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A Kinetic Description of the Fast Relaxation of Coexisting Spherical and Cylindrical Micelles

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Abstract—A kinetic description of the fast relaxation of coexisting spherical and cylindrical micelles is given. The complete spectrum of the times of the comparatively fast establishment of separate quasi-equilibria of surfactant monomers and spherical and cylindrical micelles was found in an analytic form by solving the linearized kinetic aggregation equation complemented by material balance equation at surfactant concentrations above the second critical micelle concentration. The results are compared with the earlier data on the kinetics of fast relaxation in solutions of surfactants in the absence of either cylindrical or spherical micelles.

INTRODUCTION

Separate quasi-equilibria of surfactant monomers and micelles are established at the stage of the fast relaxation of micellar solutions. The transition from separate quasi-equilibria to a single eventual aggregation equilibrium of a micellar solution occurs at the later stage of slow relaxation. The characteristic times of fast relaxation at surfactant concentrations above the first critical micelle concentration (CMC$_1$) but below the second critical micelle concentration (CMC$_2$), when the major fraction of the surfactant occurs in spherical micelles, were theoretically described in [1–3]. These times can also be measured experimentally by recording the ultrasound absorption spectra of micellar solutions [4, 5]. At surfactant concentrations above CMC$_2$, surfactants are largely accumulated in spherical and cylindrical micelles, and the fraction of surfactants in cylindrical micelles rapidly increases as the overall concentration grows. Accordingly, we must take into account the mutual influence of aggregates of various sizes and shapes on relaxation in a materially isolated solution at concentrations above CMC$_2$. The kinetics of the slow establishment of the eventual equilibrium particle-size distribution of coexisting spherical and cylindrical micelles was studied in [6–9].

The purpose of this work was to obtain a theoretical description of the fast relaxation of coexisting spherical and cylindrical micelles. The complete spectrum of the characteristic times of the comparatively fast establishment of separate quasi-equilibria of surfactant monomers and spherical and cylindrical micelles at surfactant concentrations higher than the CMC$_2$ can be found by solving the linearized kinetic aggregation equation augmented by the material balance equation. The results obtained can be compared with those reported in [1–3] and the data on the kinetics of fast relaxation in surfactant solutions in the absence of spherical micelles [10].

THE KINETIC EQUATIONS
OF FAST RELAXATION AT SURFACTANT
CONCENTRATIONS HIGHER
THAN THE CMC$_2$

Our consideration will be based on the approach developed in [2] for spherical micelles and in [10] for cylindrical micelles. Let a nonionic surfactant be dissolved in a polar solvent, and let the solution contain monomers and surfactant molecular aggregates with different aggregation numbers, including spherical and cylindrical micelles. The aggregation number will be denoted by n, and the concentration of molecular aggregates with the aggregation number n, by c_n. Accordingly, c_1 is the concentration of monomers. The overall concentration of the surfactant will be denoted by c, and the total concentrations of spherical and cylindrical micelles, by c_M and g. We assume that c is at least two but less than hundred times higher than the CMC$_2$. The minimum work of the formation of a molecular aggregate with the aggregation number n (for short, work of aggregation) in kT thermal units (k is the Boltzmann constant and T is the absolute temperature) will be denoted by W_n. Let us introduce the values $W_c^{(1)} \equiv W_n\big|_{n = n_c^{(1)}}$, $W_s^{(1)} \equiv W_n\big|_{n = n_s^{(1)}}$, $W_c^{(2)} \equiv W_n\big|_{n = n_c^{(2)}}$, and $W^0 \equiv W_n\big|_{n = n_0}$.

The $W_c^{(1)}$ value of the work of aggregation at the point $n = n_c^{(1)}$ of its first maximum along the axis of aggregation numbers gives the height of the activation

barrier to the formation of spherical micelles. The $W_s^{(1)}$ work of aggregation at the point $n = n_s^{(1)}$ of its first minimum characterizes the depth of the potential well in which spherical micelles are accumulated. According to [2, 3], this accumulation actually occurs inside the interval $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ on the axis of aggregation numbers; here, $n_s^{(1)}$ is the half-width of the first potential well of the work of aggregation along the n axis. Provided the strong inequality $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$ is satisfied, the work of aggregation within this interval can be approximated quadratically as

$$W_n = W_s^{(1)} + [(n - n_s^{(1)})/\Delta n_s^{(1)}]^2$$
$$(n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}). \tag{1}$$

The $W_c^{(2)} - W_s^{(1)}$ difference between the work of aggregation $W_c^{(2)}$ at the point $n = n_c^{(2)}$ of its second maximum and the $W_s^{(1)}$ value determines the height of the activation barrier for the formation of cylindrical micelles. The W^0 value of the work of aggregation is taken at the left boundary of the $n \geq n_0$ region of aggregation numbers where the core of a micelle is a prolate cylindrical body with identical ends in the form of hemispheres or almost hemispheres. These hemispherical ends correspond to the limiting packing of hydrophobic surfactant monomer moieties in a spherical molecular aggregate, and the addition of monomers to such a micelle does not cause rearrangement of its ends but only elongates its cylindrical part. As a consequence, the surface area, volume, and work of aggregation of a cylindrical micelle are linearly related to the aggregation number n at $n \geq n_0$. We can therefore write

$$W_n = W^0 + (n - n_0)/(n_* - n_0) \quad (n \geq n_0), \tag{2}$$

where n_* is the mean aggregation number of cylindrical micelles [11]. Clearly, $n_c^{(1)} < n_s^{(1)}$ and $n_s^{(1)} < n_c^{(2)} < n_0 < n_*$. Let us assume that $n_s^{(1)} \sim 10^2$, $n_0 \sim 3 \times 10^2$, and $\Delta n_s^{(1)} \sim 10$ [11]. If the overall surfactant concentration is at least two but less than hundred times higher than the CMC_2, we have $n_* \sim 10^3$–10^4 [11], and $n_* \gg n_0$.

At quasi-equilibrium of spherical micelles at aggregation numbers $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and at quasi-equilibrium of cylindrical micelles at aggregation numbers $n > n_0$, the concentrations of spherical and cylindrical micelles are $c_n = c_s^{(1)} \exp[-(W_n - W_s^{(1)})]$ and $c_n = c^0 \exp[-(W_n - W^0)]$, according to the Boltzmann principle. Here, $c_s^{(1)} \equiv c_n|_{n = n_s^{(1)}}$ and $c_0 \equiv c_n|_{n = n_0}$.

According to (1) and (2), these quasi-equilibrium distributions can be represented as

$$c_n = \begin{cases} c_s^{(1)} \exp\{-[(n - n_s^{(1)})/\Delta n_s^{(1)}]^2\} \\ (n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}) \\ c^0 \exp[-(n - n_0)/(n_* - n_0)] \quad (n > n_0). \end{cases} \tag{3}$$

Clearly, the $n_* - n_0$ value determines the distribution width of c_n according to aggregation numbers at $n > n_0$. At $n_* \gg n_0$, this width virtually coincides with the mean aggregation number of cylindrical micelles n_*.

Changes in the concentrations of coexisting spherical and cylindrical micelles at times of the establishment of quasi-equilibrium distributions (3) are described by the general kinetic equation of aggregation [2, 10],

$$\frac{\partial c_n}{\partial t} = -\frac{\partial}{\partial n}\left[\hat{j}_n^+ \hat{c}_n \left(\frac{j_n^+}{\hat{j}_n^+} \frac{c_n}{\hat{c}_n} - \frac{c_{n+1}}{\hat{c}_{n+1}}\right)\right]. \tag{4}$$

The values with $\cap$ above symbols correspond to quasi-equilibrium states. It is shown below that these states are established in the regions $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and $n > n_0$ after the fast relaxation of coexisting spherical and cylindrical micelles. The j_n^+ coefficient is the number of surfactant monomers absorbed from solution in unit time by an aggregate of n molecules. The value in square brackets in (4) is the flux of molecular aggregates in the space of aggregation numbers. Equation (4) shows that the distribution $\hat{c}_n$ reduces this flux to zero and is therefore a time-independent solution to (4), which satisfies the detailed balance equations for aggregate transitions in the regions $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and $n > n_0$. The j_n^+ value is proportional to the concentration of surfactant monomers c_1 and the surface area of a micelle. At $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and at $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$, the dependence of j_n^+ on n can be ignored for spherical micelles; we then have $j_n^+ = j_s^+$, where $j_s^+ \equiv j_n^+|_{n = n_s^{(1)}}$, with a high degree of accuracy. At $n > n_0$, the surface area of a cylindrical micelle is proportional to the aggregation number n (see above). We eventually have

$$j_n^+ = \begin{cases} \hat{j}_s^+ \dfrac{c_1}{\hat{c}_1} \quad (\hat{n}_s^{(1)} - \Delta \hat{n}_s^{(1)} \lesssim n \lesssim \hat{n}_s^{(1)} + \Delta \hat{n}_s^{(1)}) \\ \\ \hat{j}_{\hat{n}_*}^+ \dfrac{c_1}{\hat{c}_1} \dfrac{n}{\hat{n}_*} \quad (n > n_0). \end{cases} \tag{5}$$

Let us introduce the notation

$$\xi_n = (c_n - \hat{c}_n)/\hat{c}_n \tag{6}$$

for the relative deviation of the current concentration c_n from the quasi-equilibrium concentration $\hat{c}_n$. We assume that the fast relaxation under consideration occurs as the ejection and absorption of monomers largely by spherical micelles in the region $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and cylindrical micelles at $n > n_0$. Equation (6) will therefore be applied to only these micelles and monomers at $n = 1$. Along with the aggregation number n, spherical micelles in their region $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ will be described by the variable

$$r \equiv (n - \hat{n}_s^{(1)})/\Delta \hat{n}_s^{(1)}, \tag{7}$$

and cylindrical micelles in their region $n > n_0$, by the variable

$$s \equiv (n - n_0)/(\hat{n}_* - n_0). \tag{8}$$

The variable r changes over the interval $-1 \lesssim r \lesssim 1$, and s, over the interval $0 < s < \infty$. Labeling the c_n, $c_s^{(1)}$, $n_s^{(1)}$, $\Delta n_s^{(1)}$, c^0, and n_* values in quasi-equilibrium distributions (3) by the $\cap$ symbol and taking into account (7), (8), and the inequality $\Delta \hat{n}_s^{(1)}/\hat{n}_s^{(1)} \ll 1$, we obtain the total quasi-equilibrium concentrations $\hat{c}_M$ and $\hat{g}$ of spherical and cylindrical micelles

$$\hat{c}_M = \pi^{1/2} \Delta \hat{n}_s^{(1)} \hat{c}_s^{(1)}, \quad \hat{g} = \hat{c}^0 (\hat{n}_* - \hat{n}_0) \tag{9}$$

with a high degree of accuracy by integration in r and s. Quasi-equilibrium distributions (3) can then be written as

$$\hat{c}_n = \begin{cases} \dfrac{\hat{c}_M}{\pi^{1/2} \Delta \hat{n}_s^{(1)}} e^{-r^2} & (-1 \lesssim r \lesssim 1) \\[3mm] \dfrac{\hat{g}}{\hat{n}_* - n_0} e^{-s} & (0 < s < \infty). \end{cases} \tag{10}$$

Using (6), let us represent the current concentrations c_1 and c_n as

$$c_1(t) = \hat{c}_1[1 + \xi_1(t)], \quad c_n(t) = \hat{c}_n[1 + \xi_n(t)]. \tag{11}$$

We have $|\xi_1| \ll 1$ and $|\xi_n| \ll 1$ as the system approaches quasi-equilibrium, which is established after the fast relaxation of micelles. Just in the region of small deviations $|\xi_1| \ll 1$ and $|\xi_n| \ll 1$, relaxation becomes slowest, and the characteristic times of exponential damping virtually coincide with the total times of fast relaxation. We can therefore ignore the $\xi_1 \xi_n$ product compared with ξ_1 and ξ_n. Because of (11) and (5), kinetic equation

(4) can then be reduced at the fast relaxation stage to linear kinetic equations for $\xi_n(t)$,

$$\hat{c}_n \frac{\partial \xi_n(t)}{\partial t} = \hat{j}_s^+ \frac{\partial}{\partial n}\left(\hat{c}_n \frac{\partial \xi_n(t)}{\partial n}\right) - \xi_1(t) \hat{j}_s^+ \frac{\partial \hat{c}_n}{\partial n}$$

$$(n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}),$$

$$\hat{c}_n \frac{\partial \xi_n(t)}{\partial t} = \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*} \frac{\partial}{\partial n}\left(n \hat{c}_n \frac{\partial \xi_n(t)}{\partial n}\right) - \xi_1(t) \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*} \frac{\partial}{\partial n}(n \hat{c}_n) \tag{12}$$

$$(n > n_0).$$

To determine the current concentration of monomers, we must use the balance equation for the surfactant

$$c_1 = c - \sum_{n=2}^{\infty} n c_n$$

in unit solution volume. Substituting (11) into this equation and taking into account that the overall concentration c in a materially isolated solution remains virtually unchanged during fast relaxation, we obtain

$$\hat{c}_1 \xi_1(t) = -\sum_{n=2}^{\infty} n \hat{c}_n \xi_n(t) \quad (n \geq n_0), \tag{13}$$

where the second equation from (11) is extended to all $n \geq 2$.

THE SOLUTION OF KINETIC EQUATIONS FOR FAST RELAXATION

At $|r| > 1$, the exponential function e^{-r^2} becomes very small. We can therefore formally extend the domain of the variable r in (10) to the interval $-\infty < r < \infty$. This allows us to seek a solution to (12) in the form of the expansions

$$\xi_n(t) = \begin{cases} \displaystyle\sum_{i=0}^{\infty} m_i(t) H_i(r) \\[2mm] (\hat{n}_s^{(1)} - \Delta \hat{n}_s^{(1)} \lesssim n \lesssim \hat{n}_s^{(1)} + \Delta \hat{n}_s^{(1)}) \\[4mm] \displaystyle\sum_{i=0}^{\infty} q_i(t) L_i(s) \quad (n > n_0) \end{cases} \tag{14}$$

in the complete system of Hermitean $H_i(r)$ and Laguerre $L_i(s)$ polynomials, where $m_i(t)$ and $q_i(t)$ are expansion modes independent of r and s, that is, the sought functions of time t. Modes $m_i(t)$ relate to spherical, and $q_i(t)$, to cylindrical micelles. The Hermitean and Laguerre polynomials satisfy the equations

$$\frac{d^2 H_i(r)}{dr^2} - 2r \frac{dH_i(r)}{dr} + 2i H_i(r) = 0 \quad (-\infty < r < \infty),$$

$$H_0 = 1, \quad H_1(r) = 2r, \tag{15}$$

$$\int_{-\infty}^{\infty} e^{-r^2} H_i(r)H_k(r)dr = \begin{cases} 0 & (k \neq i) \\ 2^i i! \pi^{1/2} & (k = i), \end{cases}$$

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

$$L_0 = 1, \quad L_1(s) = 1 - s, \tag{16}$$

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

The integrals in r and s in (15) and (16) are the scalar products of Hermitean and Laguerre polynomials, respectively, and the values of the integrals themselves are the well-known orthogonality for these polynomials.

We suppose that $m_0 = 0$ and $q_0 = 0$ in (14); this assumption will be explained physically in the next section. Let us substitute (14) with $m_0 = 0$ and $q_0 = 0$ into (13). We suggest that the major contribution to the sum on the right-hand side of (13) is made by spherical micelles at $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and cylindrical micelles at $n > n_0$. Let us pass in (13) from the summation over n to integration in r and s taking into account (7) and (8) and the comments made in the beginning of this section. In view of (10) and the second, third, and fourth equations in (15) and (16), we obtain

$$\xi_1(t) = \frac{\hat{g}}{\hat{c}_1}(\hat{n}_* - n_0)q_1(t) - \frac{\hat{c}_M}{\hat{c}_1}\Delta\hat{n}_s^{(1)}m_1(t). \tag{17}$$

Next, let us substitute (10), (14), and (17) into kinetic equations (12) taking into account (7), (8), and the equalities $m_0 = 0$ and $q_0 = 0$. This yields two equations,

$$\sum_{m=1}^{\infty} \frac{dm_m(t)}{dt} H_m(r) = \frac{\hat{j}_s^+}{(\Delta\hat{n}_s^{(1)})^2}\sum_{k=1}^{\infty} m_k(t)$$

$$\times \left[\frac{d^2 H_k(r)}{dr^2} - 2r\frac{dH_k(r)}{dr}\right] \tag{18}$$

$$+ \frac{\hat{j}_s^+}{\Delta\hat{n}_s^{(1)}}\left[\frac{g}{\hat{c}_1}(\hat{n}_* - n_0)q_1(t) - \frac{\hat{c}_M}{\hat{c}_1}\Delta\hat{n}_s^{(1)}m_1(t)\right]2r,$$

$$\sum_{m=1}^{\infty} \frac{dq_m(t)}{dt}L_m(s) = \frac{\hat{j}_n^+}{\hat{n}_*(\hat{n}_* - n_0)^2}\sum_{k=1}^{\infty} q_k(t)$$

$$\times \left[\left(s + \frac{n_0}{\hat{n}_* - n_0}\right)\frac{d^2 L_k(s)}{ds^2} + \left(1 - s - \frac{n_0}{\hat{n}_* - n_0}\right)\frac{dL_k(s)}{ds}\right]$$

$$- \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*}\left[\frac{\hat{g}}{\hat{c}_1}(\hat{n}_* - n_0)q_1(t) - \frac{\hat{c}_M}{\hat{c}_1}\Delta\hat{n}_s^{(1)}m_1(t)\right] \tag{19}$$

$$\times \left(1 - s - \frac{n_0}{\hat{n}_* - n_0}\right).$$

Taking into account the comments made in the beginning of this section, let us form the scalar products of both sides of (18) by H_i ($i = 1, 2, \ldots$) and both sides of (19) by L_i ($i = 1, 2, \ldots$). Using (15) and (16), we obtain

$$\frac{dm_1(t)}{dt} = -\frac{2\hat{j}_s^+}{(\Delta\hat{n}_s^{(1)})^2}\left[1 + \frac{\hat{c}_M(\Delta\hat{n}_s^{(1)})^2}{2\hat{c}_1}\right]m_1(t)$$

$$+ \frac{\hat{j}_s^+}{\Delta\hat{n}_s^{(1)}}\frac{\hat{g}\hat{n}_*}{\hat{c}_1}q_1(t), \tag{20}$$

$$\frac{dm_i(t)}{dt} = -\frac{2i\hat{j}_s^+}{(\Delta\hat{n}_s^{(1)})^2}m_i(t) \quad (i = 2, 3, \ldots), \tag{21}$$

$$\frac{dq_1(t)}{dt} = \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*}\frac{\hat{c}_M\Delta\hat{n}_s^{(1)}}{\hat{c}_1}m_1(t)$$

$$- \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*^2}\left(\frac{1 + \hat{g}\hat{n}_*^2}{\hat{c}_1}\right)q_1(t), \tag{22}$$

$$\frac{dq_i(t)}{dt} = -\frac{i\hat{j}_{\hat{n}_*}^+}{\hat{n}_*^2}q_i(t) \quad (i = 2, 3, \ldots). \tag{23}$$

To uncouple Eqs. (22) and (23) for q_i with different i indices, we, as is seen from (19), ignored the contributions of the relative order $n_0/\hat{n}_*$ to the scalar products. This corresponds to surfactant solutions with concentrations at which $n_0/\hat{n}_* \ll 1$. Accordingly, the $\hat{n}_* - n_0$ multiplier in the last term on the right-hand side of (20) is replaced by $\hat{n}_*$.

The integration of (21) and (23) yields

$$m_i(t) = m_i(0)e^{-t/\tau_{si}}, \quad q_i(t) = q_i(0)e^{-t/\tau_i} \tag{24}$$
$$(i = 2, 3, \ldots),$$

where $m_i(0)$ and $q_i(0)$ are the modes $m_i(t)$ and $q_i(t)$ ($i = 2, 3, \ldots$) at the initial fast relaxation time $t = 0$. The characteristic times τ_{si} and τ_i are given by the equalities

$$\tau_{si} = \frac{(\Delta\hat{n}_s^{(1)})^2}{2\hat{j}_s^+}\frac{1}{i} \quad (i = 2, 3, \ldots), \tag{25}$$

$$\tau_i = \frac{\hat{n}_*^2}{\hat{j}_{\hat{n}_*}^+}\frac{1}{i} \quad (i = 2, 3, \ldots). \tag{26}$$

Let us turn to Eqs. (20) and (22), which form a closed system. The general solution to this system has the form

$$\begin{aligned} m_1(t) &= A_1 e^{-t/\tau_{s1}} + A_2 e^{-t/\tau_1}, \\ q_1(t) &= B_1 e^{-t/\tau_{s1}} + B_2 e^{-t/\tau_1}. \end{aligned} \tag{27}$$

Here, A_1 and A_2 are the constants of integration determined by the initial deviations $m_1(0)$ and $q_1(0)$. The B_1 and B_2 constants are related to A_1 and A_2 as

$$\frac{B_1}{A_1} = \frac{1}{\beta_{12}}\left(\frac{1}{\tau_{s1}} - \beta_{11}\right), \quad \frac{B_2}{A_2} = \frac{1}{\beta_{12}}\left(\frac{1}{\tau_1} - \beta_{11}\right), \tag{28}$$

and the τ_{s1} and τ_1 values are given by the equalities

$$\begin{aligned} \frac{1}{\tau_{s1}} &= \frac{\beta_{11} + \beta_{22}}{2} + \left[\left(\frac{\beta_{11} - \beta_{22}}{2}\right)^2 + \beta_{12}\beta_{21}\right]^{1/2}, \\ \frac{1}{\tau_1} &= \frac{\beta_{11} + \beta_{22}}{2} - \left[\left(\frac{\beta_{11} - \beta_{22}}{2}\right)^2 + \beta_{12}\beta_{21}\right]^{1/2}, \end{aligned} \tag{29}$$

where β_{11}, β_{12} and β_{21}, β_{22} are the coefficients of $m_1(t)$ and $q_1(t)$ on the right-hand sides of (20) and (22), respectively taken with the sign minus. Expanding these coefficients with the use of (20) and (22) and taking into account (25) and (26) at $i = 2$, we obtain

$$\beta_{11} \equiv \frac{\hat{c}_M(\Delta\hat{n}_s^{(1)})^2}{4\tau_{s2}\hat{c}_1}\left[1 + \frac{2\hat{c}_1}{\hat{c}_M(\Delta\hat{n}_s^{(1)})^2}\right], \quad \beta_{12} \equiv -\frac{\hat{g}\hat{n}_*\Delta\hat{n}_s^{(1)}}{4\tau_{s2}\hat{c}_1},$$

$$\beta_{21} \equiv -\frac{\hat{c}_M\hat{n}_*\Delta\hat{n}_s^{(1)}}{2\tau_2\hat{c}_1}, \quad \beta_{22} \equiv \frac{\hat{g}\hat{n}_*^2}{2\tau_2\hat{c}_1}\left(1 + \frac{c_1}{\hat{g}n_*^2}\right) \tag{30}$$

for times τ_{s2} and τ_2.

According to (30), the product $\beta_{12}\beta_{21}$ is positive (although $\beta_{12} < 0$ and $\beta_{21} < 0$). We therefore see from (29) that τ_{s1} and τ_1 have real values and $\tau_{s1} > 0$. Let us show that τ_1 is positive also. It follows from (29) that

$$1/\tau_{s1}\tau_1 = \beta_{11}\beta_{22} - \beta_{12}\beta_{21}. \tag{31}$$

Using (30) and (31), we obtain

$$\begin{aligned} \frac{1}{\tau_{s1}\tau_1} &= \frac{\hat{c}_M\hat{g}\hat{n}_*^2(\Delta\hat{n}_s^{(1)})^2}{8\tau_{s2}\tau_2\hat{c}_1^2} \\ &\times\left\{\left[1 + \frac{2\hat{c}_1}{\hat{c}_M(\Delta\hat{n}_s^{(1)})^2}\right]\left(1 + \frac{\hat{c}_1}{\hat{g}n_*^2}\right) - 1\right\}. \end{aligned} \tag{32}$$

According to (32), $\tau_{s1}\tau_1 > 0$. It was shown above that $\tau_{s1} > 0$. It follows that $\tau_1 > 0$ also. The inequalities $\tau_{s1} > 0$ and $\tau_1 > 0$ allow these values in (27) to be treated as relaxation times.

As a result, Eqs. (24) and (27) determine all modes $m_i(t)$ and $q_i(t)$ ($i = 1, 2, \ldots$) in expansions (14) at $m_0 = 0$ and $q_0 = 0$, and Eqs. (25), (26) and (29), and (30) give the complete spectrum of relaxation times of various modes in the distributions of coexisting spherical and cylindrical micelles during the establishment of quasi-equilibria. According to (11), (17), and (27), the τ_{s1} and τ_1 times also determine the relaxation of the concentration of surfactant monomers to its quasi-equilibrium value.

THE HIERARCHY OF FAST RELAXATION TIMES

Let us compare the relaxation times of various modes of the distributions of spherical and cylindrical micelles during the establishment of separate quasi-equilibrium states obtained in the preceding section for the $n_s^{(1)} - \Delta n_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta n_s^{(1)}$ and $n > n_0$ regions. Clearly, the longest times characterize the duration of the attainment of the corresponding quasi-equilibria. It follows from (25) and (26) that

$$\tau_{s2} > \tau_{si}, \quad \tau_2 > \tau_i \quad (i = 3, 4, \ldots). \tag{33}$$

The ratio between the τ_{s2} and τ_2 times is given by

$$\frac{\tau_{s2}}{\tau_2} = \frac{1}{2}\frac{\hat{j}_{\hat{n}_*}^+}{\hat{j}_s^+}\frac{(\Delta\hat{n}_s^{(1)})^2}{\hat{n}_*^2}. \tag{34}$$

Let L be the length of a cylindrical micelle and v_C and l_C be the volume of the hydrocarbon chain of the surfactant molecule and its length in the uncoiled state. The surface area of a spherical micelle will be denoted by $A^{(s)}$, and that of a cylindrical micelle, by $A^{(c)}$. We have $A^{(s)} \simeq 4\pi l_C^2$. At $\hat{n}_s^{(1)} < n_0 \ll \hat{n}_*$, we also have $A^{(c)} \simeq 2\pi l_C L$. Taking into account what was said about the $\hat{j}_{\hat{n}_*}^+$ and $\hat{j}_s^+$ values in the first section, the $\hat{j}_{\hat{n}_*}^+/\hat{j}_s^+$ ratio can be set equal to $A^{(c)}/A^{(s)}$. This yields

$$\hat{j}_{\hat{n}_*}^+/\hat{j}_s^+ \simeq L/2l_C. \tag{35}$$

Next,

$$\hat{n}_s^{(1)}v_C \simeq 4\pi l_C^3/3, \quad \hat{n}_*v_C \simeq \pi l_C^2 L, \tag{36}$$

where the values on the right-hand side approximate the volume of a spherical micelle and (at $n_s^{(1)} < n_0 \ll \hat{n}_*$) the volume of a cylindrical micelle. It follows from (35) and (36) that

$$\hat{j}_{\hat{n}_*}^+/\hat{j}_s^+ \simeq 2\hat{n}_*/3\hat{n}_s^{(1)}. \tag{37}$$

Substituting (37) into (34) and taking into account the approximate equality $(\Delta \bar{n}_s^{(1)})^2 \simeq \bar{n}_s^{(1)}$, which is characteristic of spherical micelles, we obtain

$$\tau_{s2}/\tau_2 \simeq 1/3\bar{n}_*. \qquad (38)$$

Let us consider the first equation in (29). At surfactant concentrations at least two but less than 100 times higher than the CMC_2, the following estimates hold [11]:

$$\bar{n}_* \sim 10^3 - 10^4, \quad \frac{\hat{c}_1}{\hat{c}_M} \sim \frac{\hat{c}_1}{\hat{g}} \sim 10, \quad (\Delta \bar{n}_s^{(1)})^2 \sim 10^2. \quad (39)$$

Using (39), we obtain

$$\frac{\hat{c}_1}{\hat{c}_M (\Delta \bar{n}_s^{(1)})^2} \sim 10^{-1}, \quad \frac{\hat{c}_1}{\hat{g}\bar{n}_*^2} \sim 10^{-5} - 10^{-7}. \qquad (40)$$

These estimates allow us to replace the multipliers in square brackets and parentheses in (30) by one. Using the resulting equations and taking (38) into account, we can write

$$\frac{\beta_{22} \pm \beta_{11}}{2} \simeq \frac{\hat{g}\bar{n}_*^2}{4\tau_2 \hat{c}_1}\left[1 \pm \frac{3}{2}\frac{\hat{c}_M(\Delta \bar{n}_s^{(1)})^2}{\hat{g}\bar{n}_*}\right]. \qquad (41)$$

It follows from (39) that

$$\hat{c}_M(\Delta \bar{n}_s^{(1)})^2/\hat{g}\bar{n}_* \sim 10^{-1} - 10^{-2}. \qquad (42)$$

This estimate can be used to approximately reduce (41) to

$$\frac{\beta_{22} \pm \beta_{11}}{2} \simeq \frac{\hat{g}\bar{n}_*^2}{4\tau_2 \hat{c}_1}. \qquad (43)$$

Using (30) and (38) once more, let us write

$$\beta_{12}\beta_{21} \simeq \frac{3}{8}\frac{\hat{g}\bar{n}_*^3 \hat{c}_M(\Delta \bar{n}_s^{(1)})^2}{\tau_2^2 \hat{c}_1^2} \qquad (44)$$

(this does not require estimates (40)). According to (43) and (44), we have

$$\left(\frac{\beta_{11} - \beta_{22}}{2}\right)^2 + \beta_{12}\beta_{21} \simeq \frac{\hat{g}^2 \bar{n}_*^4}{16\tau_2^2 \hat{c}_1^2}\left[1 + 6\frac{\hat{c}_M(\Delta \bar{n}_s^{(1)})^2}{\hat{g}\bar{n}_*}\right]. \quad (45)$$

Substituting estimate (42) into (45) yields the approximation

$$\left[\left(\frac{\beta_{11} - \beta_{22}}{2}\right)^2 + \beta_{12}\beta_{21}\right]^{1/2} \simeq \frac{\hat{g}\bar{n}_*^2}{4\tau_2 \hat{c}}. \qquad (46)$$

Using (43) and (46) in the first equation from (29), we obtain

$$\tau_{s1} \simeq \frac{2\hat{c}_1}{\hat{g}\bar{n}_*^2}\tau_2. \qquad (47)$$

The second value of those estimated in (40) is negligibly small compared with the first one and can therefore be ignored in (32). Equation (32) then yields

$$\frac{1}{\tau_{s1}\tau_1} \simeq \frac{\hat{g}\bar{n}_*^2}{4\tau_{s2}\tau_2 \hat{c}_1}. \qquad (48)$$

With (47) in (48), we obtain

$$\tau_1 \simeq 2\tau_{s2}. \qquad (49)$$

As distinct from the first equation in (29), the main contributions are cancelled in the second one because of the minus sign of the second term. This cancellation requires the explicit inclusion of increasingly complex corrections for determining the $1/\tau_1$ value directly by the second equation from (29). This emphasizes the effectiveness of the approach applied above, when Eq. (32) was used instead of the second equation from (29).

Let us now consider the hierarchy of time scales augmenting inequalities (33). According to Eqs. (38) and (47), $\tau_{s2}/\tau_{s1} \simeq \hat{g}\bar{n}_*/6\hat{c}_1$. It follows from the first and second estimates in (39) that

$$\hat{g}\bar{n}_*/\hat{c}_1 \sim 10^2 - 10^3. \qquad (50)$$

This allows us to write the strong inequality

$$\tau_{s2} \gg \tau_{s1}. \qquad (51)$$

Next, (38) and (49) give $\tau_2/\tau_1 = 3\bar{n}_*/2$, which, because of the first estimate in (39), gives the strong inequality

$$\tau_2 \gg \tau_1. \qquad (52)$$

Lastly, it directly follows from (49) that

$$\tau_1 > \tau_{s2}. \qquad (53)$$

Inequalities (51)–(53) give the chain of inequalities

$$\tau_2 \gg \tau_1 > \tau_{s2} \gg \tau_{s1}, \qquad (54)$$

which, together with (33), describe the hierarchy of time scales in relaxation to separate quasi-equilibrium distributions of coexisting spherical and cylindrical micelles. Recall that the $m_i(t)$ and $q_i(t)$ modes ($i = 1, 2, \ldots$) correspond to spherical and cylindrical micelles, respectively. It then follows from (24), (27), (33), and (54) that the longest relaxation times for the distributions of spherical and cylindrical micelles are τ_1 and τ_2, respectively.

Bearing in mind (25), (26), and (49), let us rewrite the times τ_1 and τ_2 as

$$\tau_1 = (\Delta \bar{n}_s^{(1)})^2/2\bar{j}_s^+, \quad \tau_2 = \bar{n}_*^2/2\bar{j}_{\bar{n}_*}^+. \qquad (55)$$

It follows from (11), (14), (24), and (27) and inequalities (33) and (54) that, at $m_0 = 0$ and $q_0 = 0$,

$$c_n(t)|_{t \gg \tau_1} = \hat{c}_n \quad (n_s^{(1)} - \Delta \bar{n}_s^{(1)} \lesssim n \lesssim n_s^{(1)} + \Delta \bar{n}_s^{(1)}),$$

$$c_n(t)|_{t \gg \tau_2} = \hat{c}_n \quad (n > n_0). \qquad (56)$$

It follows that the quasi-equilibrium distribution of spherical micelles independent of time t does indeed become established in time τ_1, and the establishment of the quasi-equilibrium distribution of cylindrical micelles also independent of time takes much longer time τ_2. Therefore, the times τ_1 and τ_2 are the characteristic times of the fast relaxation of coexisting spherical and cylindrical micelles to their aggregation quasi-equilibria. In addition, because of (11), (17), (27), and (54), we have

$$c_1(t)|_{t \gg \tau_1} = \hat{c}_1, \qquad (57)$$

that is, the concentration c_1 of surfactant monomers approaches the quasi-equilibrium value $\hat{c}_1$ in time τ_1.

The total concentrations c_M and g of spherical and cylindrical micelles in the corresponding ranges of aggregation numbers are

$$c_M = \int_{n_s^{(1)} - \Delta n_s^{(1)}}^{n_s^{(1)} + \Delta n_s^{(1)}} c_n dn, \quad g = \int_{n_0}^{\infty} c_n dn.$$

Taking this into account and using (11), (7)–(10), (14) and Eqs. (15) and (16) for Hermitean and Laguerre polynomials, we obtain $c_M(t) = \hat{c}_M(1 + m_0)$ and $g(t) = \bar{g}(1 + g_0)$. It then follows from the equalities $m_0 = 0$ and $q_0 = 0$ that $c_M(t) = \hat{c}_M$ and $g(t) = \bar{g}$. The assumptions $m_0 = 0$ and $q_0 = 0$ introduced in the preceding section therefore ensure not only the fulfillment of equalities (56) and (57) but also constant values of the total concentrations of spherical and cylindrical micelles during the establishment of their quasi-equilibria. The equalities $m_0 = 0$ and $q_0 = 0$, which play the role of boundary conditions in solving fast relaxation kinetic equations, can then be physically explained as follows. During fast relaxation, forward and reverse fluxes of molecular aggregates over the potential humps of the work of aggregation do not have time to appear. Only these fluxes are capable of changing the total concentrations of spherical and cylindrical micelles; they appear in longer times of the slow relaxation of micellar solutions and cause the gradual establishment of a unique eventual aggregation equilibrium [8].

The total concentrations of spherical and cylindrical micelles given at the initial time $t = 0$ and, if the solution is materially isolated, the overall surfactant concentration remain constant up to the attainment of quasi-equilibria of spherical and cylindrical micelles, which allows us to unambiguously determine $\hat{c}_1$, $\hat{n}_s^{(1)}$, $\Delta \hat{n}_s^{(1)}$, $\hat{c}_M$, $\bar{n}_*$, and $\bar{g}$ from these values and also quasi-equilibrium distributions (3) or (10) themselves.

System of equations (20)–(23) for fast relaxation modes and its solutions (24)–(30) can be applied also in the absence of spherical or cylindrical micelles. In particular, with $\bar{g} = 0$ in (20), Eqs. (20) and (21) become

equations for the fast relaxation modes of solutions with spherical micelles [1–3] (Eqs. (22) and (23) then become physically meaningless). Conversely, with $\hat{c}_M = 0$ in (22), Eqs. (22) and (23) become equations for the fast relaxation modes of solutions with cylindrical micelles [10] (Eqs. (20) and (21) then become physically meaningless). This is an important argument in favor of the suggested kinetic theory.

A comparison of (55)–(57) with the results obtained in [1–3] and [10] leads us to the following conclusions. In the absence of cylindrical micelles (however, if the estimate $\hat{c}_1/\hat{c}_M \sim 10$ in (39) remains valid), fast relaxation time for spherical micelles remains virtually unchanged, whereas the relaxation time of surfactant monomers becomes shorter approximately by a factor of $\hat{c}_M(\Delta \hat{n}_s^{(1)})^2/2\hat{c}_1 \sim 10$. In the absence of spherical micelles, fast relaxation time for cylindrical micelles remains virtually unchanged, whereas the relaxation time of surfactant monomers becomes shorter approximately by a factor of $\bar{g}\bar{n}_*/3\hat{c}_1 \sim 10^2$–$10^3$.

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