Kinetics of Fast Relaxation of Cylindrical Micelles

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Abstract—On the basis of the kinetic description of stepwise aggregation upon the release and absorption of surfactant monomers by micelles, the complete spectrum of relaxation times is found for relatively fast establishment of a quasi-equilibrium distribution of cylindrical micelles. These times also include the time required for the establishment of the corresponding quasi-equilibrium concentration of surfactant monomers. The resultant times are compared to an earlier diffusion estimate for the characteristic time of the establishment of quasi-equilibrium state of cylindrical micelles in a solution with a surfactant concentration much higher than the second critical micellization concentration CMC_2.

INTRODUCTION

A phenomenon important for the kinetic theory of micellization in surfactant solutions is a sufficiently fast establishment of quasi-equilibrium size distributions of molecular aggregates of surfactants outside the regions of the potential barriers of the minimum aggregate formation work on the aggregation number axis. The data of the distribution set the total numbers of aggregates outside these regions and also determine the boundary conditions for quasi-steady-state overcoming of potential work barriers by the aggregates; in this process, relatively slow establishment of the final complete equilibrium of the micellar solution takes place. The characteristic times of the establishment of separate quasi-equilibria among monomers, premicellar aggregates, and spherical micelles were considered earlier in [1–3] at surfactant concentrations above the first critical micellization concentration (CMC_1) but below the second critical micellization concentration (CMC_2). These times, at which the total number of micelles per unit volume of the solution remains virtually invariable, were termed (Aniansson [1]) the times of fast relaxation in contrast to characteristic times of slow relaxation, at which the total number of micelles and other parameters of the quasi-equilibrium distribution gradually attain their final equilibrium values.

At surfactant concentrations above CMC_2, the major share of the surfactant is distributed between spherical and cylindrical micelles. At concentrations significantly higher than CMC_2, most of the surfactant in solution is already contained in cylindrical micelles. The kinetics describing the establishment of the final equilibrium size distribution of coexisting spherical and cylindrical micelles at surfactant concentrations much higher than CMC_2 was recently studied in [4–7]. In [6], the time required for the establishment of separate quasi-equilibrium of cylindrical micelles was also estimated on the basis of the diffusion approximation of the kinetic micellization equation. The aim of this study is to find the entire spectrum of characteristic times corresponding to relatively fast establishment of quasi-equilibrium of cylindrical micelles throughout their size range of practical importance. The calculation is based on solving the linearized general kinetic equation of micellization. At the same time, the times corresponding to the establishment of quasi-equilibrium concentration of surfactant monomers in the solution will also be found.

1. MAIN RELATIONSHIPS DESCRIBING THE MICELLIZATION KINETICS AT SURFACTANT CONCENTRATIONS ABOVE CMC_2

Let us consider a solution of a nonionic surfactant in a polar solvent, where monomers and molecular aggregates of the surfactant (including cylindrical micelles) coexist. Let us denote the aggregation number (the number of surfactant molecules in a molecular aggregate) by n. The concentration of the molecular aggregates (the number of aggregates per unit volume of the solution) with aggregation number n will be denoted by c_n. Accordingly, c_1 is the concentration of the monomers. The overall concentration of the surfactant (the total number of the surfactant molecules per unit volume of the solution) will be denoted by c, whereas the total concentration of cylindrical micelles (the total number of cylindrical micelles per unit volume) is denoted by g. Let us assume that c is notably (but no more than by two orders of magnitude) higher than CMC_2. Therefore, the share of the surfactant contained in spherical micelles is hereafter neglected in comparison with the share of the surfactant in cylindrical micelles. The designation W_n will be used for the minimum formation work (in kT

units, where k is Boltzmann's constant and T is the absolute temperature) of a molecular aggregate with aggregation number n; for brevity, let us term it the aggregation work. Further, $W^0 \equiv W_n|_{n = n_0}$ will denote the work at aggregation number n_0; this is the starting number up from which the attachment of monomers to a cylindrical micelle does not lead to the rearrangement of the micelle ends but only increases its length. Hence, the surface area, volume, and aggregation work of a cylindrical micelle are linearly related with the aggregation number at $n \geq n_0$. Therefore, let us write

$$W_n = W^0 + (n - n_0)/(n_* - n_0) \quad (n \geq n_0), \quad (1.1)$$

where n_* is the average aggregation number of cylindrical micelles (n_* depends on the overall concentration of the surfactant in solution as $n_* \sim \sqrt{c}$) [4]. Let us assume the estimates $n_0 \sim 3 \times 10^2$ [8] and $n_* \geq 10^3$.

In the quasi-equilibrium of cylindrical micelles in the range of aggregation numbers $n > n_0$, the concentrations of cylindrical micelles are distributed according to Boltzmann's law as

$$c_n = c^0 \exp[-(W_n - W^0)],$$

where $c^0 \equiv c_n|_{n = n_0}$. With allowance for Eq. (1.1), this quasi-equilibrium distribution can be represented in the form

$$c_n = c^0 e^{-(n - n_0)/(n_* - n_0)} \quad (n > n_0). \quad (1.2)$$

Evidently, the $(n_* - n_0)$ value determines the width of the distribution c_n over aggregation numbers at $n > n_0$. At $n_* \gg n_0$, this width is virtually equal to average aggregation number n_* of cylindrical micelles.

To describe the changes in the concentrations of cylindrical micelles with different aggregation numbers at times corresponding to the establishment of quasi-equilibrium distribution (1.2), let us use the general Becker–Doering–Zel'dovich kinetic equation [9, 10] of stepwise aggregation in the form

$$\frac{\partial c_n}{\partial t} = -\frac{\partial}{\partial n}\left[\hat{j}_n^+ \hat{c}_n \left(\frac{j_n^+ c_n}{\hat{j}_n^+ \hat{c}_n} - \frac{c_{n+1}}{\hat{c}_{n+1}} \right) \right]. \quad (1.3)$$

The "overarc" $\cap$ is used to mark the quantities in the state of quasi-equilibrium, which, as is shown below, is established in the $n > n_0$ range after the completion of fast relaxation of cylindrical micelles. Coefficient j_n^+ is determined as the number of surfactant monomers absorbed from the solution by a micelle of n surfactant molecules per unit time. The quantity under the derivative sign $\partial/\partial n$ in Eq. (1.3) is the flux of micelles in the space of aggregation numbers. As is seen from Eq. (1.3), the distribution of $\hat{c}_n$ is a time-independent solution to Eq. (1.3), satisfying the equations of detailed

balance in the $n > n_0$ range. The j_n^+ value is proportional to the concentration of surfactant monomers c_1 and to the micelle surface area. At $n > n_0$, the surface area of a cylindrical micelle, according to the above statements, is proportional to aggregation number n. Therefore,

$$j_n^+ = \hat{j}_{\hat{n}_*}^+ \frac{c_1}{\hat{c}_1} \frac{n}{\hat{n}_*} \quad (n > n_0). \quad (1.4)$$

Let us denote the relative deviation of current concentration c_n from quasi-equilibrium concentration $\hat{c}_n$ by

$$\xi_n = (c_n - \hat{c}_n)/\hat{c}_n. \quad (1.5)$$

Assuming that the studied fast relaxation at solution concentrations considered here (much higher than CMC_2) takes place via the release and absorption of monomers by mostly cylindrical micelles at $n > n_0$, let us consider only such micelles and monomers with $n = 1$ in Eq. (1.5). Along with the aggregation number n, we will also characterize cylindrical micelles in the $n > n_0$ range by the variable

$$s \equiv (n - n_0)/(\hat{n}_* - n_0). \quad (1.6)$$

Variable s changes in the $0 < s < \infty$ interval. Marking the c_n, c^0, and n_* values in quasi-equilibrium distribution (1.2) with an arc symbol $\cap$, we arrive at the following expression for total quasi-equilibrium concentration $\hat{g}$ of cylindrical micelles via the integration with respect to s:

$$\hat{g} \simeq \hat{c}^0(\hat{n}_* - n_0). \quad (1.7)$$

Quasi-equilibrium distribution (1.2) can be written with allowance for formulas (1.6) and (1.7) as

$$\hat{c}_n = \frac{\hat{g}}{\hat{n}_* - n_0} e^{-s} \quad (0 < s < \infty). \quad (1.8)$$

Using Eq. (1.5), let us represent current concentrations c_1 and c_n as

$$c_1(t) = \hat{c}_1[1 + \xi_1(t)], \quad c_n(t) = \hat{c}_n[1 + \xi_n(t)]. \quad (1.9)$$

On approaching the quasi-equilibrium states established after the completion of fast relaxation of cylindrical micelles, we arrive at $|\xi_1| \ll 1$, $|\xi_n| \ll 1$. It is precisely in the range of small deviations $|\xi_1| \ll 1$, $|\xi_n| \ll 1$ that the relaxation process has the lowest rate and the characteristic time of exponential decay practically coincides with the total time of fast relaxation. Therefore, we neglect product $\xi_1\xi_n$ in comparison with ξ_1 and ξ_n. Then, by virtue of Eqs. (1.9) and (1.4), kinetic equation (1.3) at the stage of fast relaxation can be reduced to a linear kinetic equation for $\xi_n(t)$:

$$\widehat{c}_n\frac{\partial \xi_n(t)}{\partial t} = \frac{\widehat{j}^+_{\widehat{n}_*}}{\widehat{n}_*}\frac{\partial}{\partial n}\left(n\widehat{c}_n\frac{\partial \xi_n(t)}{\partial n}\right)$$

$$-\xi_1(t)\frac{\widehat{j}^+_{\widehat{n}_*}}{\widehat{n}_*}\frac{\partial}{\partial n}(n\widehat{c}_n) \quad (n > n_0). \tag{1.10}$$

To determine the current monomer concentration, one should use the equation of surfactant balance in a unit volume of the solution: $c_1 = c - \sum_{n=2}^{\infty} nc_n$. Substituting Eqs. (1.9) into this equation and taking into account that the overall concentration c in a materially isolated solution remains virtually the same after the completion of fast relaxation (we neglect volume effects associated with the aggregation of surfactant monomers), we arrive at

$$\widehat{c}_1\xi_1(t) = -\sum_{n=2}^{\infty} n\widehat{c}_n\xi_n(t), \tag{1.11}$$

where the second of Eqs. (1.9) is extended to all $n \geq 2$.

2. SOLUTION OF KINETIC EQUATION

The form of kinetic equation (1.10) with allowance for Eq. (1.8) and for the $0 < s < \infty$ range of variable s enables us to search for the solution to Eq. (1.10) in the form of an expansion

$$\xi_n(t) = \sum_{i=0}^{\infty} q_i(t)L_i(s) \quad (n > n_0) \tag{2.1}$$

over the complete set of Laguerre polynomials $L_i(s)$, where $q_i(t)$ are s-independent expansion modes, which are the desired functions of time t. For Laguerre polynomials, the following relationships are true:

$$s\frac{d^2L_i(s)}{ds^2} + (1-s)\frac{dL_i(s)}{ds} + iL_i(s) = 0 \quad (0 < s < \infty),$$

$$L_0 = 1, \quad L_1(s) = 1 - s, \tag{2.2}$$

$$\int_0^{\infty} e^{-s}L_i(s)L_k(s)ds = \begin{cases} 0 & (k \neq i) \\ (i!)^2 & (k = i). \end{cases}$$

The integrals with respect to s in Eqs. (2.2) are scalar products of Laguerre polynomials.

Let us set $q_0 = 0$ in Eq. (2.1). This choice will be explained in the next section. Assuming that the major contribution to the sum in the right-hand side of Eq. (1.11) is due to cylindrical micelles at $n > n_0$, substituting Eq. (2.1) at $q_0 = 0$ into Eq. (1.11), and proceeding in the right-hand side of Eq. (1.11) from the summation over n to the integration with respect to s with allowance for Eq. (1.6), we arrive at the following formulas by virtue of Eq. (1.8) and the second, third, and fourth relationships in Eqs. (2.2):

$$\xi_1(t) = \frac{\widehat{g}}{\widehat{c}_1}(\widehat{n}_* - n_0)q_1(t). \tag{2.3}$$

Now let us substitute Eqs. (1.8), (2.1), and (2.3) into kinetic equation (1.10) and consider Eq. (1.6) and $q_0 = 0$. Then we obtain

$$\sum_{k=1}^{\infty} \frac{dq_k(t)}{dt}L_k(s) = \frac{\widehat{j}^+_{\widehat{n}_*}}{\widehat{n}_*(\widehat{n}_* - n_0)}$$

$$\times \sum_{k=1}^{\infty} q_k(t)\left[\left(s + \frac{n_0}{\widehat{n}_* - n_0}\right)\frac{d^2L_k(s)}{ds^2}\right.$$

$$\left. + \left(1 - s - \frac{n_0}{\widehat{n}_* - n_0}\right)\frac{dL_k(s)}{ds}\right] \tag{2.4}$$

$$- \frac{\widehat{j}^+_{\widehat{n}_*}}{\widehat{n}_*}\frac{\widehat{g}}{\widehat{c}_1}(\widehat{n}_* - n_0)q_1(t)\left(1 - s - \frac{n_0}{\widehat{n}_* - n_0}\right).$$

Performing scalar multiplication of both sides of Eq. (2.4) by L_i ($i = 1, 2, \ldots$) and using Eqs. (2.2), we find

$$\frac{dq_1(t)}{dt} = -\frac{\widehat{j}^+_{\widehat{n}_*}}{\widehat{n}_*^2}\left(1 + \frac{\widehat{g}\widehat{n}_*^2}{\widehat{c}_1}\right)q_1(t), \tag{2.5}$$

$$\frac{dq_i(t)}{dt} = -\frac{i\widehat{j}^+_{\widehat{n}_*}}{\widehat{n}_*^2}q_i(t) \quad (i = 2, 3, \ldots). \tag{2.6}$$

In the derivation of Eqs. (2.5) and (2.6), in order to separate equations for q_i with different subscripts i, we neglected the contributions of relative order $n_0/\widehat{n}_*$ to the scalar products in Eq. (2.4). Considering the meanings of quantities n_0 and $\widehat{n}_*$, this is justified if the surfactant solutions in question have concentrations notably higher than CMC_2 and estimates $n_0 \sim 3 \times 10^2$ and $n_* \geq 10^3$ from section 1 are true.

Integrating Eqs. (2.5) and (2.6), we arrive at

$$q_i(t) = q_i(0)e^{-t/\tau_i} \quad (i = 1, 2, \ldots), \tag{2.7}$$

where $q_i(0)$ are the values of modes $q_i(t)$ ($i = 1, 2, \ldots$) at the initial moment of fast relaxation $t = 0$. Relaxation times τ_i of modes with different subscripts i are described by the equalities

$$\tau_1 = \frac{\widehat{n}_*^2}{\widehat{j}^+_{\widehat{n}_*}[1 + \widehat{g}\widehat{n}_*^2/\widehat{c}_1]}, \tag{2.8}$$

$$\tau_i = \frac{\widehat{n}_*^2}{i\widehat{j}^+_{\widehat{n}_*}} \quad (i = 2, 3, \ldots). \tag{2.9}$$

As a result, Eqs. (2.7) determine all modes $q_i(t)$ ($i = 1, 2, \ldots$) in expansion (2.1) at $q_0 = 0$, whereas Eqs. (2.8) and (2.9) provide the complete spectrum of relaxation times of different modes in the distribution of cylindrical micelles upon the establishment of quasi-equilib-

rium state. According to formulas (1.9), (2.3), and (2.7), time τ_1 also determines the relaxation of surfactant monomer concentration to its quasi-equilibrium value.

3. RELATIONSHIPS BETWEEN TIMES OF FAST RELAXATION

Let us compare the relaxation times (found in the previous section) corresponding to different modes of the distribution of cylindrical micelles upon the establishment of quasi-equilibrium state in the $n > n_0$ range. We will concentrate on the longest times as those characterizing the duration of the attainment of quasi-equilibrium for the entire distribution. As follows from Eq. (2.9), the following inequalities are true:

$$\tau_2 > \tau_i \quad (i = 3, 4, \ldots). \tag{3.1}$$

For the ratio of times τ_1 and τ_2, formulas (2.8) and (2.9) yield

$$\frac{\tau_1}{\tau_2} = \frac{2}{1 + \widehat{g}\widehat{n}_*^2/\widehat{c}_1}. \tag{3.2}$$

At surfactant concentrations above CMC_2, the following strong inequality is necessarily true:

$$\widehat{g}\widehat{n}_*^2/\widehat{c}_1 \gg 1. \tag{3.3}$$

Indeed, even at CMC_2, we obtain $\widehat{g}\widehat{n}_*/\widehat{c}_1 \sim 1/10$ and $\widehat{n}_* \sim 10^3$ by virtue of [4], and the fulfillment of inequality (3.3) is ensured. With allowance for (3.3), Eq. (3.2) implies that

$$\tau_2 \gg \tau_1. \tag{3.4}$$

Thus, as follows from formulas (3.1) and (3.4), the longest among the times describing the relaxation of the distribution of quasi-cylindrical micelles to the quasi-equilibrium state is time τ_2.

Let us denote τ_2 by τ and write, by virtue of Eqs. (2.9),

$$\tau \equiv \tau_2 = \widehat{n}_*^2/2\widehat{j}_{\widehat{n}_*}^+. \tag{3.5}$$

As follows from Eqs. (1.9), (2.1), and (2.7) with allowance for formulas (3.1), (3.4), and (3.5) and provided that $q_0 = 0$, we have $c_n(t)|_{t \gg \tau} = \widehat{c}_n \ (n > n_0)$. Thus, the quasi-equilibrium distribution of cylindrical micelles, independent of time t, is indeed established over the course of time τ. Hence, τ is the characteristic time of the fast relaxation of cylindrical micelles to their aggregative quasi-equilibrium. At the same time, in view of Eqs. (1.9), (2.1), and (2.7), the concentration of the surfactant monomers c_1 approaches the corresponding quasi-equilibrium value $\widehat{c}_1$ within time τ_1, which is much shorter than time τ.

According to the definition of total concentration g of cylindrical micelles $g = \int_{n_0}^{\infty} c_n \, dn$, with allowance for Eqs. (1.6), (1.8), (1.9), and (2.1), and relations for Laguerre polynomials (2.2), we obtain $g(t) = \widehat{g}(1 + q_0)$. Apparently, equality $q_0 = 0$ entails equality $g(t) = \widehat{g}$. Thus, the assumption that q_0 is equal to zero (used in the previous section) implies that the total concentration of cylindrical micelles upon the establishment of their quasi-equilibrium remains invariable. Actually, equality $q_0 = 0$ is ensured by the fact that the flux of molecular aggregates between spherical and cylindrical micelles over relatively short time τ does not notably alter the total concentration of cylindrical micelles. Since the total concentration of cylindrical micelles set at the initial moment $t = 0$ and (if the solution is materially isolated) the overall concentration of surfactant remain invariable upon the attainment of quasi-equilibrium of cylindrical micelles, we can use these values for the unambiguous determination of $\widehat{n}_*$, $\widehat{c}_1$, and $\widehat{g}$, as well as quasi-equilibrium distribution (1.2) [or (1.8)] itself. The conservation of the total concentration of cylindrical micelles and of the overall surfactant concentration plays the role of boundary conditions in the problem concerning fast relaxation of cylindrical micelles.

The $\widehat{n}_*$, $\widehat{c}_1$, and $\widehat{g}$ values attained after the completion of the fast relaxation of cylindrical micelles may markedly differ from the values corresponding to the complete equilibrium of micellar solution. Then, subsequently, at much longer times, the total concentration of cylindrical micelles and their average size [as well as quasi-equilibrium distribution (1.2)] will change relatively slowly owing to direct and inverse fluxes of molecular aggregates over the potential barriers of aggregation work until total aggregative equilibrium is established in the micellar solution.

Let us compare resultant analytical expression (3.5) for time τ of the relaxation of cylindrical micelles to their quasi-equilibrium state with the earlier diffusion estimate [6, Eq. (3.10)]. In the notation used in that paper, this estimate is written as $\tau \simeq 0.28 n_1^2/\widehat{j}_{n_1}^+$, where n_1 is the right boundary of the range at the aggregation number axis after which the distribution of cylindrical micelles over their aggregation numbers is virtually nullified. The n_1 value can be estimated as $n_1 \sim 4\widehat{n}_*$. Comparing Eq. (3.5) with formula $\tau \simeq 0.28 n_1^2/\widehat{j}_{n_1}^+$ and considering Eq. (1.4), we see that the τ value found in this communication is approximately two times lower than the estimate of τ from [6]. Taking into account that the estimate for time τ was obtained in [6] as an upper estimate on the basis of the solution to the boundary problem for the diffusion approximation of the kinetic equation for cylindrical micelles, this agreement should be regarded as quite satisfactory.

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