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Theoretical Study on the Formation of Spherical Micelles

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Synopsis. From the Tanford theory for the formation of spherical micelles and a modification of this theory, the aggregation number n_w and monomer concentration x_1 are calculated as a function of total surfactant concentration x. The definition of cmc of $d^3x_1/dx^3=0$ is adequate. Empirical equations for the estimation of n_w and cmc are obtained.

When the concentration of surfactant is raised above the critical micelle concentration (cmc), to a first approximation all added molecules go into micelles. Then the question arises if the micelles grow in size or if only the number of the micelle is increased.[1] Recently, a number of experimental researches have been done, but there is still a matter of controversy whether the micelle of nonionic surfactant grows with increasing concentration or not.[2] Another question arises if the monomer concentration of the surfactant remains constant above the cmc.[3]

By gel-filtration chromatography, we determined the monomer concentration as a function of total surfactant concentration and further calculated the micellar aggregation number from this result.[3–5] These data may be used to test several theories for micellization or to estimate the micelle size distribution and other properties on the basis of these theories. Among these theories, the Tanford theory seems to be of greatest promise.[6] Warr and White modified it for computational simplicity and calculated the concentration dependence of the monomer concentration and aggregation number for spherical micelles.[7]

In this work we compare these theories and obtain useful relations to fit these theories to our experimental data.

Thermodynamic Basis

According to Tanford,[6] the free energy (per RT) of transfer of i surfactant molecules to a spherical micelle of aggregation number i may be expressed as[7,8]

$$\Delta G_i^\circ = -ai + bi^{2/3} + ci^{4/3} - (-a+b+c). \tag{1}$$

This equation holds for all micelles of aggregation number greater than unity. The coefficient a is a bulk free-energy term for transfer of an alkyl chain from water into the micelle core, b is the surface free energy per surfactant at the micelle/solution interface, and c is a term for repulsions etc. between the head groups in the micelle. The mole fraction of micelles of aggregation number i may be given by

$$x_i = x_1{}^i \exp(-\Delta G_i^\circ). \tag{2}$$

Using this equation, one can express the total surfactant mole fraction x and the weight average aggregation number n_w as

$$x = \sum_{i=1}^{\infty} ix_i, \tag{3}$$

and

$$n_w = \sum_{i=2}^{\infty} i^2 x_i / \sum_{i=2}^{\infty} ix_i. \tag{4}$$

From Eqs. 1 and 2, one can obtain a scaled mole fraction of i-mer as a function of a scaled monomer concentration from

$$x_i e^a = (x_1 e^a)^i \exp[-b(i^{2/3}-1)-c(i^{4/3}-1)]. \tag{5}$$

Furthermore Tanford defined the cmc as x at which $x_1/x=0.95$.[6]

For computational simplicity Warr and White modified Eq. 1 as

$$\Delta G_i^\circ = -a(i-1) + b(i-1)^{2/3} + c(i-1)^{4/3}, \tag{6}$$

and gave useful expressions for the cmc and other properies.[7] They defined scaling parameters for ΔG_i° and i:

$$\Gamma = b^2/c, \tag{7}$$

and

$$I = (b/c)^{3/2}. \tag{8}$$

The Γ value varies linearly with ΔG_i° and I gives a rough value of n_w. Furthermore they considered cmc values on the basis of the following equation:

$$d^3x_1/dx^3 = 0. \tag{9}$$

This is a form of the general definition of cmc by Phillips.[9] From Eq. 2 we can obtain

$$d^3x_1/dx^3 = M/x_1{}^2 \, [\sum_{i=1}^{\infty} i^2 x_1{}^{i-1} \exp(-\Delta G_i^\circ)]^5, \tag{10}$$

where

$$M = 3[\sum_{i=1}^{\infty} i^2 (i-1) x_1{}^{i-1} \exp(-\Delta G_i^\circ)]^2 - [\sum_{i=1}^{\infty} i^2(i-1)(i-2) x_1{}^{i-1} \exp(-\Delta G_i^\circ)] [\sum_{i=1}^{\infty} i^2 x_1{}^{i-1} \exp(-\Delta G_i^\circ)]. \tag{11}$$

From Eq. 9 the cmc is the value of x at which $M=0$.

Results and Discussion

Figure 1 shows plots of n_w against the logarithm of total concentration scaled by exp a in the case of $I=60$. The solid lines were calculated from the Tanford theory, viz., Eq. 1 and the dashed lines were from the Warr and White theory, viz., Eq. 6. The numerals attached to these lines denote the Γ values. Results similar to Fig. 1 were obtained in the cases of $I=20$ and 150. As Fig. 1 shows, at high concentrations the I value is similar to the n_w values calculated from the Warr and White theory, but is slightly larger than those from the Tanford theory. These results are useful to estimate the values of b and c from observed n_w values and show that n_w is determined by the balance of the b term to the c term in Eqs. 1 and 6.

Figure 2 shows plots of monomer concentration against total concentration calculated from Eq. 1 (solid lines) and Eq. 6 (dashed lines) in the cases of I=60. Similar results were obtained in the cases of I=20 and 150. The monomer concentrations calculated from Eq. 1 are smaller than those from Eq. 6.

Figure 3 shows the logarithm of cmc against the square root of the product bc, calculated from Eq. 1. The filled symbols denote the cmc values calculated from the definition by Tanford, viz., x_1/x=0.95 and the hollow symbols are those from the definition of Eq. 9. Similar results were obtained from Eq. 6. The plots in Fig. 2 show part of these results. Empirically, these cmc values are expressed by the following equation:

$$\ln x_{\mathrm{cmc}} = -a + \beta (bc)^{1/2} + \gamma. \qquad (12)$$

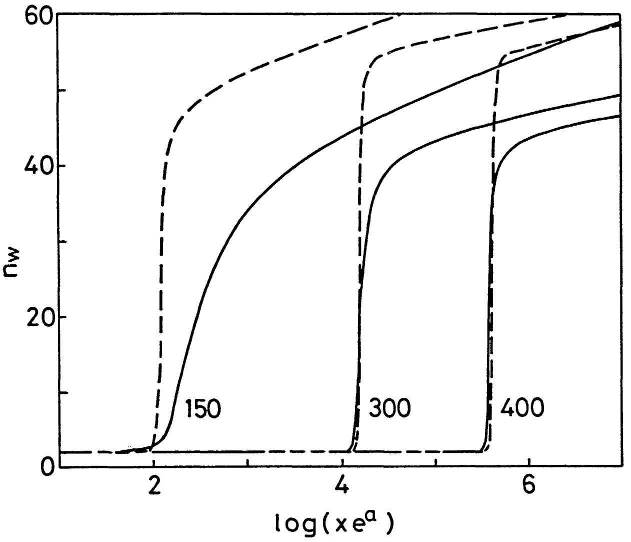

Fig. 1. Weight average aggregation numbers calculated from Eqs. 1 (solid lines) and 6 (dashed lines) as a function of the logarithm of scaled total concentration at different Γ values for I=60.

Table 1 shows the coefficients β and γ in Eq. 12 and the correlation coefficient of linearity determined by a linear least-squares method. In the case of Eq. 6, the cmc values determined by the two definitions are close to each other and also close to the predictions by Eq. 12, as can be seen from the values of the correlation coefficient and the standard deviations of β and γ in Table 1. In the case of Eq. 1 the cmc values determined by the two definitions are far, as shown in Fig. 2 and Table 1. From Fig. 2 we can conclude that the definition of cmc by Eq. 9 is better than that by Tanford. Figure 1 shows the n_w values predicted by Eq. 1 are smaller than those by Eq. 6. As a result, in the case of Eq. 1 the cmc values defined by Tanford

Table 1. The Coefficients β and γ and the Correlation Coefficient r Fitted to Eq. 12

Eq	Definition	β±sd[a]	γ±sd[a]	r
1	x_1/x=0.95	1.96±0.04	−1.23±0.82	0.9978
1	Eq. 9	1.87±0.01	0.25±0.26	0.9998
6	x_1/x=0.95	1.99±0.01	−0.12±0.13	0.9999
6	Eq. 9	1.98±0.00	−0.10±0.10	1.0000

a) Standard deviation.

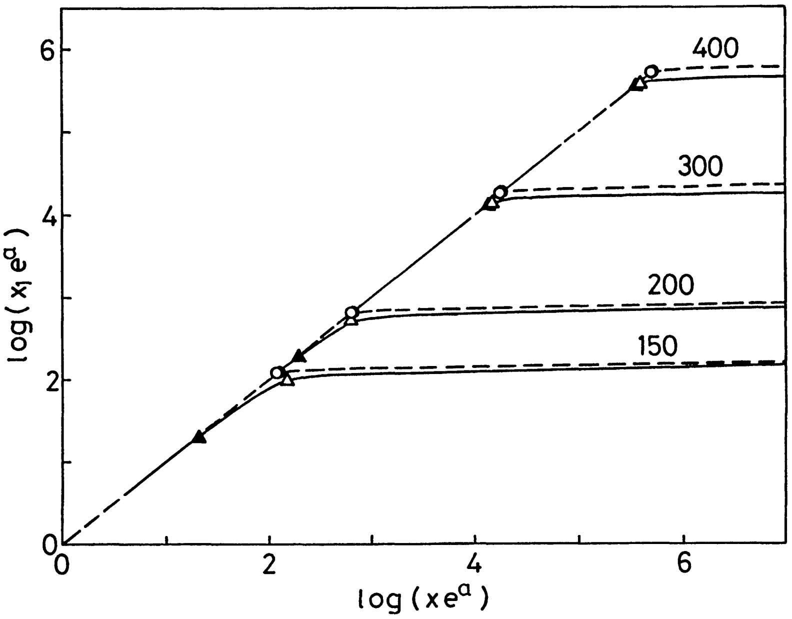

Fig. 2. Plots of scaled monomer concentrations against scaled total concentrations, calculated from Eqs. 1 (solid lines) and 6 (dashed lines) for I=60 at different Γ values. The hollow symbols ○ and △ show the cmc values defined by Eq. 9 and the filled symbols ● and ▲ show those defined by x_1/x=0.95.

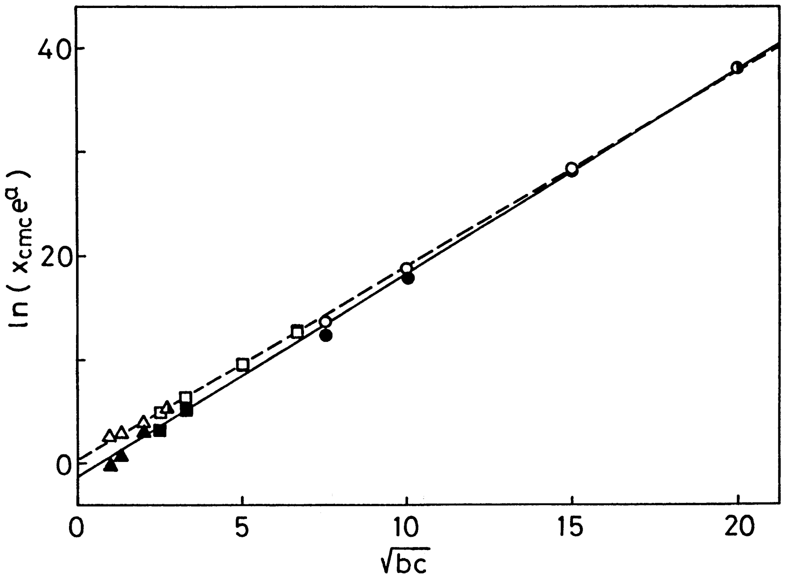

Fig. 3. Plots of scaled cmc values against the square root of the product bc for Eq. 1, calculated from the definitions of Eq. 9 (hollow symbols) and $x_1/x=0.95$ (filled symbols) at different I values: ○ and ●; I=20, □ and ■; I=60, △ and ■; I=150. The dashed line is fitted to the hollow symbols and the solid line is fitted to the filled symbols.

become too small. From Eq. 12 we can see that the cmc value is controlled mainly by term a viz., interactions between alkyl groups and water, and further by terms b and c, viz., interactions between head groups at the micellar surface. The definition of cmc by Ruckenstein and Nagarajan,[8] viz., $d^2\Delta G_i^\circ/di^2=0$, yielded too small cmc values (data not shown).

In conclusion, the Warr and White theory (Eq. 6) is simple and useful to understand the predictions from the Tanford theory (Eq. 1). In Eq. 1 as well as in Eq. 6, the micelle size parameter I is a good measure of n_w, and the cmc value is empirically given by Eq. 12. These results are useful to fit Eqs. 1 and 6 to experimental data of cmc and n_w.[10] The values of n_w and x_1 predicted by Eq. 1 are significantly different from those predicted by Eq. 6. This result means that the physical meanings of the coefficients a, b, and c in Eq. 1 are different from, though similar to, those in Eq. 6. Therefore Eq. 6 is not a very good approximation of Eq. 1. The definition of cmc by Eq. 9 gives reasonable cmc values for both Eqs. 1 and 6.

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