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Ionic Equilibria in Micellar Solutions

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Synopsis. Ionic equilibria in micellar solutions are discussed on the basis of micelle-monomer equilibrium, mass-conservation, and electroneutrality. The present treatment gives a larger degree of counterion dissociation from micelles than ever estimated. Another conclusion is a decreasing concentration of monomeric surface-active ion as micellar concentration increases.

Since Botré *et al.* firstly applied the membrane potential measurement to elucidate a degree of dissociation of counterion from micelles,(1) many investigators have followed the same kind of trials by using either ion-exchange membrane or pNa glass electrode.(2–5) As a starting point of discussion, Eq. (1) has been assumed,

$$a = \gamma(C_0 + \alpha n C_m) \qquad (1)$$

where a is the activity of counterion, γ activity coefficient, α a degree of counterion dissociation from micelle, n aggregation number of a micelle and C_m a micellar concentration. This expression is based on "*formal separation*"(1) of counterions originated from micelles and those from free surfactant ions. However no one can make this distinguishment *a priori.*

Alternatively, we express, as an approximation, the pseudo-phase model for a 1 : 1 type ionic surfactant forming a micellar solution in the absence of extraneous electrolyte,

$$C_c C_s f_\pm^2 = (C_0 f_0)^2 \qquad (2)$$

where f_0 and $f_\pm$ are the activity coefficients of surfactant at cmc and at any arbitrary concentration above cmc, C_c and C_s are the concentrations of, respectively, counterion and surface-active ion in equilibrium with micelles. Eq. (2) is considered to hold to a good approximation, even when a more general mass action law model is taken into account. Furthermore one obtains Eq. (3) as a consequence of mass balance,

$$C = C_s + nC_m \qquad (3)$$

where C is the total (analytical) concentration of the surfactant. Electroneutrality also requires the following relation.

$$C_c = C_s + \alpha n C_m \qquad (4)$$

Combing Eq. (3) with Eq. (4), one has

$$C_c = C_s + \alpha(C - C_s) \qquad (5)$$

or introducing Eq. (2), one obtains

$$C_c = (C_0^2/C_c)(f_0/f_\pm)^2 + \alpha[C - (C_0^2/C_c)(f_0/f_\pm)^2] \qquad (6)$$

Note that Eq. (1) can be reproduced only if C_s is replaced by C_0, or at the limit $C \to C_0$.

Rearrangement of Eq. (6) gives

$$C_c - (C_0^2/C_c)(f_0/f_\pm)^2 = \alpha[C - (C_0^2/C_c)(f_0/f_\pm)^2] \qquad (7)$$

With the knowledge of C, C_c and the activity coefficients, α can be calculated. In order to do so, the potentiometry of micellar solution is very useful. Such potentiometry is schematically shown in Fig. 1, where an electronic potential, E motivated from the counterion activity is plotted against log C. Tracing $C \to B \to A \to C_c$, one obtains C_c at a total concentration C. It is rather difficult to estimate the ratio of the activity coefficients in micellar solution. In the present treatment as well as any other theories using a parameter α, all the effects arising from micelles are included in the parameter, and the coexisting coions and counterions (unbound) are considered to behave as if they were in a solution of the same concentration. This idea is identical with so-called additivity rule well accepted in the field of polyelectrolyte solutions.(6) Therefore we

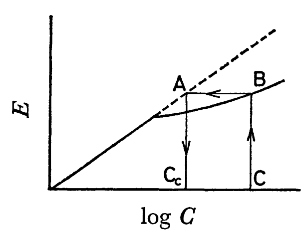

Fig. 1. A schematic representation of potential E *vs.* log C profile.

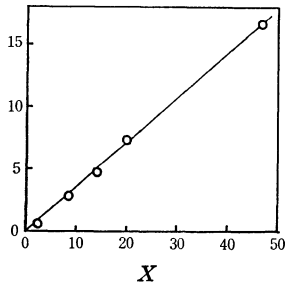

Fig. 2. Y *vs.* X plot. See the text for detail. The original data are already published by us.(5)

TABLE 1. THE DEGREE OF COUNTERION DISSOCIATION OF SODIUM DODECYLSULFATE

Author	Degree of dissociation α previous	Degree of dissociation α present	Ref.
Botré *et al.* (1959)	0.16		1
Shedlovsky *et al.* (1963)	0.22	0.32	2
Satake *et al.* (1969)	0.25	0.40	4
Shirahama (1972)	0.29	0.36	5
Birch and Clarke (1972)	0.25	0.30[a]	13

[a] They calculated the value of α on the basis of mass-action law, which also predicts a decrease of surface-active ion above cmc, as in the present treatment.

set $(f_0/f_\pm) \fallingdotseq 1$. In Fig. 2 $Y=C_c-(C_0^2/C_c)$ is plotted against $X=C-(C_0^2/C_c)$ for sodium dodecylsulfate. As is seen, a linear relation with the slope α is obtained. The published data are recalculated for sodium dodecylsulfate and shown in Table 1, from which it is clear that, in any case, the value of α is larger than those ever estimated by the assumption of Botre *et al.*, or Eq. (1). Another conclusion obtainable from Eq. (2) and an increasing counterion concentration even above cmc (experimental facts) is that the concentration of monomeric surface-active ion in equilibrium with micelles is decreasing as the total concentration increases. The same results have been derived in a little different manner in the works of Elworthy *et al*,[7] and of Birch and Clarke.[13] It is misleading that the monomer concentration in equilibrium with micelles is constant. Thus, the studies based on the incorrect assumption, such as conductivity,[8] surfactant-polymer interaction,[9] calorimetry,[10] solubilization,[11] and nmr[12] are required to be re-investigated.

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