

Concentrations of Monomers and Cylindrical Micelles above the Second CMC

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Abstract—Based on thermodynamically substantiated linear dependence of the work of cylindrical micelle formation on the aggregation number within a wide range of aggregation numbers where the cylindrical micelles are accumulated in a surfactant solution, the second critical micellization concentration (CMC) is introduced as an overall surfactant concentration at which the ratio of the total amount of substance in cylindrical micelles to the amount of substance in monomers is equal to 0.1, i.e., it is already noticeable. It is shown that this ratio increases rather rapidly with a monomer concentration. The coefficient of the linear dependence of the work of cylindrical micelle formation on the aggregation number in the important practical situation where the ratios of the total concentration of cylindrical micelles and total amount of substance in these micelles to the monomer concentration are equal by the order of magnitude to 1 and 10^5 , respectively, while disc micelles and extended bilayers are still not appeared. In the same situation, the ratios of the total concentration of spherical micelles and total amount of substance in these micelles to the monomer concentration are equal by the order of magnitude to 1 and 10^2 , respectively. The relationship between the overall surfactant concentration and monomer concentration is found. It is shown that the second CMC exceeds by two orders of magnitude the first CMC corresponding to the onset of the noticeable accumulation of surfactant in spherical micelles. The distribution of cylindrical micelles over the aggregation numbers is analyzed. It is demonstrated that, in agreement with the experiment, the distribution is almost uniform in the considerable part of the wide range of aggregation numbers and drops exponentially in the remaining (right-hand) part of this range. Experimental result is confirmed that the total concentration of cylindrical micelles, the mean value, and the mean statistical scatter of aggregation numbers in a cylindrical micelle is proportional to the square root of the overall surfactant concentration. The balance equation of surfactant amount in the vicinity of the final equilibrium state of a materially isolated solution is linearized. This linearization makes it possible to express the deviations of monomer and aggregate concentrations from their equilibrium values at the lower boundary of the region of the linear dependence of the work of cylindrical micelle formation on the aggregation numbers via the deviations of experimentally observed total concentrations of spherical and cylindrical micelles from their equilibrium values. The case of the solutions of such surfactants, for which spherical shape appeared to be unrealizable due to their molecular structure and packing conditions, is considered separately.

INTRODUCTION

The ability of amphiphilic surfactant molecules to the aggregation and micellization in aqueous solutions is of significant interest due to a large number of various physicochemical and technological applications [1, 2], as well as due to peculiarities of micellization mechanism [2, 3]. The approach based on the methods of nucleation theory can be very helpful in describing the micellization mechanism. The kinetics and thermodynamics of spherical micelle formation (within the framework of the droplet and quasi-droplet models) and the relaxation of micellar solution have been recently considered using such an approach [4–12].

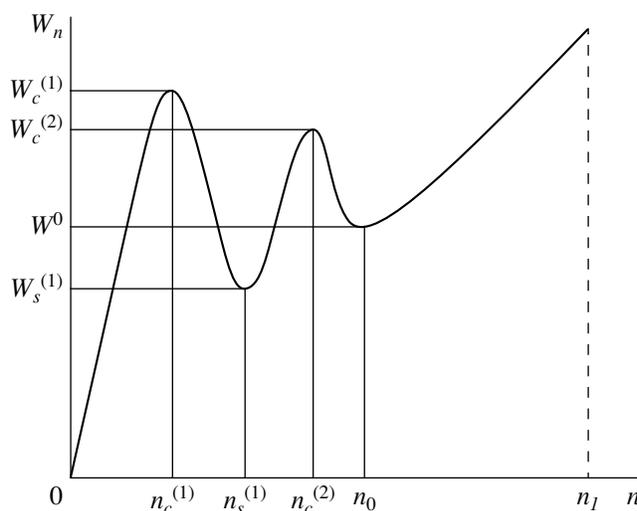
It is known that, as the concentration in the solution above the critical micellization concentration (CMC) corresponding to the onset of the accumulation of surfactant in spherical micelles increases, one should expect the emergence of cylindrical micelles with aggregation numbers much higher than for spherical

micelles [2, 3, 13–17]. The emergence of cylindrical micelles (in addition to spherical ones) is referred to as the polymorphous transformation in a micellar solution [2, 3]. As was shown in [13], the formation of cylindrical micelles is preceded by the overcoming of the second potential barrier of the work of their formation by the molecular aggregates; this process becomes markedly notable when the overall surfactant concentration exceeds a certain value called the second CMC. The accumulation of surfactants occurs precisely in the cylindrical micelles upon further increase in the overall solution concentration within a rather wide range before the onset of the formation of disc micelles and extended bilayers in the solution [13–15].

In this publication, we systematize the notions of the structure of surfactant solution in the presence of spherical and cylindrical micelles and retrieve the detailed information on the solution from their rather general characteristics accessible for experimental observation.

Based on thermodynamically substantiated linear dependence of the formation work of surfactant cylindrical molecular aggregate on the aggregation number, we will determine the second CMC as the overall surfactant concentration at which the ratio of the total amount of substance in cylindrical micelles to the amount of substance in monomers is equal to 0.1, i.e., it is already noticeable. We will find the coefficient of the linear dependence of the work of cylindrical micelle formation on the aggregation number. We will establish the relationship between the overall surfactant concentration and monomer concentration and demonstrate that the second CMC by two orders of magnitude exceeds the first CMC corresponding to the onset of the noticeable accumulation of surfactant in spherical micelles. We will show that, above the second CMC, the amount of substance in cylindrical micelles is much more sensitive to the monomer concentration than the amount of substance in spherical micelles above the first CMC. We will study the distribution of cylindrical micelles over the aggregation numbers above the second CMC and compare the results obtained with the available experimental and theoretical estimates [13–16]. We will find the dependence of the total concentration of cylindrical micelles, the mean value, and the mean statistical scatter of the aggregation numbers in a cylindrical micelle on the overall surfactant concentration. We will perform the linearization of the balance equation of surfactant amount in the vicinity of the final state of solution equilibrium in a materially isolated solution. This linearization will make it possible to express the deviations of the concentrations of monomers and aggregates from their equilibrium values at the lower boundary of the region of the linear dependence of the work of cylindrical micelle formation on the aggregation numbers via the deviations of experimentally observed total concentrations of spherical and cylindrical micelles from their equilibrium values. We will consider separately the case of solutions of such surfactants for which the spherical shape of micelles appeared to be unrealizable due to their molecular structure and packing conditions.

The main attention in this paper we focus on the experimentally important range of the overall surfactant concentration where the ratio of this concentration to the surfactant monomer concentration by the order of magnitudes lies in the vicinity of 10^5 where almost the whole dissolved surfactant is accumulated in cylindrical micelles, but disc micelles and extended bilayers are still not formed in the solution. The study reported in this paper is not related to whether the height of the second barrier of aggregation work is lower (in accordance with [13]) or higher than that of its first barrier. Moreover, the study and relevant determination of the second CMC are not related even to the fact whether the second barrier of the aggregation work really exists or not.



The work of aggregation W_n as a function of aggregation number n at the simultaneous existence of spherical and cylindrical micelle modifications at the overall surfactant concentration in a solution above the second CMC.

1. THE WORK OF CYLINDRICAL MICELLE FORMATION IN SURFACTANT SOLUTION

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 in 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. Overall surfactant concentration (the total number of surfactant molecules in solution unit volume) is denoted by c .

The represented in the figure dependence of the work of molecular aggregate formation in a solution on the aggregation numbers at the monomer concentration, at which the fraction of a substance accumulated in cylindrical micelles becomes significant, is a generalization of the known experimental and theoretical data [13–16]. 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) (for brevity, hereafter we call the W_n value the work of aggregation)

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

The $W_c^{(1)}$ value of 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 of the work of aggregation in point $n = n_s^{(1)}$ of its first min-

imum characterizes the depth of the potential well where the spherical micelles are accumulated; and the $W_c^{(2)}$ value of the work of aggregation in point $n = n_c^{(2)}$ of its second maximum defines the height of the activation barrier needed for the formation of cylindrical micelles. If there is no second barrier of the work of aggregation (the formation of cylindrical micelles from cylindrical ones is a barrierless process), the $n_c^{(2)}$ and $W_c^{(2)}$ values are absent. 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.

In the $n_0 \leq n \leq n_1$ range, the micelle core is an elongated cylindrical body with identical ends in the form of hemispheres or quasi-hemispheres. Such a shape of considered micelle modification is responsible for their second name as spherocylindrical micelles. Because the limiting state of the packing of the hydrophobic portions of surfactant monomers into spherical molecular aggregate corresponds to hemispherical ends, the addition of a monomer to such a micelle does not cause the rearrangement of its ends but increases only the length of its cylindrical portion. As a result, the length and, hence, the surface area and volume of a micelle become linearly connected with aggregation number n . Within the framework of the droplet and quasi-droplet models of a micelle [2, 3, 9–11], the work of aggregation involves the hydrophobic (due to the gain in the work of the transfer of hydrophobic parts of surfactant monomers from the solution to the micelle core), surface (related to the surface tension of the micelle core), electrical (due to the electrical double layer formed on the micelle surface by the hydrophilic parts of surfactant monomers), and concentration (due to the difference in monomer concentrations in the solution and micelle) contributions. As for spherical micelles, hydrophobic and concentration contributions to the work of aggregation of cylindrical micelle are proportional (in the principal order) to aggregation number n . At the already mentioned linear dependence of n on the surface area of cylindrical micelle, the surface and electrical contributions to the work of aggregation W_n of cylindrical micelle are also linear functions of n . The preceding explains the linear dependence of the total work of aggregation W_n on the aggregation number in the $n_0 \leq n \leq n_1$ range shown in the figure and used in further discussion. The knowledge of the specific properties of surfactant monomers is not needed for finding the parameters of this dependence.

Since the concentration contribution to the work of aggregation has universal (independent of the choice of

model of molecular aggregate or specific polymorphous shape of micelles) pattern, and, as is known [4], for the case of dilute surfactant solutions depends on concentration c_1 of surfactant monomers in the solution via term $-(n-1)\ln c_1$, we have

$$\begin{aligned} \partial W_n / \partial c_1 &= -(n-1)/c_1, \\ \partial W_s^{(1)} / \partial c_1 &= -(n_s^{(1)} - 1)/c_1, \quad \partial W^0 / \partial c_1 = -(n_0 - 1)/c_1. \end{aligned} \quad (1.2)$$

With allowance for what have been said above on the dependence of the work of aggregation W_n on monomer concentration c_1 and aggregation number n , it is convenient to express the relation for W_n within the $n_0 \leq n \leq n_1$ aggregation number range as

$$W_n = W^0 + [b - \ln(c_1/c_{1c})](n - n_0) \quad (1.3)$$

$(n_0 \leq n \leq n_1),$

where b and c_{1c} are positive values independent of solution concentration c_1 and $b - \ln(c_1/c_{1c})$ is the coefficient of the linear dependence of work W_n on n . Physical meaning of the c_{1c} value will be elucidated in Section 3. Evidently, the $b + \ln(c_{1c})$ sum can be explicitly expressed via the parameters of hydrophobic, surface, and electrical contributions to the work of aggregation within the framework of the droplet model of a micelle; therefore, the b and c_{1c} values appeared to be interrelated; furthermore, the c_{1c} value acts as a certain characteristic monomer concentration in the solution. Hereafter, we assume that the c_1 concentration is so low (in the situation that is of interest to us) that inequality $b - \ln(c_1/c_{1c}) > 0$ (accounted for in the figure) takes place. As this inequality is violated, the work W_n of cylindrical micelle formation would decrease with n , and the avalanche-like increase in the amount of substance in cylindrical micelles would occur.

Along with the b value, it is also convenient to deal with parameter β which is related to b by the equality

$$b \equiv \beta \ln 10/n_0. \quad (1.4)$$

As we will see below in Section 4, in the experimentally important region of the values of overall surfactant solution concentration c where $c/c_1 \sim 10^5$ is valid by the order of magnitude, as well as at estimate $n_1/n_0 \sim 10^3$ [15] typical of many surfactants, we arrive at the approximate (but not estimating) relation

$$\beta \approx 2, \quad (1.5)$$

ensuring positive b values. Under the same conditions, we find the $b - \ln(c_1/c_{1c})$ value of Eq. (1.3) in Section 4.

2. CONCENTRATION OF CYLINDRICAL MICELLES IN SURFACTANT SOLUTION

It is natural that the most of micelle numbers will be in the ranges of the sizes belonging to the potential wells (shown in the figure) at $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$ and $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$, where $\Delta n_c^{(1)}$ and $\Delta n_c^{(2)}$

are the half-widths of the first and second barrier of the work of aggregation on the n axis, respectively; at $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$, in the form of spherical micelles; and at $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$, in the form of cylindrical micelles.

The large excess of micelles in regions $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$ and $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$ allows us to assume that, even in the solution nonequilibrium state, micelle concentrations in these regions are maintained separately as quasi-equilibrium quantities, regardless of the variations in the number of micelles through the fluxes over the potential barrier of the work of aggregation W_n . Let us introduce the notation:

$$c_s \equiv c_n|_{n=n_0}. \quad (2.1)$$

Then, according to Boltzmann's principle and the definition of work W^0 in Eq. (1.1), the quasi-equilibrium distribution of cylindrical micelles at $n_c^{(2)} + \Delta n_c^{(2)} < n < n_1$ can be written as

$$c_n = c_s e^{-(W_n - W^0)} \quad (n_c^{(2)} + \Delta n_c^{(2)} < n < n_1) \quad (2.2)$$

and, at $n_0 < n < n_1$, it can be written, with allowance for Eq. (1.3), as

$$c_n = c_s e^{(a-b)(n-n_0)} \quad (n_0 < n < n_1), \quad (2.3)$$

where

$$a \equiv \ln(c_1/c_{1c}). \quad (2.4)$$

At the equilibrium state of surfactant solution covering all the aggregation numbers, from Eq. (2.1) and the definition of work W^0 in Eq. (1.1), according to Boltzmann's principle, we have

$$c_s = c_1 e^{-W^0}. \quad (2.5)$$

As was demonstrated in [5], at the equilibrium state of surfactant solution, the total concentration c_M of spherical micelles in the $n_c^{(1)} + \Delta n_c^{(1)} < n < n_c^{(2)} - \Delta n_c^{(2)}$ range is related to the concentration of surfactant monomers in solution by the expression

$$c_M = \pi^{1/2} c_1 \Delta n_s^{(1)} e^{-W_s^{(1)}}, \quad (2.6)$$

where $\Delta n_s^{(1)}$ is the half-width of the potential well of work W_n on the aggregation number axis for spherical micelles.

According to [5], the condition

$$\Delta n_s^{(1)}/n_s^{(1)} \ll 1 \quad (2.7)$$

should be fulfilled for the applicability of relation (2.6).

Let us assume that conditions

$$n_0 \gg n_s^{(1)}, \quad n_1 \gg n_0 \quad (2.8)$$

should also be satisfied.

We also accept the estimates of $n_s^{(1)}$, $\Delta n_s^{(1)}$, n_0 , and n_1 values

$$n_s^{(1)} \sim 10^2, \quad \Delta n_s^{(1)} \sim 15, \quad n_0 \sim 10^3, \quad n_1 \sim 10^6, \quad (2.9)$$

that satisfy conditions (2.7) and (2.8) and are based on experiment [1, 9, 15]. These estimates are consistent with estimate $n_1/n_0 \sim 10^3$ made at the end of Section 1.

Estimates of the $W_s^{(1)}$ and W^0 values related to estimates (2.9) will later be used in Eqs. (3.8) and (4.37). The estimates of other (shown in the figure) values $n_c^{(1)}$, $n_c^{(2)}$, $W_c^{(1)}$, and $W_c^{(2)}$ will not be needed in this paper.

Up to Section 8, we consider only the equilibrium states of surfactant solution. Then, Eqs. (2.5) and (2.6) will be valid. In this case, concentrations c_s , c_M , as well as overall concentration c , are determined unambiguously by concentration c_1 of surfactant monomers.

Let us denote the total number of surfactant molecules (the total amount of substance) in cylindrical micelles in solution unit volume by N . Then, we have

$$N \equiv \int_{n_c^{(2)} + \Delta n_c^{(2)}}^{n_1} n c_n dn. \quad (2.10)$$

The $n_c^{(2)} + \Delta n_c^{(2)} < n < n_0$ region is fairly narrow compared to the $n_0 < n < n_1$ region due to estimates (2.9), whereas work W_n increases with the deviation of n from n_0 much faster in the $n_c^{(2)} + \Delta n_c^{(2)} < n < n_0$ region than in $n_0 < n < n_1$ region. Because of this, we replace the lower limit of integration in Eq. (2.10) by n_0 . Then, performing integration with the use of relation (2.3), we obtain

$$N = \frac{c_s n_0}{a-b} [e^{(a-b)(n_1-n_0)} - 1] + \frac{c_s n_1}{a-b} e^{(a-b)(n_1-n_0)} - \frac{c_s}{(a-b)^2} [e^{(a-b)(n_1-n_0)} - 1], \quad (2.11)$$

where $n_1 - n_0$ in the pre-exponential factor of the second term is replaced by n_1 with a high accuracy due to estimations (2.9).

Let us denote the total concentration of cylindrical micelles (the total number of cylindrical micelles in solution unit volume) by g . Then we have

$$g \equiv \int_{n_c^{(2)} + \Delta n_c^{(2)}}^{n_1} c_n dn. \quad (2.12)$$

Replacing, as for the N value, the lower limit of integration in Eq. (2.12) by n_0 and integrating with the use of relation (2.3), we arrive at

$$g = \frac{c_s}{a-b} [e^{(a-b)(n_1-n_0)} - 1]. \quad (2.13)$$

If there is no second barrier for the work of aggregation, the limit $n_c^{(2)} + \Delta n_c^{(2)}$ replaces in Eqs. (2.10) and (2.12) the lower limit of integration $n_s^{(1)} + \Delta n_s^{(1)}$; slightly above this limit, micelles exist already in the cylindrical modification. It is significant that this limit can be still replaced by n_0 . Indeed, in the absence of the second barrier, work W_n increases with aggregation number n from $n_s^{(1)} + \Delta n_s^{(1)}$, moreover, much faster at the beginning. Then in view of estimates (2.9), the relative values of contributions from range $n_s^{(1)} + \Delta n_s^{(1)} < n < n_0$ to the total amount N of substance in cylindrical micelles and to the total concentration g of cylindrical micelles will be fairly small.

In view of Eqs. (2.2), (2.5), and the first equation of relations (1.2), we have $\partial(c_n/c_1)\partial c_1 > 0$. Then, according to definitions (2.10) and (2.12), inequalities

$$\partial(N/c_1)/\partial c_1 > 0, \quad \partial(g/c_1)/\partial c_1 > 0, \quad (2.14)$$

indicating the important (for further discussion) monotonous rise of the total number of surfactant molecules in cylindrical micelles and the total number of cylindrical micelles relative to monomer concentration with an increase in the monomer concentration, are fulfilled.

3. THE SECOND CMC AND ITS RELATIONSHIP WITH THE FIRST CMC

Let us write the balance equation of the amount of surfactant in solution for the overall concentration c of surfactant solution as

$$c = c_1 + n_s^{(1)}c_M + N, \quad (3.1)$$

where, in view of Eq. (2.7), the second term accounts for the contribution of spherical micelles and the third term, that of cylindrical micelles, to the overall solution concentration.

In accordance with the law of mass action, the micellization is theoretically possible at any concentration; however, this is revealed in practice beginning with the first CMC when some part of a substance is already accumulated in spherical micelles. The exact determination of the CMC is rather conditional and realized in dozens of procedures allowing to estimate the critical degree of micellization (that is often close to 0.1 by the order of magnitude) [2]. Therefore, it is much simpler to determine the CMC from the preset numerical values of the degree of micellization or the ratio between the amounts of micellar and monomeric forms of surfactant. We assume that monomer concentration

c_{1m} corresponding to the first CMC satisfies the condition

$$\frac{n_s^{(1)}c_M}{c_1} \Big|_{c_1=c_{1m}} \equiv \frac{1}{10}. \quad (3.2)$$

According to Eq. (3.1), definition (3.2) indicates that, at $c_1 = c_{1m}$, the role of spherical micelles in the balance of the amount of surfactant is already noticeable. Definition (3.2) slightly differs from the similar definition accepted in [12] with the replacement of 1/10 for 1/9.

It was shown [12] that, within a wide interval of the variations in the total concentration c_M of spherical micelles where c_M/c_1 ratio varies from about 10^{-3} to the value of the order of unity, the $n_s^{(1)}$ value remains almost constant. According to [12], it follows from Eq. (3.2) that

$$\frac{n_s^{(1)}c_M}{c_1} \Big|_{c_1=c_{1m}[1+(3/n_s^{(1)})\ln 10]} = 10^2. \quad (3.3)$$

In accordance with Eq. (3.1), equality (3.3) implies that, at $c_1 = c_{1m}[1+(3/n_s^{(1)})\ln 10]$, the role of spherical micelles in the balance of the amount of surfactant is already rather significant.

In formula (1.3), the c_{1c} is taken as the monomer concentration corresponding to the second CMC. Let us determine the second CMC as the overall surfactant concentration at which the ratio between the total amount of substance in cylindrical micelles to the amount of substance in monomers is equal to 1/10; i.e., in accordance with Eq. (3.1), it is already noticeable in the balance of surfactant content. Then, we have

$$\frac{N}{c_1} \Big|_{c_1=c_{1c}} \equiv \frac{1}{10}. \quad (3.4)$$

We will be convinced in Section 4 that formula (1.3) ensures a rapid increase in the N/c_1 ratio, as concentration c_1 starts to exceed concentration c_{1c} . This and Eq. (3.4) confirm that the c_{1c} value in Eq. (1.3) really represents the monomer concentration corresponding to the second CMC above which the role of cylindrical micelles in the balance of surfactant content, in accordance with Eq. (3.1), grows fairly fast. Common approach to definitions (3.2) and (3.4) of the first and second CMCs used in this work is worth noting.

Let us assume (this assumption will be discussed a little bit later) that the role of cylindrical micelles in the balance of surfactant content starts to be noticeable already when concentration c_{1c} is close to $c_{1m}[1+(3/n_s^{(1)})\ln 10]$ and, hence, according to equality (3.3), the role of spherical micelles in the balance of surfactant content is already fairly large. Thus, we have

$$c_{1c} \approx c_{1m}[1+(3/n_s^{(1)})\ln 10]. \quad (3.5)$$

Correspondingly, Eq. (3.3) is written as

$$\left. \frac{n_s^{(1)} c_M}{c_1} \right|_{c_1 = c_{1c}} \approx 10^2. \quad (3.6)$$

In accordance with Eq. (3.5), concentration c_{1c} is higher than concentration c_{1m} ; however, in view of the first estimate of (2.9), this excess is small.

From Eq. (3.6) and the first estimate of (2.9), it follows that

$$\left. \frac{c_M}{c_1} \right|_{c_1 = c_{1c}} \sim 1. \quad (3.7)$$

Taking Eqs. (2.6), (2.9), and (3.7) into account, we obtain

$$W_s^{(1)} \Big|_{c_1 = c_{1c}} \approx 3.3. \quad (3.8)$$

It could be assumed that the role of cylindrical micelles in the balance of surfactant content starts to be noticeable when c_{1c} exceeds c_{1m} slightly more than in Eq. (3.5). For example, instead of Eq. (3.5), we could use relation $c_{1c} \approx c_{1m}[1 + (4/n_s^{(1)})\ln 10]$. Then, the right-hand sides of relations (3.6) and (3.7) would increase tenfold and, correspondingly, the key role of spherical micelles in the balance of surfactant content at $c_1 = c_{1c}$ would be still larger. Further, this will show up only in a tenfold increase in the second CMC.

4. THE GROWTH OF THE AMOUNT OF SURFACTANT IN CYLINDRICAL MICELLES AND THE NUMBER OF CYLINDRICAL MICELLES WITH THE MONOMER CONCENTRATION

Let us consider the behavior of the total amount of surfactant in micelles and the total number of micelles at surfactant monomer concentrations in solution slightly exceeding concentration c_{1c} . Let us represent positive value a determined at these concentrations by relation (2.4) as

$$a \equiv (\alpha/n_0) \ln 10, \quad (4.1)$$

where α is the parameter satisfying double inequality

$$0 \leq (\alpha/n_0) \ln 10 \ll 1. \quad (4.2)$$

Somewhat below we obtain, using Eq. (1.5), constraint $\alpha < 2$ refining the upper limit in relation (4.2). From Eqs. (1.4) and (4.1), we have

$$a - b = [(\alpha - \beta)/n_0] \ln 10 \quad (4.3)$$

and, correspondingly

$$e^{(a-b)n_1} = 10^{(\alpha-\beta)n_1/n_0}. \quad (4.4)$$

According to Eqs. (2.4), (4.1), and (4.2), concentrations c_1 of surfactant monomers (which are of interest to us) slightly exceeding concentration c_{1c} are expressed via parameter α , using relation

$$c_1 = c_{1c}[1 + (\alpha/n_0) \ln 10]. \quad (4.5)$$

At such concentrations, for the work of aggregation at $n = n_0$, from relations (1.2), (2.9), and (4.5), we have

$$W^0 = W_0^0 - \alpha \ln 10, \quad (4.6)$$

where

$$W_0^0 \equiv W^0 \Big|_{c_1 = c_{1c}}. \quad (4.7)$$

From Eq. (4.6), we obtain

$$e^{-W^0} = e^{-W_0^0} 10^\alpha. \quad (4.8)$$

It is convenient to represent n_1/n_0 ratio as

$$n_1/n_0 \equiv 10^\gamma, \quad (4.9)$$

where parameter γ , as follows from estimates (2.9), satisfies approximate (albeit not estimated) relation $\gamma \approx 3$. Hereafter, we assume that, at monomer concentrations (which are of interest to us) slightly exceeding concentration c_{1c} , relations

$$\beta - \alpha \geq (\gamma + 1)n_0/n_1 \quad (4.10)$$

or, in view of Eq. (4.3)

$$b - a \geq [(\gamma + 1)/n_1] \ln 10 \quad (4.11)$$

are fulfilled.

Inequalities (4.10) and (4.11) are significant, because the avalanche-like increase in the amount of substance in cylindrical micelles occurs almost immediately upon their violation. Note that Eq. (4.11) ensures inequality $b - \ln(c_1/c_{1c}) > 0$ mentioned in Section 1.

Based on Eqs. (4.9) and (4.11), we find

$$e^{(a-b)(n_1-n_0)} \leq \frac{n_0}{10n_1} \ll \frac{n_0}{n_1}. \quad (4.12)$$

It is seen from (2.9) and (4.12) that relations (2.11) and (2.13) for the total amount N of surfactant molecules in cylindrical micelles in solution unit volume and at the total concentration g of cylindrical micelles with a high accuracy can be reduced to:

$$N = \frac{c_s n_0}{b - a} + \frac{c_s}{(b - a)^2}, \quad (4.13)$$

$$g = \frac{c_s}{b - a}. \quad (4.14)$$

Let us consider the relative role of monomers, as well as spherical and cylindrical micelles, at surfactant monomer concentrations in solution satisfying relations (4.2), (4.5), and (4.11). From Eqs. (4.13) and (4.14) with allowance for Eqs. (2.5), (4.3), (4.5), and (4.8), we find

$$\frac{N}{c_1} \Big|_{c_1 = c_{1c}[1 + (\alpha/n_0)\ln 10]} = e^{-W_0^0} 10^\alpha \frac{n_0^2}{(\beta - \alpha)\ln 10} \left[1 + \frac{1}{(\beta - \alpha)\ln 10} \right], \quad (4.15)$$

$$\frac{g}{c_1} \Big|_{c_1 = c_{1c}[1 + (\alpha/n_0)\ln 10]} = e^{-W_0^0} 10^\alpha \frac{n_0}{(\beta - \alpha)\ln 10}. \quad (4.16)$$

Using Eqs. (2.6) and (3.6), taking into account that $n_s^{(1)}$ and $\Delta n_s^{(1)}$ slightly depend on c_1 , and, in view of the second of relations (1.2), estimates (2.9), and inequality $\alpha \leq 2$ followed from Eqs. (1.5) and (4.10), the relation

$$\begin{aligned} & \exp(-W_s^{(1)}) \Big|_{c_1 = c_{1c}[1 + (\alpha/n_0)\ln 10]} \\ &= \exp(-W_s^{(1)}) \Big|_{c_1 = c_{1c}} \exp[(\alpha n_s^{(1)}/n_0)\ln 10] \\ &\approx \exp(-W_s^{(1)}) \Big|_{c_1 = c_{1c}} \end{aligned}$$

is valid, we arrive at

$$\frac{n_s^{(1)} c_M}{c_1} \Big|_{c_1 = c_{1c}[1 + (\alpha/n_0)\ln 10]} \approx 10^2. \quad (4.17)$$

Relations (4.15) and (4.17) demonstrate that, in Eq. (3.1) of the balance of surfactant content, the role of cylindrical micelles increases and the role of spherical micelles “freezes” with an increase in surfactant monomer concentration above concentration c_{1c} (with an increase in parameter α). It is evident that estimate (3.7), which guarantees the diluted state of solution relative to spherical micelles, and estimate (3.8) taken into account in the figure, remain valid.

In particular, at $\alpha = 0$, from Eq. (4.15) with allowance for Eq. (1.5), we have

$$\frac{N}{c_1} \Big|_{c_1 = c_{1c}} = e^{-W_0^0} \frac{n_0^2}{\beta \ln 10} \left[1 + \frac{1}{\beta \ln 10} \right] \approx e^{-W_0^0} \frac{n_0^2}{\beta \ln 10}. \quad (4.18)$$

In view of Eq. (3.4), from Eq. (4.18) follows the equality

$$e^{-W_0^0} = \frac{\beta \ln 10}{10 n_0^2}, \quad (4.19)$$

that is important for further discussion; wherefrom, with account of Eq. (1.5) and estimate $n_0 \sim 10^3$ in (2.9), we find approximate (albeit not estimated) value W_0^0 : $W_0^0 \approx 14$. Taking in Eq. (4.16) $\alpha = 0$, we arrive at

$$\frac{g}{c_1} \Big|_{c_1 = c_{1c}} = e^{-W_0^0} \frac{n_0}{\beta \ln 10}. \quad (4.20)$$

The account of equality (4.19) yields

$$\frac{g}{c_1} \Big|_{c_1 = c_{1c}} = \frac{1}{10 n_0}. \quad (4.21)$$

Substituting equality (4.19) into relations (4.15) and (4.16), we have

$$\begin{aligned} & \frac{N}{c_1} \Big|_{c_1 = c_{1c}[1 + (\alpha/n_0)\ln 10]} \\ &= 10^{\alpha-1} \frac{\beta}{(\beta - \alpha)} \left[1 + \frac{1}{(\beta - \alpha)\ln 10} \right], \end{aligned} \quad (4.22)$$

$$\frac{g}{c_1} \Big|_{c_1 = c_{1c}[1 + (\alpha/n_0)\ln 10]} = 10^{\alpha-1} \frac{\beta}{(\beta - \alpha)} \frac{1}{n_0}. \quad (4.23)$$

In particular, at $\alpha = 1$ that is compatible with Eqs. (1.5) and (4.10), from Eqs. (4.22) and (4.23) with allowance for Eq. (1.5), we find

$$\frac{N}{c_1} \Big|_{\alpha=1} \approx 3, \quad (4.24)$$

$$\frac{g}{c_1} \Big|_{\alpha=1} \approx \frac{2}{n_0}. \quad (4.25)$$

Relations (3.4) and (4.24) confirm that the c_{1c} value represents the surfactant monomer concentration corresponding to the second CMC above which surfactant is rapidly accumulated in cylindrical micelles.

Let us choose for parameter α the values $\alpha = \beta - 2(\gamma + 1)n_0/n_1$ and $\alpha = \beta - (\gamma + 1)n_0/n_1$ satisfying inequality (4.10) [the second value satisfies inequality (4.10) only as the limiting value]. Substituting these values into formula (4.22), accounting for definition (4.9), as well as for strong inequalities $(\gamma + 1) \times 10^{-\gamma} \ll 1$ and $(\beta - \alpha) \ll 1$ that are also valid at $n_1/n_0 \sim 10^3$ and $\gamma \approx 3$, we obtain

$$\frac{N}{c_1} \Big|_{\alpha = \beta - 2(\gamma + 1)n_0/n_1} = 10^{\beta + 2\gamma - 1} \frac{\beta}{4(\gamma + 1)^2 \ln 10}, \quad (4.26)$$

$$\frac{N}{c_1} \Big|_{\alpha = \beta - (\gamma + 1)n_0/n_1} = 10^{\beta + 2\gamma - 1} \frac{\beta}{(\gamma + 1)^2 \ln 10}. \quad (4.27)$$

Similarly, substituting $\alpha = \beta - 2(\gamma + 1)n_0/n_1$ and $\alpha = \beta - (\gamma + 1)n_0/n_1$ into Eq. (4.23) and accounting for Eq. (4.9), we find

$$\frac{g}{c_1} \Big|_{\alpha = \beta - 2(\gamma + 1)n_0/n_1} = 10^{\beta + \gamma - 1} \frac{\beta}{2(\gamma + 1)n_0}, \quad (4.28)$$

$$\frac{g}{c_1} \Big|_{\alpha = \beta - (\gamma + 1)n_0/n_1} = 10^{\beta + \gamma - 1} \frac{\beta}{(\gamma + 1)n_0}. \quad (4.29)$$

It is seen from Eqs. (4.26)–(4.29) that, when parameter α approaches up to parameter β from even at a rel-

atively small increase in parameter α (at a relatively small increase in surfactant monomer concentration), the amount of surfactant in cylindrical micelles and the amount of cylindrical micelles with respect to surfactant monomer concentration increases manifold.

Let us discuss in more detail an interesting situation when parameter α approaches up to parameter β . We assume

$$\alpha = \beta - 2(\gamma + 1)n_0/n_1, \quad (4.30)$$

that satisfies inequality (4.10) with twofold excess. Such an excess is sufficient to vary later (in Sections 7 and 8) parameter α with no violation of inequality (4.10), as well as to ignore the emergence of disc micelles in surfactant solution. For simplicity, we neglect the indication that α -dependent values refer to the value of parameter α introduced in Eq. (4.30). From Eqs. (4.26) and (4.28) with allowance for definition (4.9) and the fact that, at $n_1/n_0 \sim 10^3$, equality $\gamma = 3$ is approximately fulfilled, we have

$$\frac{N}{c_1} = 10^{\beta-1} \frac{\beta}{64 \ln 10} \left(\frac{n_1}{n_0}\right)^2, \quad (4.31)$$

$$\frac{g}{c_1} = 10^{\beta-1} \frac{\beta n_1}{8 n_0^2}. \quad (4.32)$$

In the experimentally important region of the values of overall surfactant solution concentration c , where $c/c_1 \sim 10^5$ ratio is valid by the order of magnitude, the dominant role in Eq. (3.1) for the surfactant amount balance is played, as is seen from Eq. (4.17), by the third term of this equation. Then, $N = c$ and it follows from Eq. (4.31):

$$\beta \times 10^{\beta-1} = 64 \frac{c}{c_1} \left(\frac{n_0}{n_1}\right)^2 \ln 10, \quad (4.33)$$

that gives the equation for parameter β at the preset experimental values of c/c_1 and n_0/n_1 . Since $\beta \times 10^{\beta-1}$ rather strongly depends on β , Eq. (4.33) allows us to approximately find parameter β even when the right-hand side of equation is known only by the order of magnitude. In the experimentally important region of the values of overall concentration c of surfactant solution, where $c/c_1 \sim 10^5$ ratio is valid by the order of magnitude, as well as at estimate $n_1/n_0 \sim 10^3$ that is typical of many surfactants, Eq. (4.33) leads to the approximate (albeit not to estimated) equality (1.5) for parameter β .

From relation (4.32) at the found value of $\beta \times 10^{\beta-1}$ with the use of Eq. (4.33), we obtain

$$\frac{g}{c_1} = 8 \frac{c}{c_1} \frac{\ln 10}{n_1}. \quad (4.34)$$

At $c/c_1 \sim 10^5$ and estimate $n_1 \sim 10^6$ typical of many surfactants, this equation leads to estimate $g/c_1 \sim 2$ which

guarantees the diluted state of solution with respect to cylindrical micelles. According to Eqs. (4.3) and (4.30) and already mentioned approximate equality $\gamma = 3$, we have

$$b - a = (8/n_1) \ln 10, \quad (4.35)$$

that determines the $b - \ln(c_1/c_{1c})$ coefficient of the linear dependence of work W_n on n in Eq. (1.3). Using Eqs. (4.8) and (4.19), accounting that, in view of Eq. (4.30), parameter α is rather accurately close to parameter β , and finding then the value of $\beta \times 10^{\beta-1}$ from Eq. (4.33), we obtain

$$e^{-W^0} = 64 (\ln 10)^2 \frac{c}{c_1 n_1^2}. \quad (4.36)$$

At $c/c_1 \sim 10^5$ and $n_1 \sim 10^6$, formula (4.36) yields the estimate

$$e^{-W^0} \sim 10^{-4}, \quad (4.37)$$

according to which $W^0 \approx 9.2$ is approximately valid that was taken into account in the figure.

5. RELATIONSHIP BETWEEN THE OVERALL CONCENTRATION AND MONOMER CONCENTRATION IN SURFACTANT SOLUTION

Relations derived in Sections 3 and 4 illustrating the accumulation of surfactants in spherical and cylindrical micelles with an increase in monomer surfactant concentration beginning with concentration c_{1m} and ending with the monomer concentrations slightly exceeding concentration c_{1c} allow us, together with balance equation (3.1) of monomer amount, to monitor the relationship between the overall concentration and surfactant monomer concentration. This relationship is important for the interpretation of experimental results, because, in contrast to the overall concentration, the surfactant monomer concentration can be measured independently with a high accuracy only up to the first CMC.

At $c_1 = c_{1m}$ (at the monomer concentration corresponding to the first CMC), from Eq. (3.1) with allowance for Eq. (3.2) and equality $N|_{c=c_{1m}} = 0$, we have

$$c/c_1 \approx 1 \quad (c_1 = c_{1m}), \quad (5.1)$$

that can easily be verified in experiment. At $c_1 = c_{1c}$ (at the monomer concentration corresponding to the second CMC), from Eq. (3.1) with allowance for Eqs. (3.4) and (3.6), we obtain

$$c/c_1 \approx n_s^{(1)} c_M / c_1 \approx 10^2 \quad (c_1 = c_{1c}). \quad (5.2)$$

According to relation (3.5) and estimate $n_s^{(1)} \sim 10^2$, the relative difference between concentrations c_{1c} and c_{1m} is much less than unity. Then, as follows from Eqs. (5.1) and (5.2), the second CMC exceeds the first CMC by two orders of magnitude. Further, in order to have val-

ues $n_s^{(1)} c_M/c_1 \sim 1$ and $N/c_1 \sim 1$, provided that Eqs. (3.2) and (3.4) are satisfied, it is required, according to [12] and formula (4.24), to have concentrations $c_1 = c_{1m}[1 + (1/n_s^{(1)})\ln 10]$ and $c_1 = c_{1c}(1/n_0)\ln 10$, respectively. At $n_0/n_s^{(1)} \sim 10$, this indicates that the amount of substance in cylindrical micelles above the second CMC is much more sensitive to the monomer concentration than the amount of substance in spherical micelles above the first CMC.

Although the amount of substance in cylindrical micelles rapidly increases with monomer concentration above the c_{1c} value, the relationship between the overall concentration and monomer concentration first remains unchanged due to a rather large amount of surfactant accumulated in spherical micelles. For instance, at $c_1 = c_{1c}[1 + (1/n_0)\ln 10]$ (at concentration c_1 only slightly exceeding concentration c_{1c}), from Eq. (3.1) with allowance for Eqs. (4.17) and (4.24), we find

$$\begin{aligned} c/c_1 &\approx n_s^{(1)} c_M/c_1 \approx 10^2, \\ (c_1 = c_{1c}[1 + (1/n_0)\ln 10]). \end{aligned} \quad (5.3)$$

If, in accordance with all what have been said at the end of Section 3, we increased the $n_s^{(1)} c_M/c_1$ ratio tenfold, then in Eqs. (5.2) and (5.3) we would have 10^3 instead of 10^2 . As a result, the second CMC would exceed the first one by three orders of magnitude.

As in Section 4, let us describe in more detail an interesting situation where parameter α approaches up to parameter β . Let us assume consecutively $\alpha = \beta - 4(\gamma + 1)n_0/n_1$, $\alpha = \beta - 2(\gamma + 1)n_0/n_1$, and $\alpha = \beta - (\gamma + 1)n_0/n_1$ that agrees with condition (4.10). At these values of parameter α , from Eqs. (3.1), (4.17), and (4.22) with allowance for $\beta = 2$, $n_1/n_0 \sim 10^3$, and approximate equality $\gamma = 3$, we obtain

$$\begin{aligned} c/c_1 &\approx N/c_1 \approx \frac{10^5}{4}, \quad n_s^{(1)} c_M/c_1 \approx 10^2 \\ \left(c_1 = c_{1c} \left[1 + \frac{(2 - 16n_0/n_1)\ln 10}{n_0} \right] \right), \end{aligned} \quad (5.4)$$

$$\begin{aligned} c/c_1 &\approx N/c_1 \approx 10^5, \quad n_s^{(1)} c_M/c_1 \approx 10^2 \\ \left(c_1 = c_{1c} \left[1 + \frac{(2 - 8n_0/n_1)\ln 10}{n_0} \right] \right), \end{aligned} \quad (5.5)$$

$$\begin{aligned} c/c_1 &\approx N/c_1 \approx 4 \times 10^5, \quad n_s^{(1)} c_M/c_1 \approx 10^2 \\ \left(c_1 = c_{1c} \left[1 + \frac{(2 - 4n_0/n_1)\ln 10}{n_0} \right] \right). \end{aligned} \quad (5.6)$$

Relations (5.4)–(5.6) demonstrate that, as the overall solution concentration increases above $10^4 c_{1m}$ (that corresponds to the approach of parameter α up to parameter β), almost the whole of added surfactant is transferred to cylindrical micelles. In this case, the

amount of surfactant in the form of monomers and spherical micelles remains virtually unchanged presenting a negligible fraction of the total content of surfactant in the solution.

6. THE WIDTH OF CYLINDRICAL MICELLE DISTRIBUTION OVER THE AGGREGATION NUMBERS

Let us represent the $b - a$ value determining coefficient $b - \ln(c_1/c_{1c})$ by the linear dependence of work W_n on n in Eq. (1.3) via parameters γ and n_1 at the monomer concentration

$$c_1 = c_{1c}[1 + (1/n_0)(\beta - 2(\gamma + 1)n_0/n_1)\ln 10], \quad (6.1)$$

at which Eq. (4.30) is fulfilled and cylindrical micelles already play the dominant role in balance equation (3.1) of surfactant amount. With account of Eqs. (4.3) and (4.30), we have

$$b - a = 2[(\gamma + 1)/n_1]\ln 10. \quad (6.2)$$

Substituting Eq. (6.2) into relation (2.3), for the distribution c_n of cylindrical micelles over the aggregation numbers in the $n_0 \leq n \leq n_1$ region, we obtain

$$c_n = c_s e^{-[2(\gamma + 1)(n - n_0)/n_1]\ln 10} \quad (n_0 \leq n \leq n_1). \quad (6.3)$$

Let us determine width $n_2 - n_0$ of distribution c_n set by relation (6.3) from the condition

$$[2(\gamma + 1)(n_2 - n_0)/n_1]\ln 10 \equiv 1, \quad (6.4)$$

stating that the distribution at this width decreases by a factor of e . Then, we have

$$n_2 - n_0 = \frac{n_1}{2(\gamma + 1)\ln 10} = \frac{n_1}{2\ln(10n_1/n_0)}, \quad (6.5)$$

where definition (4.9) of parameter γ is taken into account. It is seen that, with an increase in parameter n_1 setting the upper limit of the region of aggregation numbers, the denominator in Eq. (6.5) increases slower than the numerator. At $n_0 = 10^3$ and $n_1 = 10^6$, concentrations c_n of cylindrical micelles in the $10^3 \leq n \leq 10^5$ range are almost equal to c_s . At $n \geq 10^5$, the concentrations rapidly decrease. In particular, at $n = n_1$, from Eq. (6.3) we find $c_n|_{n=n_1} = c_s e^{-8\ln 10} = c_s \times 10^{-8}$. Thus, at the chosen values of problem parameters, in accordance with experimental data, the distribution of cylindrical micelles is almost uniform in the most part of the wide region of aggregation numbers and decays exponentially in the remaining part lying to the right of this region.

From Eqs. (6.3) and (6.5) at $\gamma = 3$, we have

$$\frac{\int_{n_1}^{n_2} nc_n dn}{\int_{n_0}^{n_1} nc_n dn} = \frac{2}{e}, \quad (6.6)$$

$$\frac{\int_{n_1}^{n_1/2} nc_n dn}{\int_{n_0}^{n_1} nc_n dn} \approx (\gamma + 1) \times 10^{-(\gamma+1)} \ln 10 \approx 9.2 \times 10^{-4}.$$

It is seen that the fraction of surfactant contained in cylindrical micelles in the $n_2 \leq n \leq n_1$ range is still significant, whereas in the $n_1/2 \leq n \leq n_1$ range it is already negligibly small. A rather fast decrease in the amount of surfactant in cylindrical micelles within the n range from n to n_1 , occurring as the aggregation number n approaches up to its limiting value n_1 , implies that the limiting value of n_1 can be observed experimentally with a fair accuracy.

7. DEPENDENCE OF THE TOTAL CONCENTRATION OF CYLINDRICAL MICELLES, MEAN VALUE, AND MEAN STATISYICAL SCATTER OF AGGREGATION NUMBERS IN A CYLINDRICAL MICELLE ON THE OVERALL SURFACTANT CONCENTRATION

Together with total concentration g of cylindrical micelles and total amount N of surfactant molecules in cylindrical micelles defined by relations (2.10) and (2.12), we introduce value Q , according to

$$Q \equiv \int_{n_c^{(2)} + \Delta n_c^{(2)}}^{n_1} n^2 c_n dn. \quad (7.1)$$

Replacing, as in the determination of N and g in Eqs. (2.11) and (2.13), the lower limit of integration in Eq. (7.1) by n_0 and, with allowance for Eq. (2.3), we reduce relation (7.1) for Q to relation (7.4) at surfactant monomer concentrations in solution, which are of interest to us, because at these concentrations, in accordance with Eq. (4.35), the estimate

$$b - a \sim (8/n_1) \ln 10 \quad (7.2)$$

is valid and, in view of $n_1/n_0 \gg 1$, strong inequality

$$(b - a)n_0 \ll 1 \quad (7.3)$$

is also valid;

$$Q = \frac{2c_s}{(b - a)^3}. \quad (7.4)$$

Accounting for Eqs. (2.10), (2.12), and (7.1), let us determine mean number \bar{n} , mean square \bar{n}^2 , and mean statistical scatter σ of the aggregation numbers of cylindrical micelle as

$$\bar{n} \equiv \frac{N}{g}, \quad \bar{n}^2 \equiv \frac{Q}{g}, \quad \sigma \equiv (\bar{n}^2 - \bar{n}^2)^{1/2}. \quad (7.5)$$

Substituting relation (4.14), equality

$$N = c_s/(b - a)^2, \quad (7.6)$$

followed from Eqs. (4.13) and (7.3), as well as relation (7.4), into Eq. (7.5), we find

$$\bar{n} = 1/(b - a), \quad \bar{n}^2 = 2/(b - a)^2, \quad \sigma = 1/(b - a). \quad (7.7)$$

In view of relations (5.4)–(5.6), total amount N of surfactant molecules in cylindrical micelles coincides with a high accuracy with overall concentration c at the monomer concentrations which are of interest to us. Then, it follows from Eq. (7.6)

$$b - a \approx (c_s/c)^{1/2}. \quad (7.8)$$

Substitution of Eq. (7.8) into Eqs. (4.14) and (7.7) yields

$$\begin{aligned} g &\approx (c_s c)^{1/2}, \quad \bar{n} \approx (c/c_s)^{1/2}, \\ \bar{n}^2 &\approx 2c/c_s, \quad \sigma \approx (c/c_s)^{1/2}. \end{aligned} \quad (7.9)$$

Let us estimate the dependence of concentration c_s on overall concentration c at interesting to us surfactant monomer concentrations at which relations (7.2) and (7.3) are fulfilled. Since at these surfactant monomer concentrations, $c \approx N$, the relation

$$dc_s/dc \approx dc_s/dN = \frac{dc_s/dc_1}{dN/dc_1} \quad (7.10)$$

is valid.

Using Eqs. (2.5), (1.2), (7.2), (7.3), and (7.6), we have $dc_s/dc_1 = n_0 \exp(-W^0)$ and $dN/dc_1 \sim 2n_1^3 \times \exp(-W^0)/(8 \ln 10)^3$. According to Eq. (7.10) with allowance for estimates (2.9), we have

$$dc_s/dc \sim 10^{-12} \ll 1, \quad (7.11)$$

that enables us to assume that concentration c_s in formulas (7.9) remains almost constant when varying overall concentration c . Taking in (7.9) $c_s = \text{const}$, we obtain

$$g \propto c^{1/2}, \quad \bar{n} \propto c^{1/2}, \quad \sigma \propto c^{1/2}. \quad (7.12)$$

Direct proportional dependence of the total concentration of cylindrical micelles, mean value, and mean statistical scatter of the aggregation numbers in a cylindrical micelle on the square root of overall surfactant concentration demonstrated by relations (7.12) is confirmed by

the experiment and the other theoretical models of the formation of cylindrical micelles [3, 13, 15].

8. LINEARIZATION OF THE EQUATION OF SUBSTANCE AMOUNT BALANCE IN THE VICINITY OF FINAL EQUILIBRIUM STATE OF A MATERIALLY ISOLATED SURFACTANT SOLUTION

Let us consider Eq. (3.1) of surfactant amount balance in the vicinity of the final equilibrium state of a materially isolated solution. In this vicinity, the state of solution is not equilibrium and, hence, as was mentioned in Section 2, Eqs. (2.5) and (2.6) are invalid, and concentrations c_s and c_M , as well as overall concentration c , are not determined unambiguously by the concentration c_1 of surfactant monomers. Denoting the values for the final equilibrium state of solution by the wavy vertical bar, and their deviations from equilibrium state by symbol δ to the left of the value, we then see that the relationship of deviations δc_s , δc_M , and δc with δc_1 is not known in advance. However, Eq. (3.1) of surfactant amount balance in a materially isolated solution, where δc is equal to zero, leads to the relationship of deviations δc_1 and δc_s with deviations δc_M and δg of the total concentrations of spherical and cylindrical micelles available for experimental observations. Let us elucidate this relationship upon the linearization of Eq. (3.1) of surfactant amount balance in the vicinity of the final equilibrium state of a materially isolated surfactant solution where, according to Eq. (7.2), the relation

$$b - \tilde{a} \sim (8/n_1) \ln 10 \quad (8.1)$$

takes place.

From Eqs. (2.4), (7.6), and (4.14) with allowance for the fact that Eq. (2.5) is valid for the final state of a solution, we obtain

$$\delta a = \frac{1}{\tilde{c}_1} \delta c_1 = \frac{1}{\tilde{c}_s} e^{-\tilde{w}^0} \delta c_1, \quad (8.2)$$

$$\delta N = \frac{1}{(b - \tilde{a})^2} \delta c_s + 2e^{-\tilde{w}^0} \frac{1}{(b - \tilde{a})^3} \delta c_1, \quad (8.3)$$

$$\delta g = \frac{1}{(b - \tilde{a})} \delta c_s + e^{-\tilde{w}^0} \frac{1}{(b - \tilde{a})^2} \delta c_1. \quad (8.4)$$

We derive the condition of linearization of N and g values by deviation δc_1 , using Eq. (8.3), as a condition of the neglect of next (quadratic with respect to δc_1) term compared to the second term in the right-hand side of Eq. (8.3). Then, we have $|\delta c_1/\tilde{c}_1| \ll (2/3)(b - \tilde{a})$ or, in view of Eq. (8.1),

$$|\delta c_1/\tilde{c}_1| \ll \frac{16}{3n_1} \ln 10. \quad (8.5)$$

From Eq. (8.4), we find

$$\delta c_s = -e^{-\tilde{w}^0} \frac{1}{b - \tilde{a}} \delta c_1 + (b - \tilde{a}) \delta g. \quad (8.6)$$

Substituting (8.6) into the right-hand side of Eq. (8.3), we obtain

$$\delta N = e^{-\tilde{w}^0} \frac{1}{(b - \tilde{a})^3} \delta c_1 + \frac{1}{b - \tilde{a}} \delta g. \quad (8.7)$$

According to the material isolation of solution, we have from Eq. (3.1) of surfactant amount balance in solution

$$\delta c_1 + \tilde{n}_s^{(1)} \delta c_M + \delta N = 0, \quad (8.8)$$

where, in view of Eq. (8.5), it is assumed (with a high accuracy) that $\tilde{n}_s^{(1)} = \tilde{n}_s^{(1)}$. Substituting Eq. (8.7) into (8.8), we arrive at

$$\delta c_1 + \tilde{n}_s^{(1)} \delta c_M + e^{-\tilde{w}^0} \frac{1}{(b - \tilde{a})^3} \delta c_1 + \frac{1}{b - \tilde{a}} \delta g = 0. \quad (8.9)$$

According to Eqs. (4.37) and (8.1) and at $n_1 \sim 10^6$, strong inequality $e^{-\tilde{w}^0} (b - \tilde{a})^{-3} \sim 10^{10} \gg 1$ is valid so that the first term in the left-hand side of Eq. (8.9) can be ignored. Then, from Eq. (8.9) we have with a high accuracy

$$\delta c_1 = -e^{\tilde{w}^0} \tilde{n}_s^{(1)} (b - \tilde{a})^3 \delta c_M - e^{\tilde{w}^0} (b - \tilde{a})^2 \delta g. \quad (8.10)$$

Canceling [with the aid of Eq. (8.10)] δc_1 in the right-hand side of Eq. (8.6), we find

$$\delta c_s = \tilde{n}_s^{(1)} (b - \tilde{a})^2 \delta c_M + 2(b - \tilde{a}) \delta g. \quad (8.11)$$

Equations (8.10) and (8.11) disclose the desired relationship of deviations δc_1 and δc_s with deviations δc_M and δg .

It follows from Eqs. (8.7) and (8.10) that

$$\delta N = -\tilde{n}_s^{(1)} \delta c_M. \quad (8.12)$$

Equation (8.12) expresses the relationship between deviations δN and δc_M for N and c_M values available for experimental observation.

9. THE CASE OF THE ABSENCE OF SPHERICAL MICELLES

The relations cited above referred to the most complex case when first spherical and then cylindrical micelles are consecutively formed in the surfactant solution and the micelles of both types 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 molecular structure and packing conditions and the micellization starts just with the formation of cylindrical micelles. In this section, we summarize briefly formulas and conclusions for the case of the isolated existence of cylindrical micelles.

In the case of the absence of spherical micelles, the reference point in the figure should be displaced formally to the point with coordinates $n_s^{(1)}$ and $W_s^{(1)}$. To the right of this point, the dependence of the work of molecular aggregate formation in the solution on the aggregation number at the monomer concentration at which the fraction of substance accumulated in cylindrical micelles is already significant, will be qualitatively the same as upon the coexistence of spherical and cylindrical micelles. Correspondingly, the second barrier of the work of aggregation plays the role of the first barrier.

In formulas involving c_M , we should now assume

$$c_M = 0. \quad (9.1)$$

There is only the second CMC whose definition (3.4) persists; the first CMC is absent. Correspondingly, relation (5.1) is invalid. Now we can independently measure (with an adequate accuracy) the surfactant monomer concentration up to the second CMC. Instead of Eqs. (5.2) and (5.3), with allowance for Eq. (4.24), we now have

$$c/c_1 \approx 1 \quad (c_1 = c_{1c}), \quad (9.2)$$

$$c/c_1 \approx 4 \quad (c_1 = c_{1c}[1 + (1/n_0) \ln 10]). \quad (9.3)$$

Equations (5.4)–(5.6) persist; however, now there is no need to indicate the value of $n_s^{(1)} c_M/c_1$, because, in accordance with Eq. (9.1), it is equal to zero. Sections 6 and 7 are completely valid. In formulas cited in Section 8, in accordance with Eq. (9.1), now we should assume $\delta c_M = 0$. Instead of final equations (8.10)–(8.12) in Section 8, we have

$$\delta c_1 = -e^{\tilde{W}^0} (b - \tilde{a})^2 \delta g, \quad (9.4)$$

$$\delta c_s = 2(b - \tilde{a}) \delta g, \quad (9.5)$$

$$\delta N = 0. \quad (9.6)$$

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