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Correlation between Critical Solution Phenomena and Ultralow Interfacial Tensions in a Surfactant/Water/Oil System

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A three-phase region consisting of surfactant (D), water (W), and oil (O) phases appeared due to the superposition of two critical phenomena of D–W and O–D in a nonionic surfactant/water/oil system. Three interfacial tensions, γ_{O-W}, γ_{O-D}, and γ_{D-W}, among the three phases were determined at various temperatures. The generalized Antonoff's rule ($\gamma_{O-W}=\gamma_{O-D}+\gamma_{D-W}$) holds approximately in the three-phase region. γ_{O-D} and γ_{D-W} disappear at the respective critical solution temperatures, and ultralow interfacial tensions are attained in the vicinity of both critical temperatures. The oil–water interfacial tension, γ_{O-W}, reaches its minimum in the midst of the temperature range of the three-phase region, and the narrower the temperature range of the three-phase region, the lower the interfacial tension. The correlation between the interfacial tensions and the types of emulsions is also discussed.

There exists a three-phase region consisting of surfactant, water, and oil phases around the transition-temperature range at which the surfactant changes from water-soluble to oil-soluble in a nonionic surfactant/water/oil system.[1)] A similar three-phase region has been observed in an ionic surfactant system in the presence of salt and a co-surfactant.[2–6)] Saito and Shinoda found very low interfacial tensions in a three-phase region of a nonionic surfactant system.[7)] Later Healy *et al.* found ultralow interfacial tensions between a surfactant phase (they called it a middle-phase microemulsion) and a water (or oil) phase in a petroleum sulfonate system.[3,8)] On the other hand, ultralow interfacial tensions in very dilute systems of ionic surfactants were reported by Wade *et al.*[9–11)]

In a previous paper,[12)] it was clarified that a three-phase region appears due to the superposition of three miscibility gaps *i.e.*, surfactant–oil, surfactant–water, and oil–water phases, at a constant temperature. Furthermore, it was made clear that the lower (or upper) limiting temperature of the three-phase region corresponds to the lower (or upper) critical solution temperature of surfactant–water (or surfactant–oil) phases in a nonionic surfactant system. Interfacial tensions can be expected to be very small in the vicinity of the respective critical solution temperature. Since the emulsion type changes from O/W to W/O around the three-phase region,[1)] the phase inversion in emulsion may be directly related to the balance of two interfacial tensions, *i.e.*, the oil–surfactant and water–surfactant interfaces, in the three-phase region. In this context, the correlation among the phase behavior, the ultralow interfacial tensions, and the phase-inversion in emulsions has been studied.

Experimental

Materials. Pure $C_8H_{17}(OCH_2CH_2)_3OH$ was kindly donated by POLA Chemicals, while pure $C_{12}H_{25}(OCH_2CH_2)_4$-OH was obtained from Nikko Chemicals; the purities (above 98%) were confirmed by gas-chromatographic analysis. Extra-pure-grade heptane, octane, nonane, dodecane, tetradecane, hexadecane, and 2-butoxyethanol were obtained from the Tokyo Kasei Kogyo Co. and were used without further purification.

Procedures. The interfacial tensions were measured by a sessile-drop method.[13,14)] After attaining equilibrium, a drop of a high-density phase was placed on a Teflon film immersed in a low-density phase. The maximum height of the sessile drop above the equator, y, was measured by means of a cathetometer. The interfacial tension was calculated by a large drop approximation as follows:

$$\gamma = gy^2\Delta\rho/2,$$

where γ is the interfacial tension; g, the gravitational acceleration, and $\Delta\rho$, the density difference between two liquids.[14)] In order to reduce error, x/y (x is the radius of the sessile drop at the equator) has to be at least more than 10. The density was measured by means of a digital density meter (Anton Paar DMA 40). The procedures of the determination of phase volumes and cream volumes has been described elsewhere.[15–17)]

Results and Discussion

Phase Behavior of Nonionic Surfactant in Oil–Water. A schematic ternary phase diagram for a nonionic surfactant/water/oil system at the temperature range around the three-phase region is shown in Figs. 1(a)—(c).[12)] The water, surfactant and oil phases are indicated by W, D, and O respectively. The compositions of the three coexisting liquids at a constant temperature and pressure are indicated by invariant points, α (D phase), β (O phase), and γ (W phase). There is a plait point (isothermal critical point), L, in the D+O region, but not in the D+W region in Figs. 1(b) and (c), because a lower critical solution temperature on a water-nonionic surfactant axis is usually lower than this temperature. Point α shifts toward the water apex with a decrease in the temperature, and finally Points α and γ coincide with each other at the critical end point Kc ($\alpha=\gamma$) and the three-phase region disappears, as is shown in Fig. 1(a). On the Kc-β line, the critical mixture ($\alpha=\gamma$) is in equilibrium with the oil phase, β. In this case, the D+W region usually remains in the vicinity of the water-surfactant axis.[12)] The boundary between D+O and O+W regions at this temperature is the Kc-β line, but we can not draw the boundary at temperatures below that of the critical end point, Kc. Therefore, the D($\simeq$W)+O notation is used for the two-phase

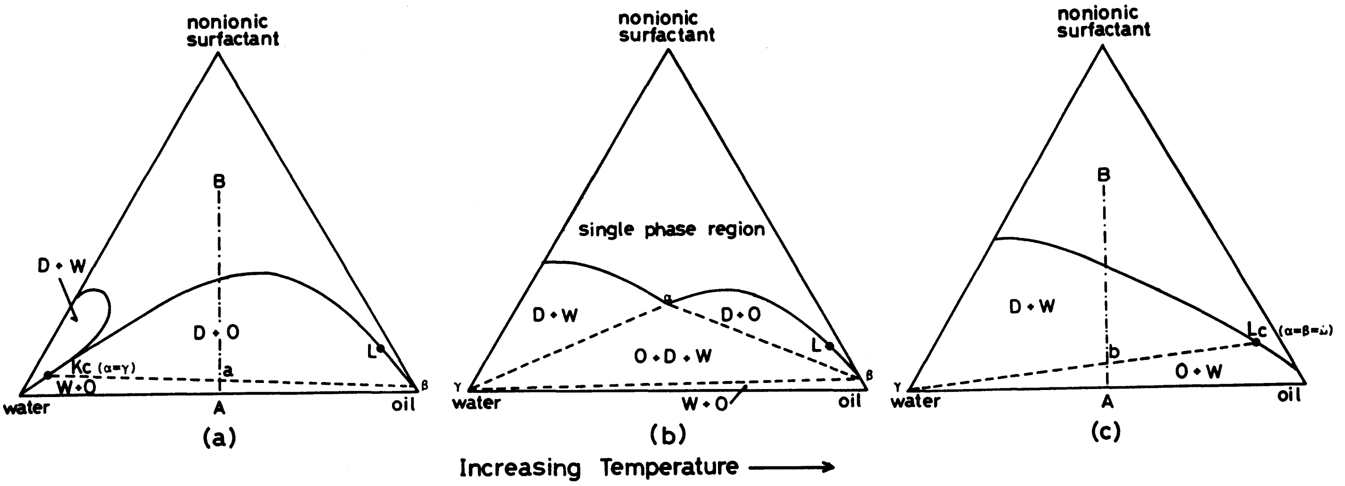


Fig. 1. Schematic phase diagram for a nonionic surfactant/water/oil system at the temperatures of a lower critical end point (Fig. 1(a)), in the midst of two critical end points (Fig. 1(b)), and of a upper critical end point (Fig. 1(c)). Kc and Lc are the lower and upper critical end points. α, β, and γ are the invariant points forming the three-phase region. O, D, and W are an oil, a surfactant, and a water phases. Points a and b correspoind to those in Fig. 2.

region at lower temperatures (*cf.* Fig. 2). D(≃W) is usually called the aqueous micellar solution phase, which solubilizes oil. On the other hand, Point α shifts toward the oil apex with an increase in the temperature, and finally Points α, β, and L become identical at another critical end point, Lc ($\alpha=\beta=$L), as is shown in Fig. 1(c). Therefore, the three-phase and D+O regions disappear at this temperature, leaving the D+W and O+W regions. The W phase is nearly pure water; its composition is indicated by γ. Since we can not draw the boundary between the D+W and O+W regions at temperatures above that of the critical end point, Lc, the D(≃O)+W notation is used for the two-phase region (*cf.* Fig. 2). D(≃O) is usually called the nonaqueous reversed micellar solution phase, which solubilizes water.

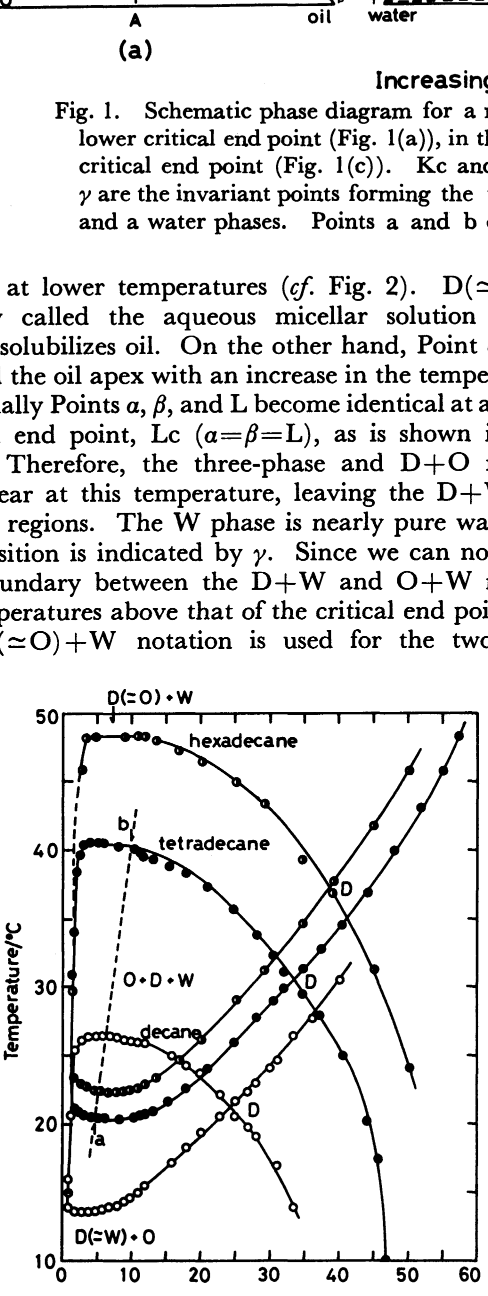


Fig. 2. Phase diagram of equal weight of water–oil containing $C_8H_{17}(OCH_2CH_2)_3OH$ as a function of temperature. The compositions correspond to the line A-B in Fig. 1.

A phase diagram consisting of equal weights of hydrocarbon and water as functions of the concentration of $C_8H_{17}(OCH_2CH_2)_3OH$ and the temperature is shown in Fig. 2. Point a in the tetradecane system, corresponds to that in Fig. 1(a), so it seems that the meniscus separating the D and W phases has just disappeared at Point a. Figure 3 shows the change in the volume fractions of respective phases as a function of the temperature in the $C_8H_{17}(OCH_2CH_2)_3OH$/water/tetradecane system. The concentration of the surfactant changes along with the broken line, a-b, in Fig. 2. The densities of the respective phases along the same line are also shown in Fig. 4. The densities of the O and W phases are almost equal to those of the pure components in the three-phase region. Accordingly, it is considered that the surfactants are singly dispersed in both phases.[7] However, the solubility of the surfactant in the O or W phase seems to increase abruptly in the vicinity of Points a and b as is shown in Fig. 4. As a

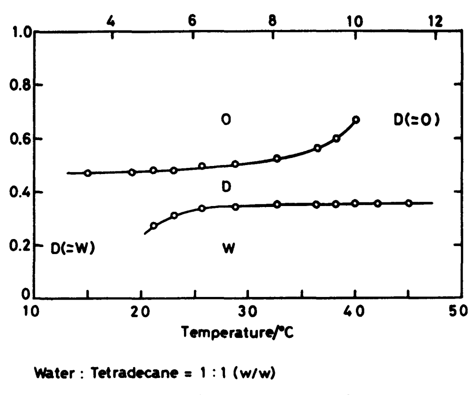


Fig. 3. The volume fractions of respective phases on the line a-b in Fig. 2.

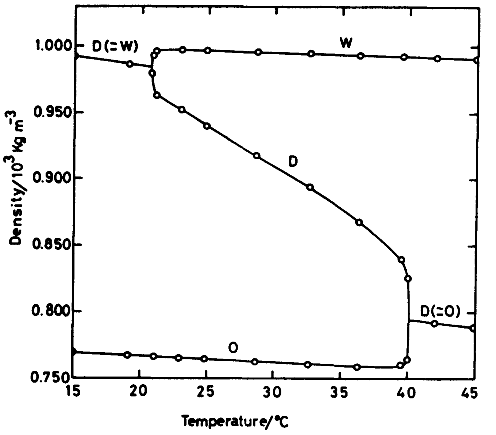


Fig. 4. The densities of respective phases on the line a-b in Fig. 2.

result, it is obvious that a three-phase region consisting of the O, W, and D phases appears in the range of two critical end temperatures, *i.e.*, a lower critical solution temperature (LCST) of the D and W phases, at which Kc exists, and an upper critical solution temperature (UCST) of the D and O phases, at which Lc exists. A similar result was obtained in an ionic surfactant system.[4,12] In the system, in which the LCST coincides with the UCST, there is a tricritical point at which the three coexisting liquids become identical.[18,19]

Correlation between Critical Solution Phenomena and Ultralow Interfacial Tensions in a Surfactant System. Since the interfacial tension becomes zero at a critical point,[20,21] and since the change in the activity of a surfactant with the concentration is very small,[22] the change in the concentration has scarcely no effect on chemical potential or interfacial tension, which is a function of the chemical potential; *i.e.*, ultralow interfacial tensions are attained in the vicinity of Point a or b in Fig. 2. Interfacial tensions between respective phases along the a-b line in Fig. 2 are shown in Fig. 5. $\gamma_{\text{O-W}}$, $\gamma_{\text{O-D}}$, and $\gamma_{\text{D-W}}$ are the interfacial tensions at the O–W, O–D, and D–W interfaces in the three-phase regions. $\gamma_{\text{D}(\simeq\text{O})\text{-W}}$ and $\gamma_{\text{O-D}(\simeq\text{W})}$ are the interfacial tensions at the D(≃O)–W and O–D(≃W) interfaces at temperatures above and below the critical temperatures. Naturally, $\gamma_{\text{O-W}}$, $\gamma_{\text{O-D}}$, and $\gamma_{\text{O-D}(\simeq\text{W})}$ coincide with one another at the LCST (at Point a), while $\gamma_{\text{O-W}}$, $\gamma_{\text{D-W}}$, and $\gamma_{\text{D}(\simeq\text{O})\text{-W}}$ coincide with one another at the UCST (Point b). $\gamma_{\text{O-D}}$ decreases with an increase in the temperature and becomes zero at Point b. On the other hand, $\gamma_{\text{D-W}}$ decreases with a decrease in the temperature and becomes zero at Point a. Accordingly, the ultralow interfacial tensions at surfactant–oil and surfactant–water interfaces are attained at temperatures in the vicinity of each critical temperature, *i.e.*, on the Lc-γ and Kc-β lines in Fig. 1. The critical point in a surfactant system usually exists in a solvent-rich region.[4,12,22,23] This is very important for such a practical purpose as the tertiary oil recovery,[8] for the amount of surfactant used to reduce the inter-

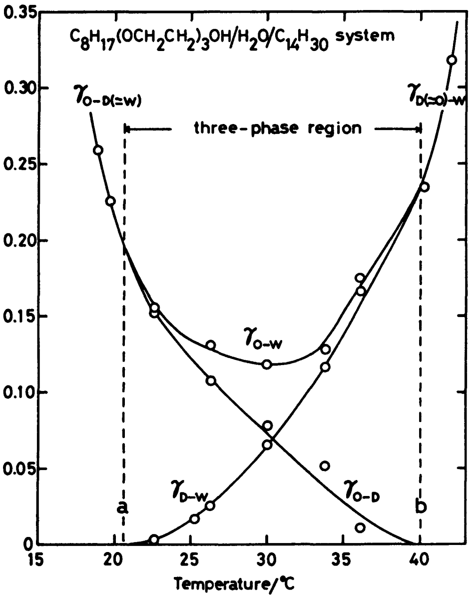
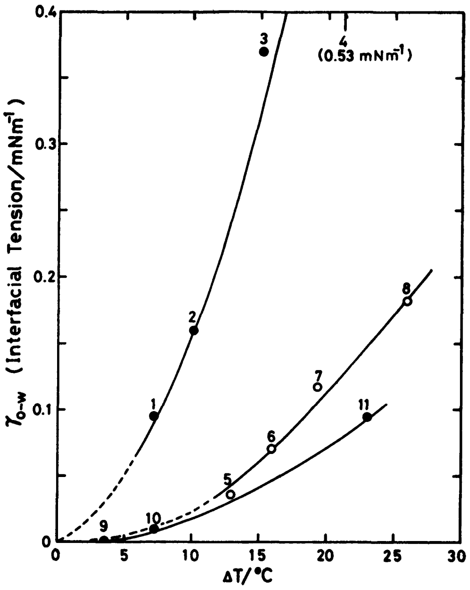


Fig. 5. The interfacial tensions between O–W, W–D, and O–D as a function of temperature on the line a-b in Fig. 2.



	system		
1	$C_4H_9OCH_2CH_2OH/H_2O/C_7H_{16}$	at	9.0 °C
2	$C_4H_9OCH_2CH_2OH/H_2O/C_8H_{18}$		17.3
3	$C_4H_9OCH_2CH_2OH/H_2O/C_9H_{20}$		26.4
4	$C_4H_9OCH_2CH_2OH/H_2O/C_{10}H_{22}$		34.4
5	$C_8H_{17}(OCH_2CH_2)_3OH/H_2O/C_{10}H_{22}$		20.1
6	$C_8H_{17}(OCH_2CH_2)_3OH/H_2O/C_{12}H_{26}$		26.2
7	$C_8H_{17}(OCH_2CH_2)_3OH/H_2O/C_{14}H_{30}$		30.0
8	$C_8H_{17}(OCH_2CH_2)_3OH/H_2O/C_{16}H_{34}$		35.5
9	$C_{12}H_{25}(OCH_2CH_2)_4OH/H_2O/C_{12}H_{26}$		22.2
10	$C_{12}H_{25}(OCH_2CH_2)_4OH/H_2O/C_{16}H_{34}$		31.1
11	$C_{12}H_{25}(OCH_2CH_2)_4OH/H_2O$/squalane		47.3

Fig. 6. Correlation between the difference in two critical end temperatures ($\Delta T = T_{\text{UCST}} T_{\text{LCST}}$) and the minima of O–W interfacial tensions in various nonionic surfactant systems. The interfacial tensions were measured at $(T_{\text{UCST}} + T_{\text{LCST}})/2$.

facial tension to the ultralow range has to be small.

At each critical temperature, a generalized Antonoff's rule, $\gamma_{O-W}=\gamma_{O-D}+\gamma_{D-W}$, automatically holds on the Lc-γ and Kc-β lines in Fig. 1,[24] because:

$$\gamma_{D-W}=0,\ \gamma_{O-W}=\gamma_{O-D} \quad \text{at LCST,} \tag{1}$$

$$\gamma_{O-D}=0,\ \gamma_{O-W}=\gamma_{D-W} \quad \text{at UCST.} \tag{2}$$

In the three-phase region, Antonoff's rule holds approximately, but, strictly speaking, γ_{O-W} is slightly smaller than $\gamma_{O-D}+\gamma_{D-W}$ as is shown in Fig. 5. A reverse inequality does not hold at true equilibrium.[24-27)]

$$\gamma_{O-W}<\gamma_{O-D}+\gamma_{D-W} \quad \text{in the three-phase region} \tag{3}$$

Since a stable lens of the surfactant phase was formed at the water–oil interface after equilibrium was attained at 30 °C (50/50 water/tetradecane, $C_8H_{17}(OCH_2CH_2)_3$-OH 1.5 wt%/system), the (3) relation surely holds. The minimum was observed on the γ_{O-W} *versus*-temperature curve in the three-phase region, as is shown in Fig. 5. It is obvious from Relations 1—3 that this minimum becomes ultralow when the two critical end temperatures approach each other. If the LCST coincides with the UCST completely, γ_{O-W} becomes zero at the tricritical point at which three coexisting phases become identical, as has been described before. The correlation between the temperature difference at two critical end points ($\Delta T=T_{UCST}-T_{LCST}$) and the minima of γ_{O-W} in various nonionic surfactant systems is shown in Fig. 6. The interfacial tensions were measured at temperatures in the midst of the three-phase region. It is clear from Fig. 6 that the ultralow interfacial tension at an oil–water interface is attained in the system in which the difference in two critical temperatures is very small, and that the longer the hydrocarbon chain length of a surfactant, the lower the oil–water interfacial tension. In this case, both the oil phase and the water phase contain only a small amount of a surfactant, *i.e.*, cmc or so, as is shown in Figs, 1, 2, and 4. Therefore, the concentration of a surfactant required to reduce the interfacial tension to the ultralow range is very small.

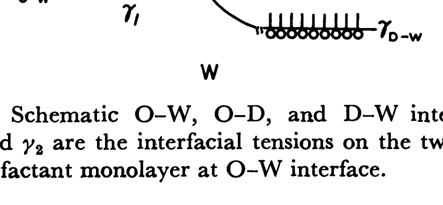


Fig. 7. Schematic O–W, O–D, and D–W interfaces. γ_1 and γ_2 are the interfacial tensions on the two sides of surfactant monolayer at O–W interface.

Correlation between the Emulsion Type and Interfacial Tension. Since the three-phase region appears in the temperature range between the two critical points of the O–D and D–W phases, the interfacial tensions at the respective interfaces will be directly relevant to the inversion of the emulsion type. If γ_1 is the interfacial tension between a water phase and a surfactant monolayer adsorbed on the O–W interface, and γ_2 that between an oil phase and a surfactant monolayer, $\gamma_{O-W}=\gamma_1+\gamma_2$ holds in the three-phase region (*cf.* Fig. 7.) $\gamma_{O-D(\simeq W)}=\gamma_1+\gamma_2$ and $\gamma_{D(\simeq O)-W}=\gamma_1+\gamma_2$ also hold at temperatures below the LCST and above the UCST. As has been described before, $\gamma_{O-D(\simeq W)}$ is the interfacial tension between an aqueous micellar solution phase and an excess oil, and $\gamma_{D(\simeq O)-W}$, that between a reversed micellar solution phase and excess water. Since Antonoff's rule holds approximately in the three-phase region, the O–W interface can be regarded as a thin film of the D phase. However, strictly,

$$\gamma_{O-D}=\gamma_2+\gamma_1',\ \gamma_{D-W}=\gamma_1+\gamma_2', \tag{4}$$

where γ_1' and γ_2' are the correction terms which are not negative, judging from Eq. 3. Since Antonoff's rule holds strictly at each critical temperature, *i.e.*, $\gamma_1'=\gamma_2'=0$, the following relations hold:

$$\gamma_1=0,\ \gamma_{O-W}=\gamma_2 \quad \text{at LCST,} \tag{5}$$

$$\gamma_2=0,\ \gamma_{O-W}=\gamma_1 \quad \text{at UCST.} \tag{6}$$

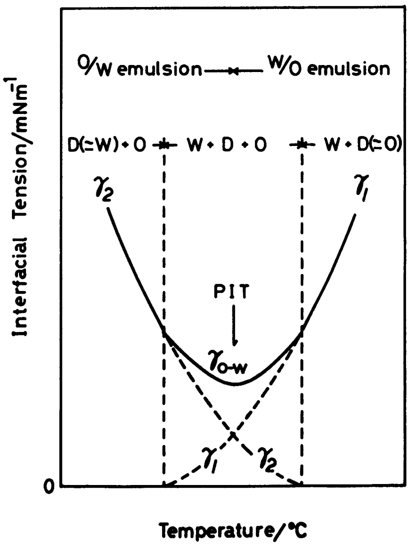


Fig. 8. Schematic change of the two interfacial tensions on the two sides of surfactant monolayer, γ_1 on the water side and γ_2 on the oil side as a function of temperature. A real curve corresponds to the interfacial tension of oil–water emulsion system.

γ_{D-W} may be zero or negative at a flat interface below the LCST, because the D–W interface is not stable at equilibrium. Therefore, $\gamma_1\leq 0$ and $\gamma_{O-D(\simeq W)}\leq\gamma_2$ hold below the LCST. Similarly, $\gamma_2\leq 0$ and $\gamma_{D(\simeq O)-W}\leq\gamma_1$ hold above the UCST. These relations are shown schematically in Fig. 8. The interface on the oil side of the surfactant monolayer tends to shrink, while that on the water side of the surfactant monolayer tends to expand, at temperatures below the LCST, because $\gamma_1\leq 0$ and $\gamma_2>0$, as is shown in Fig. 8. Therefore, in this temperature range, an O/W-type emulsion is formed. The case is the reverse above the UCST, so that a W/O-type emulsion is formed. $\gamma_1=\gamma_2$ holds at the temperature in the midst of a three-phase region. This temperature is the Hydrophile-Lipophile-Balanced (HLB) temperature and may correspond to the phase inversion temperature in emulsion. Since the interfacial tension curve is almost symmetrical, as is shown in Fig. 5, the phase inversion temperature (PIT) may be close to

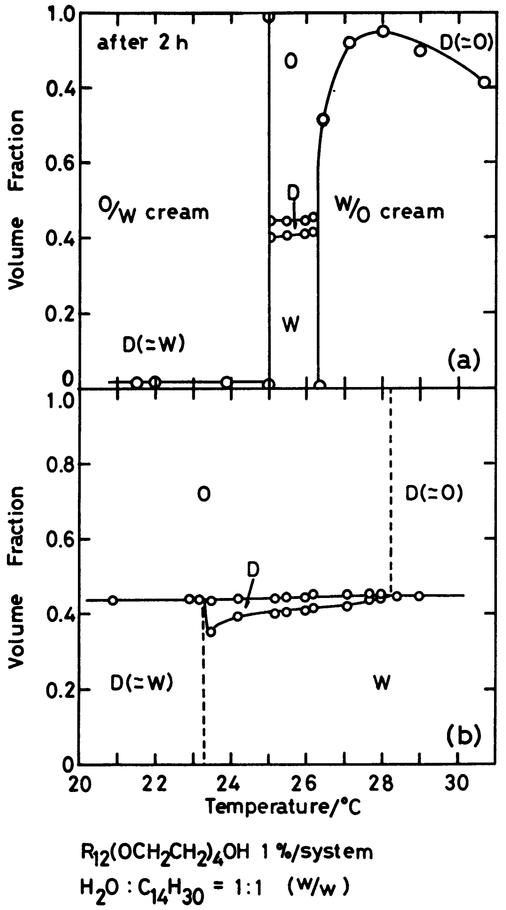


Fig. 9. The effect of emulsification temperature on the type of emulsion (a) and the volume fractions of O, W, and D phases at equilibrium (b) in $C_{12}H_{25}(OCH_2CH_2)_4$-OH/water/tetradecane system.

the temperature at which γ_{O-D} and γ_{D-W} become equal. In order to confirm this reasoning, the effect of the temperature on the emulsion type was carefully determined; it is shown in Fig. 9.[28,29] It is obvious that PIT is in the midst of the three-phase region.

References

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

2) P. A. Winsor, "Solvent Properties of Amphiphilic Compounds," Butterwoeths, London (1954), p. 68.

3) R. N. Healy, R. L. Reed, and D. G. Stenmark, *Soc. Pet. Eng. J.*, **16**, 147 (1976).

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

5) K. Shinoda, H. Kunieda, N. Obi, and S. E. Friberg, *J. Colloid Interface Sci.*, **80**, 304 (1981).

6) A. M. Bellocq, D. Bourbon, and B. Lemanceau, *J. Colloid Interface Sci.*, **79**, 419 (1981).

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

8) R. N. Healy and R. L. Reed, "Improved Oil Recovery by Surfactant and Polymer Flooding," ed by D. O. Shah and R. S. Schechter, Academic Press, New York (1977), p. 383.

9) J. L. Cayias, R. S. Schechter, and W. H. Wade, *J. Colloid Interface Sci.*, **59**, 31 (1977).

10) L. Cash, J. L. Cayias, G. Fournier, D. Macallister, T. Schares, R. S. Schechter, and W. H. Wade, *J. Colloid Interface Sci.*, **59**, 39 (1977).

11) P. H. Doe, M. El-Emary, W. H. Wade, and R. S. Schechter, *J. Am. Oil Chem. Soc.*, **55**, 505 (1978).

12) H. Kunieda and S. E. Friberg, *Bull. Chem. Soc. Jpn.*, **54**, 1010 (1981).

13) G. Quincke, *Pogg. Ann.*, **160**, 337 (1877).

14) A. W. Adamson, "Physical Chemistry of Surfaces," 3rd ed John Wiley and Sons, New York (1976), p. 31.

15) K. Shinoda and H. Saito, *J. Colloid Interface Sci.*, **30**, 258 (1969).

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

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

18) R. B. Griffiths, *J. Chem. Phys.* **60**, 195 (1974).

19) J. C. Lang, Jr., and B. Widom, *Physica*, **81A**, 190 (1975).

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

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

22) K. Shinoda, M. Hanrin, H. Kunieda, and H. Saito, *Colloids Surfaces*, **2**, 301 (1981).

23) J. C. Lang and R. D. Morgan, *J. Chem. Phys.* **73**, 5849 (1980).

24) J. C. Lang, Jr., P. K. Lim, and B. Widom, *J. Phys. Chem.*, **80**, 1719 (1976).

25) B. Widom, *J. Chem. Phys.*, **62**, 1332 (1975).

26) Ref. 14, p. 109.

27) P. D. Fleming, III, and J. E. Vinatieri, *J. Colloid Interface Sci.*, **81**, 319 (1981).

28) K. Shinoda and H. Saito, *J. Colloid Interface Sci.*, **30**, 258 (1969).

29) K. Shinoda and H. Sagitani, *J. Colloid Interface Sci.*, **64**, 68 (1978).