April, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 971—974 (1981) 971

# A New Interpretation of the Fast Relaxation in a Micellar Solution

Tohru Inoue,* Ryoichi Tashiro, and Ryosuke Shimozawa
*Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814-01*

(Received June 16, 1980)

Some contradictions are pointed out in the kinetic parameters of the fast relaxation in a micellar solution deduced from the previously proposed kinetic models. A modification of the previous models is proposed. The proposed model eliminates the contradictions and leads to a consistent interpretation of the experimental results.

In many surfactant solutions there exist two well-separated relaxation processes associated with micelle-monomer equilibria. The fast process has been attributed to the perturbation of the exchange equilibrium of the monomer between micellar and bulk phases. Thus far, two different kinetic models for this process have been widely accepted for the analysis of the fast relaxation data; one of them has been proposed by Wyn-Jones *et al.*,[1)] and the other, by Aniansson and Wall.[2)] However, as will be shown later, it seems that neither of the two models successfully lead to a consistent kinetic parameter from the experimental data. This paper will show that a consistent interpretation becomes possible by combining the two basic concepts incorporated in the previous models.

## The Treatment of Wyn-Jones *et al.*

Wyn-Jones *et al.*[1b)] have treated the monomer exchange just as the adsorption-desorption phenomena of a monomer from the bulk phase to the micelles. They assumed that the rate of the entering of the monomer into the micelle is proportional to the product of the monomer concentration in the bulk phase and the area of the micellar surface uncovered by the surfactant molecules, and that the rate of the escape of the monomer from the micelle is proportional to the area of the micellar surface covered by the surfactant molecules. On these assumptions, the rate of the disappearance of the monomer from the bulk phase is given by:

$$-\frac{\mathrm{d}A_1}{\mathrm{d}t} = k_1A_1(1-\alpha)S - k_{-1}\alpha S, \tag{1}$$

where $A_1$ represents the monomer concentration in the bulk phase; $k_1$ and $k_{-1}$, the rate constants of the entering and escaping processes of the monomer; $S$, the sum of the surface area of micelles present in the solution, and $\alpha$, the fraction of the surface area covered by monomers. Letting $a_0$ be the molar area of the micellized monomer at the micellar surface, $S$ is given by the following expression:

$$S = \sum_i iA_i\frac{a_0}{\alpha} = \frac{a_0}{\alpha}(C_0-A_1), \tag{2}$$

where $A_i$ is the concentration of the micelle with the aggregation number $i$, and $C_0$, the total surfactant concentration. From Eqs. 1 and 2, the following expression is derived for the relaxation time:

$$\begin{aligned}\tau_1{}^{-1} &= k_1a_0\frac{1-\alpha}{\alpha}C_0 - k_{-1}a_0 \\ &= k_aC_0 - k_d, \end{aligned}\tag{3}$$

where $k_a$ and $k_d$ are the apparent rate constants for the entering and escaping processes of the monomer. Furthermore, from the equilibrium condition, $k_d/k_a = \bar{A}_1 \simeq \mathrm{CMC}$, Eq. 3 is rearranged to:

$$\tau_1{}^{-1} = k_d\frac{C_0-\mathrm{CMC}}{\mathrm{CMC}}. \tag{4}$$

Equation 4 well explains the experimental finding that $\tau_1^{-1}$ increases linearly with $C_0$. However, the experimental findings for various surfactant systems indicate that $\tau_1^{-1}$ has a positive intercept when the abscissa is taken as $(C_0-\mathrm{CMC})$.[3—9)] Thus, the Wyn-Jones model can only partly explain the experimental results.

## The Treatment of Aniansson and Wall

Aniansson and Wall[2)] have explicitly taken account of the distribution of the aggregation number, $s$, for micelles. They assumed that the association rate of the monomer with $s$-mer is proportional to the product of the concentrations of the monomer and $s$-mer, and that the dissociation rate of the monomer from $s$-mer is proportional to the concentration of $s$-mer. Thus, the rate of flow into the aggregation number, $s$, is expressed by:

$$\frac{\mathrm{d}A_s}{\mathrm{d}t} = k_s^+A_1A_{s-1} - k_s^-A_s - (k_{s+1}^+A_1A_s - k_{s+1}^-A_{s+1}), \tag{5}$$

where $A_1$ and $A_s$ represent the concentrations of the monomer and $s$-mer; $k_s^+$, the rate constant of the formation of $s$-mer from the monomer and $(s-1)$-mer, and $k_s^-$, the rate constant of the degradation of $s$-mer into $(s-1)$-mer. Introducing the relative deviation from the equilibrium concentration, $\xi_s = (A_s-\bar{A}_s)/\bar{A}_s$, and assuming that the distribution curve of the aggregation number is continuous, Eq. 5 is transformed to Eq. 6, which is an analogue of the one-dimensional diffusion equation:

$$\bar{A}_s\frac{\partial\xi(s,t)}{\partial t} = \frac{\partial}{\partial s}k_s^-\bar{A}_s\left[\frac{\partial\xi(s,t)}{\partial s} - \xi_1\right]. \tag{6}$$

Solving Eq. 6 under appropriate boundary conditions and assumptions, the following expression for the relaxation time is finally obtained:

$$\tau_1{}^{-1} = \frac{k^-}{\sigma^2} + \frac{k^-}{n}\,\frac{C_0-\bar{A}_1}{\bar{A}_1}. \tag{7}$$

Furthermore, $k^+\bar{A}_1\bar{A}_{s-1} = k^-\bar{A}_s$, the equilibrium condition, leads to:

$$k^+ \simeq k^-/\bar{A}_1 \simeq k^-/\mathrm{CMC}. \tag{8}$$

In Eqs. 7 and 8, $k^-$ and $k^+$ are the dissociation and association rate constants, which are assumed to be independent of $s$ for proper micelles, $\sigma$, the parameter characterizing the width of the distribution curve of a micellar size, and $n$, the average aggregation number.

According to Eq. 7, $\tau_1^{-1}$ increases linearly with $C_0$ and has a definite value at the CMC, which corresponds to $k^-/\sigma^2$. This agrees with experimental findings on the behavior of $\tau_1^{-1}$ with $C_0$. In Table 1 the values of the kinetic parameters evaluated from Eqs. 7 and 8 are summarized for several surfactant systems. All the $k^-$ and $k^+$ values are those reported by Hoffmann *et al.*[4,5,8] The $E_A^\ddagger$'s are the apparent activation energies for the association process, estimated from the temperature dependence of $k^+$. A precise examination of the kinetic parameters in Table 1 will be given in the subsequent descriptions, (i), (ii), and (iii).

TABLE 1. VALUES OF THE KINETIC PARAMETERS EVALUATED FROM ANIANSSON AND WALL THEORY

| Surfactant | Temp/°C | $k^{-1}$/s$^{-1}$ | $k^+$/mol$^{-1}$ dm$^3$ s$^{-1}$ | $E_A{}^+$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| DPI[a)] | 25 | $1.6\times10^7$ | $3.0\times10^9$ | 38 |
| TPCl[a)] | 15 | $9.7\times10^6$ | $2.4\times10^9$ | 30 |
| TPBr[a)] | 25 | $6.3\times10^6$ | $2.5\times10^9$ | 45 |
| HPCl[a)] | 15 | $4.4\times10^5$ | $4.6\times10^8$ | 31 |
| HPBr[a)] | 25 | $3.3\times10^5$ | $5.5\times10^8$ | 29 |
| NaDS[b)] | 25 | $1.0\times10^7$ | $1.2\times10^9$ | |
| NaTS[b)] | 25 | $9.6\times10^5$ | $4.7\times10^8$ | |
| NaHS[b)] | 30 | $6\times10^4$ | $1.3\times10^8$ | |
| $NiDS_2$[c)] | 25 | $3.9\times10^6$ | $1.6\times10^9$ | 44 |
| $CoDS_2$[c)] | 25 | $2.6\times10^6$ | $1.1\times10^9$ | 49 |

DP=dodecylpyridinium, TP=tetradecylpyridinium, HP=hexadecylpyridinium, DS=dodecylsulfate, TS=tetradecyl sulfate, HS=hexadecyl sulfate.
The $k^-$ and $k^+$ are those reported by Hoffmann *et al.* a) Ref. 4. b) Ref. 5. c) Ref. 8.

(i) According to Debye,[10] the rate constant to be expected for encounter-controlled ionic reaction is given by:

$$k = \frac{4\pi N_A z_A z_B e^2}{1000\varepsilon kT}\,\frac{D_A+D_B}{\exp\,(z_A z_B e^2/\varepsilon rkT)-1}, \tag{9}$$

where $D$ and $z$ are the diffusion coefficient and the electrovalency of the reacting species respectively, $r$ is the center-to-center distance at which two reactants enter into the reaction, $\varepsilon$ is the dielectric constant of the medium, and the other symbols have their usual meanings.

Applying Eq. 9 to the present association reaction between a single surfactant ion and a micelle in an aqueous solution, the rate constant is roughly estimated to be $3\times10^9$—$1\times10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 25 °C using the appropriate numerical values; the diffusion coefficient of the monomer$\approx1\times10^{-5}$ cm$^2$ s$^{-1}$; the diffusion coefficient of the micelle is negligibly small compared with that of the monomer; the micelle radius is 15—20 Å; the micelle charge is ±10—20;[11] the radius of the spherical monomer is 5 Å; hence, $r\approx20$—25 Å and $z_A z_B\approx+10$—20. Thus, the $k^+$ values in Table 1 imply that the association of the monomer with the micelle is controlled by the diffusion of the monomer to the micelle.

(ii) The apparent activation energy expected for a diffusion-controlled ionic reaction is estimated from Eq. 10:

$$E_A = -RT^2\frac{\mathrm{d}\ln\eta}{\mathrm{d}T} + RT\Big\{LT+\frac{z_A z_B e^2}{\varepsilon rkT}(1-LT) \times[1-\exp\,(-z_A z_B e^2/\varepsilon rkT)]^{-1}\Big\}. \tag{10}$$

Equation 10 is derived from Eq. 9, taking into account the fact that the diffusion coefficient is proportional to $kT/\eta$, where $\eta$ is the viscosity of the medium, and that $\varepsilon=\varepsilon_0\exp(-LT)$, where $L$ is a constant specific to the medium. In the case of an aqueous solution at 25 °C, $-RT^2\mathrm{d}\ln\eta/\mathrm{d}T\simeq17$ kJ mol$^{-1}$ and $LT\simeq1.4$.[12] By substituting these numerical values into Eq. 10, one obtains $E_A$ values of 13—17 kJ mol$^{-1}$ for the diffusion-controlled association of the monomer with the micelle. The experimentally obtained activation energies listed in Table 1 are obviously too large to be attributed to a diffusion-controlled process.

(iii) It is expected from the conductance data that the diffusion coefficient of a surfactant ion increases by a factor of approximately 1.1 per methylene unit decrease in the chain.[13] On the other hand, as is shown in Table 1, the $k^+$ value for the homologous surfactant series is increased by a factor of about three to four per methylene unit decrease. Although the larger ionic strength due to the larger CMC of the shorter chain surfactant may cause a certain enhancement of the association rate, since the two reactants have the same sign of the charge, the variation of $k^+$ in Table 1 with alkyl chain length seems to be much larger than that expected for a diffusion-controlled association reaction.

The facts described in (ii) and (iii) are not in accordance with the order of the magnitude of $k^+$ estimated by means of the Aniansson and Wall theory. In order to obtain self-consistent rate constants and activation energies, an alternative approach will be proposed in the next section.

## Alternative Treatment

Aniansson and Wall have considered that the dissociation rate is proportional to the micelle concentration, and that the association rate is proportional to the product of the monomer concentration and the micelle concentration. However, as assumed by Wyn-Jones *et al.*,[1a] it may be reasonable to regard the dissociation rate of the monomer as proportional to the concentration of the surfactant ion which can dissociate from the micelle, *i.e.*, the product of the concentration of the micelle and the aggregation number. Also, the association rate may be regarded as proportional to the product of the concentration of the monomer and the concentration of the site in the micellar phase into which the surfactant ion can enter. The concentration of the vacant site on the micellar surface may be expressed by a manner analogous to the treatment of Wyn-Jones *et al.* Let $a_0$ be the area occupied by a monomer on the micellar surface; $\alpha$, the fraction of the surface area occupied by monomers, and $m$, the aggregation number. Then, the vacant area on the surface of a micelle is expressed by $m(1-\alpha)/\alpha \cdot a_0$. We assume here that the number of vacant sites per micelle is given by dividing the vacant area by $a_0$, *i.e.*, $m(1-\alpha)/\alpha$. Then, the concentration of the vacant site is expressed by $m(1-\alpha)/\alpha \cdot A_m$ for the micelle with the aggregation number $m$. Thus, the following relations are obtained:

$$\text{association rate} = k_{\mathrm{a},m+1}A_1 m\frac{1-\alpha}{\alpha}A_m = mk'_{\mathrm{a},m+1}A_1A_m \qquad (11)$$

$$\text{dissociation rate} = mk_{\mathrm{d},m}A_m, \qquad (12)$$

where $k_{\mathrm{a},m+1}$ and $k_{\mathrm{d},m}$ are the elementary rate constants for the monomer to enter into, and to escape from, the micelle with the aggregation number $m$, and where $k'_{\mathrm{a},m+1}=(1-\alpha)/\alpha \cdot k_{\mathrm{a},m+1}$. Taking account of the probable dependence of $k'_{\mathrm{a},m+1}$ and $k_{\mathrm{d},m}$ on $m$, and the size distribution of the micelle, the rate expression for the monomer-concentration change in the bulk phase induced by the exchange process is given by:

$$\frac{\mathrm{d}A_1}{\mathrm{d}t} = \sum_{m'}^{m''}[mk_{\mathrm{d},m}A_m-(m-1)k'_{\mathrm{a},m}A_1A_{m-1}], \qquad (13)$$

where the aggregates with the aggregation numbers $m' \leq m \leq m''$ are regarded as micelles and where the concentrations of the oligomers are neglected. Then, according to the usual procedure of relaxation kinetics, one obtains:

$$\frac{\mathrm{d}\Delta A_1}{\mathrm{d}t} = \sum_{m'}^{m''}mk_{\mathrm{d},m}\left(\Delta A_m - \frac{\bar{A}_m}{\bar{A}_{m-1}}\Delta A_{m-1} - \frac{\bar{A}_m}{\bar{A}_1}\Delta A_1\right), \qquad (14)$$

where $\Delta A_1 = A_1 - \bar{A}_1$, *etc.*; the bar indicates the concentration at the equilibrium for the fast relaxation process, *i.e.*, pseudo-equilibrium. If $k_{\mathrm{d},m}$ is assumed to be independent of $m$ in the region of $m' \leq m \leq m''$ and is replaced by $k_\mathrm{d}$, Eq. 14 leads to:

$$\frac{\mathrm{d}\Delta A_1}{\mathrm{d}t} = k_\mathrm{d}\sum_{m'}^{m''}m\left(\Delta A_m - \frac{\bar{A}_m}{\bar{A}_{m-1}}\Delta A_{m-1}\right) - \frac{k_\mathrm{d}}{\bar{A}_1}\sum_{m'}^{m''}m\bar{A}_m\Delta A_1. \qquad (15)$$

If we choose the $m'$—$m''$ range properly, the first term on the right-hand side of Eq. 15 is transformed to:

$$k_\mathrm{d}\sum_{m'}^{m''}m\left(\Delta A_m - \frac{\bar{A}_m}{\bar{A}_{m-1}}\Delta A_{m-1}\right) \simeq k_\mathrm{d}\sum_{m'}^{m''}m\Delta A_m\left(1 - \frac{\bar{A}_{m+1}}{\bar{A}_m}\right),$$

Assuming the distribution of the aggregates to be Gaussian, *i.e.*,

$$\bar{A}_m = \bar{A}_{\tilde{m}}\mathrm{e}^{-(m-\tilde{m})^2/2\sigma^2},$$

where $\tilde{m}$ represents the average aggregation number at the pseudo-equilibrium, and $\sigma^2$, the variance of the distribution curve, we obtain:

$$\frac{\bar{A}_{m+1}}{\bar{A}_m} = \mathrm{e}^{-1/2\sigma^2}\mathrm{e}^{-(m-\tilde{m})/\sigma^2} \simeq 1 - \frac{m-\tilde{m}}{\sigma^2}. \qquad (16)$$

Equation 16 is obtained by expanding the exponential terms and neglecting the higher terms, since $\sigma \approx 10$, and $|m-\tilde{m}|$ is usually about 20 at most. Thus,

$$\sum_{m'}^{m''}m\left(1 - \frac{\bar{A}_{m+1}}{\bar{A}_m}\right)\Delta A_m \simeq \frac{1}{\sigma^2}\sum_{m'}^{m''}m\left(m-\tilde{m}\right)\Delta A_m = \frac{1}{\sigma^2}\sum_{m'}^{m''}\left[\left(m-\tilde{m}\right)^2 - \tilde{m}^2 + m\tilde{m}\right]\Delta A_m. \qquad (17)$$

In Eq. 17, $(m-\tilde{m})^2$ can be neglected compared with $m\tilde{m}$, and the $\tilde{m}^2$ term can be dropped out since $\sum_{m'}^{m''}\Delta A_m = 0$ under the assumption that the distribution curve undergoes a parallel shift during the fast relaxation process. Then, under conditions of mass balance, $\Delta A_1 + \sum_{m'}^{m''}m\Delta A_m \simeq 0$, the following relation is obtained from Eq. 17:

$$\text{First term of Eq. 15} = -\frac{\tilde{m}k_\mathrm{d}}{\sigma^2}\Delta A_1. \qquad (18)$$

Furthermore, the total concentration of the surfactant is expressed by:

$$C_0 \simeq \bar{A}_1 + \sum_{m'}^{m''}m\bar{A}_m$$

since the concentrations of the oligomers are much smaller than those of the monomer and the micelle. Therefore,

$$\text{Second term of Eq. 15} = -k_\mathrm{d}\frac{C_0-\bar{A}_1}{\bar{A}_1}\Delta A_1. \qquad (19)$$

From Eqs. 15, 18, and 19, one obtains:

$$\frac{\mathrm{d}\Delta A_1}{\mathrm{d}t} = -\left(\frac{\tilde{m}k_\mathrm{d}}{\sigma^2} + k_\mathrm{d}\frac{C_0-\bar{A}_1}{\bar{A}_1}\right)\Delta A_1. \qquad (20)$$

Thus, the reciprocal of the fast relaxation time is expressed by:

$$\tau_1^{-1} = \frac{\tilde{m}k_\mathrm{d}}{\sigma^2} + k_\mathrm{d}\frac{C_0-\bar{A}_1}{\bar{A}_1}, \qquad (21)$$

which becomes equivalent to the expression of Aniansson and Wall (Eq. 7) when $k_\mathrm{d}$ in Eq. 21 is read as $k^-/n$. According to Eq. 21, the dissociation rate constant of the monomer from the micelle, $k_\mathrm{d}$, is obtained from the slope of the $\tau_1^{-1}$ *vs.* $C_0$ plot. Here, $\bar{A}_1$ is the monomer concentration at the pseudo-equilibrium, but it may be practically assumed to be the CMC since the relaxation measurements are carried out under the condition of a small perturbation.

The equilibrium condition gives:

$$mk_\mathrm{d}\bar{A}_m = (m-1)\,k'_\mathrm{a}\bar{A}_1\bar{A}_{m-1}.$$

Since $\bar{A}_m \simeq \bar{A}_{m-1}$ for a broad distribution ($\sigma \approx 10$) and $m \simeq m-1$ for a usual, proper micelle, one obtains:

$$k'_\mathrm{a} \simeq k_\mathrm{d}/\bar{A}_1 \text{ and } k_\mathrm{a} = \frac{\alpha}{1-\alpha}k'_\mathrm{a}. \qquad (22)$$

In the above expressions, $k'_\mathrm{a}$ and $k_\mathrm{a}$ are assumed to be independent of the aggregation number in the region of $m' \leq m \leq m''$. This assumption necessarily implies that $\alpha$, the fraction of the occupied surface, is virtually invariant with $m$. Thus, from Eq. 22, $k_\mathrm{a}$, the elementary association rate constant, can be determined if $\alpha$ is known. The precise value of $\alpha$ is not available at the present time, but an approximate estimation of it is possible. According to Tanford's calculation[14] based on geometrial considerations, $S/m$ is 80—70 Å$^2$ in the range of $50 \leq m \leq 80$ for a globular micelle formed from the surfactant molecule with 12 carbon atoms. There-

TABLE 2. VALUES OF $k_d$ AND $k_a$ EVALUATED FROM Eqs. 21 AND 22

| Surfactant | Temp/°C | $k_d/\mathrm{s}^{-1}$ | $k_a/\mathrm{mol}^{-1}$ $\mathrm{dm}^3\ \mathrm{s}^{-1}$ |
|---|---|---|---|
| DPI | 25 | $2.5\times10^5$ | $2.0\times10^7$ |
| TPCl | 15 | $1.1\times10^5$ | $1.2\times10^7$ |
| TPBr | 25 | $7.8\times10^4$ | $1.3\times10^7$ |
| $\mathrm{TPC_3H_7SO_3}$a) | 15 | $9.6\times10^4$ | $1.4\times10^7$ |
| $\mathrm{TPC_4H_9SO_3}$a) | 15 | $4.4\times10^4$ | $8.6\times10^6$ |
| $\mathrm{TPC_5H_{11}SO_3}$a) | 15 | $2.0\times10^4$ | $6.0\times10^6$ |
| HPCl | 15 | $4.0\times10^3$ | $1.8\times10^6$ |
| HPBr | 25 | $3.3\times10^3$ | $2.4\times10^6$ |
| NaDS | 25 | $1.6\times10^5$ | $8.1\times10^6$ |
| NaTSb) | 25 | $1.2\times10^4$ | $2.5\times10^6$ |
| NaHS | 30 | $6\times10^2$ | $5.6\times10^5$ |
| $\mathrm{NiDS_2}$ | 25 | $4.0\times10^4$ | $6.9\times10^6$ |
| $\mathrm{CoDS_2}$ | 25 | $2.4\times10^4$ | $4.2\times10^6$ |

a) From the data in Ref. 6. b) From the data in Refs. 5 and 9.

fore, taking the value of 2—3 Å as a radius of the head group, $\alpha$ can be estimated to be 0.2—0.4.

Table 2 lists the $k_d$ and $k_a$ values evaluated from Eqs. 21 and 22 for several surfactant systems. For the evaluation of $k_a$, we adopted $\alpha=0.3$. Although the $k_a$ values have some uncertainty associated with $\alpha$, they may be reliable at least to the order of magnitude. When $\alpha$ is varied from 0.2 to 0.4, $k_a$ increases by a factor of 2.7.

As is shown in Table 2, the alternative treatment proposed in this work gives $k_a$ values of the order of $10^6$—$10^7$ $\mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{s}^{-1}$, smaller by about $10^2$ than the $k^+$ values deduced from the Aniansson-Wall model. This difference in rate constants results from the $m$ and $\alpha$ factors in Eq. 11 ($m\approx10^2$ and $\alpha\approx0.2$—$0.4$). These values of $k_a$ suggest the non-diffusion-controlled association reaction of a monomer with a micelle and are reasonably consistent with the facts described in (ii) and (iii) of the preceding section.

It is considered that the association proceeds *via* the activated state, which exists in the course of the incorporation of a monomer present at the micellar surface into the interior. This activated state probably consists of the hydrocarbon tail of a monomer being partly inserted into the micellar hydrocarbon core, just to the depth where further incorporation tends to be favored by the hydrophobic interaction. For the attainment of this state, a vacant space must be formed in the hydrocarbon core where the terminal group of a hydrocarbon tail can enter. Furthermore, it is necessary for the water molecules attached to the hydrocarbon tail of the entering monomer to be released. Thus, it is likely that the energies required for such processes contribute mainly to the activation energy for the association reaction.

## References

1) a) P. J. Sams, E. Wyn-Jones, and J. Rassing, *Chem. Phys. Lett.*, **13**, 233 (1972); b) J. Rassing, P. J. Sams, and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1247 (1974).

2) a) E. A. G. Aniansson and S. N. Wall, *J. Phys. Chem.*, **78**, 1024 (1974); b) E. A. G. Aniansson and S. N. Wall, *ibid.*, **79**, 857 (1975).

3) R. Folger, H. Hoffmann, and W. Ulbricht, *Ber. Bunsenges. Phys. Chem.*, **78**, 986 (1974).

4) H. Hoffmann, R. Nagel, G. Platz, and W. Ulbricht, *Colloid Polym. Sci.*, **254**, 812 (1976).

5) E. A. G. Aniansson, S. N. Wall, M. Almgren, H. Hoffmann, K. Kielmann, W. Ulbricht, R. Zana, J. Lang, and C. Tondre, *J. Phys. Chem.*, **80**, 905 (1976).

6) H. Hoffmann, H. Nüsslein, and W. Ulbricht, "Micellization, Solubilization, and Microemulsions," ed by K. L. Mittal, Plenum Press, New York (1977), Vol. 1, p. 263.

7) S.-K. Chan, U. Herrmann, W. Ostner, and M. Kahlweit, *Ber. Bunsenges. Phys. Chem.*, **81**, 396 (1977).

8) W. Baumüller, H. Hoffmann, W. Ulbricht, C. Tonder, and R. Zana, *J. Colloid Interface Sci.*, **64**, 418 (1978).

9) T. Inoue, Y. Shibuya, and R. Shimozawa, *J. Colloid Interface Sci.*, **65**, 370 (1978).

10) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

11) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York (1963), p. 16.

12) E. A. Moelwyn-Hughes, "The Chemical Statics and Kinetics of Solutions," Academic Press, New York (1971), Chaps. 5 and 7.

13) a) A. N. Campbell and R. Lakshminarayanan, *Can. J. Chem.*, **43**, 1729 (1965); b) J. S. Clunie, J. F. Goodmann, and P. C. Symons, *Trans. Faraday Soc.*, **63**, 754 (1967).

14) C. Tanford, *J. Phys. Chem.*, **76**, 3020 (1072).