyond the potential humps of the aggregation work, are maintained in the quasi-equilibrium states. Then the distributions of concentration of the molecular aggregates in the regions of the first and second potential humps are quasi-steady. They are time-independent over sufficiently long time intervals, which, on the other hand, are too short for the concentrations c_1, c_M and g to change markedly during the slow process of approaching the state of complete equilibrium of the micellar solution. Along with that, the fluxes $J'^{(1)}$, $J''^{(1)}$, $J'^{(2)}$, and $J''^{(2)}$ are quasi-steady too. This significantly simplifies the whole investigation.

We denote as $c_n'^{(1)}$ and $c_n''^{(1)}$ the quasi-steady distributions of concentration of molecular aggregates participating in the quasi-steady direct, $J'^{(1)}$, and reverse, $J''^{(1)}$, fluxes over the first hump of the aggregation work. Following the ideas of the kinetic theory of nucleation, we set the boundary conditions

$$c_n'^{(1)}/c_n \simeq \begin{cases} 1 & (n \simeq n_c^{(1)} - \Delta n_c^{(1)}), \\ 0 & (n \simeq n_c^{(1)} + \Delta n_c^{(1)}), \end{cases}$$

$$c_n''^{(1)}/c_n \simeq \begin{cases} 0 & (n \simeq n_c^{(1)} - \Delta n_c^{(1)}), \\ 1 & (n \simeq n_c^{(1)} + \Delta n_c^{(1)}) \end{cases} \qquad (4.3)$$

on the boundaries of the first hump. The aggregate concentration c_n on the left-hand sides of eqs 4.3 refers to a quasi-equilibrium state and is determined by the first (at $n \simeq n_c^{(1)} - \Delta n_c^{(1)}$) and the second (at $n \simeq n_c^{(1)} + \Delta n_c^{(1)}$) of eqs 2.1. Taking into account the inequalities of eqs 4.1, one can obtain the following analytical expressions for the quasi-steady fluxes $J'^{(1)}$ and $J''^{(1)}$:[9]

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

$$J''^{(1)} = c_M j_c^{+(1)} \exp[-(W_c^{(1)} - W_s^{(1)})]/\pi \Delta n_c^{(1)} \Delta n_s^{(1)} \qquad (4.4)$$

in which $j_c^{+(1)}$ is the number of surfactant monomers absorbed ($j_c^{+(1)} > 0$), from solution, by a spherical molecular aggregate composed of $n_c^{(1)}$ molecules, per unit time. The first of eqs 4.4 is analogous to the equation for the steady nucleation rate in the theory of nucleation. The second of eqs 4.4 gives the rate of steady breakup of spherical micelles. Equations 4.4 are similar in their structure. The natural difference is that the breakup of spherical micelles is prevented by the aggregation work barrier of the height $W_c^{(1)} - W_s^{(1)}$, and the breakup intensity is proportional to the concentration $c_s^{(1)} = c_M/\pi^{1/2}\Delta n_s^{(1)}$ of molecular aggregates with $n = n_s^{(1)}$.

The quasi-equilibrium distribution c_n is given on the left and right boundaries of the second potential hump by the second (at $n \simeq n_c^{(2)} - \Delta n_c^{(2)}$) and, correspondingly, by the third (at $n \simeq n_c^{(2)} + \Delta n_c^{(2)}$) of eqs 2.1. Using the same approach as that used when deriving eqs 4.4, one can write analytical expressions for the quasi-steady direct, $J'^{(2)}$, and reverse, $J''^{(2)}$, fluxes of molecular aggregates over the second potential hump as

$$J'^{(2)} = c_M j_c^{+(2)} \exp[-(W_c^{(2)} - W_s^{(1)})]/\pi \Delta n_c^{(2)} \Delta n_s^{(1)}$$

$$J''^{(2)} = c^0 j_c^{+(2)} \exp[-(W_c^{(2)} - W^0)]/\pi^{1/2}\Delta n_c^{(2)} \qquad (4.5)$$

in which $j_c^{+(2)}$ is the number of surfactant monomers absorbed ($j_c^{+(2)} > 0$) by a nonspherical molecular aggregate composed of $n_c^{(2)}$ molecules, per unit time.

If we pass to the concentration $c_s^{(1)} = c_M/\pi^{1/2}\Delta n_s^{(1)}$ at $n = n_s^{(1)}$, the quantity $\pi^{1/2}\Delta n_s^{(1)}$ disappears in the denominators of the second of eqs 4.4 and the first of eqs 4.5. Then the relation of these equations to the first of eqs 4.4 and the second of eqs 4.5 is more apparent. However, it is better to keep the total concentration c_M of the spherical micelles in eqs 4.4 and 4.5 because c_M is more readily accessible from experiment than $c_s^{(1)}$. Additionally, we can state the following: Because the aggregate concentration c_n is in quasi-equilibrium in the region $n > n_c^{(2)} + \Delta n_c^{(2)}$, then, according to the Boltzmann principle, we can replace n_0 in the definition $c^0 \equiv c_n|_{n=n_0}$ and in the second of eqs 4.5 by any value of n within this region. Even so, the factor $c^0 \exp(W^0)$ in the second of eqs 4.5 does not change. However, it is better to keep the value $n = n_0$ in this equation, from which eqs 1.2 and 2.4 become applicable.

Relaxation in a materially isolated micellar solution leads to a state of complete equilibrium. Since the direct and reverse fluxes of molecular aggregates over the potential humps of the aggregation work mutually compensate each other in the state of equilibrium, then

$$\tilde{J}'^{(1)} = \tilde{J}''^{(1)}, \quad \tilde{J}'^{(2)} = \tilde{J}''^{(2)} \qquad (4.6)$$

where the tilde marks the fluxes in the state of equilibrium. Equations 4.4−4.6 lead to eqs 2.2 and 2.3 obtained in section 2 for solution equilibrium without using the concept of the direct and reverse fluxes of molecular aggregates over the potential humps. This confirms eqs 4.4 and 4.5 along with the concept itself (although the direct and reverse fluxes enter eqs 4.2 in the form of their differences only).

In view of eqs 4.4 and 4.5, the right-hand sides of kinetic eqs 4.2 depend on the concentrations c_1, c_M, and c^0. The dependence on c_M and c^0 is linear, while the dependence on c_1 turns out to be more complicated because the quantities $j_c^{+(1)}$, $j_c^{+(2)}$, $W_c^{(1)}$, $W_s^{(1)}$, $W_c^{(2)}$, W^0, $\Delta n_c^{(1)}$, $\Delta n_s^{(1)}$, and $\Delta n_c^{(2)}$ are functions of the surfactant monomer concentration. The quantities $j_c^{+(1)}$ and $j_c^{+(2)}$ are directly proportional to c_1. The quantities $W_c^{(1)}$, $W_s^{(1)}$, $\Delta n_c^{(1)}$, and $\Delta n_s^{(1)}$ can be found as functions of c_1 within the droplet and quasi-droplet models of nonionic spherical micelles.[14,15] To determine $W_c^{(2)}$ and W^0 as functions of c_1, one can use the first and third of eqs 1.1, while the dependence of $\Delta n_c^{(2)}$ on c_1 can be neglected in the first approximation. In view of the first of eqs 2.7 and the definition $a \equiv \ln(c_1/c_{1c})$, the concentration g on the left-hand side of the second of eqs 4.2 is a function of c_1 and a linear function of c^0. There is one more equation relating the concentrations c_1, c_M, and c^0, where c_M and c^0 enter linearly. It is given by the surfactant amount balance, eq 3.2, jointly with eqs 2.7 and 3.1. As a result, we see that kinetic eqs 4.2 jointly with the expressions for the fluxes given by eqs 4.4 and 4.5, as well as the balance eq 3.2 jointly with eqs 2.7 and 3.1 constitute a closed set of equations. This equation set determines a variation in the concentrations c_1, c_M, and g in time and describes slow relaxation in materially isolated solutions with spherical and cylindrical micelles at total concentrations above the CMC_2.

5. Accounting for the Dependence of Work W^0 on the Monomer Concentration

We are interested in the range of variation of the average aggregation number n_* of cylindrical micelles defined as

$$n_* \sim 10^4/p \quad (1 \leq p \lesssim 5) \tag{5.1}$$

where p is just a numerical parameter. As follows from the estimate $n_0 \sim 3 \times 10^2$, the inequality $n_* \gg n_0$ still holds at the upper limit of p noted in eq 5.1. Thus, the difference $n_* - n_0$ practically coincides with n_*. Equations 2.6 and 5.1 yield

$$b - a = 1/n_* \sim p/10^4 \quad (1 \leq p \lesssim 5) \tag{5.2}$$

Therefore, n_* may be regarded as both the width of the distribution of cylindrical micelles and the average aggregation number of cylindrical micelles. Since b is independent of the surfactant monomer concentration c_1 and the quantity $a \equiv \ln(c_1/c_{1c})$ depends on c_1 by means of the term $\ln(c_1)$, eq 5.2 assigns the range of variation of c_1, which we will study below. Equation 5.2 and the inequality $n_* \gg n_0$ bring us to $n_0(b - a) \ll 1$. This allows us to reduce the second of eqs 2.7 to

$$N = \frac{c^0}{(b-a)^2} \quad (b - a = 1/n_*) \tag{5.3}$$

As we will confirm at the end of this section, the condition

$$\mathrm{c} \gg N_s \simeq \mathrm{CMC}_2 \tag{5.4}$$

is valid if eqs 3.6 are fulfilled. In view of eqs 3.2 and 5.4, we have

$$N \simeq c \tag{5.5}$$

that is, cylindrical micelles give the main contribution to the surfactant amount balance in the solution.

Using the third of eqs 1.1, the definition $a \equiv \ln(c_1/c_{1c})$, and the inequality $n_0 \gg 1$, we have

$$\mathrm{e}^{-W^0} = \mathrm{e}^{-W_0{}^0}\mathrm{e}^{an_0} \tag{5.6}$$

where $W_0^0 \equiv W^0|_{c_1=c_{1c}}$. If the quantity a satisfies the limitation expressed in (5.2), eq 5.6 can be rewritten at $n_0/n_* \ll 1$ with sufficient accuracy as

$$\mathrm{e}^{-W^0} = \mathrm{e}^{-W_0{}^0}\mathrm{e}^{bn_0} \tag{5.7}$$

Thus, the exponent e^{-W^0} is independent of p at $1 \leq p \lesssim 5$.

Using eqs 2.3 and 5.3, the independence of e^{-W^0} on p, and the proportionality between $b - a$ and p that follows from eq 5.2, we have

$$\frac{N}{c_1} = \frac{N}{c_1}\bigg|_{p=1}\frac{1}{p^2} \quad (1 \leq p \lesssim 5) \tag{5.8}$$

Equations 5.5 and 5.8 yield

$$\frac{c}{c_1} \simeq \frac{c}{c_1}\bigg|_{p=1}\frac{1}{p^2} \quad (1 \leq p \lesssim 5) \tag{5.9}$$

According to eqs 5.1 and 5.9, the quantities n_* and c/c_1 are inversely proportional to p and p^2, respectively. This leads to the known result[4,19] that n_* is directly proportional to $(c/c_1)^{1/2}$.

Equations 5.2, 5.3, and 5.5, with the help of eq 2.3, allow us to write

$$\mathrm{e}^{W^0} \simeq \frac{c_1}{c}n_*{}^2, \quad \mathrm{e}^{W^0}(b-a) \simeq \frac{c_1}{c}n_*, \quad \mathrm{e}^{W^0}(b-a)^2 \simeq \frac{c_1}{c}$$

$$\mathrm{e}^{W^0}(b-a)^3 \simeq \frac{c_1}{c}\frac{1}{n_*} \quad (b - a = 1/n_*) \tag{5.10}$$

Equation 5.5 and the equality $n_* = N/g$ noted at the end of section 2 give

$$g \simeq c/n_* \tag{5.11}$$

Using the second of eqs 2.7 at $a = 0$ (at $c_1 = c_{1c}$), taking into account eq 2.3 and the definition $W_0^0 \equiv W^0|_{c_1=c_{1c}}$, we obtain

$$\frac{N}{c_1}\bigg|_{c_1=c_{1c}} = \frac{n_0}{b}\left(1 + \frac{1}{bn_0}\right)\mathrm{e}^{-W_0{}^0} \tag{5.12}$$

Expressing $\mathrm{e}^{-W_0{}^0}$ in eq 5.12 with the use of the definition found in eq 3.5 and substituting the result in eq 5.7, we have

$$\mathrm{e}^{-W^0} = \frac{b}{10n_0}\left(1 + \frac{1}{bn_0}\right)^{-1}\mathrm{e}^{bn_0} \tag{5.13}$$

Using eq 5.13 and the first of eqs 5.10 leads to the equation

$$bn_0\left(1 + \frac{1}{bn_0}\right)^{-1}\mathrm{e}^{bn_0} \simeq 10\frac{c}{c_1}\left(\frac{n_0}{n_*}\right)^2 \tag{5.14}$$

The parameter b is determined by the nature of cylindrical micelles and is independent of the monomer concentration c_1. The parameter n_0 corresponds to a reference point chosen and, naturally, is also constant. Therefore, the right-hand side of eq 5.14 as a whole should be constant to produce again the above relation $n_* \propto (c/c_1)^{1/2}$. On the other side, eq 5.14, as an equation for bn_0, provides a direct method of estimation of the parameter b that is usually calculated with the aids of models.

The root bn_0 of eq 5.14 is not very sensitive to variation in the right-hand side of the equation. This considerably simplifies all our study. In particular, we can choose

$$\frac{c}{c_1}\bigg|_{p=1} \sim 10^3 \tag{5.15}$$

in accordance with eq 5.4 at the upper limit of the variation of n_* at $p = 1$. Then, estimating the right-hand side of eq 5.14 (independent of p), with the help of eqs 5.1 and 5.9 and $n_0 \sim 3 \times 10^2$, as 9, we obtain the approximate value $bn_0 \simeq 2$ for the root bn_0. If we chose $(c/c_1)|_{p=1} \sim 10^4$, keeping the estimate $n_*|_{p=1} \sim 10^4$, we would obtain $bn_0 \simeq 3.5$. Subsequently, we will keep the estimate of eq 5.15. Then the parameter b equals

$$b \simeq 2/n_0 \tag{5.16}$$

As follows from eqs 5.9 and 5.15, the ratio c/c_1 is not too high. In view of eqs 3.6 and 3.7, the total concentration c exceeds the CMC_2 by no more than 2 orders of magnitude. According to eq 5.1, the average aggregation number n_* of cylindrical micelles is not too large at such total concentrations. Thus, micelle collisions, leading to the recombination and splitting of micelles, are not yet important, and the Boltzmann distribution in eq 2.4 for cylindrical micelles is still applicable. Along with that, eqs 5.9 and 5.15 determine the total surfactant concentration c that markedly exceeds the CMC_2. The range of variation of c envelops almost 2 orders of magnitude.

Equation 5.16 allows us to obtain several important results at the total concentration c, satisfying eqs 5.9 and 5.15. Using eqs 5.2 and 5.16 and $a \equiv \ln(c_1/c_{1c})$, we have

$$c_1 \simeq c_{1c}(1 + 2/n_0 - 1/n_*) \tag{5.17}$$

where the strong inequalities $1/n_0 \ll 1$ and $1/n_* \ll 1$ are taken into account. As follows from eq 5.17, $c_1 \simeq c_{1c}$. Equations 5.13 and 5.16 give $\mathrm{e}^{W^0} \simeq n_0{}^2$. Bearing this in mind and using eqs 2.3, 2.7, and 5.2 and $n_0 \sim 3 \times 10^2$, we find $g/c_1 \sim 1/10p$ ($1 \leq p \lesssim 5$). The latter ensures that the surfactant solution is dilute with respect to the cylindrical micelles.

We can also add the following: Because of the second of eqs 1.1, the exponent $\mathrm{e}^{-W_s^{(1)}}$ grows by $\exp[n_s^{(1)}(2/n_0 - 1/n_*)]$ times with increasing monomer concentration c_1 from the value c_{1c} up to values defined by eq 5.17. As follows from eq 5.1 and the estimates $n_s^{(1)} \sim 10^2$ and $n_0 \sim 3 \times 10^2$, the exponent $\mathrm{e}^{-W_s^{(1)}}$ does not increase significantly. Then, in view of eqs 3.1 and 2.2, N_s and c_M exceed their values $N_s|_{c_1=c_{1c}}$ and $c_M|_{c_1=c_{1c}}$ insignificantly. Therefore the estimates

$$N_s/c_1 \sim 10, \quad c_M/c_1 \sim 1/10 \tag{5.18}$$

are valid along with eqs 3.6. In view of eqs 5.9 and 5.15, this means that eq 5.4 is fulfilled, even at the upper limit of p noted in eq 5.9.

6. Linearization of the Surfactant Balance Equation in the Vicinity of the Equilibrium State of a Materially Isolated Solution

We now consider a vicinity of the equilibrium state of a materially isolated surfactant solution. Since the solution is nonequilibrium in this vicinity, eqs 2.2 and 2.3 are inapplicable. As a corollary, the concentrations c^0, c_M, and c are not determined uniquely by the surfactant monomer concentration c_1. As previously done in section 4, we will mark quantities in the state of equilibrium with a tilde and denote the deviation of quantities from their equilibrium value by adding the symbol δ to the left of the quantities. The deviation δc of the total surfactant concentration can be considered to be zero in a materially isolated solution. Then the surfactant amount balance given by eq 3.2 establishes a relation between the deviations δc_1 and δc^0 and the deviations δc_M and δg of the total concentrations of spherical and cylindrical micelles. We will find this relation.

It is sufficient for our study if the relation

$$b - \tilde{a} = 1/\tilde{n}_* \sim p/10^4 \quad (1 \leq p \lesssim 5) \tag{6.1}$$

holds in accordance with eq 5.2 in the final equilibrium state of a materially isolated surfactant solution, as well as eqs 5.1, 5.9, 5.10, and 5.15. Below, we will indeed see that the possibility of linearization of eq 3.2 in the vicinity of the equilibrium state imposes a severe restriction on the smallness of the relative deviation of $b - a$ from $b - \tilde{a}$. This restriction provides that, in addition to eq 6.1, eq 5.2 holds with a high accuracy in the whole vicinity of the final equilibrium state, allowing the linearization of eq 3.2. Along with eq 5.2, eq 5.3 and the first of eqs 2.7 are valid in the same vicinity.

To simplify the study, we perform the linearization of these formulas and the definition $a \equiv \ln(c_1/c_{1c})$. Using eq 2.3 in the final equilibrium state of solution, we obtain

$$\delta a = \frac{1}{\tilde{c}_1}\delta c_1 = \frac{1}{\tilde{c}^0}\mathrm{e}^{-\tilde{W}^0}\delta c_1$$

$$\delta N = \frac{1}{(b-\tilde{a})^2}\delta c^0 + 2e^{-\tilde{W}^0}\frac{1}{(b-\tilde{a})^3}\delta c_1$$

$$\delta g = \frac{1}{(b-\tilde{a})}\delta c^0 + \mathrm{e}^{-\tilde{W}^0}\frac{1}{(b-\tilde{a})^2}\delta c_1 \tag{6.2}$$

The condition of linearization with respect to δc_1 in eqs 6.2 can be written as the condition of neglecting the quadratic in the δc_1 term in the second of eqs 6.2 (which is the most sensitive to δc_1) compared with the linear in the δc_1 term kept in this equation. We then have

$$|\delta c_1|/\tilde{c}_1 \ll (2/3)(b - \tilde{a}) \tag{6.3}$$

The inequality given in eq 6.3 gives the required condition of linearization of the balance eq 3.2. With linear dependence on c^0 in eq 5.3 and the first of eqs 2.7, a restriction on the smallness of the deviation δc^0 is not required in eqs 6.2. Let us rewrite the left-hand side of eq 6.3 with the help of the first of eqs 6.2 as $|\delta(b-a)|$ (the parameter b is independent of c_1 and, consequently, $\delta b = 0$). Then eq 6.3 confirms that eq 5.2 holds, together with eq 6.1, with a high accuracy within the whole vicinity of the final equilibrium state, allowing the linearization of eq 3.2. With the aid of eq 6.1, the condition given in eq 6.3 can be rewritten as

$$|\delta c_1|/\tilde{c}_1 \ll 2/3\tilde{n}_* \tag{6.4}$$

Using the third of eqs 6.2, we find

$$\delta c^0 = -\mathrm{e}^{-\tilde{W}^0}\frac{1}{b-\tilde{a}}\delta c_1 + (b-\tilde{a})\delta g \tag{6.5}$$

Substituting eq 6.5 in the right-hand side of the second of eqs 6.2, we obtain

$$\delta N = \mathrm{e}^{-\tilde{W}^0}\frac{1}{(b-\tilde{a})^3}\delta c_1 + \frac{1}{b-\tilde{a}}\delta g \tag{6.6}$$

With allowance for eq 3.1 to be valid for spherical micelles at quasi-equilibrium, the balance eq 3.2 linearized leads for a materially isolated solution to

$$\delta c_1 + \tilde{n}_s^{(1)}\delta c_M + \delta N = 0 \tag{6.7}$$

Here, we set $n_s^{(1)} = \tilde{n}_s^{(1)}$ with good accuracy because of eq 6.4 and low sensitivity of the quantity $n_s^{(1)}$ to the monomer concentration c_1.[16] Putting eq 6.6 in eq 6.7, we have

$$\delta c_1 + \tilde{n}_s^{(1)}\delta c_M + \mathrm{e}^{-\tilde{W}^0}\frac{1}{(b-\tilde{a})^3}\delta c_1 + \frac{1}{b-\tilde{a}}\delta g = 0 \tag{6.8}$$

Applying eqs 5.1, 5.9, 5.15, and the last of eqs 5.10 to the final equilibrium state of solution, we obtain $\mathrm{e}^{\tilde{W}^0}(b-\tilde{a})^{-3} > 10^5 \gg 1$. Thus, the first term on the left-hand side of eq 6.8 can be omitted. Then eq 6.8 gives, with high accuracy,

$$\delta c_1 = -e^{\tilde{W}^0}\tilde{n}_s^{(1)}(b-\tilde{a})^3\delta c_M - e^{\tilde{W}^0}(b-\tilde{a})^2\delta g \qquad (6.9)$$

Excluding the deviation δc_1 on the right-hand side of eq 6.5 with the help of eq 6.9, we find

$$\delta c^0 = \tilde{n}_s^{(1)}(b-\tilde{a})^2\delta c_M + 2(b-\tilde{a})\delta g \qquad (6.10)$$

Equations 6.9 and 6.10 reveal the sought-after relation of the deviations δc_1 and δc^0 to the deviations δc_M and δg.

Substituting eq 6.9 in eq 6.6 yields

$$\delta N = -\tilde{n}_s^{(1)}\delta c_M \qquad (6.11)$$

Equation 6.11 expresses the relation between the deviations δN and δc_M of the quantities N and c_M that is accessible from experiment.

Applying eq 6.1 and the last two of eqs 5.10 to the final equilibrium state of solution, we rewrite eqs 6.9 and 6.10 in the form

$$\delta c_1 \simeq -\frac{\tilde{c}_1}{\tilde{c}}\frac{\tilde{n}_s^{(1)}}{\tilde{n}_*}\delta c_M - \frac{\tilde{c}_1}{\tilde{c}}\delta g \qquad (6.12)$$

$$\delta c^0 \simeq \frac{\tilde{n}_s^{(1)}}{\tilde{n}_*^{\,2}}\delta c_M + \frac{2}{\tilde{n}_*}\delta g \qquad (6.13)$$

where the coefficients of δc_M and δg are expressed through the characteristics of an equilibrium surfactant solution. All these characteristics are accessible from experiment. The ranges of variation of the quantities $\tilde{n}_*$ and $\tilde{c}$ are determined by eqs 5.1, 5.9, and 5.15 applied to the final equilibrium state. Equations 6.11−6.13 cover the situation when spherical and cylindrical micelles are not in mutual quasi-equilibrium and are not equilibrated with premicellar molecular aggregates.

7. The Set of Linearized Relaxation Equations for the Total Concentrations of Spherical and Cylindrical Micelles

To simplify the study, let us now perform a linearization of the kinetic equations of micellization, eqs 4.2, with respect to small deviations of quantities from their final equilibrium values in a materially isolated surfactant solution. As a result, we obtain

$$\begin{aligned} d(\delta c_M)/dt &= \delta(J'^{(1)} - J''^{(1)}) - \delta(J'^{(2)} - J''^{(2)}) \\ d(\delta g)/dt &= \delta(J'^{(2)} - J''^{(2)}) \end{aligned} \qquad (7.1)$$

Below, we derive analytical expressions for the deviations on the right-hand sides of eqs 7.1.

We start from the deviation $\delta(J'^{(1)} - J''^{(1)})$. According to eqs 4.4, the dependences of $J'^{(1)}$ and $J''^{(1)}$ on $j_c^{+(1)}$, $W_c^{(1)}$, and $\Delta n_c^{(1)}$ are identical. In view of the equality $\tilde{J}''^{(1)} = \tilde{J}'^{(1)}$ (the first of eqs 4.6), the variations of $j_c^{+(1)}$, $W_c^{(1)}$, and $\Delta n_c^{(1)}$ are then mutually canceled when finding $\delta(J'^{(1)} - J''^{(1)})$. To find the deviation of the exponent $e^{W_s^{(1)}}$ that is very sensitive to c_1, we employ the second of eqs 1.1. Ignoring the dependence of $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1, which will be justified below, and taking into account the inequality $n_s^{(1)} \gg 1$, we finally arrive, with the help of eqs 4.4 and 4.6, at

$$\delta(J'^{(1)} - J''^{(1)}) = \tilde{J}'^{(1)}\left(\frac{\tilde{n}_s^{(1)}}{\tilde{c}_1}\delta c_1 - \frac{1}{\tilde{c}_M}\delta c_M\right) \qquad (7.2)$$

In accordance with the second of eqs 1.1, the condition of applicability of linearized eq 7.2 (the condition of neglecting quadratic and higher-order corrections in the deviation δc_1) is $|\delta c_1|/\tilde{c}_1 \ll 2/\tilde{n}_s^{(1)}$. The high relative smallness of the deviation δc_1 following from this and the estimate $n_s^{(1)} \sim 10^2$ justifies neglecting the dependences of the quantities $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1 in view of their weak sensitivity to c_1.[16]

Let us now pass to the deviation $\delta(J'^{(2)} - J''^{(2)})$. According to eqs 4.5, the dependences of $J'^{(2)}$ and $J''^{(2)}$ on $j_c^{+(2)}$, $W_c^{(2)}$, and $\Delta n_c^{(2)}$ are identical. In view of the equality $\tilde{J}''^{(2)} = \tilde{J}'^{(2)}$ (the second of eqs 4.6), the variations of $j_c^{+(2)}$, $W_c^{(2)}$, and $\Delta n_c^{(2)}$ are then mutually canceled when finding $\delta(J'^{(2)} - J''^{(2)})$. To find the deviation of the exponent $e^{W_s^{(1)}}$, we again employ the second of eqs 1.1. To find the deviation of the exponent e^{W^0} that is even more sensitive to c_1 than is $e^{W_s^{(1)}}$, we use the third of eqs 1.1. Ignoring again the dependences of $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1 and accounting for eqs 4.5 and 4.6, we finally obtain

$$\delta(J'^{(2)} - J''^{(2)}) = \tilde{J}'^{(2)}\left(\frac{n_0 - \tilde{n}_s^{(1)}}{\tilde{c}_1}\delta c_1 + \frac{1}{\tilde{c}_M}\delta c_M - \frac{1}{\tilde{c}^0}\delta c^0\right) \qquad (7.3)$$

In accordance with the second and third of eqs 1.1, the conditions of applicability of linearized eq 7.3 are $|\delta c_1|/\tilde{c}_1 \ll 2/\tilde{n}_s^{(1)}$ and $|\delta c_1|/\tilde{c}_1 \ll 2/n_0$. In view of the estimates $n_s^{(1)} \sim 10^2$ and $n_0 \sim 3 \times 10^2$, the second condition is slightly stronger than the first one. Therefore, neglecting the dependences of $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1 in eq 7.3 is even more justified than it is in eq 7.2. Although eqs 7.2 and 7.3 refer to the deviations of the differences of the direct and reverse fluxes of molecular aggregates, the separate expressions for the direct and reverse fluxes were important in deriving eqs 7.2 and 7.3.

To build a relaxation theory, we have to add linearized eqs 6.12 and 6.13 to eqs 7.2 and 7.3. The condition of applicability of eqs 6.12 and 6.13 is eq 6.4. As is seen from eq 5.1 and the estimates $n_s^{(1)} \sim 10^2$ and $n_0 \sim 3 \times 10^2$, the condition expressed in eq 6.4 is much stronger than the aforementioned conditions of applicability of eqs 7.2 and 7.3. Therefore, the condition in eq 6.4 determines the degree of accessible-for-theory closeness of a materially isolated surfactant solution to its final complete equilibrium state.

Equations 6.12 and 6.13 permit us to express the deviations δc_1 and δc^0 in eqs 7.2 and 7.3 through the deviations δc_M and δg that are accessible from experiment. Taking this into account, let us represent the right-hand sides of eqs 7.2 and 7.3 in the form of linear combinations of the deviations δc_M and δg to write eqs 7.1 as

$$\begin{aligned} d(\delta c_M)/dt &= -\alpha_{11}\delta c_M - \alpha_{12}\delta g \\ d(\delta g)/dt &= -\alpha_{21}\delta c_M - \alpha_{22}\delta g \end{aligned} \qquad (7.4)$$

where the coefficients α_{11}, α_{12}, α_{21}, and α_{22} are to be determined.

Applying eq 2.3 and the first of eqs 5.10 to the final equilibrium state and using eqs 6.12, 6.13, and 7.1−7.4 yield

$$\alpha_{11} \simeq \left[\frac{(\tilde{n}_s^{(1)})^2}{\tilde{n}_*\tilde{c}} + \frac{1}{\tilde{c}_M}\right]\tilde{J}'^{(1)} - \left[\frac{(n_0 - \tilde{n}_s^{(1)})\tilde{n}_s^{(1)}}{\tilde{n}_*\tilde{c}} + \frac{\tilde{n}_s^{(1)}}{\tilde{c}} - \frac{1}{\tilde{c}_M}\right]\tilde{J}'^{(2)}$$

$$\alpha_{12} \simeq \frac{\tilde{n}_s^{(1)}}{\tilde{c}}\tilde{J}'^{(1)} - \left(\frac{n_0 - \tilde{n}_s^{(1)}}{\tilde{c}} + \frac{2\tilde{n}_*}{\tilde{c}}\right)\tilde{J}'^{(2)}$$

$$\alpha_{21} \simeq \left[\frac{(n_0 - \tilde{n}_s^{(1)})\tilde{n}_s^{(1)}}{\tilde{n}_*\tilde{c}} + \frac{\tilde{n}_s^{(1)}}{\tilde{c}} - \frac{1}{\tilde{c}_M}\right]\tilde{J}'^{(2)}$$

$$\alpha_{22} \simeq \left(\frac{n_0 - \tilde{n}_s^{(1)}}{\tilde{c}} + \frac{2\tilde{n}_*}{\tilde{c}}\right)\tilde{J}'^{(2)} \tag{7.5}$$

Only the direct fluxes $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$ of molecular aggregates over the first and second potential humps enter eqs 7.5, both the fluxes being taken at the final equilibrium state. The fluxes are given, in view of the equalities $\tilde{J}'^{(1)} = \tilde{J}''^{(1)}$ and $\tilde{J}'^{(2)} = \tilde{J}''^{(2)}$, by any of eqs 4.4 and 4.5 with referring the quantities in them to the final equilibrium state of the solution (marking the quantities with a tilde). Evidently, $\tilde{J}'^{(1)} > 0$ and $\tilde{J}'^{(2)} > 0$.

The ranges of the accessible-for-theory variations of quantities $\tilde{n}_*$ and $\tilde{c}$ are determined by eqs 5.1, 5.9, and 5.15 applied to final equilibrium. Taking them and the estimates $n_s^{(1)} \sim 10^2$ and $n_0 \sim 3 \times 10^2$ into account, we reduce eqs 7.5, with the relative error on the order of the small parameter $\tilde{N}_s/\tilde{c} = \tilde{n}_s^{(1)}\tilde{c}_M/\tilde{c}$ in eq 5.4, to considerably simpler formulas:

$$\alpha_{11} \simeq \frac{1}{\tilde{c}_M}(\tilde{J}'^{(1)} + \tilde{J}'^{(2)}), \quad \alpha_{12} \simeq \frac{\tilde{n}_s^{(1)}}{\tilde{c}}\tilde{J}'^{(1)} - \frac{2\tilde{n}_*}{\tilde{c}}\tilde{J}'^{(2)}$$

$$\alpha_{21} \simeq -\frac{1}{\tilde{c}_M}\tilde{J}'^{(2)}, \quad \alpha_{22} \simeq \frac{2\tilde{n}_*}{\tilde{c}}\tilde{J}'^{(2)} \tag{7.6}$$

There is no need for preliminary assumptions on the flux values $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$ in eqs 7.6. The factors before $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$ in eqs 7.6 are expressed through the characteristics $\tilde{n}_s^{(1)}$, $\tilde{n}_*$, $\tilde{c}_M$, and $\tilde{c}$ of the equilibrium surfactant solution, which are accessible in experiment. The dependence on n_0 has been dropped out in the factors.

Equations 7.4 and 7.6 form a closed set of two linearized relaxation equations describing the molecular mechanism of the time development of deviations δc_M and δg of total concentrations of spherical and cylindrical micelles from their values in the final equilibrium state of the materially isolated surfactant solution. The condition of linearization is given by eq 6.4. This set of equations determines the establishment of the mutual quasi-equilibrium of the spherical and cylindrical micelles as well as the establishment of their total equilibrium with premicellar molecular aggregates. Finding δc_M and δg from the equation set allows one to easily find the deviations δN and δc_1 by using eqs 6.11 and 6.12.

If the spherical shape of a micelle becomes unrealizable because of the structure and packing conditions of surfactant monomers, micellization starts with the formation of cylindrical micelles at once. In this case, when spherical micelles are absent, eq 6.12, with allowance for eq 5.11 in the final equilibrium of solution, shows that eq 6.4 guarantees the fulfillment of the condition $|\delta g|/\tilde{g} \ll 2/3$. The analysis of the set of relaxation equations under the coexistence of spherical and cylindrical micelles would confirm that eq 6.4 guarantees not only the condition $|\delta g|/\tilde{g} \ll 2/3$, but also the condition $|\delta c_M|/\tilde{c}_M \ll 4/3$. Thus, although eq 6.4 requires, in view of eq 5.1, the relative deviation $|\delta c_1|/\tilde{c}_1$ of the surfactant monomer concentration to be very small compared with unity, eq 6.4 permits the relative deviations $|\delta c_M|/\tilde{c}_M$ and $|\delta g|/\tilde{g}$ of the total concentrations of spherical and cylindrical micelles to be not too small compared with unity. Therefore, the deviations of the total concentrations of spherical and cylindrical micelles from their values in the final equilibrium state of surfactant solution can be observable in experiment.

Two independent functions of time, δc_M and δg, upon entering eqs 7.4, correspond to two slow relaxation modes and, with that, two relaxation times of micellar solution markedly above the CMC$_2$. The general solution of eqs 7.4 is

$$\delta c_M = A_1 e^{-\theta_1 t} + A_2 e^{-\theta_2 t}, \quad \delta g = B_1 e^{-\theta_1 t} + B_2 e^{-\theta_2 t} \tag{7.7}$$

where A_1 and A_2 are two arbitrary constants of integration. The constants B_1 and B_2 are related to A_1 and A_2 as

$$\frac{B_1}{A_1} = \frac{1}{\alpha_{12}}(\theta_1 - \alpha_{11}), \quad \frac{B_2}{A_2} = \frac{1}{\alpha_{12}}(\theta_2 - \alpha_{11}) \tag{7.8}$$

The quantities θ_1 and θ_2 are determined by the expressions

$$\theta_1 = \frac{\alpha_{11} + \alpha_{22}}{2} + \left[\left(\frac{\alpha_{11} - \alpha_{22}}{2}\right)^2 + \alpha_{12}\alpha_{21}\right]^{1/2},$$

$$\theta_2 = \frac{\alpha_{11} + \alpha_{22}}{2} - \left[\left(\frac{\alpha_{11} - \alpha_{22}}{2}\right)^2 + \alpha_{12}\alpha_{21}\right]^{1/2} \tag{7.9}$$

Evidently, the integration constants A_1 and A_2 are associated with the initial deviations $\delta c_M|_{t=0}$ and $\delta g|_{t=0}$.

The inequalities $\theta_1 > 0$ and $\theta_2 > 0$, which mean that the quantities θ_1 and θ_2 are real and positive, can be proved from eqs 7.9 and 7.6 by taking into account the inequality $\tilde{c} > \tilde{N}_s = \tilde{n}_s^{(1)}\tilde{c}_M$ (which certainly holds because of eq 5.4) and the positiveness of $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$. Jointly with eqs 7.7, the inequalities $\theta_1 > 0$ and $\theta_2 > 0$ give a kinetic substantiation for monotonically approaching (without oscillations) the state of final equilibrium for a materially isolated solution with spherical and cylindrical micelles. Although the fact that approaching the final equilibrium is natural, its kinetic substantiation is an important argument to the benefit of the above kinetic theory.

The inequalities $\theta_1 > 0$ and $\theta_2 > 0$ show that θ_1 and θ_2 in eqs 7.7 have the meaning of relaxation rates. Correspondingly, the quantities t_{r1} and t_{r2}, defined as $t_{r1} \equiv 1/\theta_1$ and $t_{r2} \equiv 1/\theta_2$, stand for the relaxation times. Analytical expressions for these times follow from eqs 7.9.

Concluding Remarks

The introduction of quasi-equilibrium Boltzmann distributions, eqs 2.1, and the direct and reverse fluxes (eqs 4.4 and 4.5) of molecular aggregates over the first and second potential humps of the aggregation work are important for the description of the molecular mechanism of slow relaxation in surfactant solutions with spherical and cylindrical micelles. This allows us to construct and analyze the kinetic eqs 4.2 for micellization in solutions with a total surfactant concentration above the CMC$_2$. The study conducted is not limited by the choice of a specific micellar model.

Equation 5.14 plays a significant role in the study of internal ties between the equilibrium characteristics of a micellar solution markedly above the CMC$_2$. In particular, it links the parameter b of the aggregation work of a cylindrical micelle, which is independent of the monomer concentration c_1, with the ratio $(c/c_1)/n_*^2$, which is independent[4,19] of the total surfactant concentration c because the average aggregation number n_* for cylindrical micelles and the concentration c belong to the ranges given by eqs 5.1, 5.9, and 5.15 (where n_* is proportional to $(c/c_1)^{1/2}$). Equation 5.14 allows for finding an approximate equality (eq 5.16) for the parameter b and proving that estimates given by eqs 3.6 for N_s/c_1 and c_M/c_1 at the CMC$_2$ stay valid at the total surfactant concentration markedly exceeding the CMC$_2$.

The linear relations between the deviations of N, c_1, c^0 and c_M, g given by eqs 6.11−6.13 and linearized eqs 7.2 and 7.3 for differences in the direct and reverse fluxes of molecular aggregates over the first and second humps of the aggregation work are basic in constructing an analytical theory of relaxation of micellar solutions. As a result, eqs 7.2, 7.3, and 6.11−6.13 allow us to write the closed set of two linearized relaxation equations (eqs 7.4) with coefficients disclosed by eqs 7.6. The set of eqs 7.4 is valid for the situation when the main contribution to the surfactant amount in solution is made by cylindrical micelles (but below the total surfactant concentrations at which the net micellar structure and ordering transitions become important[27]). The equation set cannot be expanded to the situation when cylindrical micelles are not the main contributors to the surfactant balance or, moreover, are absent altogether. The set of eqs 7.4 describes the molecular mechanism of the time development of the total concentrations of spherical and cylindrical micelles in the vicinity of final equilibrium of a materially isolated surfactant solution and leads to analytical expressions for two characteristic rates, θ_1 and θ_2, and two characteristic times, $t_{r1} \equiv 1/\theta_1$ and $t_{r2} \equiv 1/\theta_2$, of slow relaxation in micellar solution markedly above the CMC$_2$.

Acknowledgment. The work is done under the financial support of Russian Foundation for Basic Research (Grant 04-03-32134).

LA052136M