A Correction Factor for Electrostatic Free Energy in Micelle Formation

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It is well known that the critical micelle concentration (CMC) of a surfactant changes markedly with the concentration of counter-ions, c_i. There is in general a linear relation between log CMC and log c_i.[1-5] However, the log-log relation which we have obtained for straight-chain sodium decylbenzene sulfonate (SDBS) over a wide range of counter-ion concentrations is discrepant from the linear relation.*[1] The present paper will discuss a correction factor for electrostatic free energy in micelle formation based on the dependence of CMC on the concentration of counter-ions.

Figure 1 shows the relation between log CMC and log c_i for SDBS.*[2] The curves I and II are, respectively, the best-fitting straight and quadratic lines for the observed values in the sense of least squares. These two curves are written in the following forms:

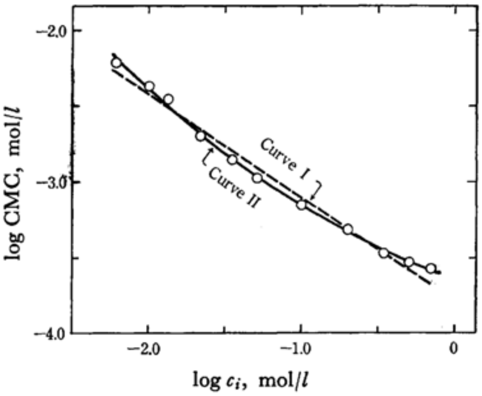

Fig. 1. The relation between log CMC and log c_i for SDBS at 25°C. The CMC values were taken from the sharp breaks in the solubilization curves for an oil-soluble dye, Yellow-OB, the method being described in previous papers.[7,8]

For the curve I,

$$\log \mathrm{CMC} = A + B \log c_i \tag{1}$$

$$A = -3.77, \text{ and } B = -0.67$$

For the curve II,

$$\log \mathrm{CMC} = A' + B' \log c_i + C' (\log c_i)^2 \tag{2}$$

$$A' = -3.66,\ B' = -0.40, \text{ and } C' = 0.12$$

Comparing the curves I and II, we may take the latter curve as the log CMC *vs.* log c_i relation for SDBS, since the curve II may be seen to be more fitting to the values experimentally determined than the curve I.

The micelle formation of ionic surfactants is generally governed by two energies: the cohesive energy among the hydrocarbon chains and the repulsive energy among the charged groups.[5,9,10] Thus, the CMC is expressed as:

$$\boldsymbol{k}T \ln \mathrm{CMC} = \Delta G_{\mathrm{HC}} + \lambda \varepsilon \psi_0 + K \tag{3}$$

or:

$$\log \mathrm{CMC} = (0.434/\boldsymbol{k}T)(\Delta G_{\mathrm{HC}} + \lambda \varepsilon \psi_0 + K) \tag{4}$$

where ΔG_{HC} is the free energy change in the hydrocarbon part by micelle formation; ψ_0, the surface potential of the micelle; $\boldsymbol{k}$, the Boltzmann constant; T, the absolute temperature; ε, the elementary charge, and K, the constant which appears when the CMC value is expressed in moles per liter. The λ in Eq. (3) is the correction factor for the electrostatic free energy; that is, $\lambda\varepsilon\psi_0$ is the effective electrical energy.[7] If we assume a charged flat surface for the micelle, the surface potential of the micelle and the concentration of counter-ions are related by the Gouy-Chapman equation[11]:

$$\begin{aligned} \varepsilon\psi_0/2\boldsymbol{k}T &= \sinh^{-1}\Theta c_i^{-1/2} \\ &= \ln\{\Theta c_i^{-1/2} + [1 + (\Theta c_i^{-1/2})^2]^{1/2}\} \end{aligned} \tag{5}$$

$$\Theta = (1000\pi\sigma^2/2\boldsymbol{N}_{\mathrm{A}}D\boldsymbol{k}T)^{1/2} \tag{6}$$

where σ is the charge density; $\boldsymbol{N}_{\mathrm{A}}$, the Avogadro number, and D, the dielectric constant. The

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*[1] Such a deviation from the linear log-log relation has also been reported by Mysels.[6]

[1] M. E. Hobbs, *J. Phys. Chem.*, **55**, 675 (1951).

[2] H. Lange, *Kolloid-Z.*, **121**, 66 (1951).

[3] K. Shinoda, *J. Phys. Chem.*, **59**, 432 (1955).

[4] M. J. Schick and F. M. Fowkes, *ibid.*, **61**, 1062 (1957).

[5] K. Shinoda *et al.*, "Colloidal Surfactants," Academic Press, New York, N. Y. (1963).

[6] E. K. Mysels and K. J. Mysels, *J. Colloid Sci.*, **20**, 315 (1965).

*[2] The SDBS was prepared by the sulfonation of pure decylbenzene; it was neutralized with sodium hydroxide. The sample was purified by removing the unreacted material and inorganic salt.

[7] F. Tokiwa and K. Ohki, *J. Colloid Interface Sci.*, **23**, 456 (1967).

[8] F. Tokiwa, This Bulletin, **36**, 222 (1963).

[9] M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, **69**, 3718 (1965).

[10] K. Shinoda, This Bulletin, **26**, 101 (1953).

[11] E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Co., New York, N. Y. (1948).

quantity of $(\Theta c_i^{-1/2})^2$ is much greater than unity, as will be shown later; therefore, Eq. (5) may be reduced to:

$$\varepsilon\psi_0/2\boldsymbol{k}T \simeq \ln 2\Theta c_i^{-1/2} = 2.30(\log 2\Theta - \tfrac{1}{2}\log c_i) \quad (7)$$

or:

$$\log c_i \simeq 2\log 2\Theta - (0.434/\boldsymbol{k}T)\varepsilon\psi_0 \quad (8)$$

By inserting Eq. (8) into Eq. (2) and comparing Eq. (2) with Eq. (4), we obtain the relation:

$$\lambda = C'(0.434/\boldsymbol{k}T)\varepsilon\psi_0 - (B' + 4C'\log 2\Theta) \quad (9)$$

The λ in Eq. (3) or (4) is thus a linear function of ψ_0, as may be seen in Eq. (9). The value of λ can be calculated in terms of Eq. (9) when B', C', and Θ are known. The B' and C' constants have already been given in Eq. (2). The value of Θ is estimated to be 2.26 $(\text{mol}/l)^{1/2}$ from Eq. (6) by assuming a reasonable value of 8.0×10^4 esu/cm^2 for σ. The area of the micellar surface in cm^2/molecule, S, is assumed to be approximately 6.0×10^{-15},[12] which gives the above σ value, since $\sigma=\varepsilon/S$.

Figure 2 shows the λ *vs.* ψ_0 plots, ψ_0 being calculated in terms of Eq. (7). The value of λ is not constant, but increases with an increasing ψ_0 value. A similar result has been obtained for a nonionic-cationic surfactant, dimethyldodecylamide oxide (DDAO), which is also shown in Fig. 2.[7] Figure 2 suggests that the extent of interaction among the charged heads changes with the surface potential of the micelle. The difference in the λ *vs.* ψ_0 plots between SDBS and DDAO may be attributed to different ways of interaction among the charged heads. Further, the molecular structure of these surfactants probably has some relation with the interaction.

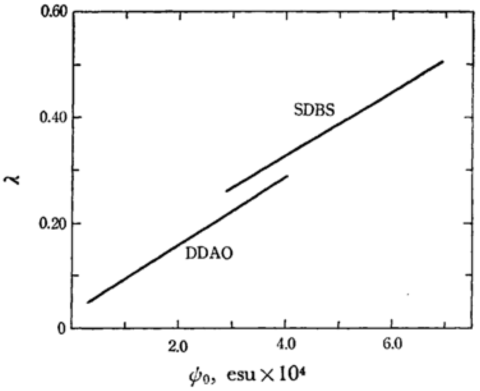

Fig. 2. The values of λ plotted against ψ_0. The plots for dimethyldodecylamine oxide is also shown for comparison.[7]

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12) F. van Voorst Vader, *Trans. Faraday Soc.*, **56**, 1067 (1960).