Bull. Chem. Soc. Jpn., 56, 980—984 (1983) [Vol. 56, No. 4

Phase Behavior and Tricritical Phenomena in a Bile Salt System

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(Received July 22, 1982)

A three-phase region consisted of a water (W), a surfactant (D) and an oil (O) phases was found in a sodium taurocholate (NaTC)/brine/co-surfactant (monoglyceride or its model compound)/oil (triglyceride) system. A required concentration of cosurfactant to produce the three-phase region was decreased with increasing salinity. The three-phase region becomes narrower and finally vanishes with decreasing salinity at constant temperature or with the rise in temperature at constant salinity in a NaTC/brine/glycerol mono (2-ethylhexyl) ether/glycerol tris (2-ethylhexanoic) ester system. Since the critical end points of O–D and D–W phases approach and coincide in the system, the three-phase region disappears at a tricritical point at which three coexisting liquid phases become identical. According to the phase rule, there is a line of tricritical points in the space of T and compositions in this five-component system and it moves toward higher temperatures with the increase in salinity. Therefore, the three-phase region exists at temperatures below the tricritical temperature at constant salinity.

In a three-fluid-phase system (a liquid-liquid-gas type or a liquid-liquid-liquid type), two fluid phases become identical in the presence of a third phase at a critical end point.1–3) There are two kinds of critical end phenomena as is shown schematically in Figs. 1(a) and (b). One is the critical phenomenon between upper (A) and middle (B) phases, and the other is that between middle (B) and lower (C) phases. But, the critical phenomenon between upper and lower phases is not observed in the presence of the middle phase.4) If these two critical end points coincide each other, three coexisting phases become identical at a high-order critical point, *i.e.*, a tricritical point as is shown in Fig. 1(c).1–4) This kind of critical phenomenon has been observed in some systems.5–9)

In a surfactant/water/oil system, three coexisting liquid phases consisted of a water (W), a surfactant (D) and an oil (O) phases appear under certain conditions. For example, a three-phase region is observed at a certain temperature range in a nonionic surfactant/water/oil system and its upper limit corresponds to a critical end temperature of O–D phases, while its lower limit is that of D–W phases.10–12) The equilibrium of three coexisting phases in a surfactant system at atmospheric pressure is shown schematically in Fig. 2.10–12) The orientation of X axis corresponds to the oil–water ratio and that of Y axis corresponds to the concentration of surfactant. The Z axis is perpendicular to the plane (X–Y plane) of a three-phase triangle and it corresponds to temperature in a nonionic surfactant system. In Fig. 2(a), K and L are critical curves of D–W and O–D which exist outside the three-phase region and terminate at respective critical end points Kc and Lc. Curves, α, β, γ, are the loci of D, O, and W phases forming a three-phase triangle. The points on α and β curves coincide at Lc point at which O and D phases become identical. The critical mixture of O–D is in

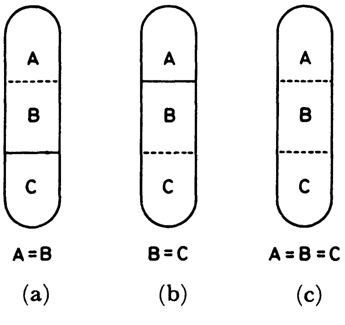

Fig. 1. Schematic figures of critical end points, (a), (b), and a tricritical point, (c).
(a): A and B phases become identical in the presence of C phase, (b): B and C phases become identical in the presence of A phase, (c): A, B, and C phases become identical at a tricritical point.

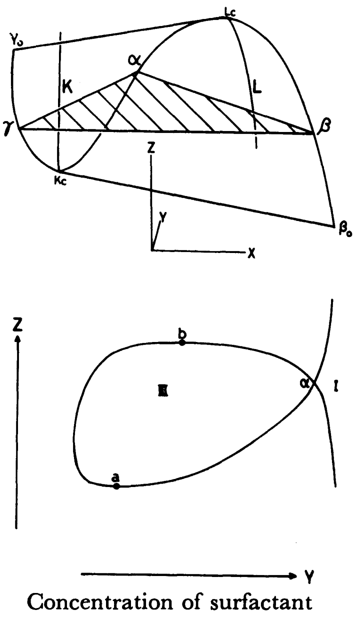

Fig. 2. (a) Schematic diagram of three coexisting phases in a surfactant/water/oil system at constant pressure. Curves α, β, and γ show the loci of compositions of a surfactant(D), and oil(O), and a water(W) phases forming a three-phase region. K and L are the critical curves of D–W and O–D phases. Lc and Kc are the critical end points of D–W and O–D. One of three-phase triangles is shown. (b) Vertical section of Fig. 2(a) at equal amount of water–oil. Points a and b are the intersections of this plane and Kc-β_0, Lc-γ_0 lines respectively. The orientation of X axis is vertical to this plane. III is the three-phase region.

equilibrium with W phases (γ_0 point) on the Lc-γ_0 line which is called a critical tie line.[13] Therefore, the critical end phenomenon as is shown in Fig. 1(a) occurs on this line. Similarly the critical end phenomenon occurs on another critical tie line, Kc-β_0 on which the phenomenon in Fig. 1(b) is observed. A three-phase region exists between two critical tie lines.

Vertical section (Z–Y plane) of Fig. 2(a) at a composition of equal amount of water and oil is also shown in Fig. 2(b).[10–12] A three-phase region exists inside a closed loop. Point **a** is the intersection of this plane and a critical tie line Kc-β_0 in Fig. 2(a). Point **b** is that of this plane and Lc-γ_0 line.

If these two critical end points strictly coincide, a tricritical phenomenon as is shown in Fig. 1(c) occurs. But, in a nonionic surfactant systems, it may not appear at atmospheric pressure, because a tricritical point is an invariant point in the space of T, P and compositions in a three-component system.[4,12] On the other hand, similar three-phase region appears in an ionic surfactant/brine/(co-surfactant)/oil system.[10,14–17] In these systems, one or two degrees of freedom increase in comparison with a nonionic surfactant system so that it seems to be easier to find a tricritical phenomenon despite of the difficulty of determining X, Y, Z axes exactly. Although the solution behavior of surfactant in a water–oil system is generally very complicated due to formation of a liquid crystalline phase,[18,19] it is known that there is no liquid crystalline phase in a bile salt system.[19] Therefore, a three-phase region and tricritical phenomenon may appear in a bile salt/brine/co-surfactant(monoglyceride)/oil(triglyceride) system, which can be regarded as a model of biological system.

Experimental

Materials. Sodium taurocholate (NaTC) was obtained from Sibma Chemicals Co. Its purity is above 98%. 3-(2-ethylhexyloxy)-1,2-propanediol (glycerol mono(2-ethylhexyl) ether, MEH) and 3-(*cis*-9-octadecenyloxy)-1,2-propanediol (glycerol monooleyl ether, MO) were obtained from Nikko Chemicals Co. and their purities are above 99%. 1,2,3-propanetriyl tris(2-ethylhexanoate) (glycerol tris(2-ethylhexanoic) ester, TEH) was obtained from Nisshin Seiyu Co. (above 97%) Extra-pure-grade 1,2,3-propanetriyl tris(*cis*-9-octadecenoate) (triolein, TO) was obtained from Nakarai Chemicals Co. Extrapure-grade *cis*-9-octadecenoic acid (oleic acid, OA) and 2,3-dihydroxypropyl dodecanoate (monolaurin, ML) were obtained from Tokyo Kasei Kogyo Co. These reagents were used without further purifications.

Procedures. Various amounts of brine, oil, surfactant and co-surfactant were sealed in ampoules. A series of ampoules kept in a thermostat were well shaken and left at constant temperature from 1 d to one week depending on the stability of solution and the three-phase boundary and the change in volumes of respective phases were determined.

Results and Discussion

Phase Behavior in Sodium Taurocholate (NaTC)/Brine/Co-surfactant/Oil Systems. Figure 3 shows three-phase regions consisted of a water (W), a surfactant (D) and an oil (O) phases in various systems of NaTC/brine/co-surfactant/oil at 35 °C. The concentration of NaTC is 3 wt%/system and (co-surfactant+oil)/brine ratio is unity. The weight percent of co-surfactant, *i.e.*, co-surfactant/(oil+co-surfactant)is plotted vertically and the salinity is plotted horizontally. At constant salinity, D phase is separated from W phase in the presence of O phase with the increase in co-surfactant content and a three-phase region appears. With further increase in co-surfactant content, D and O phases dissolve each other and the three-phase region turns to a two-phase system. The required concentration of co-surfactant to produce a three-phase region becomes low at high salinity. These results completely correspond with that in an ordinary ionic surfactant/brine/co-surfactant/oil system.[16] The change in solution behavior of NaTC from water-soluble to oil-soluble as a function of the concentration of co-surfactant corresponds to that of a nonionic surfactant/water/oil system as a function of temperature.[10,20,21] It is known that solubilization of oil or water in a surfactant solution reaches maximum and ultralow interfacial tensions are attained around a three-phase region due to critical solution phenomena of O–D and D–W phases.[11,21] The solubilization of MEH–TEH mixture in an aqueous NaTC solution has been determined and is shown in Fig. 4. It is clear that the optimum ratio of oil–co-surfactant is very important for large solubilization and the solution behavior of NaTC is highly affected by salinity.

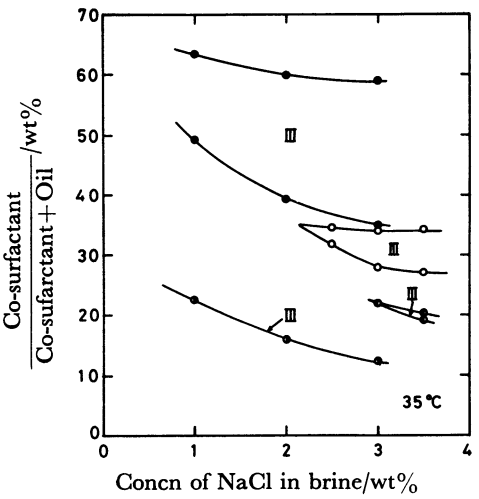

Fig. 3. The effect of salinity on the required concentration of co-surfactant to produce a three-phase region in a NaTC/brine/co-surfactant/oil system at 35 °C. The concentration of NaTC is 3 wt%/system and (oil+co-surfactant)/brine ratio is unity. III, the three-phase region.

	co-surfactant	oil
●	MO	TO
○	MEH	TEH
◐	MEH	OA
◑	ML	OA

The Effect of Salinity and Temperature on the Three-phase Region. Three-phase regions become narrower and finally diminishes with the decrease in salinity in the systems of NaTC/brine/MEH/TEH and NaTC/brine/MEH/OA as is shown in Fig. 3. In order to clarify this

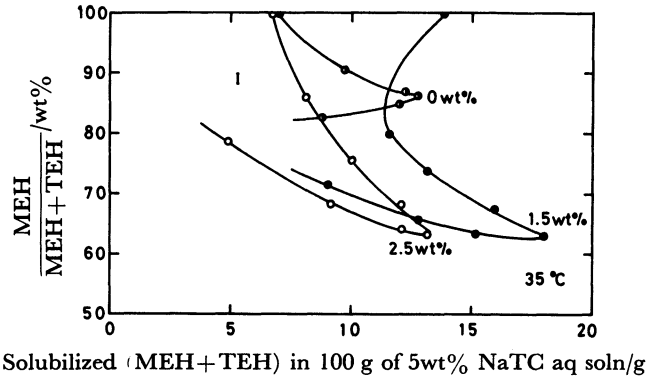

Fig. 4. The effect of NaCl on the solubilization of (TEH +MEH) mixture in brines containing 5 wt% of NaTC at 35 °C. The numerical values indicate concentrations of NaCl in brine.

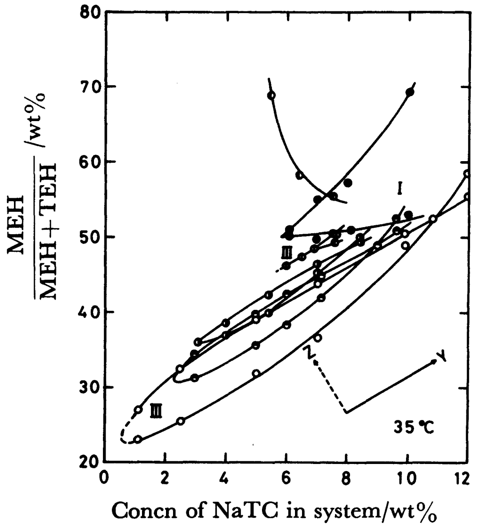

Fig. 5. The effect of NaCl on the three-phase region in NaTC/brine/MEH/TEH system at 35 °C. (MEH+TEH)/brine ratio is unity. The three-phase region becomes very narrow at 1.5 wt% NaCl.
◐: 0 wt% NaCl, ●: 1 wt% NaCl, ⦶: 1.5 wt% NaCl, ◑: 2 wt% NaCl, ◓: 2.5 wt% NaCl, ○: 3.5 wt% NaCl.

phenomenon, the effect of the concentration of NaTC on the three-phase region has been determined at 35 °C in the NaTC/brine/MEH/TEH system and is shown in Fig. 5. The vertical axis is the same as that of Fig. 3 and the concentration of NaTC in system is plotted horizontally. A three-phase region changes to one-phase region with increasing NaTC content, because O and W phases dissolve into D phase. On the other hand, the volume of D phase is decreased and finally, diminishes at the left-hand boundary of the three-phase region. Since inorganic salt is practically soluble only in water, brine can be regarded as a pseudo one component, then a pseudo four-component system of ionic surfactant/brine/co-surfactant/oil is represented by a tetrahedron at constant temperature and salinity as is shown in Fig. 6. In this pseudo four-component system, degree of freedom of respective regions is the same as that in a nonionic surfactant/water/oil system as is shown in Fig. 2

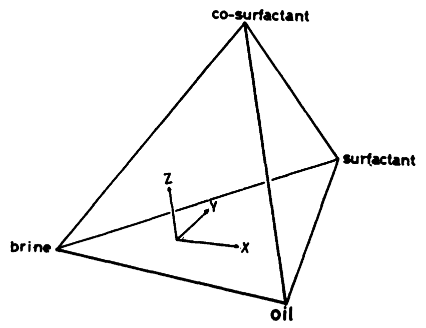

Fig. 6. Composition tetrahedron at constant T and P in a pseudo four-component system.

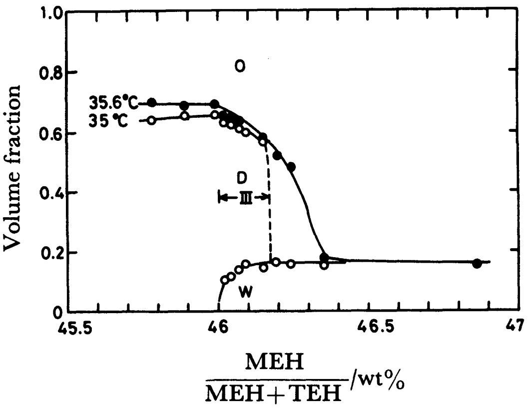

Fig. 7. The effect of $\frac{\text{MEH}}{\text{MEH+TEH}}$ on the volume fractions of respective phases at 1.5 wt% NaCl. The three-phase region diminishes at 35.6 °C. (MEH+TEH)/brine ratio is unity. The concentration of NaTC is 6 wt%/system.

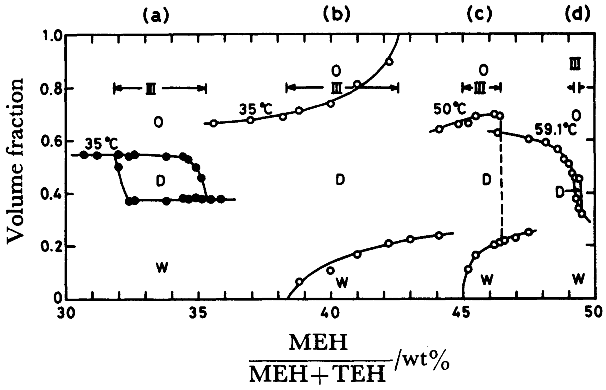

Fig. 8. The effect of temperature and the concentration of co-surfactant on the volume fractions of respective phases at various temperatures in a NaTC/brine(2.5 wt% NaCl)/MEH/TEH system. The concentrations of NaTC are 6 wt%/system (○) and 3 wt%/system (●).

because temperature and salinity are fixed. Therefore, two critical end points are invariant points and two critical tie lines are also fixed in a composition tetrahedron. Accordingly X, Y, Z, coordinate system similar to that in Fig. 2 can be taken in this tetrahedron. The orientation of Y axis in Fig. 5 corresponds to that in Fig. 2, because the volume fraction of D phase is in-

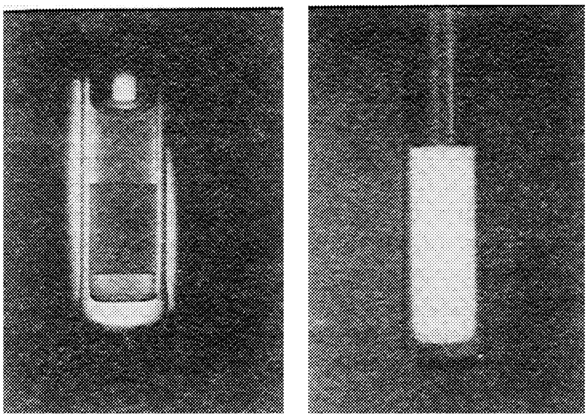
(a) (b)

Fig. 9. The photographs of the three coexisting phases near the tricritical point at 35 °C in transmitted light (a) and in scattered light (b). (NaTC, 6 wt%/system. (MEH+TEH)/brine (1.5 wt% NaCl) is unity. MEH/(MEH+TEH) is 46.05 wt%.)

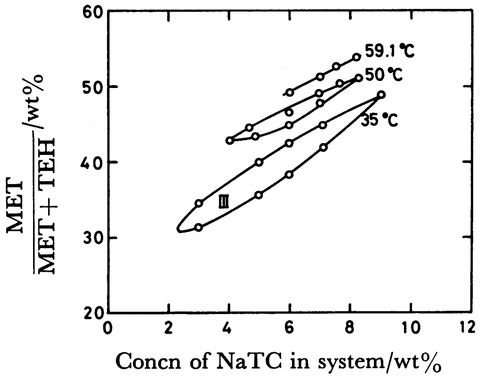

Fig. 10. The effect of temperature on the three-phase region at constant salinity (2.5 wt% NaCl) in a NaTC/brine/MEH/TEH system. The three-phase region vanishes slightly above 59.1 °C. (MEH+TEH)/brine ratio is unity.

creased in this direction. The three-phase region becomes narrower with the decrease in salinity and vanishes slightly below 1.5wt% NaCl. The change in volume fractions of respective phases as a function of co-surfactant content is shown in Figs. 7 and 8(a), (b) at 35 °C. As is shown in Figs. 8(a) and (b), when the concentration of NaTC is low (3 wt%), D phase dissolves into O or W phase and disappers at the right- or left-hand boundaries of the three-phase region. On the other hand, when the concentration of NaTC is high (6 wt%), O or W phase dissolves into D phase and disappears at those boundaries. This means that the critical end phenomena between O–D or D–W phases occur in the presence of a third phase (W or O phase) at a concentration of NaTC between 3—6 wt% on the curve in Fig. 5.[10,11,16] Those points correspond to the intersection between the plane of Fig. 5 and the critical tie lines in a composition tetrahedron (*cf.* points **a** and **b** in Fig. 2). Therefore, Z axis in Fig. 5 corresponds to that in Fig. 2 but is not completely in parallel with the plane of Fig. 5 as described later. Since these two points exist on the closed curve of Fig. 5, the width of a three-phase region at respective salinity represents the relative distance between two critical tie lines and it corresponds to the difference in critical end temperatures in a nonionic surfactant system. As is shown in Fig. 5, that distance shortens with the decrease in salinity and at last becomes zero slightly below 1.5 wt% NaCl at constant temperature (35 °C). In other words, the three-phase region in the composition tetrahedron becomes smaller and smaller with decreasing in salinity. Therefore, a tricritical point exists slightly below 1.5 wt% NaCl. In fact, all three coexisting phases show critical opalescence at 1.5 wt% NaCl as is shown in Fig. 9.

On the other hand, at constant salinity (2.5 wt% NaCl), a three-phase region also becomes narrow and vanishes with the rise in temperature as is shown in Fig. 10. The change in volume fractions of respective phases at 35, 50, and 59.1 °C are also shown in Figs. 8(b), (c), and (d). Hence, it is considered that a tricritical point also exists slightly above 59.1 °C at 2.5 wt% NaCl. From these results, a tricritical point shifts toward higher temperatures with increasing salinity.

Correlation between a Tricritical Phenomenon and the Degree of Freedom.[22] If the number of components are increased, a tricritical phenomenon can be observed more easily. The degree of freedom (f) of pth order critical point is expressed by following relation.[22]

$$f = c - 2p + 3, \tag{1}$$

where p is the number of phases becoming identical, and c is the number of components. Therefore, at a tricritical point, $f = c - 4$ at constant pressure. This means that there is a line of tricritical points in the space of T and compositions in a five component system and it becomes an invariant point when temperature or composition of one component is fixed. In other words, a tricritical temperature is invariant at constant salinity, while the salinity at a tricritical point is invariant at constant temperature.

The Shape of a Three-phase Region Near the Tricritical Point. Figure 11 shows the shape of the three-phase region at 1.5 wt% NaCl on the plane almost perpen-

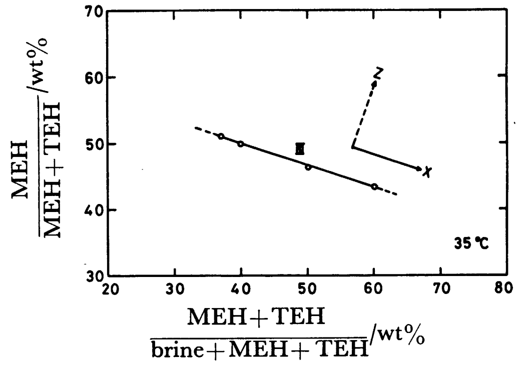

Fig. 11. The effect of (MEH+TEH)/brine ratio on the three-phase region in a NaTC/brine(1.5 wt% NaCl)/MEH/TEH system at 35 °C. The concentration of NaTC in system is 6 wt%. This figure is almost perpendicular to the plane of Fig. 5 in a composition tetrahedron.

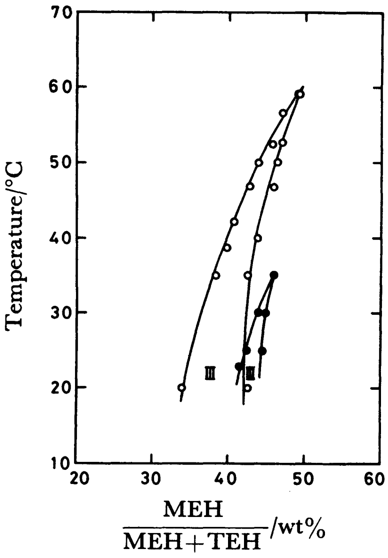

Fig. 12. The effect of temperature on the three-phase region in a NaTC/brine(●, 1.5 wt% NaCl; ○, 2.5 wt% NaCl)/MEH/TEH system. The concentration of NaTC in system is 6 wt%. (MEH+TEH)/brine ratio is unity. The three-phase region vanishes in the vicinity of a tricritical temperature.

dicular to that in Fig. 5 in the composition tetrahedron at 1.5 wt% NaCl. X axis and Y axis are approximately parallel to the respective figures. But Z axis in the figures is the projection of true axis on respective planes judging from Figs. 5 and 11. Although we could not determine the edges of the three-phase region in Fig. 11 because of their narrownesses, it is clear that near the tricritical point, the order of the sizes of the three-phase region in three directions is X>Y>Z. As described before, a three-phase region shrinks to a point, *i.e.*, a tricritical point in a composition tetrahedron with the rise in temperature at constant salinity or with increasing salinity at constant temperature. Griffiths predicted theoretically the shape of a three-phase region as a function of temperature in his coordinate system ξ_1, ξ_2, ξ_3, which is intrinsic to the figure of a three-phase region.[1] Present coordinate system, X, Y, Z, approximately corresponds with his system near a tricritical point.[1,2] According to his theory, the dimensions of the three-phase region vanish at different rates. The size in the ξ_1 direction diminishes proportionally to $(T_{\text{Tcp}}-T)^{1/2}$, that in the ξ_2 direction vanishes proportionally to $(T_{\text{Tcp}}-T)$ and that in the ξ_3 direction disappears proportionally to $(T_{\text{Tcp}}-T)^{3/2}$, where T_{Tcp} is a tricritical temperature.[1,2] Therefore, on approach to the tricritical point the region first becomes flat (the size in the ξ_3 (or Z) direction shrinks), then slender (that in the ξ_2 (or Y) direction shrinks) and finally of vanishing length (that in the ξ_1 (or X) direction shrinks).[1,2] His prediction is qualitatively in correspondence with the NaTC system as is shown in Figs. 5 and 11.

Correlation between a Tricritical Point and a Three-phase Region. As described before, a tricritical point is shifted to higher temperatures with increasing salinity. Accordingly, at fixed salinity, a three-phase region exists at temperatures below the tricritical temperature as is shown in Fig. 12. If the salinity is approached to zero, the tricritical temperature becomes below 0 °C and the three-phase region cannot be observed. This is the reason why it is difficult to obtain a three-phase region in an ionic surfactant/water/co-surfactant/oil system without adding salt.

The authors wish to thank Mr. M. Tanaka for his technical assistance.

References

1) R. B. Griffiths, *J. Chem. Phys.*, **60**, 195 (1974).
2) J. C. Lang, Jr., and B. Widom, *Physica*, **81A**, 190 (1975).
3) M. L. McGlashan, "Chemical Thermodynamics," Academic Press Inc., London (1979), Chap. 17.
4) B. Widom, *J. Phys. Chem.*, **77**, 2196 (1973).
5) J. Specovius, M. A. Leiva, R. L. Scott, and C. M. Knobler, *J. Phys. Chem.*, **85**, 2313 (1981).
6) G. S. Radyshevskaya, N. I. Nikurashina, and R. V. Mertslin, *J. Gen. Chem. USSR*, **32**, 673 (1962).
7) I. R. Krickevskii, G. D. Efremova, R. O. Pryanikova, and A. V. Serebryakova, *Russ. J. Phys. Chem.*, **37**, 1046 (1963).
8) G. D. Efremova and A. V. Shvarts, *Russ. J. Phys. Chem.*, **40**, 486 (1966).
9) R. B. Griffiths, *Phys. Rev. Lett.*, **24**, 715 (1970).
10) H. Kunieda and S. E. Friberg, *Bull. Chem. Soc. Jpn.*, **54**, 1010 (1981).
11) H. Kunieda and K. Shinoda, *Bull. Chem. Soc. Jpn.*, **55**, 777 (1982).
12) H. Kunieda, *Bull. Chem. Soc. Jpn.*, **56**, 625 (1983).
13) B. M. Knickerbocker, C. V. Pesheck, H. T. Davis, and L. E. Scriven *J. Phys. Chem.*, **86**, 393 (1982).
14) P. A. Winsor, "Solvent Properties of Amphiphilic Compounds," Butterworths, London (1950), p. 68.
15) R. L. Reed and R. N. Healy, "Improved Oil Recovery by Surfactant and Polymer Flooding," ed by D. O. Shah and R. S. Schecther, Academic Press Inc., New York (1977), p. 383.
16) H. Kunieda and K. Shinoda, *J. Colloid Interface Sci.*, **75**, 601 (1980).
17) H. Kunieda and K. Shinoda, *Yukagaku*, **29**, 676 (1980).
18) H. Kunieda and K. Shinoda, *J. Dispersion Sci. Tech.*, **3**, 233 (1982).
19) P. Ekwall, L. Mandell, and K. Fontell, *Mol. Cryst. Liquid Cryst.*, **8**, 157 (1969).
20) K. Shinoda and H. Saito, *J. Colloid Interface Sci.*, **26**, 70 (1968).
21) K. Shinoda and H. Kunieda, *J. Colloid Interface Sci.*, **42**, 381 (1973).
22) J. Zernike, *Recl. Trav. Chim. Pays-Bas*, **68**, 585 (1949).