

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

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Abstract—The micellization theory previously elaborated based on the determination of critical micelle concentration using the constant of the law of mass action is refined for ionic surfactants. The degree of micellization is used as a parameter to obtain implicit dependences of monomer and micelle concentrations on overall surfactant concentration in an ideal micellar solution. As expected, the counterion concentration increases monotonically, while the surface-active ion concentration passes through a maximum immediately after the critical micelle concentration. Repeated calculations performed at different degrees of counterion binding show that, as this parameter is decreased, the maximum becomes sharper, disappearing when the parameter becomes equal to unity. The complex character of the exact analytical description of the concentration functions for monomers and micelles is in contrast to their simple graphical representations. This fact makes it possible to derive simple analytical approximations for them in the form of explicit functions useful for calculations.

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INTRODUCTION

As applied to micellization of an ionic surfactant that dissociates completely into two ions, the law of mass action is formulated as follows (see, e.g., [1]):

$$c_M f_M = K_a (c_1 f_1)^{n_1} (c_2 f_2)^{n_2}, \quad (1)$$

where c_M and f_M are the concentration (number of particles per unit volume) and activity coefficient of micelles, respectively; K_a is the true constant of the law of mass action; and c_i , f_i , 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:

$$c_M = K c_1^{n_1} c_2^{n_2}, \quad (2)$$

where, strictly speaking, coefficient K is not a constant any longer. However, as has been verified by direct calculations for a sodium dodecyl sulfate solution, the relative difference between $\ln K$ and $\ln K_a$ near the CMC is as small as 1% [1]. Hence, the law of mass action written as Eq. (2) is appreciably accurate in the considered concentration range. It should also be noted that, in theoretical studies, it is used in combination with the material balance condition, which cannot comprise the activity coefficients.

The material balance condition is written as

$$c v_i = c_i + n_i c_M \quad (i = 1, 2), \quad (3)$$

where c is the overall concentration of a surfactant and v_i is a stoichiometric coefficient (the number of i -type ions resulting from dissociation of one electrolyte molecule), so that $c v_i$ is the overall concentration of the ions of this type in the solution. The degree of micellization is an important parameter of the theory,

$$\alpha_i \equiv \frac{n_i c_M}{c v_i}. \quad (4)$$

It is clear from Eq. (4) that micelle concentration can be expressed via the degree of micellization of any ion (it is convenient to use a surface-active ion), while the concentrations of monomeric surface-active ions (subscript 1) and counterions (subscript 2) depend only on their own degrees of micellization as follows:

$$c_M = \frac{c v_1 \alpha_1}{n_1}, \quad c_i = c v_i (1 - \alpha_i) \quad (i = 1, 2). \quad (5)$$

Substitution of relations (5) into Eq. (2) yields

$$\frac{c v_1 \alpha_1}{n_1} = K [c v_1 (1 - \alpha_1)]^{n_1} [c v_2 (1 - \alpha_2)]^{n_2}. \quad (6)$$

Using degree β of counterion binding, α_2 can be expressed via α_1 as

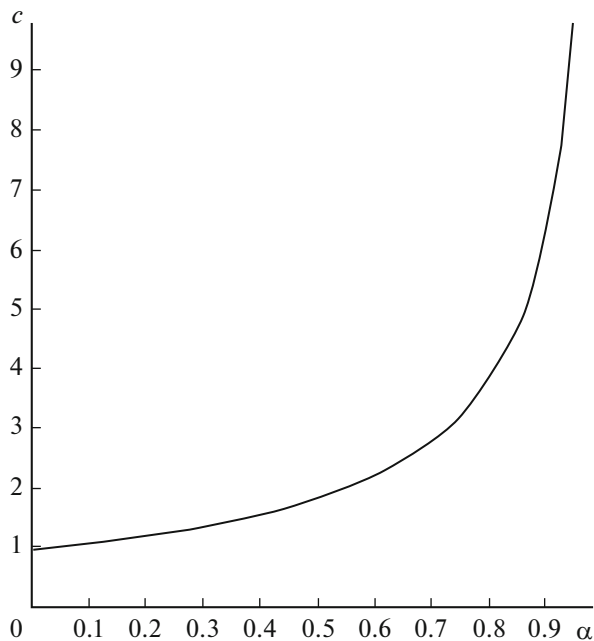


Fig. 1. Overall concentration of an ionic surfactant as a function of the degree of micellization according to Eq. (13) at $n = 100$ and $\beta = 0.8$.

$$\alpha_2 = \alpha_1\beta, \quad \beta \equiv -\frac{z_2 n_2}{z_1 n_1} = \frac{v_1 n_2}{v_2 n_1}, \quad (7)$$

where z_i is the charge number of an i -type ion. Then, Eq. (6) may be written as follows:

$$\frac{c v_1 \alpha}{n_1} = K [c v_1 (1 - \alpha)]^{n_1} [c v_2 (1 - \alpha \beta)]^{n_2}, \quad (8)$$

where $\alpha \equiv \alpha_1$. Equation (8) explicitly determines the monotonic $c(\alpha)$ dependence with the only inflection point, which can be taken as the CMC [1].

There are many other definitions of CMC in the literature [1]. The definition based on the relation between the CMC and the constant of the law of mass action [2, 3] is especially remarkable. After being generalized to a multicomponent situation [4], this relation is written as

$$K = c_{1m}^{1-n_i}, \quad (9)$$

where c_{1m} is the CMC and $n_i \equiv \sum_i n_i$ is the total aggregation number for particles of all types. The substitution of Eq. (9) into Eqs. (2) and (8) transforms these equations as follows:

$$\tilde{c}_M = \tilde{c}_1^{n_1} \tilde{c}_2^{n_2}, \quad (10)$$

$$\frac{\tilde{c} v_1 \alpha}{n_1} = [\tilde{c} v_1 (1 - \alpha)]^{n_1} [\tilde{c} v_2 (1 - \alpha \beta)]^{n_2}, \quad (11)$$

where the tilde symbol indicates that the concentration is measured in the CMC units. Equations (10)

and (11) are obviously 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 goal of this communication is to refine and extend them to the case of an ionic micellar solution, as has already been done for nonionic micelles [5]. We shall confine ourselves to the simplest case, in which an ionic surfactant is a strong 1 : 1 electrolyte. To make the notation simpler, we assume that all concentrations are measured in CMC units and omit the tilde symbol below.

RELATIONSHIPS FOR CONCENTRATIONS

According to relations (7), in the case of a 1 : 1 electrolyte, the degrees of micellization of ions and their aggregation numbers are related using the degree of counterion binding

$$n_2 = n_1 \beta, \quad (12)$$

and Eqs. (10) and (11) can be written as

$$c_M = c_1^n c_2^{n\beta}, \quad (13)$$

$$c = \left[\frac{\alpha}{n(1-\alpha)^n (1-\alpha\beta)^{n\beta}} \right]^{\frac{1}{n(1+\beta)-1}}, \quad (14)$$

where $n \equiv n_1$ is now the only aggregation number, which, as does degree of micellization α , refers to the surface-active ion. As in the case of a nonionic surfactant [5], we consider the problem within the framework of the quasi-chemical approach and assume that the aggregation number and the degree of counterion binding are constant values in the vicinity of CMC, $1 < c < 100$. At specified n and β values, Eq. (14) unambiguously determines surfactant concentration as a function of the degree of micellization. Figure 1 shows the plot of the $c(\alpha)$ function at $n = 100$ and $\beta = 0.8$. 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 the range of $c < 1$ that, in the selected scale, the curve almost coincides with the vertical axis of the coordinate system in this region. In accordance with definition (9) and Eq. (14), critical degree of micellization α_m , which corresponds to CMC ($c = 1$), is determined from the condition

$$\frac{\alpha_m}{n(1-\alpha_m)^n (1-\alpha_m\beta)^{n\beta}} = 1 \quad (15)$$

and varies depending on the preset n and β values. At $n = 100$ and $\beta = 0.8$, we have $\alpha_m \approx 0.046$, while the inflection point has coordinates $\alpha \approx 0.052$, $c \approx 1.006$. It can be seen that the CMC values determined using Eq. (9) and the inflection point in the $c(\alpha)$ curve differ by less than 1%.

If the $c(\alpha)$ function is known, the concentration dependences can be determined for all types of particles in a micellar system according to Eq. (5). Let us

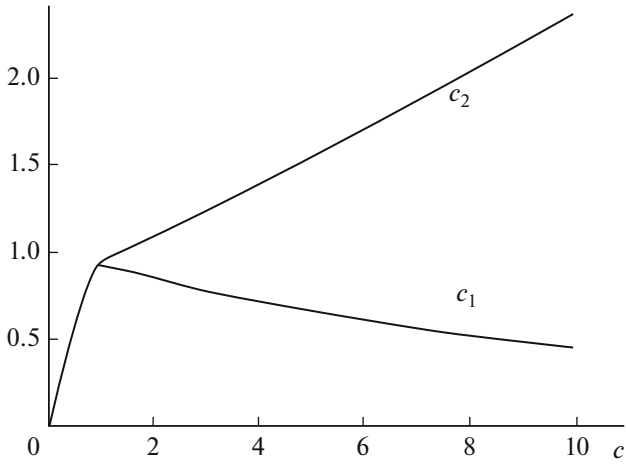


Fig. 2. Concentrations of monomeric surface-active ions (c_1) and counterions (c_2) as functions of the overall surfactant concentration in the range of degrees of micellization $0 < \alpha < 0.95$.

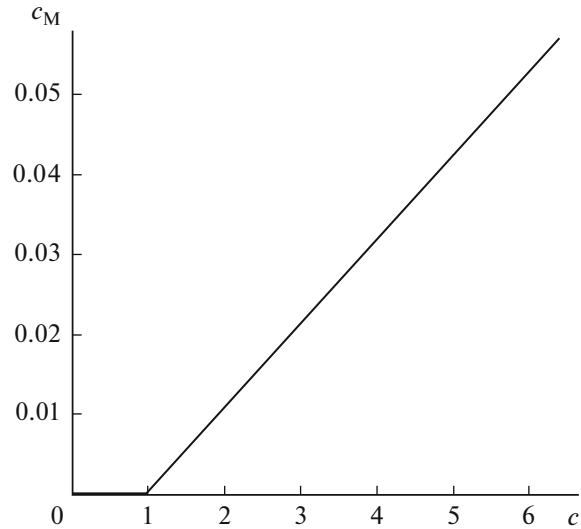


Fig. 3. Micelle concentration as a function of the overall surfactant concentration in the range of degrees of micellization $0 < \alpha < 0.95$.

start with the concentration of monomeric surface-active ions:

$$c_1 = c(1 - \alpha). \quad (16)$$

By substituting Eq. (14) into Eq. (16), we find

$$c_1 = \left[\frac{\alpha(1 - \alpha)^{n\beta-1}}{n(1 - \alpha\beta)^{n\beta}} \right]^{\frac{1}{n(1+\beta)-1}}. \quad (17)$$

As can be seen from Eq. (17), c_1 is nullified at both $\alpha = 0$ and $\alpha = 1$, thereby indicating that the concentration of free surface-active ions passes through a maximum. This fact has, for a long time, been known [6] and experimentally studied (see references in [4]).

The concentration of monomeric counterions is specified as

$$c_2 = c(1 - \alpha\beta), \quad (18)$$

or, after substituting Eq. (14),

$$c_2 = \left[\frac{\alpha(1 - \alpha\beta)^{n-1}}{n(1 - \alpha)^n} \right]^{\frac{1}{n(1+\beta)-1}}. \quad (19)$$

As opposed to the concentration of surface-active ions, it is a monotonically ascending function of the degree of micellization and the overall surfactant concentration. Taken together, Eqs. (14) and (17) present the dependence of c_1 on c , parametrically (via α), while the dependence of c_2 on c is specified by Eqs. (14) and (19) at given n and β values. Both these dependences are shown in Fig. 2 at $n = 100$ and $\beta = 0.8$ in a range of $0 < \alpha < 0.95$. At CMC ($c = 1$), there are values $c_{1m} \approx 0.9541$ and $c_{2m} \approx 0.963$. The point of the maximum c_1 corresponds to degree of micellization $\alpha \approx 0.0595$; its coordinates in Fig. 2 are

$c \approx 1.0147$ (higher than the CMC by 1.5%) and $c_1 \approx 0.9543$ (while $c_2 \approx 0.966$). At other points of the $c_1(c)$ curve, the c_1 values will lie even lower; hence, the concentration of surfactant-active ions never reaches $c_1 = 1$. On the contrary, the $c_2 = 1$ value is reached very soon at $\alpha \approx 0.232$ and $c \approx 1.228$.

Now let us consider the concentration of micelles. In accordance with Eq. (5), we have

$$c_M = \frac{c\alpha}{n}. \quad (20)$$

By substituting Eq. (14) into Eq. (20), we obtain

$$c_M = \left[\frac{\alpha^{n(1+\beta)}}{n^{n(1+\beta)}(1 - \alpha)^n(1 - \alpha\beta)^{n\beta}} \right]^{\frac{1}{n(1+\beta)-1}}. \quad (21)$$

Together with Eq. (14), Eq. (21) parametrically specifies the dependence of micelle concentration on the overall surfactant concentration. Figure 3 exemplifies function $c_M(c)$, which is obtained from Eqs. (14) and (21) at $n = 100$ and $\beta = 0.8$. The graphical simplicity of this function is truly astonishing (it is almost an ideal straight line), and its analytical description is very complex. At the CMC ($c = 1$), the micelle concentration is $c_{Mm} \approx 4.6 \times 10^{-4}$.

Degree of counterion binding β is the least reliable calculation parameter of those used above. This parameter cannot be determined unambiguously by theoretical methods and depends on a method used for measurements in practice [1]. In the calculations, the role of a fitting parameter is demanded. Therefore, we have intentionally studied the effect of the numerical value of β on the pattern of the most complex con-

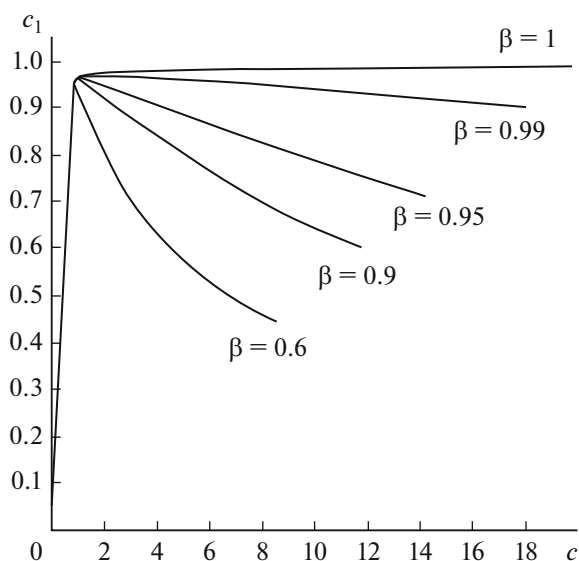


Fig. 4. Isotherms of surface-active ion concentration at different degrees of counterion binding.

centration dependence $c_1(c)$. The calculation results are shown in Fig. 4. The smaller the β value, the sharper the maximum of c_1 , and, the closer the β value to unity, the more similar the plot to the case of a non-ionic surfactant [5] (the maximum disappears at $\beta = 1$).

Since the $c_M(c)$ function is monotonically ascending and the $c_1(c)$ function is monotonically descending after its maximum, their curves intersect. At the intersection point (shown with the asterisk), the right-hand sides of Eqs. (16) and (20) are equal and yield

$$\alpha^* = \frac{n}{n+1}. \quad (22)$$

The substitution of Eq. (22) into Eqs. (14), (16), (18), and (20) determines all parameters of the intersection point as follows:

$$c^* = \frac{n+1}{[n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}}}, \quad (23)$$

$$c_1^* = c_M^* = [n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}}, \quad (24)$$

$$c_2^* = [n(1-\beta)+1]^{\frac{n-1}{n(1+\beta)-1}} \quad (25)$$

(at $n = 100$ and $\beta = 0.8$, we have $\alpha^* \approx 0.990$, $c^* \approx 25.9$, $c_1^* = c_M^* \approx 0.256$, and $c_2^* \approx 5.386$). Thus, using the law of mass action, we may calculate all concentration dependences for an ideal micellar system.

APPROXIMATION OF THE CONCENTRATION DEPENDENCES

The formulas obtained above for the $c_1(c)$, $c_2(c)$, and $c_M(c)$ functions have two drawbacks: they are rather cumbersome and, more importantly, are defined implicitly via parameter α . Such complicated analytical definition makes them difficult to use in practice. At the same time, the graphical representation of these functions is relatively simple, thus suggesting simple analytical approximations (although with some loss of accuracy). The simplest approximation consists in connecting two reference points that lie relatively far from one another with straight lines. These are the CMC and the intersection point of plots $c_1(c)$ and $c_M(c)$. This approximation is expressed by the following formulas:

$$c_1 = 1 - k_1(c - 1), \quad (26)$$

$$c_2 = 1 + k_2(c - 1), \quad (27)$$

$$c_M = k_M(c - 1), \quad (28)$$

where k_1, k_2 , and k_M are positive coefficients and it is assumed that $c_1 = c_2 \approx 1$ and $c_M \approx 0$ at $c = 1$. These formulas are, naturally, valid only for a range of $1 \leq c \leq c^*$. In accordance with Eqs. (23)–(25), the values of the coefficients are specified as

$$k_1 \equiv \frac{1 - c_1^*}{c^* - 1} = \frac{[n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}} - 1}{n+1 - [n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}}}, \quad (29)$$

$$k_2 \equiv \frac{c_2^* - 1}{c^* - 1} = \frac{n(1-\beta)+1 - [n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}}}{n+1 - [n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}}}, \quad (30)$$

$$k_M \equiv \frac{c_M^*}{c^* - 1} = \frac{1}{n+1 - [n(1-\beta)+1]^{\frac{n\beta}{n(1+\beta)-1}}}. \quad (31)$$

Expressions (29)–(31) look rather cumbersome; however, the coefficients need to be calculated only once. Then, formulas (26)–(28) can be used to explicitly describe the desired dependences. For example, at $n = 100$ and $\beta = 0.8$, we have $k_1 \approx 0.0298$, $k_2 \approx 0.176$, and $k_M \approx 0.010$. Of course, this simple approach will be used in calculations.

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