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Critical Phenomena in a Surfactant/Water/Oil System. Basic Study on the Correlation between Solubilization, Microemulsion, and Ultralow Interfacial Tensions

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The phase equilibrium in $C_8H_{17}(OCH_2CH_2)_3OH$/water/decane system was studied at 13.6, 15.8, 21.5, 26.0, and 30.0 °C. An upper critical solution point for the surfactant and oil phases, and a lower critical solution point for the surfactant and water phases were found. Strong critical opalescence was observed in the vicinity of the critical points. In a temperature range between two critical points, a three-phase region appeared due to the superposition of three miscibility gaps, *i.e.*, 1) surfactant+water; 2) surfactant+oil, and 3) oil+water phases. The correlations between the phase equilibria and the ultralow interfacial tensions were straightforward. An ionic surfactant/cosurfactant/brine/oil system gave similar phase equilibria as the nonionic surfactant system, but the effect of temperature was the reverse.

In ordinary binary-liquid systems, mutual solubility of two phases increases with the increase of temperature and the compositions of the two phase coincide at the critical temperature, at which the interfacial tension between them becomes zero.[1–3] In a critical region, due to the large concentration fluctuation large clusters of molecules develop since the dimensions of the clusters are of the order of the wave length of light. Such systems scatter light strongly and the phenomenon is called critical opalescence.[4]

In surfactant solutions, the micelles present may be interpreted as large concentration fluctuations in a wider range of temperature than that in ordinary binary mixtures. According to the traditional interpretation[5–6] micelles grow with increasing temperature in nonionic surfactant aqueous solutions and their aggregation number becomes infinite in the vicinity of the solubility curve (cloud point curve), above which a surfactant and a water phases coexist. The recent NMR investigations by Tiddy and collaborators[7] have given results at variance with this interpretation. Their evaluation rather pointed to the presence of aggregates of flocculated micelles instead of larger ones.

In nonionic surfactant/water/oil systems, the surfactant mainly dissolves in water at lower temperature, whereas it dissolves in oil at higher temperature. At the transition temperature range of the surfactant from water-soluble to oil-soluble, there is a three-phase region consisted of a water phase, an oil phase and a surfactant phase which solubilizes a large amount of water and oil.[8–10] In this region, following phenomena are observed; 1) the amount of the solubilization of oil or water in a surfactant phase is attained to maximum, and the surfactant phase scatters a considerable amount of light, 2) ultralow interfacial tensions between the surfactant and oil (water) phases are obtained.[11] It is considered that these resemble critical phenomena in ordinary liquid systems. But the correlation between these phenomena and phase equilibria has not been clarified.

In this paper, solution behavior of $C_8H_{17}(OCH_2CH_2)_3OH$ in water and oil has been studied and compared with phase equilibria in ordinary binary or ternary mixtures. The solution behavior of ionic surfactant has also been evaluated for comparison.

Experimental

Materials. Pure $C_8H_{17}(OCH_2CH_2)_3OH$ was synthesized by POLA Research Laboratory and pure $C_{12}H_{25}(OCH_2CH_2)_5OH$ was synthesized by Nikko Chemicals; the high purity was confirmed by gas chromatographic analysis. *p*-$C_8H_{17}C_6H_4SO_3Na$ was kindly supplied by Kao Soap Company. Extra pure grade decane, hexadecane, 2,2,4-trimethylpentane were obtained from Tokyo Kasei Kogyo Company, and used without further purification.

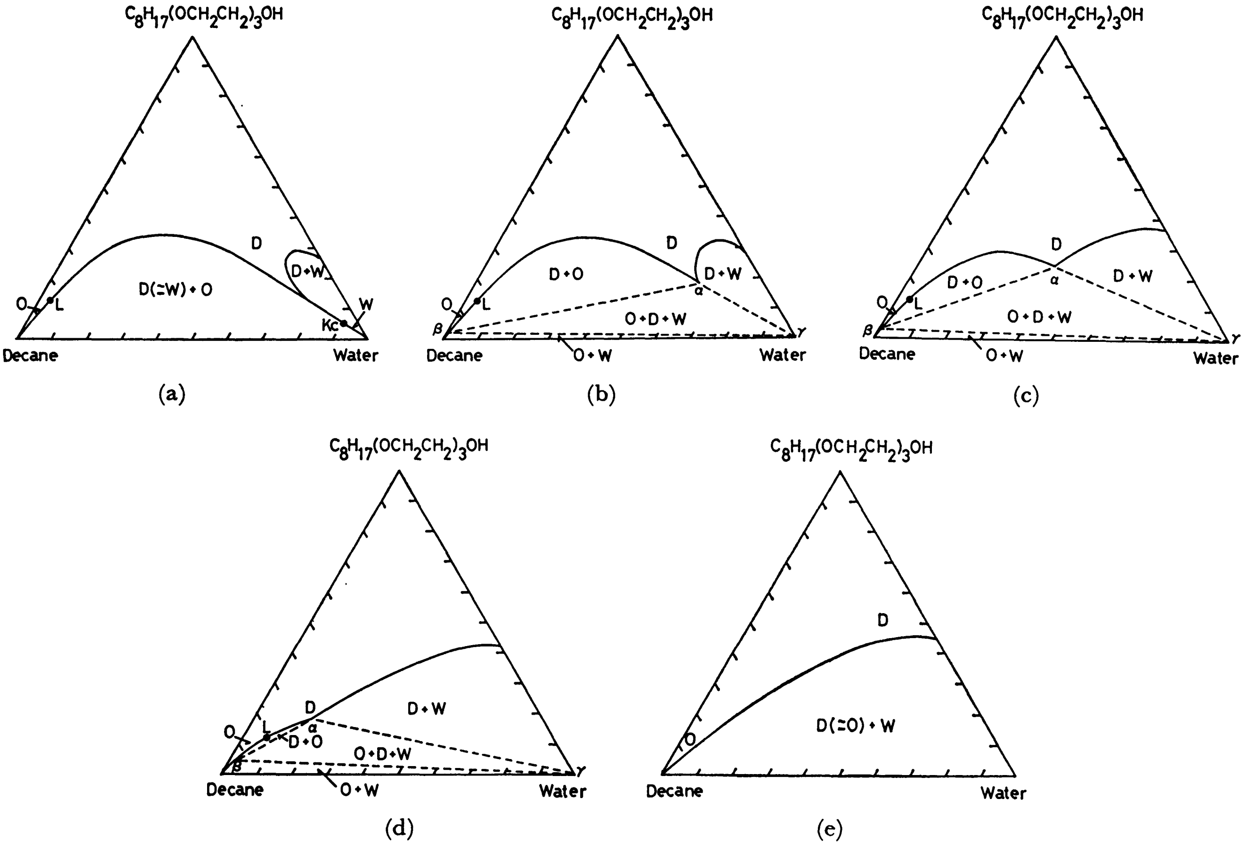
Procedures. The procedures for the determinations of the phase diagrams were described in previous papers.[9–12]

Results and Discussion

$C_8H_{17}(OCH_2CH_2)_3OH$/Water/Decane System. Complicated phase equilibria are observed in long-chain surfactant/water/oil system, since liquid crystalline phases exist in a wide range of composition.[8–13] Therefore, the use of a short-chain surfactant is of advantage in order to understand the basic solution behavior of nonionic surfactant in oil and water. The short hydrocarbon chain is not sufficient to stabilize a liquid crystalline phase, hence the phase equilibria involving only liquid phases are more easily achieved.

With this fact in mind phase diagrams for $C_8H_{17}(OCH_2CH_2)_3OH$/water/decane system were determined at 13.6, 15.8, 21.5, 26.0, and 30.0 °C and are shown in Figs. 1(a)—(e).

There are two two-phase regions in Fig. 1(a). One contains a surfactant phase (D) and an aqueous phase (W) located in the vicinity of water apex. Compositions of coexisting D phase and W phase coincide at the plait point K (isothermal critical point) on the miscibility curve. Kc means the upper limit of K as described later. The other two-phase region is comprised of a surfactant (or water) phase and an oil phase (O). Compositions of both phases coincide at the plait point L on the miscibility curve, but the boundary between the surfactant phase and the water phase cannot be distinguished since there is no plait point between these phases.



(a) (b) (c)

(d) (e)

Fig. 1. Phase diagrams for $C_8H_{17}(OCH_2CH_2)_3OH$/water/decane system at various temperatures. (a) 13.6 °C, (b) 15.8 °C, (c) 21.5 °C, (d) 26.0 °C, (e) 30.0 °C. O, an oil phase; W, a water phase; D, a surfactant phase; α, β and γ, invariant points; K and L, plait points. Kc and Lc are upper limits of K and L (*cf.* Fig. 3).

The water phase continuously changes to the surfactant phase with increasing the content of a surfactant/decane solution of the ratio 1.2. Therefore, this latter two-phase region contains two miscibility gaps, *i.e.*, D+O and W+O so that the notation, D(≃W) is used. Below this temperature the two-phase D(≃W)+O region becomes wider, whereas D+W region becomes narrower and the plait point K approaches to water apex and the plait point L approaches the oil-surfactant axis (*cf.* Fig. 3).

Point Kc is still in contact with the miscibility curve between D(≃W) and O at 13.6 °C as shown in Fig. 1(a). Slightly above this temperature, the single-phase region splits into two realms, *i.e.*, the surfactant phase and the water phase at point Kc, and a three-phase region is formed consisted of a water, and oil and a surfactant phases. In other words, the equilibrium of three liquid phases causes the superposition of three miscibility gaps, *i.e.*, O+W, D+W, and D+O. The three coexisting liquids are the point, α, β, and γ as shown in Fig. 1(b).

This kind of phenomenon is also known in ordinary ternary systems, such as water/ether/succinonitrile systems.[14,15] The single water-phase region abruptly falls to the water apex in a very narrow range of temperature. The plait point Kc is the lower critical point between the surfactant and the water phases in the presence of oil. W or D phase in the vicinity of the plait point Kc scatters light and looks blue. The system is called a microemulsion.[10]

Point α shifts to the oil apex and the three-phase and D+W phase regions become wider with increasing temperature as shown in Fig. 1(c). Point α in Fig. 1(c) is the minimum concentration of $C_8H_{17}(OCH_2CH_2)_3OH$ to make equal amount of oil and water a single phase. Three points, α, β, and L approach each other with increasing temperature as shown in Fig. 1(d) and coalesce at 26.6 °C which is the upper critical point, (Lc) between the surfactant and the oil phases in the presence of water. Three-phase and D+O regions disappear and only the two-phase D(≃O)+W phase region is observed above this temperature as shown in Fig. 1(e).

Since the plait point does not exist on the miscibility curve in Fig. 1(e), the boundary between an oil phase and a surfactant phase cannot be distinguished. In other words, this two-phase region contains two miscibility gaps, *i.e.*, D+W and O+W so that the notation D(≃O) is used.

It is clear that the mutual dissolution between the surfactant phase and the water phase is increased with decreasing temperature, whereas that between the surfactant phase and the oil phase is increased with increasing temperature as shown in Figs. 1(a)—(e).

The correlations between phase equilibria and ultralow interfacial tensions are also made clear from Figs. 1(a)—(e). It is known that the interfacial tension becomes zero at a critical point in ordinary liquid system.[3,16] The interfacial tension between the surfactant phase and the water phase approaches zero at the plait point K, because the compositions of both phases become equal. On the other hand, the interfacial tension between a surfactant phase and an oil phase approaches zero at the plait point L. Since no plait points exists above 26.6 °C as shown in Fig. 1(e), the interfacial tension does not become zero at any points in two-phase region. In three-phase region, the interfacial tension between a surfactant and a water phase becomes zero on the line at which the two lines, α-β and β-γ coalesce each other at 13.6 °C. On the other hand, the interfacial tension between a surfactant phase and an oil phase becomes zero on the line at which the two lines, α-γ and β-γ coalesce each other at 26.6 °C.

These results are in excellent accordance with those by Friberg and coworkers,[17,18] whose more complex equilibria were due to the influence of longer hydrocarbon chains. These favor the formation of lamellar phases.[19]

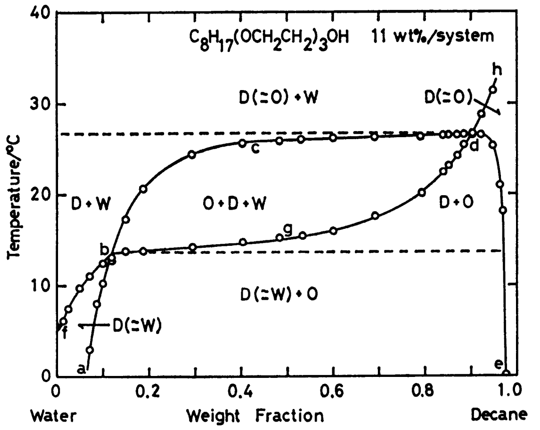


Fig. 2. Phase diagrams for water–decane containing 11 wt% of $C_8H_{17}(OCH_2CH_2)_3OH$/system as a function of temperature.

The effect of temperature on the phase equilibria of water-decane containing 11 wt% of $C_8H_{17}(OCH_2CH_2)_3$-OH was also studied and is shown in Fig. 2. This kind of phase diagrams have been extensively investigated by Shinoda and coworkers.[8–10] D($\simeq$O) and D($\simeq$W) are single-phase regions. (*cf.* Fig. 1). Above the curve a-b-c-d-e which is the miscibility curve of an oil and a surfactant phases, O and D phases cannot coexist in equilibrium. On the other hand, the surfactant phase and the water phase cannot coexist in equilibrium below the miscibility curve f-b-g-d-h. Hence the surfactant phase may coexist with the oil and the water phases only in the closed region, b-c-d-g. The curve a-b-c-d-e is smoothly continuous but the curve f-b-g-d-h has a break at point b in Fig. 2. From Fig. 2, it is clear that the solubilization of oil or water attains maximum in the vicinity of critical point (Kc or Lc).

Figure 3 is the polythermal projection of Figs. 1(a)—(e). Broken line means the locus of invariant point α and in the region of lower side of this line, a single liquid phasc does not appear at any temperatures.

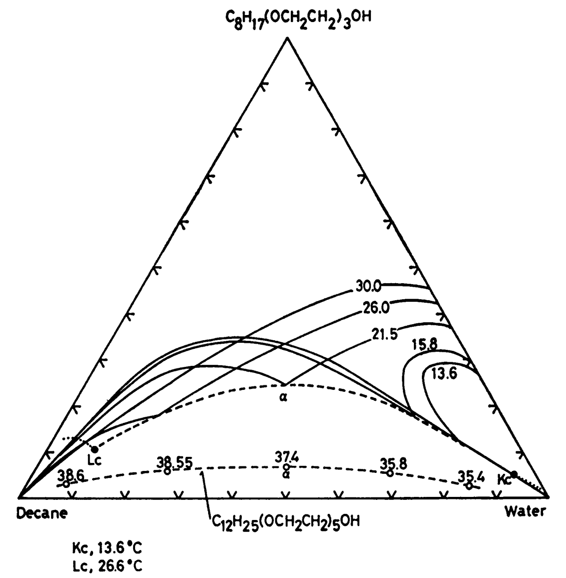
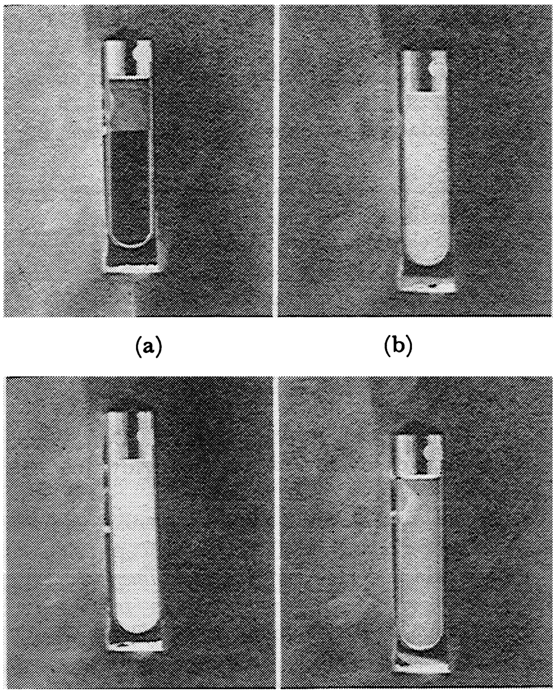


Fig. 3. Polythermal projection of Figs. 1(a)—(e). Dotted lines are the loci of plait points. —○— is a locus of α in $C_{12}H_{25}(OCH_2CH_2)_5OH$/water/decane system. Numerical numbers indicate the temperature (°C). Kc, $C_8H_{17}(OCH_2CH_2)_3OH$ 5 wt%, water 91 wt%, decane 4 wt%; Lc, $C_8H_{17}(OCH_2CH_2)_3OH$ 11 wt%, water 9 wt%, decane 80 wt%.

Dotted lines represent the loci of the plait points K and L. Since the locus of α is far from water–oil axis in $C_8H_{17}(OCH_2CH_2)_3OH$/water/decane system, the solubilizations of oil and water in surfactant phase are relatively small. The locus of α in $C_{12}H_{25}(OCH_2CH_2)_5$-OH/water/decane system (open circles) is also shown in Fig. 3. α is very close to oil–water axis so that the solubilization is very large. But, the composition of α is rapidly changed with increasing temperature.

The critical phenomenon at the composition of point Kc in Fig. 1(a) is captured in the sequence of the photographs shown in Figs. 4(a)—(d). Well above the critical temperature, both an upper surfactant phase and a lower water phase are clear and there is no appreciable scattered light. With decreasing temperature, the solubilization of water in a surfactant phase is increasing and D phase (upper) begins to scatter light as shown in Fig. 4(a). Just above the critical temperature, the dissolution of D phase in W phase will strongly increase and both show pronounced phases light-scattered as shown in Fig. 4(b). At the critical temperature (13.6 °C), the boundary between two phases suddenly disappears and the scattered light attains a maximum as shown in Fig. 4(c). Below this temperature, the light-scattering weakens and excess oil is separated from D($\simeq$W) phase as shown in Fig. 4(d). (See the meniscus). It is essential to point out that the scattered light observed in microemulsion systems[9] is a critical opalescence. Except these critical points, it is known that two critical phenomena exist on the oil-surfactant axis and the water-surfactant axis in nonionic surfactant system.[20–23]

Phase diagram of equal amount of oil and water containing $C_8H_{17}(OCH_2CH_2)_3OH$ as a function of temperature is shown in Fig. 5. The curve a-b-c-d is


(a) (b)

(c) (d)

Fig. 4. The critical phenomenon captured in the sequence of the photographs at the composition of the lower critical point (Kc) in Fig. 1(a). (a) 14.0 °C, (b) 13.7 °C, (c) 13.6 °C, (d) 12.0 °C.

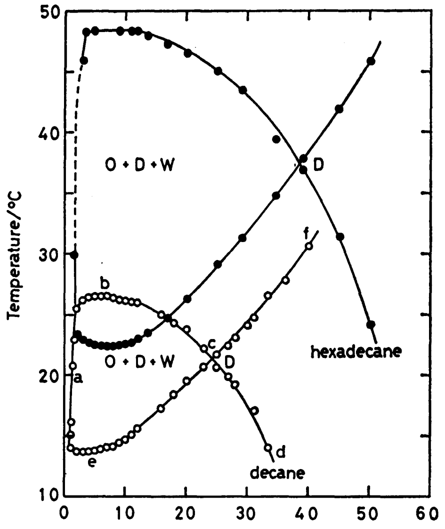


Fig. 5. The effect of the concentrations of $C_8H_{17}(OCH_2CH_2)_3OH$ on the equi-weight mixture of water and decane (or hexadecane) as a function of temperature.

the coexisting curve of the surfactant phase and the oil phase in the presence of water, whereas the curve a-e-c-f is that of the surfactant and the water phases in the presence of oil. If a molecular volume of oil is large (hexadecane), two coexisting curves shift to higher temperature as shown in Fig. 5. This fact means that a surfactant becomes more soluble in the water phase. Upper coexisting curve shifts more to higher temperature than the lower one does and the three-phase region becomes wider. Hence the minimum content of surfactant to make equal amount of oil and water a single phase is increased. This is in agreement with earlier solubilization studies.[17)]

Ionic Surfactant/Cosurfactant/Brine/Oil System. Ordinary ionic surfactant dissolves in water and solubilizes a small amount of oil and the solubilization is little affected by temperature change.[19)] Even hydrophile-lipophile balanced ionic surfactant, Aerosol OT (sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate) dissolves mainly in water in dilute system, in which aqueous micellar solution phase coexists with an excess oil.[23-24)] If brine is used instead of water, a three-phase region consisting of an oil, a water and a surfactant phases has been shown appearing in certain temperature ranges in Aerosol OT system as well as nonionic surfactant systems.[24-26)] On the other hand, it is known that the solution behavior of Aerosol OT in water is similar to that of the appropriate mixture of ordinary ionic surfactant and cosurfactant such as long-chain alcohol.[27)] Hence, it is expected that same solution behavior as that in Aerosol OT or nonionic surfactant systems appears in ordinary ionic surfactant systems if proper amounts of brine and cosurfactant are used. Phase diagram of p-$C_8H_{17}C_6H_4SO_3Na$, brine, 2,2,4-trimethylpentane and 1-hexanol as a function of temperature is shown in Fig. 6. Brine/2,2,4-trimethylpentane (containing 30 wt% of 1-hexanol) ratio is unity (W/W). Concentrations of salt in water are 1 wt% (open circles) and 3 wt% (filled circles) respectively. Below the temperature indicated by broken lines, liquid crystalline phase is separated. Below the curve which is concave downward, an excess water and a surfactant phase are separated, whereas an excess oil and a surfactant phase are separated above the curve which is concave upward. Therefore, three-phase consisted of a water, an oil and a surfactant phases appears in overlapping realm which is indicated by

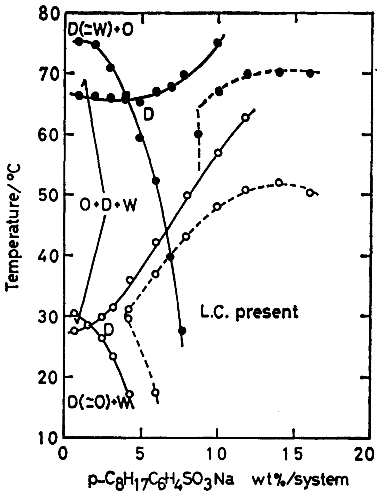


Fig. 6. The effect of the concentration of p-$C_8H_{17}C_6H_4SO_3Na$ on the equi-weight mixtures of brine (○, 1 wt% NaCl; ●, 3 wt% NaCl) and 2,2,4-trimethylpentane containing 30 wt% of 1-hexanol as a function of temperature.

O+D+W. From this result, it is clear that ionic surfactant becomes more hydrophilic with increasing temperature. Overlapping realm, *i.e.*, three-phase region shifts to lower temperature with decreasing salt content as shown in Fig. 6 and finally, it may disappear and a surfactant phase and an excess oil phase remain at room temperature in the absence of salt.

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References

1) J. H. Hildebrand and T. F. Buehrer, *J. Am. Chem. Soc.*, **42**, 2213 (1920).

2) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand Reinhold Co., New York (1970), Chap. 10.

3) D. Atack and O.K. Rice, *Discuss. Faraday Soc.*, **15**, 210 (1953).

4) H. E. Stanley, "Introduction to Phase Transitions and Critical Phenomena," Oxford University Press, New York and Oxford (1971), pp. 1—21.

5) T. Nakagawa, K. Kuriyama, and H. Inoue, *J. Colloid Sci.*, **15**, 268 (1960).

6) K. Kuriyama, *Kolloid-Z.*, **180**, 55 (1962).

7) T. A. Bostack, M. P. McDonald, G. J. T. Tiddy, and L. Haring, "Surface Active Agents," Soc. Chem. Ind., London (1979), p. 181.

8) K. Shinoda and H. Saito, *J. Colloid Interface Sci.*, **26**, 70 (1968).

9) K. Shinoda and H. Kunieda, *J. Colloid Interface Sci.*, **42**, 381 (1973).

10) K. Shinoda and H. Kunieda, "Microemulsions," ed by L. M. Prince, Academic Press Inc., New York (1977), Chap. 4.

11) H. Saito and K. Shinoda, *J. Colloid Interface Sci.*, **32**, 647 (1970).

12) H. Kunieda and K. Shinoda, *J. Phys. Chem.*, **82**, 1710 (1978).

13) S. Friberg, I. Lapczynska, and G. Gillberg, *J. Colloid Interface Sci.*, **56**, 19 (1976).

14) F. A. H. Schreinemakers, *Z. Phys. Chem.*, **25**, 543 (1898).

15) J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Tronto, New York (1951), p. 214.

16) M. P. Brun, *C. R. Acad Sci.*, **184**, 966 (1927).

17) S. E. Friberg and I. Lapczynska, *Prog. Colloid Polym. Sci.*, **56**, 16 (1975).

18) S. E. Friberg, L. Rydhag, and T. Doi, "Lyotropc Liquid Crystals," ed by S. Friberg, ACS Adv. in *Chem. Sci.* **152**, 28 (1976).

19) P. Ekwall, "Advances in Liquid Crystals," ed by G. H. Brown, Academic Press, N. Y. (1974), Vol. 7, p. 1.

20) K. Shinoda and H. Arai, *J. Colloid Interface Sci.*, **20**, 93 (1965).

21) J. S. Clunie, J. F. Goodman, and P. C. Symons, *Trans. Faraday Soc.*, **65**, 287 (1969).

22) K. Shinoda, *J. Colloid Interface Sci.*, **34**, 278 (1971).

23) H. Kunieda and K. Shinoda, *J. Colloid Interface Sci.*, **70**, 577 (1979).

24) H. Kunieda and T. Sato, *Yukagaku*, **28**, 627 (1979).

25) H. Kunieda and K. Shinoda, *J. Colloid Interface Sci.*, **75**, 601 (1980).

26) H. Kunieda, *Yukagaku*, **29**, 510 (1980).

27) H. Kunieda, *Nippon Kagaku Kaishi*, **1977**, 1428.