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System of Relaxation Equations for Materially Isolated Surfactant Solution with Spherical and Cylindrical Micelles

F. M. Kuni, A. K. Shchekin, A. I. Rusanov, and A. P. Grinin

Fock Research Institute of Physics, St. Petersburg State University, ul. Ul'yanovskaya 1, Petrodvorets, St. Petersburg, 198504 Russia

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Abstract—Analytical expressions for the direct and reverse fluxes of molecular aggregates over the first and second potential barriers of the aggregation work in the presence of spherical and cylindrical micelles in nonionic surfactant solution were derived. Expressions for the sum (entering into kinetic equations of micellization) of direct and reverse fluxes of molecular aggregates over the first and second potential barriers of the aggregation work in the vicinity of the final equilibrium state of materially isolated surfactant solution were linearized. In the experimentally important range of the values of overall surfactant concentration in solution where the predominant contribution to the total surfactant amount is introduced by cylindrical micelles, we derived a closed system of two linearized relaxation equations determining the buildup (with time) of experimentally observed total concentrations of spherical and cylindrical micelles in the vicinity of the final equilibrium state of materially isolated surfactant solution. The case of the solutions of such surfactants, for which the spherical shape of a micelle appeared to be unrealizable due to the structure and packing conditions of molecules, was considered separately.

INTRODUCTION

At present, there are different experimental and theoretical evidences that, upon the polymorphism of micelles above the second critical micellization concentration, the work of molecular aggregate formation in a surfactant solution is characterized by the maximum and minimum on the aggregation number axis related to the critical nuclei of micelles and stable spherical micelles, respectively. At larger aggregation numbers, there are also the second maximum and the broad gently sloping part where the work rises linearly and the cylindrical micelles are accumulated [1–4]. This should significantly affect the micellization kinetics compared to the situation occurring below the second CMC when only a maximum and a minimum for the formation of spherical micelles are present.

The construction of the kinetic equations of micellization at the simultaneous existence of spherical and cylindrical micelles at the overall concentration of nonionic surfactant in solution above the second CMC is the main aim of this study. In this case, we rest, to a significant extent, on the results of the study of equilibrium and slightly nonequilibrium concentrations of monomers, spherical and cylindrical micelles at the overall nonionic surfactant concentration in a solution above the second CMC [5]. In this publication, we will introduce the notions of direct and reverse fluxes of molecular aggregates over the first and second barriers of aggregation work in the presence of spherical and cylindrical micelles in surfactant solution, and the analytical expressions for these fluxes will be derived. We also perform the linearization of expressions for the sum (entering into kinetic equations) of direct and reverse fluxes of molecular aggregates over the first and second barriers of the aggregation work in the vicinity of the final equilibrium state of materially isolated surfactant solution. In the region of overall surfactant concentrations in solution where the predominant contribution to the total amount of surfactant in a solution is introduced by cylindrical micelles (albeit below the values of the overall concentration at which crosslinked micellar structures start to form [6] or the transition to liquid-crystal state takes place [7]), we will derive the closed system of two linearized relaxation equations determining the buildup (with time) of experimentally observed total concentrations of spherical and cylindrical micelles in the vicinity of the final equilibrium state of materially isolated surfactant solution.

The case of the solutions of such surfactants, for which the spherical shape appeared to be unrealizable due to the structure and packing conditions of molecules, will be considered separately. Being relatively simple, the case of the absence of spherical micelles allows us to disclose the important feature of solutions containing cylindrical micelles. Under the condition required for the linearization of kinetic equations of the extreme smallness for the relative deviation of surfactant monomer concentration from its value in the final equilibrium state of a solution, corresponding relative deviation of the total concentration of cylindrical

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micelles can be noticeable, not too small, compared to unity. Consequently, the theoretically predicted deviation of the total concentration of cylindrical micelles from its value in the final equilibrium state of a solution should be really accessible to experimental observation. In general, to confirm this statement, one needs to study the kinetic equations, which will be done in forthcoming publications.

1. DIRECT AND REVERSE FLUXES OF AGGREGATES OVER THE FIRST AND SECOND POTENTIAL BARRIERS OF THE AGGREGATION WORK

We will use the same system of designations as in [5]. The aggregation number (the number of surfactant molecules in an aggregate) is denoted by n. The concentration of molecular aggregates with aggregation number n (the number of aggregates per solution unit volume) is denoted by c_n. At $n = 1$, the aggregates are nothing other than surfactant monomers. Correspondingly, c_1 is the monomer concentration. The overall surfactant concentration (the total number of surfactant molecules per solution unit volume) is denoted by c. The W_n is understood as the formation work of molecular aggregate with aggregation number n expressed in thermal units kT (k is Boltzmann's constant and T is the absolute temperature). Note that, for cylindrical micelles, concentration c_n includes the contributions from the possible orientations of the axis of cylindrical micelle with the preset aggregation number n. All these orientations are equiprobable, because they are independent of work W_n.

According to [5], we assume

$$W_c^{(1)} \equiv W_n\big|_{n = n_c^{(1)}}, \quad W_s^{(1)} \equiv W_n\big|_{n = n_s^{(1)}}, \quad W_c^{(2)} \equiv W_n\big|_{n = n_c^{(2)}}, \quad W^0 \equiv W\big|_{n = n_0}. \tag{1.1}$$

The $W_c^{(1)}$ value for the work of aggregation in point $n = n_c^{(1)}$ of its first maximum on the aggregation number axis determines the height of the activation barrier of the formation of spherical micelles. The $W_s^{(1)}$ value for the work of aggregation in point $n = n_s^{(1)}$ of its first minimum characterizes the depth of the potential well where the spherical micelles are accumulated. The $W_c^{(2)}$ value of the work of aggregation in point $n = n_c^{(2)}$ of its second maximum on the aggregation number axis defines the height of the activation barrier needed for the formation of cylindrical micelles. The W^0 value of the work of aggregation is taken in point $n = n_0$ corresponding to the left-hand boundary of the region of aggregation numbers where the dependence of W_n on n is already linear. The right-hand boundary of this region is set by point $n = n_1$; as we approach this point, the equilibrium concentration of cylindrical micelles [proportional to $\exp(-W_n)$] decreases rapidly. Thus, the region of aggregation numbers $n > n_1$ is no longer of interest. The dependence of work W_n on the aggregation number n (generalizing the known experimental and theoretical data [1–4]), for which the fraction of a substance accumulated in cylindrical micelles becomes significant, was represented in the figure of [5].

It is evident that $n_c^{(1)} < n_s^{(1)}$ and $n_s^{(1)} < n_c^{(2)} < n_0$. As is [5], for the values of $n_s^{(1)}$, n_0, and n_1, we accept the estimates that are typical of many surfactants

$$n_s^{(1)} \sim 10^2, \quad n_0 \sim 10^3, \quad n_1 \sim 10^6. \tag{1.2}$$

Note that, according to [5], $W_s^{(1)} \sim 4$ and, according to [8], $W_c^{(1)} \sim 16$–18, are valid. Note also estimate $W^0 \sim 14$, which will follow from formula (3.2) of Section 3 of this publication.

The half-width of the first potential well of aggregation work on the axis of variable n is denoted by $\Delta n_s^{(1)}$; the half-widths of the first and second potential barriers of aggregation work on the axis of variable n, by $\Delta n_c^{(1)}$ and $\Delta n_c^{(2)}$, respectively. In accordance with [9], we assume

$$\Delta n_c^{(1)} \gg 1, \quad \Delta n_c^{(1)}/n_c^{(1)} \ll 1, \quad \Delta n_c^{(1)}/(n_s^{(1)} - n_c^{(1)}) \ll 1, \tag{1.3}$$

$$\Delta n_s^{(1)} \gg 1, \quad \Delta n_s^{(1)}/(n_s^{(1)} - n_c^{(1)}) \ll 1, \quad \Delta n_s^{(1)}/(n_c^{(2)} - n_s^{(1)}) \ll 1, \tag{1.4}$$

$$\Delta n_c^{(2)} \gg 1, \quad \Delta n_c^{(2)}/(n_c^{(2)} - n_s^{(1)}) \ll 1, \quad \Delta n_c^{(2)}/(n_0 - n_c^{(2)}) \ll 1. \tag{1.5}$$

The first constraints of (1.3)–(1.5) permit us to consider aggregation number n as continuos in the region of potential barriers and potential well of work W_n. The rest of constraints (1.3)–(1.5) denotes that both the potential barriers and the potential well of work W_n are clearly pronounced: as is shown in the figure of [5], they are distanced from points $n = 1$ and $n = n_0$, as well as from each other.

Let us introduce direct $J'^{(1)}$ and reverse $J''^{(1)}$ fluxes of molecular aggregates over the first potential barrier of the aggregation work. These fluxes determine the number of molecular aggregates overcoming (by fluctuations) the first potential barrier per unit time in the unit volume of micellar solution from region $n < n_c^{(1)} - \Delta n_c^{(1)}$ to region $n > n_c^{(1)} + \Delta n_c^{(1)}$ (direct flux) and back from region $n > n_c^{(1)} + \Delta n_c^{(1)}$ to region $n < n_c^{(1)} - \Delta n_c^{(1)}$ (reverse flux). Let us introduce direct $J'^{(2)}$ and reverse

$J''^{(2)}$ fluxes of molecular aggregates over the second potential barrier of the aggregation work. These fluxes determine the number of molecular aggregates overcoming (by fluctuations) the second potential barrier per unit time in the unit volume of micellar solution from region $n < n_c^{(2)} - \Delta n_c^{(2)}$ to region $n > n_c^{(2)} + \Delta n_c^{(2)}$ and back from region $n > n_c^{(2)} + \Delta n_c^{(2)}$ to region $n < n_c^{(2)} - \Delta n_c^{(2)}$.

In accordance with the meaning of introduced fluxes, we have

$$dc_M/dt = J'^{(1)} + J''^{(1)} - (J'^{(2)} + J''^{(2)}), \quad (1.6)$$

$$dg/dt = J'^{(2)} + J''^{(2)}, \quad (1.7)$$

where t is the time, c_M is the total concentration (total number per solution unit volume) of spherical micelles in the whole of region $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$ of their residence, and g is the total concentration (total number per solution unit volume) of cylindrical micelles in the whole of region $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$ of their residence. Adding Eqs. (1.6) and (1.7), we arrive at the evident result: $d(c_M + g)/dt = J'^{(1)} + J''^{(1)}$.

Naturally, the main number of molecular aggregates will be in the $1 \le n < n_c^{(1)} - \Delta n_c^{(1)}$, $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$, and $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$ regions outside of the potential barriers of the aggregation work. A large excess of aggregates in these regions makes it possible (even in the nonequilibrium state of a solution) to assume that aggregate concentration distributions in each region are maintained as quasi-equilibrium in spite of the variations in aggregation numbers by their fluxes over the potential barriers of the aggregation work. Quasi-equilibrium distributions of aggregate concentrations obey Boltzmann's distributions, where the aggregation work depends on the current value of monomer concentration and pre-exponential coefficients are determined by the current values of aggregate total concentrations in corresponding regions. The quasi-equilibrium distribution of cylindrical micelle concentrations over a wide range of aggregation numbers $n_0 < n < n_1$ where, according to [5], cylindrical micelles are actually present, will be confirmed in the forthcoming publication.

At the quasi-equilibrium distribution of molecular aggregate concentrations in 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 $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$, the distributions of molecular aggregate concentrations in the vicinity of the first and second potential barriers of the aggregation work will be quasi-stationary, i.e., independent of time over rather long periods of time when concentrations c_1, c_M, and g do not markedly vary yet during the slow tendency of micellar solution to its final state of complete equilibrium. The relationship between Eqs. (1.6) and (1.7) for total concentrations c_M and g of spherical and cylindrical micelles and the total kinetic equation of step-by-step aggregation follow from the definition of $J'^{(1)}$, $J''^{(1)}$, $J'^{(2)}$, and $J''^{(2)}$ as quasi-stationary direct and reverse fluxes [9] corresponding to quasi-stationary solutions of the total kinetic equation of aggregation in the vicinity of the first and second potential barriers of the aggregation work. The fact that, with the account of cylindrical micelles, the aggregation work no longer increases monotonously to infinity behind the first potential well, as was suggested in [9], has no importance for fluxes $J'^{(1)}$ and $J''^{(1)}$. Using formulas (5.8) and (5.10) of [9], we then obtain [provided that constraints (1.3) and (1.4) are fulfilled] the analytical expressions for quasi-stationary direct and reverse fluxes of molecular aggregates over the first potential barrier of the aggregation work

$$J'^{(1)} = c_1 j_c^{+(1)} \exp(-W_c^{(1)})/\pi^{1/2}\Delta n_c^{(1)}, \quad (1.8)$$

$$J''^{(1)} = -c_M j_c^{+(1)} \exp[-(W_c^{(1)} - W_s^{(1)})]/\pi\Delta n_c^{(1)}\Delta n_s^{(1)}, \quad (1.9)$$

where $j_c^{+(1)}$ is the number of surfactant monomers absorbed ($j_c^{+(1)} > 0$) from solution by the spherical molecular aggregate composed of $n_c^{(1)}$ molecules per unit time. It is evident that $J'^{(1)} + J''^{(1)}$ is the total flux of molecular aggregates transferring (by fluctuations) from region $n < n_c^{(1)} - \Delta n_c^{(1)}$ to region $n > n_c^{(1)} + \Delta n_c^{(1)}$. Relation (1.8) is analogous to that for the stationary nucleation rate in the nucleation theory. Relation (1.9) gives the rate of stationary disintegration of spherical micelles; the structure of this expression is similar to Eq. (1.8). Relations (1.9) and (1.8) differ by that the disintegration is prevented by the barrier of the aggregation work with a height of $W_c^{(1)} - W_s^{(1)}$, and the intensity of disintegration is proportional to concentration $c_M/\pi^{1/2}\Delta n_s^{(1)}$ of molecular aggregates with $n = n_s^{(1)}$.

Using the same speculations as in [9], we obtain [with the fulfillment of constraints (1.4) and (1.5)] the analytical expressions for the quasi-stationary direct and reverse fluxes of molecular aggregates over the second potential barrier of the aggregation work

$$J'^{(2)} = c_M j_c^{+(2)} \exp[-(W_c^{(2)} - W_s^{(1)})]/\pi\Delta n_c^{(2)}\Delta n_s^{(1)}, \quad (1.10)$$

$$J''^{(2)} = -c_s j_c^{+(2)} \exp[-(W_c^{(2)} - W^0)]/\pi^{1/2}\Delta n_c^{(2)}. \quad (1.11)$$

Here

$$c_s \equiv c_n|_{n = n_0} \quad (1.12)$$

is the aggregate concentration in point $n = n_0$ corresponding to the left-hand boundary of the region of

aggregation numbers where the dependence of W_n on n is already linear and $j_c^{+(2)}$ is the number of surfactant monomers absorbed ($j_c^{+(2)} > 0$) from solution per unit time by the aspherical molecular aggregate composed of $n_c^{(2)}$ molecules. It is evident that $J'^{(2)} + J''^{(2)}$ is the total flux of molecular aggregates transferring (by fluctuations) from region $n < n_c^{(2)} - \Delta n_c^{(2)}$ to region $n > n_c^{(2)} + \Delta n_c^{(2)}$.

The quasi-stationary character of fluxes (1.8)–(1.11) justifies relations (1.6) and (1.7). If, by analogy with (1.12), we introduce concentration $c_s^{(1)} \equiv c_n\big|_{n = n_s^{(1)}}$ connected (at $\Delta n_s^{(1)}/n_s^{(1)} \ll 1$) with concentration c_M by relation $c_s^{(1)} = c_M/\pi^{1/2}\Delta n_s^{(1)}$, the $\pi^{1/2}\Delta n_s^{(1)}$ value in the denominators of expressions (1.9) and (1.10) would vanish and the relationship between these expressions and expressions (1.8) and (1.11) would be then more explicit. However, we use concentration c_M, because it is more accessible for experiment than concentration $c_s^{(1)}$. Let us make one more clarification. As was already mentioned, aggregate concentration c_n in the $n > n_c^{(2)} + \Delta n_c^{(2)}$ region behind the second potential barrier of aggregation is quasi-equilibrium. Then according to Boltzmann's principle, we could use any value from this range for n (instead of n_0) in Eqs. (1.12) and (1.1): the value of multiplier $c_s\exp(W^0)$ in Eq. (1.11) would be the same. However, we used, as a reference point in Eq. (1.11), characteristic point $n = n_0$ corresponding to the left-hand side of the region of aggregation numbers where the dependence of W_n an n becomes linear.

In a materially isolated micellar surfactant solution, the state of complete aggregation equilibrium is established due to relaxation. The values in this final equilibrium state of solution are denoted by the tilde over the top. Because the direct and reverse fluxes of molecular aggregates over the potential barriers of the aggregation work are balanced in the equilibrium state, we have

$$\tilde{J}'^{(1)} + \tilde{J}''^{(1)} = 0, \quad (1.13)$$

$$\tilde{J}'^{(2)} + \tilde{J}''^{(2)} = 0. \quad (1.14)$$

It follows from Eqs. (1.8), (1.9), and (1.13) that

$$\tilde{c}_M = \pi^{1/2}\tilde{c}_1\Delta\tilde{n}_s^{(1)}e^{-\tilde{W}_s^{(1)}}, \quad (1.15)$$

in turn, from Eqs. (1.10), (1.11), and (1.14) with the account of Eq. (1.15), we obtain

$$\tilde{c}_s = \tilde{c}_1 e^{-\tilde{W}^0}. \quad (1.16)$$

Expressions (1.15) and (1.16) coincide with expressions (2.6) and (2.5) obtained in [5] without regard for the notions of direct and reverse fluxes of molecular aggregates over the potential barriers of the aggregation work. This confirms the validity of formulas (1.8)–(1.11) and the notion of direct and reverse fluxes of molecular aggregates over the potential barriers of the aggregation work (despite the fact that direct and reverse fluxes enter into Eqs. (1.6) and (1.7) only as a sum).

According to Eq. (1.8), we have

$$\tilde{J}'^{(1)} = \tilde{c}_1\tilde{j}_c^{+(1)}\exp(-\tilde{W}_c^{(1)})/\pi^{1/2}\Delta\tilde{n}_c^{(1)}. \quad (1.17)$$

Using Eqs. (1.9) and (1.13), we can represent Eq. (1.17) as

$$\tilde{J}'^{(1)} = \tilde{c}_M\tilde{j}_c^{+(1)}\exp[-(\tilde{W}_c^{(1)} - \tilde{W}_s^{(1)})]/\pi\Delta\tilde{n}_c^{(1)}\Delta\tilde{n}_s^{(1)}. \quad (1.18)$$

According to Eq. (1.10), we have

$$\tilde{J}'^{(2)} = \tilde{c}_M\tilde{j}_c^{+(2)}\exp[-(\tilde{W}_c^{(2)} - \tilde{W}_s^{(1)})]/\pi\Delta\tilde{n}_c^{(2)}\Delta\tilde{n}_s^{(1)}. \quad (1.19)$$

2. LINEARIZATION OF THE SUM OF DIRECT AND REVERSE FLUXES OF AGGREGATES OVER THE POTENTIAL BARRIERS OF AGGREGATION WORK IN THE VICINITY OF THE EQUILIBRIUM STATE OF SURFACTANT SOLUTION

We denote the deviations of parameters from their values in a final equilibrium state of materially isolated solution by symbol δ to the left of the values. In the relaxation process, these deviations become small by the absolute magnitudes; then, using these values, we can perform the linearization that considerably simplifies the study.

In this case, relations (1.6) and (1.7) acquire the following form:

$$d(\delta c_M)/dt = \delta(J'^{(1)} + J''^{(1)}) - \delta(J'^{(2)} + J''^{(2)}), \quad (2.1)$$

$$d(\delta g)/dt = \delta(J'^{(2)} + J''^{(2)}). \quad (2.2)$$

Let us now turn to deriving analytical expressions for the deviations in the right-hand sides of Eqs. (2.1) and (2.2).

We start from deviation $\delta(J'^{(1)} + J''^{(1)})$. According to Eqs. (1.8) and (1.9), the dependences of $J'^{(1)}$ and $J''^{(1)}$ on values $j_c^{+(1)}$, $W_c^{(1)}$, and $\Delta n_c^{(1)}$ are identical. In view of equality $\tilde{J}''^{(1)} = -\tilde{J}'^{(1)}$ followed from Eq. (1.13), the variations of $j_c^{+(1)}$, $W_c^{(1)}$, and $\Delta n_c^{(1)}$ are then cancelled when finding $\delta(J'^{(1)} + J''^{(1)})$. To find the deviation of exponential value $e^{W_s^{(1)}}$ that is very sensitive to c_1 we employ equality (the second of equalities (1.2) in [5])

$$\partial W_s^{(1)}/\partial c_1 = -(n_s^{(1)} - 1)/c_1, \quad (2.3)$$

which is valid for dilute surfactant solutions. Ignoring the dependence of $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1 (that will be justified below) and taking into account inequality $n_s^{(1)} \gg 1$ followed from Eq. (1.2), based on Eqs. (1.8), (1.9), and (1.13), we arrive finally at

$$\delta(J'^{(1)} + J''^{(1)}) = \tilde{J}'^{(1)}\left(\frac{\tilde{n}_s^{(1)}}{\tilde{c}_1}\delta c_1 - \frac{1}{\tilde{c}_M}\delta c_M\right). \quad (2.4)$$

As is seen from Eq. (2.3), the condition of the applicability of linearized expression (2.4) (the condition of ignoring quadratic and higher-order corrections to deviation δc_1) is $|\delta c_1/\tilde{c}_1| \ll 2/\tilde{n}_s^{(1)}$. High relative smallness of deviation δc_1 followed from the preceding and estimate $n_s^{(1)} \sim 10^2$ [Eq. (1.2)] justifies the disregard for the dependence of the $n_s^{(1)}$ and $\Delta n_s^{(1)}$ values (that, as was shown in [8], are slightly sensitive to c_1) on c_1.

Let us pass now to deviation $\delta(J'^{(2)} + J''^{(2)})$. According to Eqs. (1.10) and (1.11), dependences $J'^{(2)}$ and $J''^{(2)}$ on $j_c^{+(2)}$, $W_c^{(2)}$, and $\Delta n_c^{(2)}$ are identical. In view of equality $\tilde{J}''^{(2)} = -\tilde{J}'^{(2)}$ followed from Eq. (1.14), the variations of $j_c^{+(2)}$, $W_c^{(2)}$, and $\Delta n_c^{(2)}$ when finding $\delta(J'^{(2)} + J''^{(2)})$ are cancelled. To find the deviation of exponential value $e^{W_s^{(1)}}$ we still employ equality (2.3) and for finding the deviation of exponential value e^{W^0} that is even more sensitive to c_1 than the $e^{W_s^{(1)}}$ value, we use the equality (third equality of (1.2) in [5])

$$\partial W^0/\partial c_1 = -(n_0 - 1)/c_1, \quad (2.5)$$

which is valid for dilute surfactant solutions. Ignoring again the dependences of $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1, based on Eqs. (1.10), (1.11), and (1.14), we finally obtain:

$$\delta(J'^{(2)} + J''^{(2)}) = \tilde{J}'^{(2)}\left(\frac{n_0 - \tilde{n}_s^{(1)}}{\tilde{c}_1}\delta c_1 + \frac{1}{\tilde{c}_M}\delta c_M - \frac{1}{\tilde{c}_s}\delta c_s\right). \quad (2.6)$$

As is seen from Eqs. (2.3) and (2.5), the conditions of the applicability of linearized expression (2.6) are $|\delta c_1/\tilde{c}_1| \ll 2/\tilde{n}_s^{(1)}$ and $|\delta c_1/\tilde{c}_1| \ll 2/n_0$. According to estimates (1.2), the second condition is noticeably stronger than the first condition. Thus, the neglect of the dependences of $n_s^{(1)}$ and $\Delta n_s^{(1)}$ on c_1 in Eq. (2.6) is still more justified than in Eq. (2.4).

Although only the direct fluxes of molecular aggregates over the first and second potential barriers of the aggregation work entered into the right-hand sides of Eqs. (2.4) and (2.6), moreover, only at the final equilibrium of materially isolated solution, the role of reverse fluxes in deriving expressions (2.4) and (2.6) was large. Thus, the significance of introducing the notions of direct and reverse fluxes is evident.

Let us use relations

$$\delta c_1 = -e^{\tilde{W}^0}\tilde{n}_s^{(1)}(b - \tilde{a})^3\delta c_M - e^{\tilde{W}^0}(b - \tilde{a})^2\delta g, \quad (2.7)$$

$$\delta c_s = \tilde{n}_s^{(1)}(b - \tilde{a})^2\delta c_M + 2(b - \tilde{a})\delta g \quad (2.8)$$

(relations (8.10) and (8.11) in [5]) derived in [5] by the linearization of the balance equation of the amount of substance in the vicinity of the final equilibrium state of materially isolated surfactant solution. Here, $b - \tilde{a}$ is the coefficient of the linear dependence of work $\tilde{W}_n$ on n in region $n_0 < n < n_1$. We do not mark the b value by the tilde over the top, because it is independent of solution concentration. The condition of the applicability of linearized expressions (2.7) and (2.8) is

$$|\delta c_1/\tilde{c}_1| \ll (8/3n_1)\ln 10 \quad (2.9)$$

(condition (8.5) in [5]). As is seen from estimates (1.2), condition (2.9) is much stronger than the aforementioned conditions of the applicability of linearized expressions (2.4) and (2.6). Condition (2.9) determines, therefore, the degree of closeness of materially isolated solution to its final equilibrium accessible for the relaxation theory.

Formulas (2.7) and (2.8) permit us to express deviations δc_1 and δc_s entering into relations (2.4) and (2.6) through deviations δc_M and δg accessible for the experimental observation. Taking this into account, let us represent the right-hand sides of relations (2.4) and (2.6) in the form of linear combinations of deviations δc_M and δg, and deviations (2.1) and (2.2) in the following form:

$$d(\delta c_M)/dt = -\alpha_{11}\delta c_M - \alpha_{12}\delta g, \quad (2.10)$$

$$d(\delta g)/dt = -\alpha_{21}\delta c_M - \alpha_{22}\delta g, \quad (2.11)$$

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

Using Eqs. (2.1), (2.2), (2.4), (2.6)–(2.8), (2.10), and (2.11), we obtain

$$\alpha_{11} = \tilde{J}'^{(1)}\left[e^{\tilde{W}^0}\frac{(\tilde{n}_s^{(1)})^2}{\tilde{c}_1}(b - \tilde{a})^3 + \frac{1}{\tilde{c}_M}\right] - \tilde{J}'^{(2)}\left[e^{\tilde{W}^0}\frac{(n_0 - \tilde{n}_s^{(1)})\tilde{n}_s^{(1)}}{\tilde{c}_1}(b - \tilde{a})^3 + \frac{\tilde{n}_s^{(1)}}{\tilde{c}_s}(b - \tilde{a})^2 - \frac{1}{\tilde{c}_M}\right], \quad (2.12)$$

$$\alpha_{12} = \tilde{J}'^{(1)}\left[e^{\tilde{W}^0}\frac{\tilde{n}_s^{(1)}}{\tilde{c}_1}(b-\tilde{a})^2\right] - \tilde{J}'^{(2)}\left[e^{\tilde{W}^0}\frac{n_0-\tilde{n}_s^{(1)}}{\tilde{c}_1}(b-\tilde{a})^2+\frac{2}{\tilde{c}_s}(b-\tilde{a})\right], \quad (2.13)$$

$$\alpha_{21} = \tilde{J}'^{(2)}\left[e^{\tilde{W}^0}\frac{(n_0-\tilde{n}_s^{(1)})\tilde{n}_s^{(1)}}{\tilde{c}_1}(b-\tilde{a})^3 + \frac{\tilde{n}_s^{(1)}}{\tilde{c}_s}(b-\tilde{a})^2-\frac{1}{\tilde{c}_M}\right], \quad (2.14)$$

$$\alpha_{22} = \tilde{J}'^{(2)}\left[e^{\tilde{W}^0}\frac{n_0-\tilde{n}_s^{(1)}}{\tilde{c}_1}(b-\tilde{a})^2+\frac{2}{\tilde{c}_s}(b-\tilde{a})\right]. \quad (2.15)$$

Fluxes $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$ are given by formulas (1.17)–(1.19).

3. SYSTEM OF LINEARIZED RELAXATION EQUATIONS FOR THE TOTAL CONCENTRATIONS OF SPHERICAL AND CYLINDRICAL MICELLES

Relations (2.7) and (2.8) for materially isolated solution were derived in [5] for the experimentally important range of the values of overall surfactant concentration $\tilde{c}$ where the predominant contribution to the total amount of surfactant in solution is introduced by the cylindrical micelles. In this case, we have

$$b-\tilde{a} = (4/n_1)\ln 10, \quad (3.1)$$

$$e^{-\tilde{W}^0} = 16(\ln 10)^2\frac{\tilde{c}}{\tilde{c}_1}\frac{1}{n_1^2}, \quad (3.2)$$

where it was accounted that, for the applicability of relations (2.7) and (2.8), it is quite sufficient that condition (4.11) in [5] excluding the avalanche-like increase in the amount of substance in cylindrical micelles would be fulfilled at the limiting concentration value rather than with twofold excess as was admitted in [5]. Correspondingly, the right-hand side in relation (3.1) was taken twice as smaller as in analogous relation (4.35) in [5]; the right-hand side in relation (3.2) was taken fourfold as smaller as in analogous relation (4.36) in [5].

Let us assume the estimate

$$\tilde{c}/\tilde{c}_1 \sim 10^4. \quad (3.3)$$

Such an estimate is valid, for example, for the upper boundary of the admissible range of the overall micellar solution concentrations on the phase diagram of dodecyl hexaethylene glycol ester in water [10]. Relation (3.2) with allowance made for estimates (1.2) and (3.3) yields $\exp(-\tilde{W}^0) \sim 8.5\times10^{-7}$ and $\tilde{W}^0 \sim 14$. Note that expressions (3.1) and (3.2) do not contain the n_0 value which, by its meaning, can be determined only with some tolerance.

According to [5], $\tilde{c}_M/\tilde{c}_1 \sim 0.1$ is valid, if the second CMC exceeds the first CMC and $\tilde{c}_M/\tilde{c}_1 \sim 1$, if by two orders of magnitude. Hence, we assume the estimate

$$\tilde{c}_M/\tilde{c}_1 \sim (0.1-1). \quad (3.4)$$

From relations (3.3) and (3.4) and estimate $\tilde{n}_s^{(1)} \sim 10^2$ in (1.2) follow inequalities $\tilde{c}/\tilde{c}_1 \gg \tilde{n}_s^{(1)}\tilde{c}_M/\tilde{c}_1 \gg 1$. Because the $\tilde{n}_s^{(1)}\tilde{c}_M$ value with a high accuracy determines [with the fulfillment of constraints (1.4)] the total number of surfactant molecules in spherical micelles per solution unit volume, these inequalities confirm that the region of overall concentrations $\tilde{c}$ (which is of interest to us) lies much higher than the second CMC where cylindrical micelles predominantly contribute to the total amount of surfactant in solution.

Equations (1.16), (3.1), and (3.2), together with estimates (1.2), (3.3), and (3.4), make it possible to considerably simplify expressions (2.12)–(2.15). Let us demonstrate this situation. Preliminarily, we derive, from Eqs. (3.1) and (3.2), the following equalities:

$$e^{\tilde{W}^0}(b-\tilde{a}) = \frac{1}{4\ln 10}\frac{\tilde{c}_1}{\tilde{c}}n_1, \quad (3.5)$$

$$e^{\tilde{W}^0}(b-\tilde{a})^2 = \frac{\tilde{c}_1}{\tilde{c}}, \quad (3.6)$$

$$e^{\tilde{W}^0}(b-\tilde{a})^3 = \frac{\tilde{c}_1}{\tilde{c}}\frac{4\ln 10}{n_1}. \quad (3.7)$$

Using Eqs. (1.16), (3.6), and (3.7), as well as estimates (1.2), (3.3), and (3.4), we obtain

$$\frac{\tilde{c}_M}{\tilde{c}_1}(\tilde{n}_s^{(1)})^2 e^{\tilde{W}^0}(b-\tilde{a})^3 \sim (10^{-6}-10^{-5}), \quad (3.8)$$

$$\frac{\tilde{c}_M}{\tilde{c}_1}(n_0-\tilde{n}_s^{(1)})\tilde{n}_s^{(1)} e^{\tilde{W}^0}(b-\tilde{a})^3 \sim (10^{-5}-10^{-4}), \quad (3.9)$$

$$\frac{\tilde{c}_M}{\tilde{c}_s}\tilde{n}_s^{(1)}(b-\tilde{a})^2 \sim (10^{-3}-10^{-2}). \quad (3.10)$$

Making allowance for Eqs. (3.8)–(3.10), with a high relative accuracy of about $(10^{-3}$–$10^{-2})$ we reduce Eq. (2.12) to

$$\alpha_{11} = (\tilde{J}'^{(1)} + \tilde{J}'^{(2)})/\tilde{c}_M \quad (3.11)$$

(there was no need about assumptions on the values of $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$ fluxes).

Further, using Eqs. (1.16), (3.1), (3.5), and (3.6) and estimates (1.2), we obtain

$$e^{\tilde{W}^0}\frac{n_0-\tilde{n}_s^{(1)}}{\tilde{c}_1}\frac{\tilde{c}_s}{2}(b-\tilde{a}) \sim 10^{-2}, \quad (3.12)$$

$$e^{\tilde{W}^0}\frac{\tilde{n}_s^{(1)}}{\tilde{c}_1}(b-\tilde{a})^2 = \frac{\tilde{n}_s^{(1)}}{\tilde{c}}, \quad (3.13)$$

$$\frac{2}{\tilde{c}_s}(b-\tilde{a}) = \frac{1}{2\ln 10}\frac{n_1}{\tilde{c}}. \quad (3.14)$$

Taking account of Eqs. (3.12)–(3.14), with a high relative accuracy of $\sim 10^{-2}$ we reduce Eq. (2.13) to

$$\alpha_{12} = \tilde{J}'^{(1)}\frac{\tilde{n}_s^{(1)}}{\tilde{c}} - \tilde{J}'^{(2)}\frac{1}{2\ln 10}\frac{n_1}{\tilde{c}} \quad (3.15)$$

(there was no need about assumptions on the values of $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$ fluxes).

Finally, using Eqs. (3.9), (3.10), (3.12), and (3.14), with a high accuracy of $\sim 10^{-2}$ we reduce Eqs. (2.14) and (2.15) to

$$\alpha_{21} = -\tilde{J}'^{(2)}/\tilde{c}_M, \quad (3.16)$$

$$\alpha_{22} = \tilde{J}'^{(2)}\frac{1}{2\ln 10}\frac{n_1}{\tilde{c}} \quad (3.17)$$

(there was no need about assumption on the value of $\tilde{J}'^{(2)}$ flux).

Formulas (3.11) and (3.15)–(3.17), together with expressions (1.17)–(1.19) for fluxes $\tilde{J}'^{(1)}$ and $\tilde{J}'^{(2)}$, allow us to find coefficients α_{11}, α_{12}, α_{21}, and α_{22} in relations (2.10) and (2.11). Moreover, relations (2.10) and (2.11) form the closed system of two linearized relaxation equations determining the development (with time) of deviations δc_M and δg of the total concentrations of spherical and cylindrical micelles from their values in the final equilibrium state of materially isolated surfactant solution. The condition of the linearization of the derived system of equations is condition (2.9).

Despite the fact that condition (2.9) requires extremely small (in view of estimate $n_1 \sim 10^6$ in Eq. (1.2)) relative deviation $|\delta c_1/\tilde{c}_1|$ of surfactant monomer concentration, one can demonstrate that this condition admits noticeable, but not too small compared to unity, relative deviations $|\delta c_M/\tilde{c}_M|$ and $|\delta g/\tilde{g}|$ of the total concentrations of spherical and cylindrical micelles. Hence, the deviations of the total concentrations of spherical and cylindrical micelles predicted by the relaxation theory from their values in the final equilibrium state of materially isolated surfactant solution can really be measured in experiment.

The solution of the system of Eqs. (2.10) and (2.11) can be easily derived; however, it is necessary to thoroughly study the establishment (on the basis of this solution) of a positive definiteness of relaxation times at the arbitrary heights of the first and second potential barriers of the aggregation work, the disclosure of the hierarchy of relaxation times with a rather scarce information on the height of the second potential barriers of the aggregation work, and the formulation of the condition of maintaining quasi-equilibrium concentration distribution of cylindrical micelles within the wide range of aggregation numbers. The results of this study will be reported in the forthcoming publication.

As was already mentioned, the proposed theory was elaborated in the experimentally important region of overall surfactant concentrations in solution where the cylindrical micelles contribute predominantly to the total amount of surfactant in a solution. Thus, one cannot pass in this theory to the situation where cylindrical micelles do not make overwhelming contribution to the total amount of surfactant in solution or, moreover, they are generally absent in a solution. The kinetic theory for the case of the absence of cylindrical micelles was developed earlier in [9, 11–14].

4. THE CASE OF THE ABSENCE OF SPHERICAL MICELLES

The relations cited above referred to the most complex case when spherical and cylindrical micelles coexist above the second CMC. However, in practice, a simpler case is encountered when the spherical shape of a micelle becomes unrealizable due to the structure and packing conditions of surfactant monomers and the micellization starts just from the formation of cylindrical micelles so that the first CMC is absent. In this section, we briefly summarize the formulas and conclusions for the case of the isolated existence of cylindrical micelles.

The dependence of the work of molecular aggregate formation in a solution on the aggregation number for the case of the absence of spherical micelles at the monomer concentration, at which the fraction of a substance accumulated in cylindrical micelles is already significant, is qualitatively shown in the figure. Now instead of Eq. (1.1), we have

$$W_c \equiv W_n|_{n=n_c}, \quad W^0 \equiv W_n|_{n=n_0}. \quad (4.1)$$

The value W_c of the aggregation work in point $n = n_c$ of its the only maximum on the aggregation number axis determines the height of activation barrier for the formation of cylindrical micelles. The W^0 value of the aggregation work is still taken in point $n = n_0$ corresponding to the left-hand boundary of the region of aggregation numbers where the dependence of W_n on n is already linear. The right-hand boundary of this region is still set by point $n = n_1$; as one approaches this point, the equilibrium concentration of cylindrical micelles exponentially rapidly decreases.

It is evident that $n_c < n_0$. For the n_0 and n_1 values, we still assume previous estimates (1.2). The half-width of

the only potential barrier of the aggregation work on the n axis is denoted by Δn_c.

Then, we have

$$dg/dt = J' + J'', \tag{4.2}$$

where J' and J'' denote the direct and reverse fluxes of molecular aggregates over the potential barrier of aggregation work, respectively.

Then, under the fulfillment of constraints $\Delta n_c \gg 1$, $\Delta n_c/n_c \ll 1$, and $\Delta n_c/(n_0 - n_c) \ll 1$, we have

$$J' = c_1 j_c^+ \exp(-W_c)/\pi^{1/2}\Delta n_c, \tag{4.3}$$

$$J'' = -c_s j_c^+ \exp[-(W_c - W^0)]/\pi^{1/2}\Delta n_c, \tag{4.4}$$

where j_c^+ is the number of surfactants monomers absorbed ($j_c^+ > 0$) from a solution by the molecular aggregate composed of n_c molecules per unit time and c_s is the aggregate concentration in point $n = n_0$ determined by equality (1.12).

Further, we have

$$\tilde{J}' + \tilde{J}'' = 0. \tag{4.5}$$

Equations (4.3)–(4.5) yield previous expression (1.16) for concentration $\tilde{c}_s$. From Eq. (4.3), we obtain for $\tilde{J}'$

$$\tilde{J}' = \tilde{c}_1 \tilde{j}_c^+ \exp(-\tilde{W}_c)/\pi^{1/2}\Delta\tilde{n}_c. \tag{4.6}$$

Then, we arrive at

$$d(\delta g)/dt = \delta(J' + J''), \tag{4.7}$$

$$\delta(J' + J'') = \tilde{J}'\left(\frac{n_0}{\tilde{c}_1}\delta c_1 - \frac{1}{\tilde{c}_s}\delta c_s\right). \tag{4.8}$$

In a materially isolated solution in the experimentally important region of overall concentrations $\tilde{c}$ of surfactant solution where the predominant contribution to the total amount of surfactant in a solution is introduced by cylindrical micelles, we obtain from equalities (2.7) and (2.8) relations (under the assumption that $\delta c_M = 0$)

$$\delta c_1 = -e^{\tilde{W}^0}(b - \tilde{a})^2 \delta g, \tag{4.9}$$

$$\delta c_s = 2(b - \tilde{a})\delta g \tag{4.10}$$

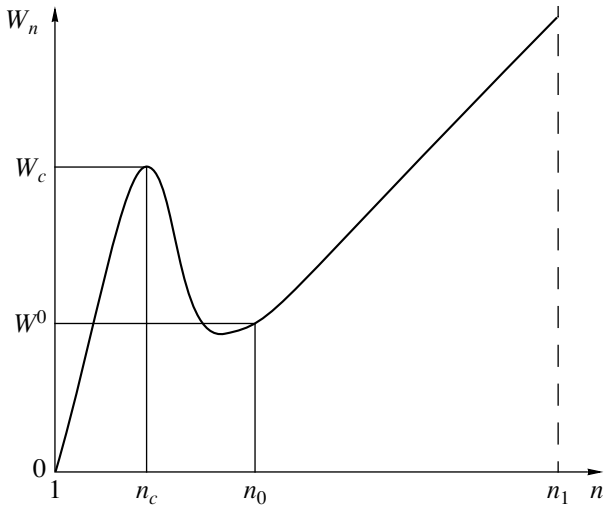
(relations (9.4) and (9.5) in [5]). The condition of the applicability of linearized equations (4.9) and (4.10) is still inequality (2.9).

From Eqs. (4.7)–(4.10), we have

$$d(\delta g)/dt = -\alpha\delta g, \tag{4.11}$$

where

$$\alpha = \tilde{J}'\left[e^{\tilde{W}^0}\frac{n_0}{\tilde{c}_1}(b - \tilde{a})^2 + \frac{2}{\tilde{c}_s}(b - \tilde{a})\right]. \tag{4.12}$$



Aggregation work W_n as a function of aggregation number n for the case of the absence of spherical micelles in a solution at the overall surfactant concentration above the second CMC.

Using estimate (3.12) (at $\tilde{n}_s^{(1)} = 0$) and equality (3.14), with a high relative accuracy of ~10^{-2}, we reduce Eq. (4.12) to

$$\alpha = \tilde{J}'\frac{1}{2\ln 10}\frac{n_1}{\tilde{c}}. \tag{4.13}$$

Formula (4.13), together with expression (4.6) for flux $\tilde{J}'$, permits us to find coefficient α in relation (4.11). In this case, relation (4.11) forms the linearized equation determining the development (with time) of deviation δg of the total concentration of cylindrical micelles from its value in the final equilibrium state of materially isolated surfactant solution. The condition of the linearization of derived equation is inequality (2.9).

Let us elucidate what constraint on the value of relative deviation $|\delta g/\tilde{g}|$ results from condition (2.9). From Eq. (4.9) with allowance made for (3.6), we arrive at

$$\delta g = -\frac{\tilde{c}}{\tilde{c}_1}\delta c_1. \tag{4.14}$$

According to [5], we have

$$\frac{\tilde{g}}{\tilde{c}_1} = 4\frac{\tilde{c}}{\tilde{c}_1}\frac{\ln 10}{n_1} \tag{4.15}$$

(relation (4.34) in [5]). It is seen from Eqs. (4.14) and (4.15) that condition (2.9) leads to the constraint

$$|\delta g/\tilde{g}| \ll 2/3. \tag{4.16}$$

Constraint (4.16) admits noticeable, not too small compared to unity, relative deviations $|\delta g/\tilde{g}|$ of the total concentration of cylindrical micelles. Consequently, theoretically predicted deviation of the total concentration of cylindrical micelles from its value in the final

equilibrium state of materially isolated surfactant solution can be really measured in the experiment.

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