Bull. Chem. Soc. Jpn., 62, 1446—1450 (1989) [Vol. 62, No. 5

Adsorption of 2-(Octylsulfinyl)ethanol at Ethanol-Water Mixture/Air Interface

Hidemi Iyota* and Kinsi Motomura†
Kagoshima Women's Jr. College, Murasakibaru, Kagoshima 890
†Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812
(Received November 11, 1988)

The surface tension of the solution of 2-(Octylsulfinyl)ethanol (OSE) in ethanol-water mixture was measured as a function of molality of OSE at constant composition of ethanol at 298.15 K under atmospheric pressure. The slope of surface tension vs. molality curve decreased with increasing composition. Two break points were observed on the curve: the break point at a low molality was attributed to the phase transition of the adsorbed film of OSE and the one at a high molality to the micelle formation of OSE. The surface excess numbers of moles per unit area of OSE and ethanol and their ratio were evaluated by applying the thermodynamic equations developed previously to the experimental results. It was clarified that the adsorbed film of OSE expels ethanol molecules from the surface region at a small composition of ethanol. The ratio of the excess number of molecules of ethanol per micelle particle to that of OSE was found to be similar to the corresponding ratio of the surface excess number of moles at the critical micelle concentration. This fact led us to the conclusion that the OSE molecules in the micelle behave similarly to those in the adsorbed film even in the mixed solvent.

The adsorption of surface active substances at various oil/water interfaces has been studied thermodynamically and the significant influence of solvent has been revealed in the previous papers.1,2) Furthermore, the thermodynamic treatment has been extended so as to be applicable to the adsorption of surfactant from mixed solvent.3) It is now necessary to examine the effect of the composition of mixed solvent on the interfacial behavior of surfactant molecules. Such examinations were rarely conducted by investigators.4—6) The present purpose is that the surface tension of the solution of 2-(octylsulfinyl)ethanol in ethanol–water mixture is measured as a function of the concentration of OSE and the composition of the mixture and analyzed thermodynamically.

Experimental

2-(Octylsulfinyl)ethanol was synthesized and purified by the method described in the previous paper.7) Its purity was checked by gas-liquid chromatography; no minimum was observed on the surface tension vs. concentration curve around the critical micelle concentration. Ethanol (Nakarai Chemicals Ltd., specially prepared reagent for spectroscopy) was dried by the refluxion over calcium oxide and then distilled. Water was triply distilled, the second and third steps being carried out from dilute alkaline permanganate solution.

Surface tension was measured by the drop volume technique8) at 298.15 K under atmospheric pressure. The error inherent in the surface tension measurement was less than 0.02 mN m^{-1} throughout this experiment. Temperature was regulated to a precision of 0.01 K by the use of thermister controller.

The surface tension γ of the solution of 2-(octylsulfinyl)ethanol (OSE) in ethanol-water mixture was measured as a function of molality of OSE, m, at a given mole fraction of ethanol, X, in the mixed solvent at 298.15 K under atmospheric pressure.

Results

Figures 1a and 1b show the γ vs. m curves at constant X. The γ value decreases steeply with increasing m and remains almost constant at concentrations above the critical micelle concentration (cmc) when X is smaller than about 0.05. Further, another break point is seen at a very small m value on γ vs. m curve, which is designated by the arrow on the curve in Fig. 1b. The m value at the break point and the cmc value increase as X increases. At larger mole fractions of ethanol, however, the slope of the γ vs. m curve

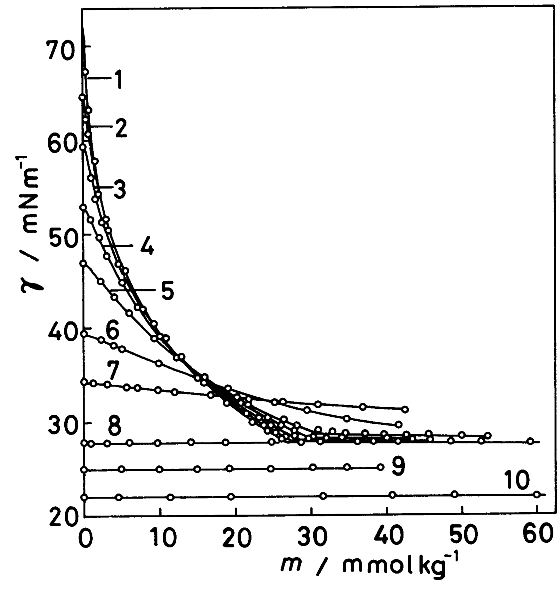

Fig. 1a. Surface tension vs. molality of OSE curves at constant mole fraction of ethanol at 298.15 K under atmospheric pressure: (1) X=0, (2) 0.0060, (3) 0.0130, (4) 0.0258, (5) 0.0439, (6) 0.0798, (7) 0.1253, (8) 0.2903, (9) 0.5694, (10) 1.

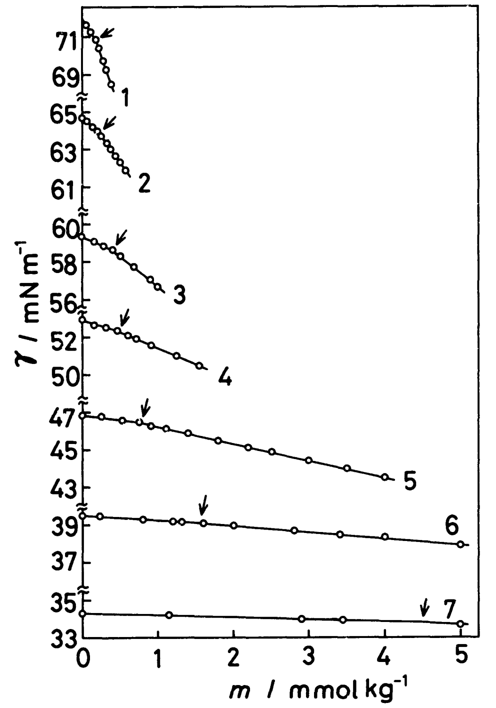

Fig. 1b. Surface tension vs. molality of OSE curves at constant mole fraction of ethanol at 298.15 K under atmospheric pressure: (1) X=0, (2) 0.0060, (3) 0.0130, (4) 0.0258, (5) 0.0439, (6) 0.0798, (7) 0.1253.

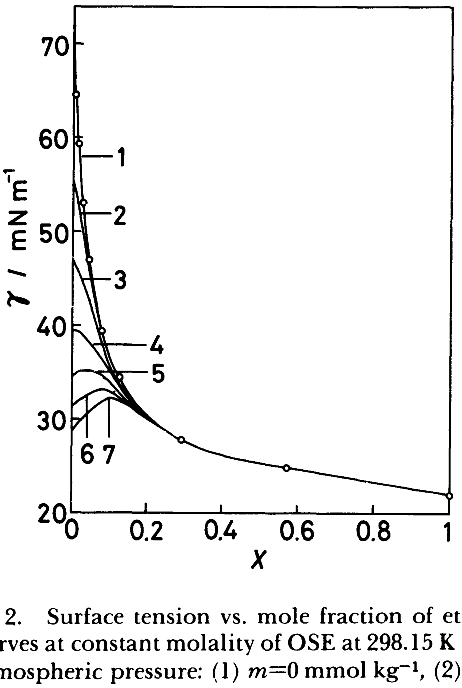

Fig. 2. Surface tension vs. mole fraction of ethanol curves at constant molality of OSE at 298.15 K under atmospheric pressure: (1) m=0 mmol kg^{-1}, (2) 2, (3) 5, (4) 10, (5) 15, (6) 20, (7) 25.

becomes gentle. It should be noticed that the γ value does not vary with m at compositions above X=ca. 0.3.

In order to examine the variation of surface tension with the composition of mixed solvent, the values of γ taken from Fig. 1a at constant m are plotted against X in Fig. 2. The γ value decreases monotonously with increasing X at low concentrations of OSE. At high concentrations of OSE, the γ vs. X curve has a distinct maximum at small X. However, all the curves approach each other above at X=ca. 0.3.

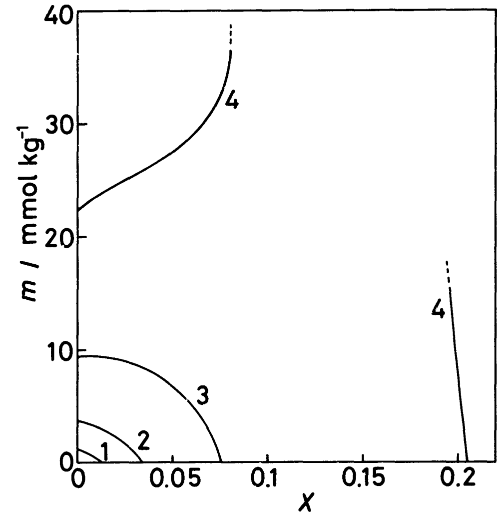

Fig. 3. Molality of OSE vs. mole fraction of ethanol curves at constant surface tension at 298.15 K under atmospheric pressure: (1) γ=60 m N m^{-1}, (2) 50, (3) 40, (4) 30.

In Fig. 3 shown is how the molality m changes with the composition X at constant surface tension. The value of m decreases with an increase in X at large γ, while the m vs. X curve has a maximum at small γ.

Discussion

Since the system under consideration consists of 2-(octylsulfinyl)ethanol, ethanol, water, and air, the information regarding the surface of the system is provided by applying the thermodynamic equations derived in the previous paper[3] to the above experimental results. Employing the molality of OSE m and the mole fraction of ethanol X as the independent variables at constant temperature T and pressure p, the fundamental equation is written in the form

$$d\gamma = -RT[(1-X)X]^{-1}[1+(\partial \ln f/\partial \ln X)_{T,p,m}]\Gamma_1^{H}dX - RTm^{-1}\Gamma_2^{H}dm, \quad (1)$$

where OSE is assumed to behave ideally at any X value and f is the activity coefficient of ethanol in the mixture. The interfacial density of ethanol Γ_1^H and that of OSE Γ_2^H are defined with respect to the dividing planes which satisfy the condition that the interfacial density of air Γ_a^H and the sum of those of ethanol and water $\Gamma_1^H+\Gamma_w^H$ are zero simultaneously. Now, the following equations derived from Eq. 1 enable us to evaluate the thermodynamic quantities $\Gamma_1^H(=-\Gamma_w^H)$, Γ_2^H, and Γ_1^H/Γ_2^H from the experimental results:

$$-(\partial\gamma/\partial m)_{T,p,X} = RTm^{-1}\Gamma_2^H, \tag{2}$$

$$-(\partial\gamma/\partial X)_{T,p,m} = RT[(1-X)X]^{-1}[1+(\partial\ln f/\partial\ln X)_{T,p,m}]\Gamma_1^H \tag{3}$$

and

$$-(\partial m/\partial X)_{T,p,\gamma} = m[(1-X)X]^{-1}[1+(\partial\ln f/\partial\ln X)_{T,p,m}]\Gamma_1^H/\Gamma_2^H. \tag{4}$$

First, the numerical values of Γ_2^H were estimated by applying Eq. 2 to the curves in Figs. 1a and 1b and plotted against m at constant X in Figs. 4a and 4b. It is seen from Fig. 4a that the Γ_2^H value increases steeply with m and then approaches that of saturation adsorption at the cmc indicated by the closed circle when X is small. With increasing X, the Γ_2^H value decreases and becomes zero at a composition above X=ca. 0.3. Therefore, it can be said that the enhancement of ethanol in the mixed solvent diminishes the adsorption of OSE. Now, let us focus our attention on the variation of Γ_2^H with m in the dilute concentration region depicted in Fig. 4b. The Γ_2^H value changes discontinuously at the concentration where the γ vs. m curve breaks. This discontinuous change in the Γ_2^H vs. m curve is attributed to the phase transition of the adsorbed film between a gaseous and an expanded state which has been observed in the previous papers.[8-10] It is also seen that the concentration at which the phase transition takes place increases with increasing X and eventually vanishes at a

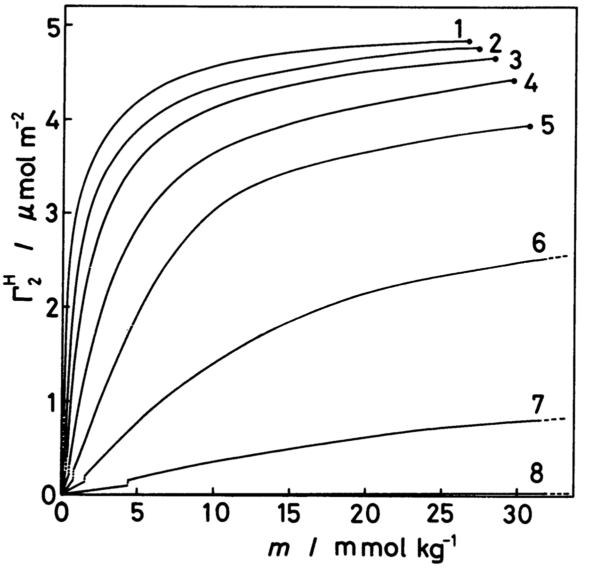

Fig. 4a. Interfacial density of OSE vs. molality of OSE curves at constant mole fraction of ethanol at 298.15 K under atmospheric pressure: (1) X=0, (2) 0.0060, (3) 0.0130, (4) 0.0258, (5) 0.0439, (6) 0.0798, (7) 0.1253, (8) 0.2903.

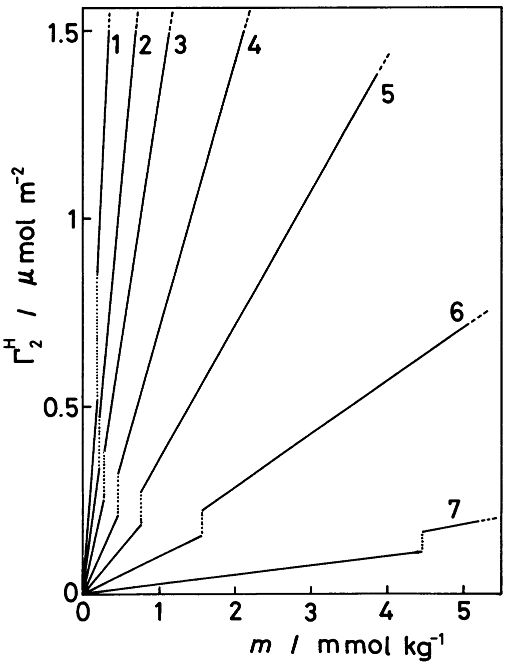

Fig. 4b. Interfacial density of OSE vs. molality of OSE curves at constant mole fraction of ethanol at 298.15 K under atmospheric pressure: (1) X=0, (2) 0.0060, (3) 0.0130, (4) 0.0258, (5) 0.0439, (6) 0.0798, (7) 0.1253.

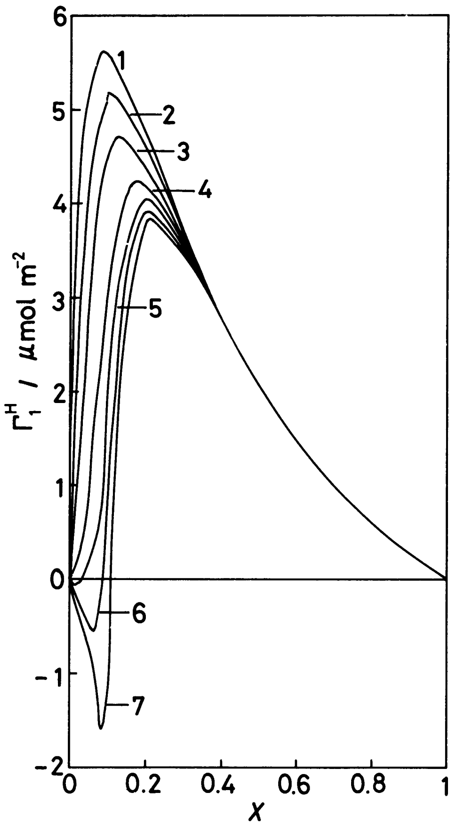

Fig. 5. Interfacial density of ethanol vs. mole fraction of ethanol curves at constant molality of OSE at 298.15 K under atmospheric pressure: (1) m= 0 mmol kg^{-1}, (2) 2, (3) 5, (4) 10, (5) 15, (6) 20, (7) 25.

composition above X=ca. 0.3. This fact is reconciled with the view that the enhancement of ethanol diminishes the adsorption of OSE.

Next, the value of Γ_1^H was evaluated by applying Eq. 3 to the γ vs. X curve drawn in Fig. 2 and using the activity coefficient of ethanol.[11] The Γ_1^H vs. X plot at constant m is shown in Fig. 5. The value of Γ_1^H at m=0 is positive over the whole range of composition and has a maximum. With increasing m, the value decreases considerably and becomes negative at a small X value, though it remains unchanged at a high X value. Taking into account that the maximum value of Γ_1^H is comparable with the value of the saturated adsorption of normal aliphatic alcohol,[12] we may say that ethanol molecules pack closely in the adsorbed film. However, the dependence of Γ_1^H on m suggests that the formation of OSE film expels ethanol molecules from the surface region. On the other hand, we notice that the surface activity of OSE becomes extinct in an ethanol-rich solution. Therefore, it seems to be useful to examine the relation of the adsorption of OSE to that of ethanol. This can be achieved by evaluating the ratio Γ_1^H/Γ_2^H.

The numerical values of Γ_1^H/Γ_2^H were evaluated by making use of Eq. 4 and the m vs. X curves in Fig. 3; they are plotted against X at fixed γ in Fig. 6, where r^H denotes Γ_1^H/Γ_2^H. The values at γ=60, 50, and 40 mN m^{-1} are seen to increase greatly with increasing X. On the other hand, the value at γ=30 mN m^{-1} first decreases and then increases steeply. These findings indicate that the competitive adsorption of OSE and ethanol molecules takes place at the surface.

Now it is useful to examine the adsorption of OSE from its micellar solution in the ethanol-water mixture. The behavior of micelles can be described by the excess thermodynamic quantities with reference to the spherical dividing surface around the micelle chosen so that the sum of the excess number of water molecules per micelle particle N_w^M and that of ethanol molecules N_1^M is equal to zero. The analogue of the Gibbs-Duhem equation for the micelle particle is written as[13]

$$N_w^M d\mu_w + N_1^M d\mu_1 + N_2^M d\mu_2 = 0, \tag{5}$$

where N_2^M is the excess number of OSE molecules per micelle particle and μ_i the chemical potential of component i. Adopting T, p, X, and m as the independent variables and assuming that OSE behaves ideally in the solution, Eq. 5 is rewritten in the following form at constant T and p

$$[(1-X)X]^{-1}[1+(\partial \ln f/\partial \ln X)_{T,p,m}]N_1^M dX + m^{-1}N_2^M dm = 0. \tag{6}$$

Combination of Eqs. 1 and 6 yields the relation representing the variation of surface tension of the micellar solution with X:

$$-d\gamma = RT[(1-X)X]^{-1}[1+(\partial \ln f/\partial \ln X)_{T,p,m}]\Gamma_2^H(r^H - r^M)dX, \tag{7}$$

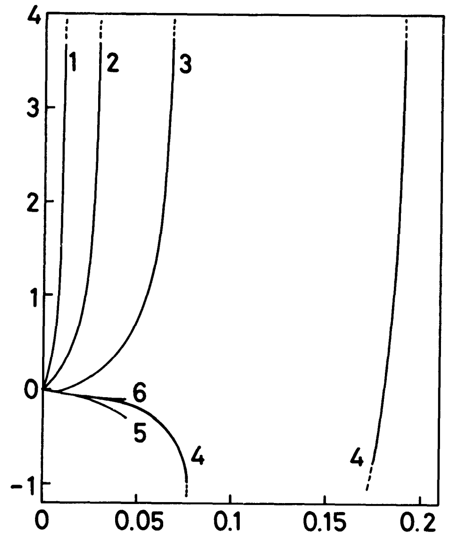

Fig. 6. Ratios r^H, $r^{H,cmc}$, and $r^{M,cmc}$ vs. mole fraction of ethanol curves at constant surface tension at 298.15 K under atmospheric pressure: (1) γ=60 mN m^{-1}, (2) 50, (3) 40, (4) 30, (5) $r^{H,cmc}$ vs. X, (6) $r^{M,cmc}$ vs. X.

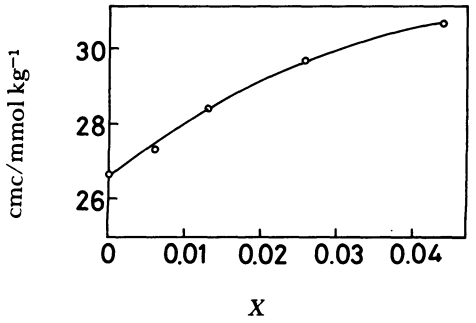

Fig. 7a. Critical micelle concentration vs. mole fraction of ethanol curve at 298.15 K under atmospheric pressure.

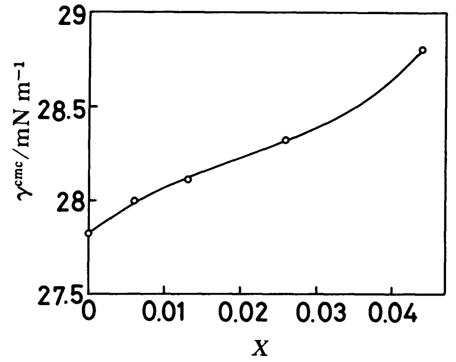

Fig. 7b. Surface tension at critical micelle concentration vs. mole fraction of ethanol at 298.15 K under atmospheric pressure.

where r^{M} expresses $N_1^{\mathrm{M}}/N_2^{\mathrm{M}}$. Since $\gamma \cong \gamma^{\mathrm{cmc}}$ and $m \cong \mathrm{cmc}$ in the vicinity of the cmc, the following equations are obtained from Eqs. 6 and 7:

$$-(\partial \mathrm{cmc}/\partial X)_{T,p} = (\mathrm{cmc})[(1-X)X]^{-1}[1+(\partial \ln f/\partial \ln X)_{T,p,m}] \times r^{\mathrm{M,cmc}} \tag{8}$$

and

$$-(\partial \gamma^{\mathrm{cmc}}/\partial X)_{T,p} = RT[(1-X)X]^{-1}[1+(\partial \ln f/\partial \ln X)_{T,p,m}] \times \Gamma_2^{\mathrm{H,cmc}}(r^{\mathrm{H,cmc}} - r^{\mathrm{M,cmc}}), \tag{9}$$

where the superscript cmc indicates that the values of the thermodynamic quantities are those at the cmc. Therefore, we can evaluate the values of $r^{\mathrm{H,cmc}}$ and $r^{\mathrm{M,cmc}}$ by applying Eqs. 8 and 9 to the experimental results.

The values of cmc and γ^{cmc} obtained from the γ vs. m curves in Fig. 1a are plotted against X at constant T and p in Figs. 7a and 7b. The cmc vs. X curve is qualitatively consistent with those observed by some other work.[4–6, 14–17] The numerical values of $r^{\mathrm{H,cmc}}$ and $r^{\mathrm{M,cmc}}$ estimated are drawn as a function of X at 298.15 K under atmospheric pressure in Fig. 6. Comparing these curves with the r^{H} vs. X curves, the values of $r^{\mathrm{H,cmc}}$ and $r^{\mathrm{M,cmc}}$ may be said to be not so different from each other. Therefore, we can conclude that the behavior of OSE molecules in the micelle is similar to that in the adsorbed film. Moreover, the negative values of $r^{\mathrm{H,cmc}}$ and $r^{\mathrm{M,cmc}}$ indicate that ethanol molecules are expelled from the adsorbed film and the micelle particle of OSE.

Further information about the interaction between OSE and ethanol molecules in the adsorbed film and the micelle will be provided by a thermodynamic treatment which regards the present system as an aqueous solution of surfactant mixture.

References

1) T. Ikenaga, N. Matubayasi, M. Aratono, K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **53**, 653 (1980).

2) H. Iyota, M. Aratono, M. Yamanaka, K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **56**, 2402 (1983).

3) K. Motomura, H. Iyota, N. Ikeda, and M. Aratono, *J. Colloid Interface Sci.*, **126**, 26 (1988).

4) L. Cantu, M. Corti, V. Degiorgio, H. Hoffmann, and W. Ulbricht, *J. Colloid Interface Sci.*, **116**, 384 (1987).

5) L. G. Ionescu, T. Tokuhiro, and B. J. Czerniawski, *Bull. Chem. Soc. Jpn.*, **52**, 922 (1979).

6) M. Koshinuma, *Bull. Chem. Soc. Jpn.*, **52**, 1790 (1979).

7) K. Motomura, S. Iwanaga, S. Uryu, H. Matsukiyo, M. Yamanaka, and R. Matuura, *Colloids and Surfaces*, **9**, 19 (1984).

8) K. Motomura, S. Iwanaga, Y. Hayami, S. Uryu, and R. Matuura, *J. Colloid Interface Sci.*, **80**, 32 (1981).

9) S. Uryu, M. Aratono, M. Yamanaka, K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **56**, 3219 (1983).

10) M. Aratono, S. Uryu, Y. Hayami, K. Motomura, and R. Matuura, *J. Colloid Interface Sci.*, **98**, 33 (1984).

11) H. J. E. Dobson, *J. Chem. Soc.*, **1925**, 2866.

12) R. Defay, I. Prigogine, and A. Bellemans, (translated by D. H. Everett), "Surface Tension and Adsorption," Longmans, London (1966), p. 94.

13) K. Motomura, S. Iwanaga, M. Yamanaka, M. Aratono, and R. Matuura, *J. Colloid Interface Sci.*, **86**, 151 (1982).

14) P. Becher, *J. Colloid Sci.*, **20**, 728 (1965).

15) A. Goto, M. Takemoto, and F. Endo, *Bull. Chem. Soc. Jpn.*, **58**, 247 (1985).

16) D. Oakenfull, *J. Colloid Interface Sci.*, **88**, 562 (1982).

17) R. Zana, S. Yiv, C. Strazielle, and P. Lianos, *J. Colloid Interface Sci.*, **80**, 208 (1981).