

Refining of Nonionic Surfactant Micellization Theory Based on the Law of Mass Action

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Abstract—Two approaches to determining critical micelle concentration (CMC) are assessed, i.e., from the inflection point in the curve for the concentration dependence of the degree of micellization and as $K^{1/(1-n)}$, where K is the constant of the law of mass action and n is the aggregation number. The latter approach makes the theory simpler, while the former explicitly expresses the critical degree of micellization via the aggregation number. The concentrations of monomers and micelles are analyzed as functions of the overall concentration of a surfactant in a micellar solution. These functions look much simpler in the graphical form as compared with their complex exact analytical representation. This has resulted in derivation of simple analytical approximations for these functions, with these approximations being useful for calculations. The concentration dependence of the surfactant diffusion coefficient has been considered based on these approximations. It turned out that this dependence not only provides the known method for determining the diffusion coefficient of micelles, but also gives the possibility in principle to determine the aggregation number from the slope of the dependence of the diffusion coefficient on the inverse concentration (counted from the CMC in the CMC units). This new method for determining the aggregation number has been tested using the literature data on the diffusion coefficient of penta(ethylene glycol)-1-hexyl ether in an aqueous solution.

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INTRODUCTION

As applied to micellization, the law of mass action is formulated as follows (see, e.g., [1]):

$$c_M f_M = K_a \prod_i (c_{il} f_{il})^{n_i}, \quad (1)$$

where c_M and f_M are the concentration and activity coefficient of micelles, respectively; K_a is the true constant of the law of mass action; and c_{il} , f_{il} , and n_i are the concentration, activity coefficient, and aggregation number of i -type monomers, respectively. When the critical micelle concentration (CMC) is low and the activity coefficients may be equated to unity (usually, in the concentration range of one to two orders of magnitude of CMC), the law of mass action is simplified as follows:

$$c_M = K \prod_i c_{il}^{n_i}, \quad (2)$$

where, strictly speaking, coefficient K is not a constant any longer. However, even for a system with Coulomb interaction, such as a sodium dodecyl sulfate solution, the relative difference between $\ln K$ and $\ln K_a$ near the CMC is as small as 1% [1]. The law of mass action written as Eq. (2) is used in the literature.

Degree of micellization

$$\alpha_i \equiv n_i c_M / c_i, \quad (3)$$

where c_i is the overall concentration of the i -type particles, is an essential value for this theory. It is clear from Eq. (3) that micelle concentration may be expressed via the degree of micellization of any micelle component (it is convenient to use the main micelle-forming substance denoted by subscript 1), while the concentration of a monomer of any type is determined only by its own degree of micellization:

$$c_M = c_1 \alpha_1 / n_1, \quad c_{il} = c_i (1 - \alpha_i), \quad (4)$$

The substitution of Eq. (4) into Eq. (2) yields

$$c_1 \alpha_1 / n_1 = K \prod_i c_i^{n_i} (1 - \alpha_i)^{n_i}. \quad (5)$$

At a fixed composition of a mixture of particles, the monotonically increasing $\alpha_1(c_1)$ function has the only inflection point, and the concentration corresponding to it may be taken as CMC, although there are many other definitions as well [1].

The definition that relates the CMC to the constant of the law of mass action [2, 3] is especially remarkable. After being generalized to a multicomponent situation [4], it corresponds to relationship

$$K = c_{1m}^{1-n}, \quad (6)$$

where c_{1m} is the CMC and $n \equiv \sum_i n_i$ is the total aggregation number for particles of all types.

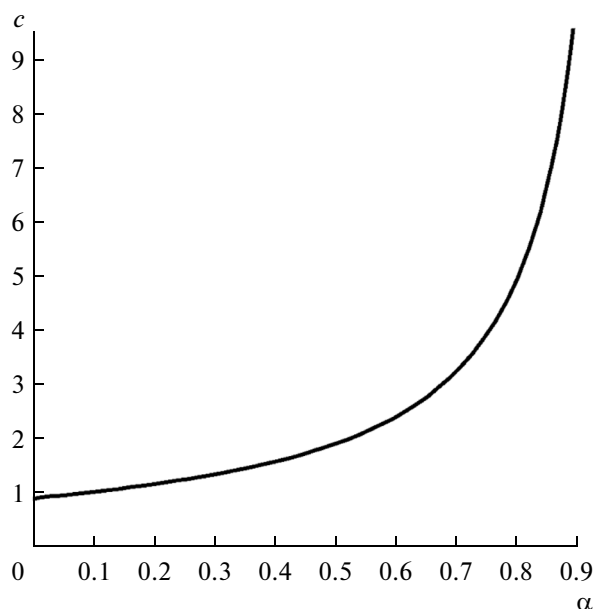


Fig. 1. Overall surfactant concentration as a function of the degree of micellization according to Eq. (10) at $n = 100$.

The substitution of Eq. (6) into Eqs. (2) and (5) transforms these relationships as follows:

$$\tilde{c}_M = \prod_i \tilde{c}_{i1}^{n_i}, \quad (7)$$

$$\tilde{c}_1 \alpha_1 / n_1 = \prod_i \tilde{c}_i^{n_i} (1 - \alpha_i)^{n_i}, \quad (8)$$

where the tilde symbol denotes that concentration is measured in the CMC units. It is evident that Eqs. (7) and (8) are attractive for the theory, since they comprise no equilibrium constant, which is difficult to calculate in the general case. Some results of this approach have been reported in [4]. The aim of this communication is to refine and complete these results for micelles of simple composition. For the sake of simplicity, we agree that all concentrations are measured in the CMC units and omit the tilde symbol below.

GENERAL RELATIONSHIPS

In the simplest case, solvated molecules of one nonionic surfactant (if solvation takes place) may play the role of the particles in question. In this case, index i in Eqs. (7) and (8) acquires only one value $i = 1$ and may be omitted. The second index (1), which indicates that monomers are concerned, remains preserved in expression (7) for the law of mass action

$$c_M = c_1^n, \quad (9)$$

while expression (8) may be written in the following form:

$$c = \left[\frac{\alpha}{(1 - \alpha)^n n} \right]^{\frac{1}{n-1}}, \quad (10)$$

which determines the overall concentration of the surfactant as an explicit function of the degree of micellization and the aggregation number. Both latter values increase with concentration; however, the aggregation number varies most slowly and is an almost constant parameter in the theory [4]. As a proper approximation, it may be considered to be a constant (which is the essence of the quasi-chemical approach) in the concentration range up to one or two orders of magnitude of CMC ($1 < c < 100$). Figure 1 shows the plot of the $c(\alpha)$ function at $n = 100$. Since the curve proceeds from the origin, it is obviously S-shaped and has an inflection point; however, the α values are so small in a range of $c < 1$ that, in the selected scale, the curve almost coincides with the vertical axis of the coordinate system in this region.

Beginning to analyze the derived relationships, we have, primarily, to verify to what extent CMC definition (6), which strongly simplifies the theory, conforms to the conventional approaches. If the CMC is determined from the inflection point, it corresponds to critical degree of micellization $\alpha_m = 0.061$ at $n = 100$ [4]. Now, our CMC corresponds to $c = 1$. Then, it is obvious that the entire bracketed expression in Eq. (10) is equal to unity, and α_m is found from equation

$$\frac{\alpha_m}{(1 - \alpha_m)^n} = n, \quad (11)$$

which determines the dependence of α_m on the specified n value (Fig. 2). At $n = 100$, the solution of Eq. (11) is $\alpha_m = 0.070$. The difference $\Delta\alpha_m = 0.009$ for the two approaches being compared is quite noticeable: 15% for α_m and slightly less than 1% for $1 - \alpha_m$ (parameter for the monomers). However, difference Δc_m is important for determining the CMC. Let us calculate it. Using formula (10), we find that

$$\frac{dc}{d\alpha} = \frac{\alpha^{\frac{2-n}{n-1}} (1 - \alpha)^{\frac{-n}{n-1}} + n \alpha^{\frac{1}{n-1}} (1 - \alpha)^{\frac{1-2n}{n-1}}}{(n-1)n^{\frac{1}{n-1}}}. \quad (12)$$

For the inflection point ($\alpha = 0.061$) at which the slope of the $c(\alpha)$ curve is smallest, formula (12) yields $dc/d\alpha \approx 1.227$ at $n = 100$. Then,

$$\Delta c_m \approx \Delta\alpha_m \frac{dc}{d\alpha} \approx 0.009 \times 1.227 \approx 0.011,$$

and, since $c_m = 1$, this deviation is as small as 1%. It is less than the accuracy of determining the CMC experimentally; moreover, the difficult removal of impurities from nonionic surfactants should be taken into account. Now, we may state that definition (6) conforms to both the theoretical and experimental approaches to determining CMC.

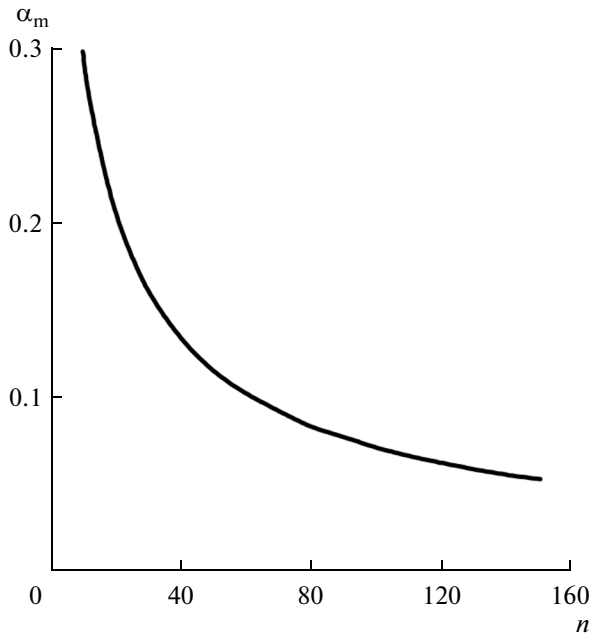


Fig. 2. Critical degree of micellization as a function of aggregation number according to Eq. (11).

In the micellization theory based on the law of mass action, Eqs. (9) and (10) are considered along with material balance condition for the surfactant

$$c = c_1 + nc_M = c_1 + nc_1^n, \quad (13)$$

where Eq. (9) has been used. As has been noted in [4], an important consequence of Eq. (13) is condition $c = n + 1$ at $c_1 = 1$, which means that monomer concentration reaches the CMC value at a surfactant concen-

tration several orders of magnitude higher than CMC. However, it has not been mentioned that, according to Eq. (9), at $c_1 = 1$, we expect to have $c_M = 1$, i.e., at $c = n + 1$, the concentrations of monomers and micelles become equal to one another and, simultaneously, to CMC. If micelle concentration at CMC is assumed to be negligible, the dependences of c_1 and c_M on c must have absolutely different patterns. To verify this hypothesis, let us, in addition to formula (10), represent c_1 and c_M as explicit functions of α . According to Eqs. (4) and (10), we have

$$c_1 = \left(\frac{\alpha}{(1-\alpha)n} \right)^{\frac{1}{n-1}}, \quad (14)$$

$$c_M = \left(\frac{\alpha}{(1-\alpha)n} \right)^{\frac{n}{n-1}}. \quad (15)$$

Equations (10) and (14) taken together specify the c_1 - c dependence parametrically (via α), while Eqs. (10) and (15) preset the c_M - c dependence at a given n value. Both these functions are shown in Fig. 3 at $n = 100$ in a range of $0 < \alpha < 0.9$. At $\alpha = 0.07$ and $n = 100$ (which correspond to $c = 1$, i.e., CMC), formulas (14) and (15) yield $c_1 \approx 0.930$ and $c_M \approx 7 \times 10^{-4}$. Taking $\alpha = 0.9$, we obtain $c_1 \approx 0.976$ and $c_M \approx 0.088$, i.e., the concentration of micelles is still lower than monomer concentration by an order of magnitude. At the point where the curves for monomer and micelle concentrations intersect and Eqs. (14) and (15) become equal to

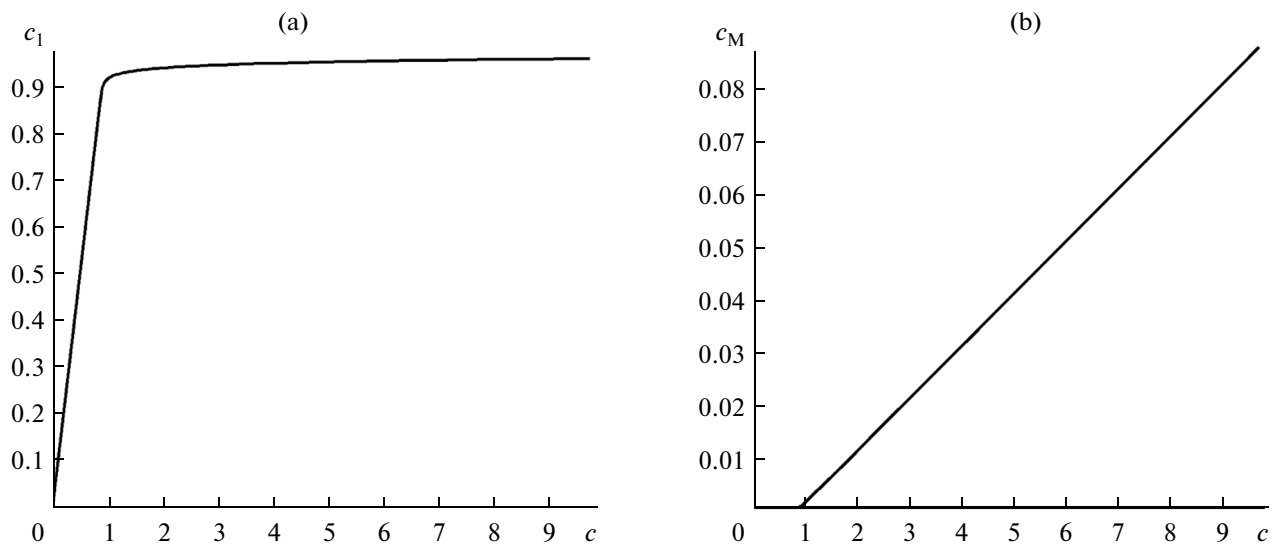


Fig. 3. Concentrations of (a) monomers and (b) micelles as functions of overall surfactant concentration at degrees of micellization $0 < \alpha < 0.9$.

unity, the degree of micellization is determined from the following condition:

$$\frac{\alpha}{1-\alpha} = n, \quad \alpha = \frac{n}{n+1}. \quad (16)$$

At $n = 100$, this yields $\alpha \approx 0.990$.

The simplicity of the graphical representation of the $c_1(c)$ and $c_M(c)$ functions shown in Fig. 3 is in contrast to the complexity of their analytical representation by formulas (10), (14), and (15). It is clear that simple analytical approximations can also be used here. For example, the curve for the $c_1(c)$ function can be approximated using two linear regions below and above the CMC:

$$c_1 = c \quad (c < 1), \quad c_1 = c_{1m} + k_1 c \quad (1 < c < n+1), \quad (17)$$

where k_1 is the positive slope coefficient. Let us calculate this value. In our approach,

$$c_{1m} = 1 - \alpha_{1m}. \quad (18)$$

The following analytical expression was found for the inflection point in the $\alpha_1(c)$ curve [1]:

$$\alpha'_m = \frac{(n/2)^{1/2} - 1}{n-1}. \quad (19)$$

As has been found above, when calculating c_{1m} , it may, with a high accuracy, be assumed that $1 - \alpha_{1m} \approx 1 - \alpha'_{1m}$. Then, omitting the linear dependence in the range from $c_1 = c_{1m}$, $c = 1$ to $c_1 = 1$, $c = n+1$, we, with allowance for relation (18), obtain

$$k_1 = \frac{1 - c_{1m}}{n} = \frac{(n/2)^{1/2} - 1}{n(n-1)}. \quad (20)$$

As a result, the second linear portion of the $c_1(c)$ function in Eq. (17) is analytically expressed as

$$c_1 = \frac{n - (n/2)^{1/2}}{n-1} + \frac{(n/2)^{1/2} - 1}{n(n-1)}(c-1) \quad (21)$$

$$(1 < c < n+1).$$

Now, let us consider the $c_M(c)$ function. By definition, for a monodisperse micellar system with aggregation number n , we have:

$$c_M = \frac{c - c_1}{n}. \quad (22)$$

The substitution of Eq. (21) into Eq. (22) yields

$$c_M = \frac{(n/2)^{1/2} - 1}{n(n-1)} + \left[1 + \frac{(n/2)^{1/2} - 1}{n(n-1)} \right] \frac{c-1}{n} \quad (23)$$

$$(1 < c < n+1).$$

At the point of CMC ($c = 1$), formula (23) (also see Eq. (19)) also determines concentration of micelles as $c_M = \alpha'_m/n$. Since we have established that the difference between α_m and α'_m is much smaller than these values themselves, the free term in the right-hand part of Eq. (23) may take place (it is small, but nonzero). The same value (as a value added to unity) is also present in square brackets. However, it is small compared with unity (always smaller than 0.02 for real aggregation numbers); therefore, it may be ignored here. Equation (23) is simplified to yield

$$c_M \approx \frac{(n/2)^{1/2} - 1}{n(n-1)} + \frac{c-1}{n} \quad (1 < c < n+1). \quad (24)$$

Formulas (21), (23), and (24) for monomer and micelle concentrations above CMC refine the commonly used approximation $c_1 \approx 1$, $c_M \approx (c-1)/n$. The comparison between Eqs. (21) and (24), shows that, although $c_M \ll c_1$ within the most part of the concentration range (these values are comparable only near $c = n+1$), derivative dc_M/dc is, on the contrary, much larger (by a factor of 16.3 at $n = 100$) than derivative dc_1/dc throughout this range.

DIFFUSION COEFFICIENT AND AGGREGATION NUMBER

The aforementioned approximations make the calculations much simpler. Let us discuss the problem of surfactant diffusion in a micellar system as an example. When the diffusion is rather slow (at a low gradient of surfactant chemical potential) and the equilibrium between monomers and micelles remains preserved during the diffusion, law of mass action (9) is valid. In this case, for low concentrations and the simplest bimodal distribution (when all micelles have the same size), surfactant diffusion coefficient D is specified by the following expression [5] (see also [6]):

$$D = \frac{c_1 D_1 + n^2 c_M D_M}{c_1 + n^2 c_M}, \quad (25)$$

where D_1 and D_M are the diffusion coefficients of monomers and micelles. The former is easily determined from experiments with a premicellar solution, while the latter can be found from the data on a micellar solution. Both coefficients could be believed to be constant but for the viscosity, which varies with concentration and directly affects the diffusion coefficients. This is evident from, e.g., the following formula for noninteracting spherical i -type particles:

$$D_i = \frac{k_B T}{6\pi\eta r_i}, \quad (26)$$

where k_B is the Boltzmann constant, T is the temperature, η is the viscosity, and r_i is the particle radius. If

particles of different types have the same or similar geometric shapes, the viscosity has the same effect on all of the diffusion coefficients. In this case, we can eliminate the effect of viscosity by using the ratio between the coefficients. In any case, after rewriting Eq. (25) as

$$\frac{D}{D_1} = \frac{c_1 + n^2 c_M D_M / D_1}{c_1 + n^2 c_M} \quad (27)$$

and assuming the D_M/D_1 ratio to be constant, we reduce the role of viscosity and make calculation of the diffusion coefficient of micelles more reliable. Let us consider this calculation procedure.

According to Eqs. (21) and (24), the relative role of the terms in the denominator of Eq. (25) is characterized by the following ratio (we denote it as κ):

$$\kappa \equiv \frac{c_1}{n^2 c_M} = \frac{n^2 - n(n/2)^{1/2} + [(n/2)^{1/2} - 1](c-1)}{n^2 [(n/2)^{1/2} - 1] + n^2 (n-1)(c-1)}. \quad (28)$$

For CMC ($c = 1$), Eq. (28) yields the result

$$\kappa = \frac{1 - (n/2)^{1/2}/n}{(n/2)^{1/2} - 1} \ll 1, \quad (29)$$

which shows that, although concentration of micelles is rather low, as compared with the concentration of monomers, the $n^2 c_M$ value is significantly higher than the concentration of monomers already at CMC ($\kappa \approx 0.154$ at $n = 100$). The κ value becomes even smaller as the concentration grows above the CMC, because the denominator in Eq. (28) increases much faster than the numerator does. At a concentration twice as high as the CMC ($c = 2$), κ decreases to negligible value

$$\kappa = \frac{n^2 - (n-1)(n/2)^{1/2} - 1}{n^2 [n + (n/2)^{1/2} - 2]} < \frac{1}{n} \quad (30)$$

($\kappa \approx 0.00885$ at $n = 100$). This means that, on exceeding the CMC, we may omit the first term in the denominator of Eq. (25) and write this equation as

$$\frac{D}{D_1} \approx \frac{D_M}{D_1} + \kappa, \quad (31)$$

where κ is specified by Eq. (28).

The latter expression can also be simplified. In the numerator of Eq. (28), as well as in formula (21), the variable component remains small, as compared with the free term throughout a broad range ($1 < c < n + 1$). If we confine ourselves to a range that does not exceed one order of magnitude with respect to the CMC, the variable component will be negligibly small and can be omitted. An opposite state of affairs holds for the denominator of Eq. (28). The variable component in it increases with concentration so rapidly that it becomes significantly higher than the free term (16.3-fold at $n = 100$) already at $c = 2$. Moreover, at $c > 2$, the

free term may be ignored and we arrive at the following approximation for κ :

$$\kappa \approx \frac{n - (n/2)^{1/2}}{n(n-1)(c-1)} \quad (2 < c < 11). \quad (32)$$

The boundaries of the range are given here approximately; the distance to the CMC value must be sufficiently large to provide a proper denominator, but not too large to meet the conditions of ideality for the entire micellar system. Now, introducing coefficient

$$k \equiv \frac{n - (n/2)^{1/2}}{n(n-1)}, \quad (33)$$

we may rewrite Eq. (31) as follows:

$$\frac{D}{D_1} \approx \frac{D_M}{D_1} + \frac{k}{c-1}. \quad (34)$$

According to Eq. (34), in the selected concentration range, the surfactant diffusion coefficient increases linearly with the $1/(c-1)$ value (i.e., decreases with growing concentration); therefore, relative diffusion coefficient D_M/D_1 of micelles can be determined as the Y-intercept when extrapolating this linear dependence to the coordinate origin ($1/(c-1) \rightarrow 0$). A similar method has been illustrated in [7] when determining the diffusion coefficient of Triton X-100 (*p*-(1,1,3,3-tetramethylbutyl)phenyl poly(ethylene glycol)) micelles. However, an analog of coefficient k in the cited study (which also included the constant of the law of mass action) remained a "thing-in-itself," leaving the feeling that nothing useful could be derived from it. In our representation of Eq. (33), coefficient k is unambiguously related to the aggregation number, thereby yielding the fundamental possibility of finding the aggregation number of micelles from the data on the concentration dependence for the diffusion coefficient of a surfactant.

Note that the approach that is adequately illustrated by formula (26), i.e., the transition from the diffusion coefficient to the aggregation number via the hydrodynamic radius of micelles, is commonly used for this purpose. However, this approach requires knowledge of, first, the geometric shape of micelles and, second, the hydration number (for finding the true volume followed by determining the aggregation number by dividing the true volume by the volume of a single surfactant molecule). Since the law of mass action is independent of micelle shape (which is often unknown) and takes into account hydration (even if the hydration number is unknown), our formula (33) is devoid of these requirements, although it still has its own limitations.

However, the use of formula (33) for determining the aggregation number encounters certain difficulties in practice. Figure 4 shows the dependence of coefficient k in Eq. (34) on the aggregation number in a range of $10 < n < 100$, where this coefficient acquires a

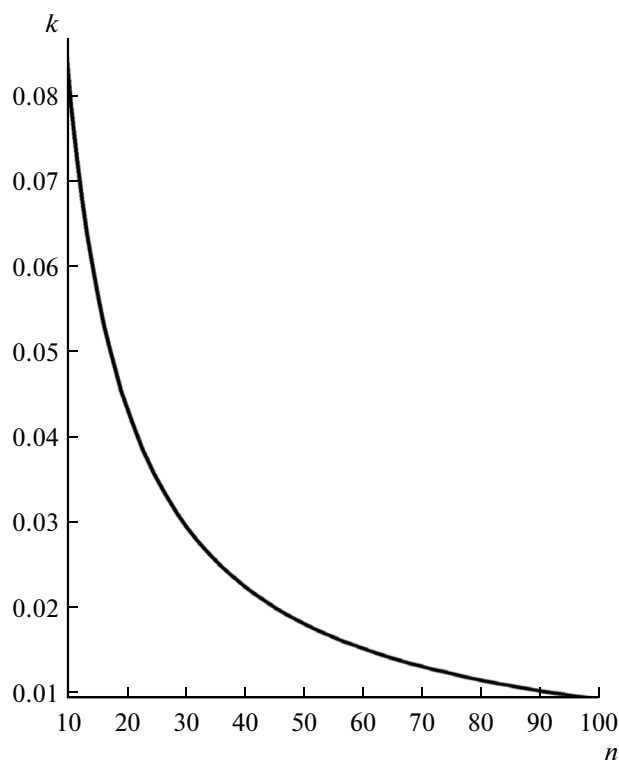


Fig. 4. Coefficient k in formula (34) as a function of aggregation number.

value of 0.086–0.0094. It can be seen that, within a reasonable range of aggregation numbers, the k value is so small that a very high accuracy is required for the measurement of the diffusion coefficient to reliably determine it in an experiment (here, the situation is similar to that observed when determining the aggregation number from the slope of the surface tension–concentration dependence above CMC, where the slope is also extremely small [8]). The data available on the diffusion coefficients of nonionic surfactants (e.g., Triton X-100 [7] and sulfobetaines [9]) are not so accurate, but this is not the sole point. It has been mentioned in the comment to formula (25) that diffusion coefficient D_1 of monomers can be easily determined from the experiments with premicellar solutions; however, if solution viscosity varies with concentration, D_1 varies as well. Hence, formula (34) does not contain the D_1 value for a premicellar solution, but rather it comprises the actual D_1 value for a solution in which total diffusion coefficient D is measured for the entire surfactant. This actual value still remains to be found. Alternatively, the D_1 value may be used as a constant for a premicellar solution with viscosity η_0 , provided that every obtained D value is recalculated from real viscosity η to viscosity η_0 . This implies that the viscosity of a solution must be measured in parallel with the measurement the surfactant diffusion coefficient in it.

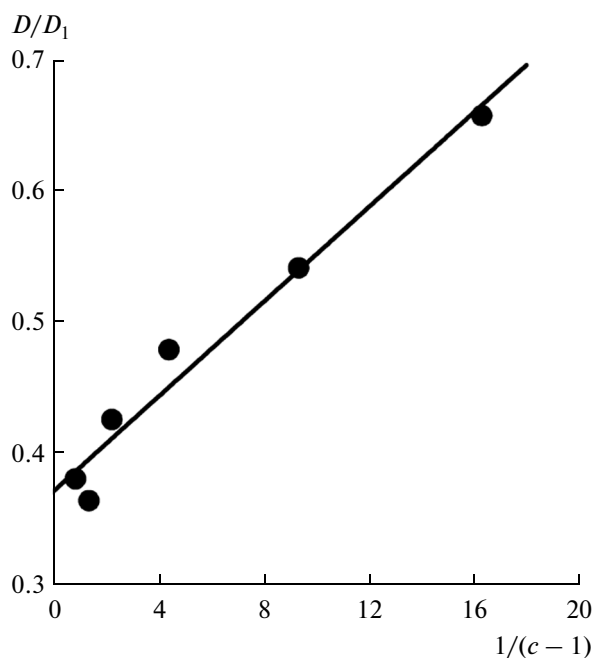


Fig. 5. To determining diffusion coefficient and the aggregation number of C_6E_5 micelles in an aqueous solution from the concentration dependence of the diffusion coefficient of the entire surfactant at 25°C [10].

This approach was demonstrated in [10] when studying an aqueous solution of penta(ethylene glycol)-1-hexyl ether (C_6E_5): each obtained diffusion coefficient was corrected by multiplying it by η/η_0 . A value of $0.49 \times 10^{-5} \text{ cm}^2/\text{s}$ was obtained for the diffusion coefficient of monomers in a premicellar solution. Variations in the diffusion coefficient of C_6E_5 were studied upon passing through CMC at 25°C. Six experimental points were located in the region above the CMC (from $c = 1.061$ to $c = 2.055$), and we used these points for the calculations by formula (34). Figure 5 exhibits the linear approximation of the experimental dependence (coefficient of determination is 0.965) at $k \approx 0.0180$ and $D_M/D_1 \approx 0.374$. At this k value, Eq. (33) yields $n = 51.1$ (see also Fig. 4), which is in good agreement with value $n = 54$ that was used in the calculations for matching with the experimental data [10]. Hence, it may be stated that an unusual method for determining the aggregation number of nonionic surfactant micelles has been tested for the first time.

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