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ORIGINAL CONTRIBUTION

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Noble phase behavior of water/propanol/polyethyleneglycol mono alkyl ether/oil system

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Abstract We studied the phase behavior of three coexisting phases in water/propanol/octaethyleneglycol mono dodecyl ether/heptane system at 45 °C. A cone-like three-phase body was found in a composition tetrahedron. In the body aqueous and surfactant phases coexist in the presence of the third coexisting phase, an oil phase, with their loci of composition drawing a closed-loop on addition of propanol. The oil phase remains in an oil-rich region without major change in its composition. The roles of propanol are discussed by using hydrophile-lipophile balance and locations of critical tie lines. Propanol mainly plays two roles; one is as a lipophilic cosurfactant and the other is as a water-soluble cosolvent. The compositions of the critical end points were also determined by a method to use the critical tie line as a clue. In other systems the same pattern phase behavior was observed.

Key words Propanol – cone-like three-phase body

Introduction

Amphiphiles or surfactant molecules self-associate in polar or nonpolar solvents and different kinds of surfactant phases appear under certain circumstances [1–12]. The nature of surfactant aggregates under a given condition dominates the state of solution. This is understood well by means of the concept of hydrophile-lipophile balance [13–17]. Depending on the hydrophile-lipophile property of surfactant, surfactant molecules are dissolved in water forming micelles or in nonpolar solvents forming reverse micelles [15–18]. When the hydrophile-lipophile property is just balanced in a given water–oil system, surfactant molecules form microemulsion [2–4, 13–16] of bicontenuous structure [13–16, 18] or other surfactant phases, that is, lamella liquid crystalline phase [19, 20] or D'phase [21]. In these phases large amounts of water and/or oil are solubilized. The microemulsion coexists with excess water and oil phases and forms a three-phase body.

Self-association of amphiphile molecules is owing to their dual property; the hydrophobicity of the lipophilic tail(s) and the lipophobicity of the hydrophilic group(s) of surfactant molecules. It is known that nonionic surfactants form micelles in some water-soluble solvents such as formamide [22, 23], glycerol [22], and some diols [22]. On the other hand, the surfactants are monomerically dissolved in other polar solvents such as dimethylformamide and short chain alcohols (methanol, ethanol) and do not form micelles [22, 24, 25]. In addition, short-chain alcohols have another effect on micelle formation of surfactants; they enhance the formation of micelles in water. In other words, the CMC values of nonionic surfactants in water decrease and reach their minimum upon addition of the short-chain alcohols [25–29]. Further addition of short-chain alcohols obstructs micelle formation. It is also known that three coexisting phases appear in brine/short-chain alcohol/oil systems, even without nonionic surfactant [30–33].

Kunieda reported that the three-phase body is shrunk upon addition of the alcohols and eventually it disappears at a tricritical point [34]. However, the effect of added short-chain alcohols on the whole three-phase behavior of nonionic surfactant in water–oil system has not been systematically studied.

In this context, the three-phase behavior of a water/propanol/polyethylene glycol alkyl ether/oil system was investigated to figure out the effect of short-chain alcohol.

Experimental

Materials

Extra pure grade propanol and oils were obtained from Tokyo Kasei Kogyo Co., Ltd. Homogeneous polyethyleneglycol mono alkyl ethers were obtained from Nikko Chemicals Co., Ltd. They were used without further purification. Water was distilled twice after being ion-changed.

Procedure to determine phase boundary

A series of composition was prepared in a glass tube. The error of composition was less than 0.5 wt%. Having being sealed in a glass tube, they were well shaken in a thermostat after thermoequilibrium and left till phase separation or a single clear phase was attained. The phase boundaries were determined by visual observation after phase separation took place. Shaking and observation of phase separation were repeated at least twice, especially at least three times in case of the nearest mixture to a boundary. There was rarely any inconsistency.

Identification of each phase

The identification of each phase was performed synthetically considering the following: 1) phase volume changes mainly across the phase boundaries; 2) the composition of each phase; 3) the pattern of phase separation comparing with well-known ones, for example D phase; 4) continuity from known phases; 5) location in relation to the critical point or the critical tie line.

Results

Phase behavior of water/propanol/octaethyleneglycol mono dodecyl ether/oil systems

Figure 1 shows the phase diagram of water/propanol/octaethyleneglycol mono dodecyl ether/cyclohexane system and the one of water/propanol/octaethyleneglycol mono dodecyl ether/heptane system at 45.0 °C and atmospheric pressure. The weight ratio of water/oil is kept constant (50/50). This figure as well as others in this paper represents a three-phase region consisting of a surfactant, excess water and excess oil phases, because amphiphiles or other components show their important functions in and near the region in surfactant systems.

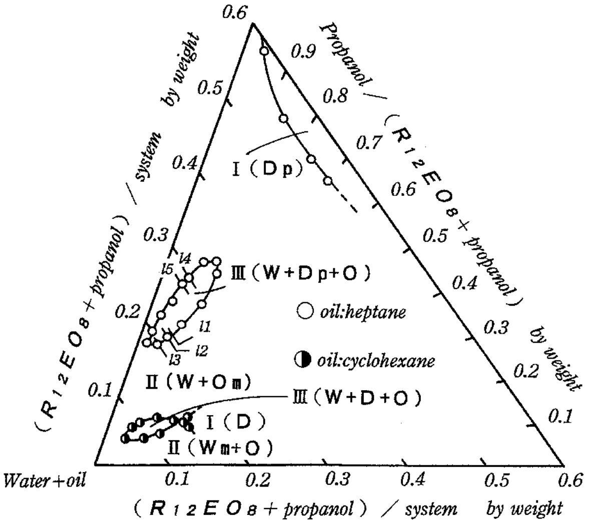


Fig. 1 Phase diagram of a water/propanol/$R_{12}EO_8$/cyclohexane system and a water/propanol/$R_{12}EO_8$/heptane system at 45.0 °C and atmospheric pressure. Water:oil is kept 1 : 1 by weight. I, II, and III indicate one-phase, two-phase and three-phase region, respectively. W, D, O, Wm and Om indicate excess aqueous, middle surfactant (microemulsion), excess oil, aqueous micellar and reversed micellar oil solution phases, respectively. Dp indicates the surfactant phase forming a closed-loop miscibility gap with water (or aqueous) phase. Only the neighborhoods of the three-phase region and the one-phase region were investigated

A typical fish-like shape of the three-phase region and single-phase region is observed in the former system; a single microemulsion or surfactant phase (D) touches the three-phase region consisting of excess water (W), surfactant, and excess oil (O) phases. This phase behavior is exactly the same as that for a mixed surfactant system including hydrophilic and lipophilic surfactants. Namely, in the present system, propanol will act as an ordinary lipophilic surfactants. Namely, in the present system, propanol will act as an ordinary lipophilic surfactant. Even if the water/oil ratio is changed, the single microemulsion phase touches the three-phase body in the present system.

On the other hand, another type of phase behavior is seen in the other system. There also is a three-phase region. Different from the cyclohexane system, the three-phase region is surrounded only by two-phase region(s), and no single-phase region touches the three-phase region. The two-phase regions are the one of the middle (indicated by

Dp) and upper (O) phases in the surfactant richer side and the one of lower (W) and upper phases in the surfactant dilute side. This is shown by the phase volume changes in the following section. This type of three-phase behavior is noble.

The phases have not been identified yet but have already been assigned the letters W, Dp and O here, for convenience of description and for consistency of symbols throughout this paper. They indicate a water (or aqueous) phase, the surfactant phase of interest in this paper, and an oil phase, respectively.

The emergence and the disappearance of the three-phase region and the locations of critical tie lines

To investigate the noble three-phase behavior, especially the emergence and disappearance of the three-phase region, the volume fraction changes of each phase have been studied and some are shown in Figs. 2(a) and (b). They are the ones on lines 11, 12, 13, 14 and 15 in Fig. 1, respectively. The letter Wm on the left-handside in Fig. 2(b) indicates an aqueous micellar solution phases. This phase continues from water/octaethyleneglycol mono dodecyl ether/heptane system. Octaethyleneglycol mono dodecyl ether is a hydrophilic surfactant in water/heptane system at 45.0 °C [35] and dissolves in water forming aqueous micellar solution [7] coexisting with an excess oil phase (O). As propanol increases on line 11, the lower phase (W) appears from Wm phase. On the other hand, on line 13 the middle phase (Dp) appears with the increase in propanol content. On line 12, which is between 11 and 13, Wm phase separates into the lower and middle phases. Their volume fractions still remained nearly equal up to within 0.0005 from the boundary by weight fraction. Critical opalescence was observed in the Wm, W and Dp phases around the separation. Conversely, the lower and middle phases become identical with each other in the presence of the upper phase with the decrease in propanol content. This phenomenon is the same as that of a microemulsion and a water phase. We consider that the lower phase is a water phase and that the middle is a surfactant phase . The addition of propanol induces the emergence of the surfactant phase. The point at which the interface of water and surfactant phases vanishes on 12 corresponds to the intersection of a critical tie line and the phase diagram of water/heptane = 50/50. This critical tie line terminates at a critical end point of the water and surfactant phases. The other terminal indicates the composition of the coexisting oil phase. (Figure 5 will help to illustrate this aspect. Point Kc corresponds to this critical end point.)

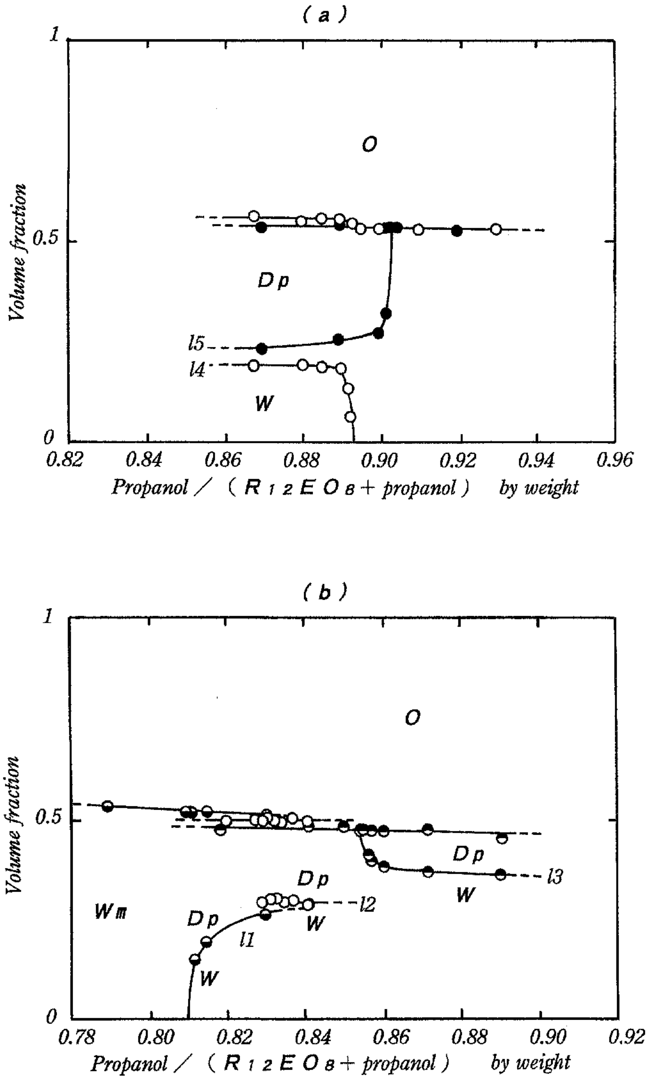


Fig. 2 Volume fraction changes of each phase along line 11, 12, 13, 14 and 15 in Fig. 1. The letters standing for the lines are attached to the corresponding curves

In the same manner, we can find the other critical tie line by Fig. 2(a). The surfactant phase swells and the lower aqueous phase disappears as the propanol content increases on line 14. On the other hand, on 15, the surfactant phase dissolves and disappears into the lower aqueous phase. The lower phase, of course, contains considerable propanol. The critical tie line passes between the lines 14 and 15. The aqueous phase and the surfactant phase become identical again. The increase of propanol causes the mutual solubilizing of the two phases. This critical tie line terminates at another critical end point. (This will be indicated by K'c in Fig. 5.)

It was confirmed that the three-phase region lies between two critical tie lines in a tetrahedron, like the ones of a microemulsion [36–38]. The noticeable feature is that the aqueous (or water) and the surfactant phases become identical at both critical end points. The oil phase remains all the while. In other words, the loci of the aqueous (or water) and surfactant phases meet twice and form a closed-loop coexistence curve in the presence of a third phase coexisting independently. The two-phase region W + Dp is insulated from the other two two-phase regions, W + O and Dp + O.

It can be seen from the above result that the three-phase region is formed by an overlap of two miscibility gaps; the closed-loop miscibility gap of water and surfactant phases and the main miscibility gap of aqueous surfactant and oil phases.

Schematic presentation of the three-phase body in a tetrahedron

Figure 3 is a series of phase diagrams of water/propanol/octaethyleneglycol mono dodecyl ether/heptane system when the weight ratio of water/heptane is varied. This provides us with the schematic presentation of the whole three-phase body, that is, loci of each phase and a stack of tie triangles. When the water/heptane ratio increases, a single-phase region touches the three-phase region twice and a two-phase region of W + Dp emerges as is shown in Figs. 3(a), (b) and (c). The single-phase region is that of the surfactant phase at water/heptane = 90/10 and indicated by I(Dp) in (c): the water and oil phases disappear as the mixed amphiphile increases. This means that the surfactant phase passes through the plane twice. In other words, the plane of water/heptane = 90/10 intersects the closed loop coexistence curve and cuts the W + Dp region. The contact-points indicate the compositions of surfactant phases of two tie triangles.

In Fig. 3(d), where water/heptane = 80/20, a single-phase region exists near but off the three-phase region and the two-phase region W + Dp is not seen. Between the ratios of 90/10 and 80/20, the two contact-points of one- and three-phase regions will coincide, where the locus of the surfactant phase saturated with water and oil will turn back. (This point will be indicated by Pturn in Fig. 5.)

When the water/heptane ratio increases up to 95/5, a one-phase region of the water (aqueous) phase touches the three-phase region twice as shown in Fig. 3(a). This region I(W) is not seen at water/heptane = 90/10. The water phase remains in water-rich regions. Figure 3(a) simultaneously shows that a considerable amount of propanol is dissolved in the water phase. This is confirmed also by Fig. 4, which is a phase diagram with propanol/$R_{12}EO_8$ = 90/10.

Figure 4 provides us with other information on the three-phase body. The ratio propanol/$R_{12}EO_8$ = 90/10 gives the minimum value of mixed amphiphile concentration for the three-phase body at almost all ratios of water/heptane as seen in Fig. 3. The content of heptane in water phase is expected to be minimum at this ratio. Even at this ratio the locus of water phase does not reach the heptane-free plane. This means that the three-phase body is completely inside the tetrahedron.

Fig. 3 A series of phase diagrams of a water/propanol/$R_{12}EO_8$/heptane system at 45.0 °C and atmospheric pressure. They are parts of sections of a tetrahedron with constant ratios of water/heptane. The ratios of water/heptane are 95/5 by weight for (a), 93/7 for (b), 90/10 for (c), 80/20 for (d), 50/50 for (e) and 5/95 for (f). Figure 3(e) is the same as that of heptane system in Fig. 1

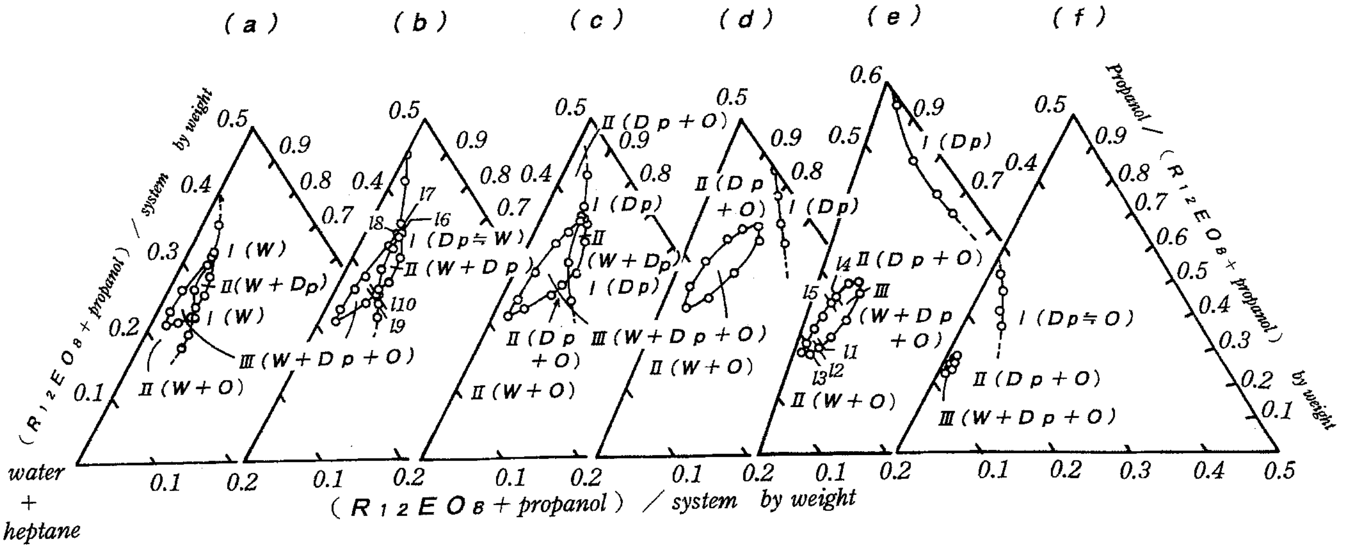
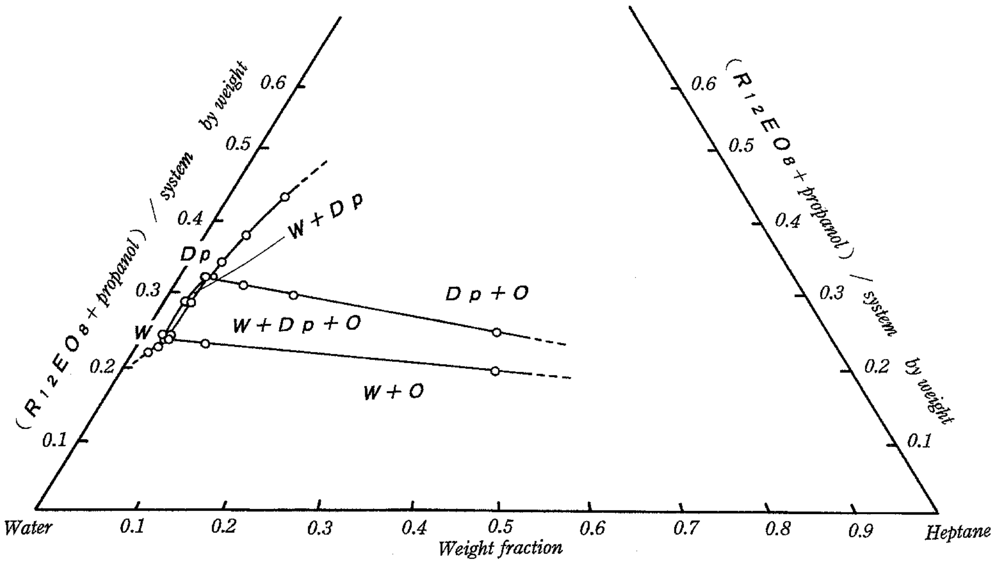


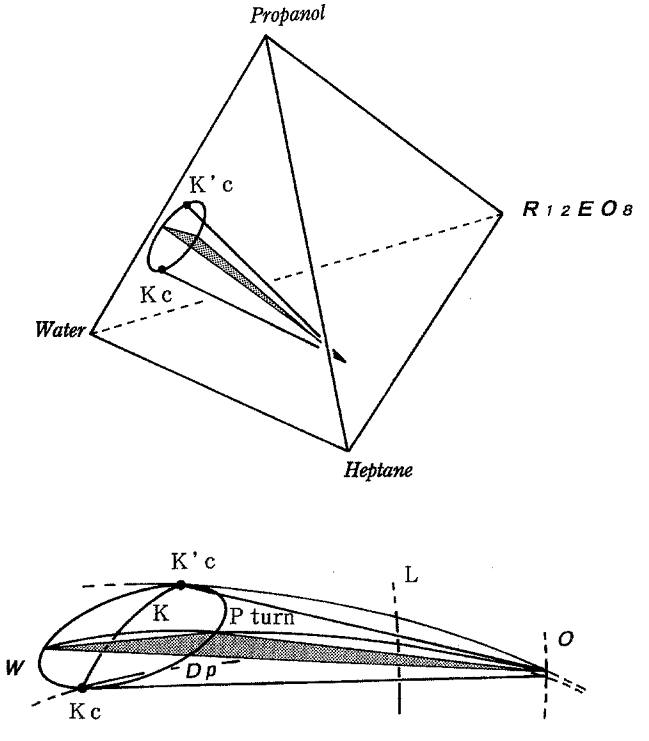
Fig. 4 A part of phase diagram of a water/propanol/$R_{12}EO_8$/heptane system at 45.0 °C and atmospheric pressure. The ratio of propanol/($R_{12}EO_8$ + propanol) is kept 0.90. The part of a three-phase region is not the one of a tie triangle; tie triangles or tie lines are not always on a plane of interest



On the other hand, as shown in Fig. 3(f), no one-phase region touches the three-phase region even when water/heptane is 5/95. The excess oil phase remains in a very low water/heptane region. Furthermore, the section of the three-phase body on a phase diagram of constant water/heptane becomes narrower with the decrease in the ratio of water/heptane. The composition of oil phase will remain nearly constant.

The novel three-phase behavior is schematically presented in Fig. 5. The loci of the water and the surfactant phases draw a closed-loop coexisting curve, whereas the oil phase remains in an oil-rich region and hardly moves. The body is enveloped by three kinds of two-phase regions; W + Dp, W + O, and Dp + O. The latter two are connected without a boundary; the first, W + Dp, is isolated from them. This cone-like three-phase body is the same as that which Knickerbocker et al. called achiral [31]. They have drawn a schematic representation in a ternary phase prism of water–nicotine–mercury system with temperature as ordinate. It seems that the closed-loop coexisting curve exists almost on the mercury-free plane and that the composition of mercury phase moves almost on the mercury axis. Mercury hardly affects the phase behavior of the other two phases and vice versa. On the other hand, the three-phase body of the present system exists in a tetrahedron phase diagram. In addition, a set of three types of two-phase regions adjoins it. The loci of the three coexisting phases, Kc-W-K′c, Kc-Dp-Pturn-K′c and line O, run inside the tetrahedron. They are the edges of the three-phase body. This means that each component affects the phase behavior. This type of phase behavior has not been observed as far as we know.

Fig. 5 Schematic presentation of a cone-like three-phase body in a tetrahedron (top) and its neighborhood (bottom). Kc indicates the lower critical end point and K′c the upper critical end point. "Pturn" is the point at which the surfactant phase turns its locus. The gray triangles are tie triangles. K and L are the critical point segments of W + Dp and Dp (or Wm) + O, respectively. Kc-W-K′c and Kc-Pturn-K′c are the loci of W and Dp, respectively. Kc-W-K′c-Pturn-Kc draws a closed-loop coexisting curve of W and Dp phases, The curves of Kc-L-O and K′c-L-O are the boundaries of two-phase regions. The loci of O phase and L stretch further: two-phase region of Wm + O also exists both above K′c-O and below Kc-O



The location of the critical end points

The locations of Kc and K′c, that is, the critical compositions of water and surfactant phases have been determined. Because propanol dissolves considerably both in water phase and in oil phase and so does $R_{12}EO_8$ in oil phase, it is a difficult task to determine a tie triangle, to say nothing of a critical tie line. A new method has been taken here, which uses a critical tie line as a clue.

A critical tie line is a limit of tie triangle and is located on the surface of the three-phase body [38]. Further, in surfactant systems, tie triangles expand nearly in parallel to the water–oil axis. Therefore, the critical tie line can be generally found on a phase diagram of fixed water/oil, being an intersection on the boundary of the three-phase and the two-phase regions. An example is the point of the intersection of 12 with the boundary of three-phase region of Fig. 1. On the other hand, the critical end point is a vertex of a tie triangle. This means that the three-phase region touches a one-phase region at the point. Accordingly, the critical end point is the point at which the intersection of critical tie line coincides with the contact point of the three-phase and the one-phase regions. The three-phase region, three kinds of two-phase regions, and two kinds of one-phase regions meet simultaneously at the critical end point. (Of course, a critical end point is an end point of a critical point segment running on the surface of a two-phase region. The segment meets the loci of vertices of tie triangle coming on the edge of the surface of two-phase bodies at the critical end point, where the two-phase region vanishes. Hence, another way to reach the critical end point is the way to chase the critical point segment.)

Figure 3(b) is the phase diagram for water/heptane = 93/7. Figures 6(a) and 6(b) are the volume fraction change of each phase along lines 16, 17, 18, 19 and 110 in Fig. 3(b). The abscissa is ($R_{12}EO_8$ + propanol)/system for 16 and 17 and propanol/($R_{12}EO_8$ + propanol) for 18. Along the line 16 a two-phase region of W + Dp is formed on the left-handside. As ($R_{12}EO_8$ + propanol) increases Dp phase swells and W phase disappears. On line 18, to the contrary, as propanol/($R_{12}EO_8$ + propanol) increases, Dp phase disappears and the three-phase region changes into the two-phase region W + O. On line 17, which is between 16 and 18, disappearance of the interface between W and Dp phases was seen. The solutions became bluish around the point; critical opalescence was observed. The point is very close to the contact-point of the three-phase and one-phase regions. Accordingly, we can estimate that the critical end point K′c is located very close to this point. The weight fraction of each component is as follows; water: 0.59, $R_{12}EO_8$: 0.05, propanol: 0.32, and heptane: 0.04.

Figure 6(a) shows volume fraction changes of each phase along the lines 19 and 110 near the other contact-point in Fig. 3(b). Along 19 the two-phase region of Wm + O changes into the three-phase region. Dp phase appears from Wm. Along 110, to the contrary, W phase appears from Wm as propanol increases: the change of Wm ~ (Wm + O) ~ (W + Dp + O) was observed. Around the boundary of two- and three-phase regions Wm, W and Dp phases became bluish: critical opalescence was observed. This contact point is very close to the other critical end point Kc. Figures 3(a) and (c) support this: the one-phase regions touching the three-phase body are those of water phase in Fig. 3(a) and of surfactant phase in

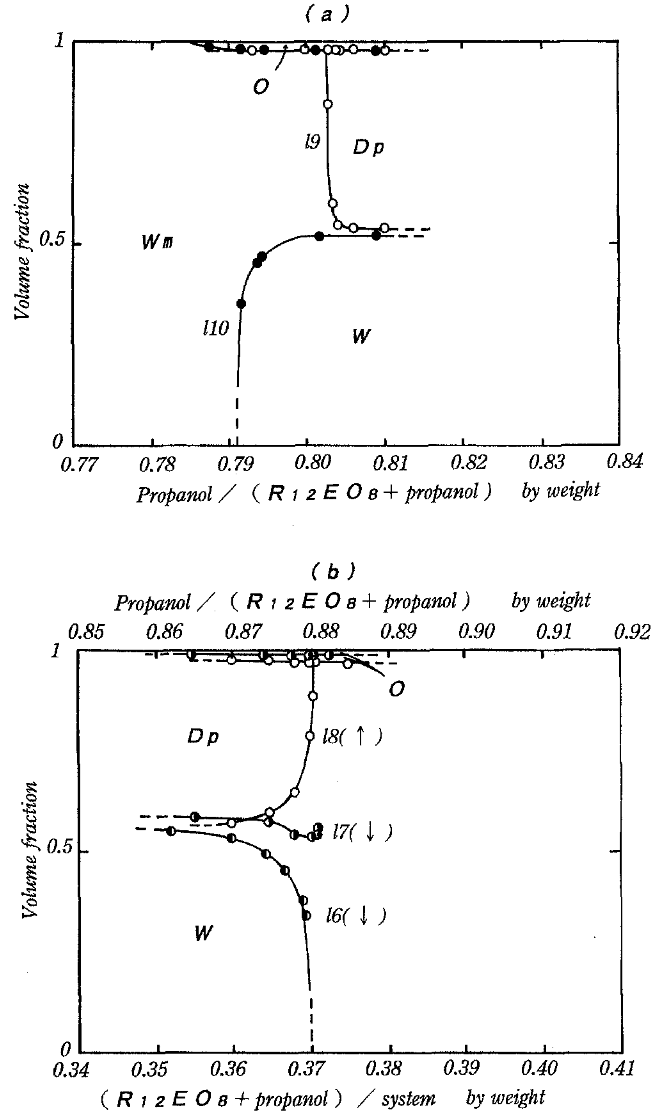


Fig. 6 Volume fraction changes of each phase along line 16, 17, 18, 19 and 110 in Fig. 3(b). The abscissas of (b) are ($R_{12}EO_8$ + propanol)/system for 16 and 17, indicated by (↓), and propanol /($R_{12}EO_8$ + propanol) for 18, indicated by (↑). The letters standing for the lines are attached to the corresponding curves

Fig. 3(c). The weight fraction of each component at the point is as follows: water: 0.65, $R_{12}EO_8$: 0.06, propanol: 0.24, and heptane: 0.05.

The two critical end points are located on almost the same plane of constant water/heptane = 93/7 inside a tetrahedron, off the heptane-free surface. As for the content of propanol, it differs considerably in both critical solutions.

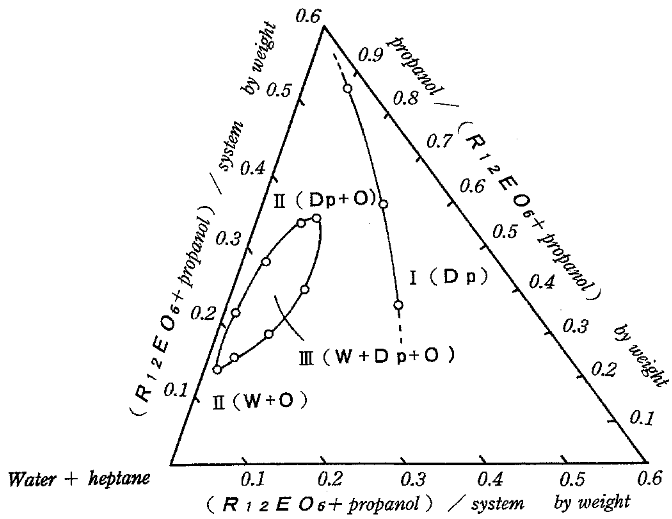
Two-phase region of the aqueous and the surfactant phases

The two-phase region of W + Dp adjoins the three-phase body at the base of the cone, the edge of which shows a closed-loop curve. Figure 4 shows that the two-phase region of W + Dp is located in a heptane-poor region. However, it does not touch the heptane-free plane. This means that heptane affects the phase separation of the surfactant phase in this system. Furthermore, if one chooses a section of this tetrahedron so as to cut the two-phase body, one will see a two-phase region of W + Dp enclosed completely by a one-phase region.

The same type of phase behavior in other systems

The same type of phase behavior was found in water/propanol/$R_{12}EO_8$/isooctane system at 50.0 °C and water/propanol/$R_{12}EO_6$/heptane system at 35.0 °C. The phase behavior of the latter one is shown in Fig. 7. Each system has a three-phase body consisting of W, Dp, and O in a propanol-rich region.

Fig. 7 Phase diagram of a water/propanol/$R_{12}EO_6$/propanol/heptane system at 30.0 °C and atmospheric pressure. Water: heptane = 1:1



Discussion

The roles of propanol in this system

Novel three-phase behavior was observed in water/nonionic surfactant/propanol/oil systems. From the location of the oil phase, the loci of aqueous and surfactant phases, and the locations of the critical end points, it can be concluded that the tie triangles pile up in the direction of increase in propanol content. In other words, the phase behavior depends greatly on the effects of propanol.

The concept of hydrophile-lipophile balance, HLB, offers help in understanding phase behavior of surfactant systems. HLB of surfactant in a system reflects all factors: temperature, the balance of functional groups of surfactant, the composition of mixed surfactant, properties of aqueous phase and oil phase, and so on. In addition, each factor for HLB may be considered to be independent and to change HLB monotonously. Hence, a single factor related with propanol is not sufficient for explanation of the phase behavior. The phase equilibrium between surfactant and aqueous phases changes in the order miscible-immiscible-miscible, on addition of propanol. Plural factors for propanol need taking into account.

Propanol is a small amphiphile and then its hydrophobicity and lipophobicity are weak. Accordingly, propanol is expected to affect HLB as a cosurfactant, as a water-soluble solvent, and as an oil-soluble solvent. The last function is, however, inconsequential here because the coexisting oil phase hardly changes its composition, judging from Fig. 3(f). The former two are conceivable major functions affecting HLB and then the phase behavior.

First, the emergence of the surfactant phase on the critical tie line of Kc can be attributed to the role of propanol as a cosurfactant. Excess addition of propanol shows the tendency to break surfactant aggregations in aqueous medium in spite of the promotion on its first addition [25–29]. This effect to break shows the reverse direction to the phase separation. In addition, $R_{12}EO_8$ is a hydrophilic surfactant in water/heptane system at 45.0 °C and atmospheric pressure, so that it dissolves in water forming micelle. Propanol will take part in forming surfactant aggregates as a cosurfactant and cause the surfactant phase to separate from the aqueous phase. It plays a role as a more lipophilic amphiphile than $R_{12}EO_8$. This interpretation is consistent with the result of the cyclohexane system in Fig. 1, which is also derived under the condition that the effect of propanol on the oil phase is a minor one. The effect of propanol as a cosurfactant dominates the effect as a water-soluble solvent.

On the other hand, a considerable amount of propanol in water prevents surfactant from aggregating, as mentioned above. Taking the view of HLB, this means that the surfactant aggregates apparently becomes hydrophilic. In other words, however, this can be also interpreted that the solvophobicity of surfactant aggregates gets relatively weaker while the aggregates is becoming more lipophilic. The effect of propanol as a solvent on property of aqueous medium will dominate the one as a cosurfactant on property of aggregates. The surfactant phase and the aqueous phase dissolve mutually again above the critical tie line of K′c. Conversely, the increase of water makes the solvent properties exclusive of nonpolar portions.

On the locations of critical tie lines

The location of critical tie lines gives a good support to the above interpretation. Figures 8(a) and (b) are the same as Fig. 3(e), except the variables are altered for this discussion. If propanol remains only in the amphiphile aggregates and plays only the role of cosurfactant, the critical tie lines are located on the top or bottom of the closed-loop coexisting curve when the ratio of propanol/$R_{12}EO_8$ is change. Figure 8(a) shows that it is inconsistent with the result. Figure 4 also shows that propanol dissolves in the water or aqueous phase. Since propanol in water has the tendency to break micelles [25], it can be thought that propanol in aqueous phase plays the role of cosolvent and make the amphiphile aggregate disorder.

On the other hand, if propanol does not take part in forming micelle and behaves only as a solvent and if the compositions of aqueous and oil domain in surfactant phase are equal to those of coexisting excess aqueous and excess oil phases respectively, then the critical tie lines are located on the top or bottom of the closed-loop coexisting curve when the ratio of propanol/(propanol + water + heptane) is changes. In this case, tie figures are always on planes determined by a tie line on the $R_{12}EO_8$-free plane and the vertex of $R_{12}EO_8$ and Fig. 8(b) can be considered to be a vertical stack of the intersections of such planes with the plane of water/oil = 1/1. The result is inconsistent with these assumptions, that is, denies one or both. It can be concluded that propanol is a water-soluble lipophilic cosurfactant.

Analogy to closed-loop coexisting curves in water–nonionic surfactant systems

Propanol plays two main roles in this system. This interpretation of the behavior of propanol is analogous to the effect of temperature on a closed-loop coexistence curve between water and surfactant phases in binary systems of water–nonionic surfactant [6]. Raising temperature makes nonionic surfactant more hydrophobic or lipophilic, and surfactant and excess water phases separate at the lower critical consolute temperature. Temperature increase corresponds to the increase of propanol in amphiphile

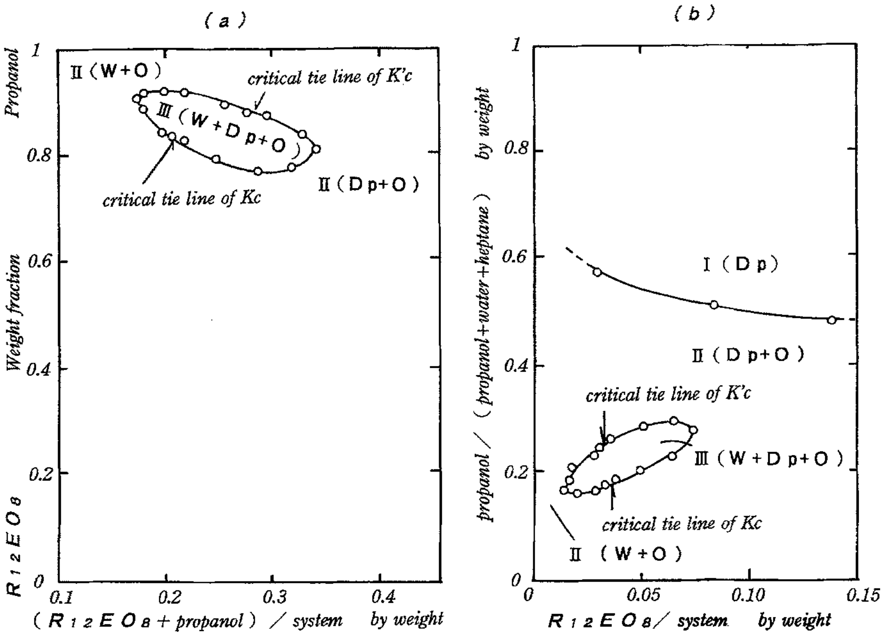


Fig. 8 Phase diagrams of a water/propanol/$R_{12}EO_8$/heptane system at 45.0 °C and atmospheric pressure. They are identical with Fig. 3(e) (or the heptane system of Fig. 1), but obtained by means of re-plotting. Figure 8(a): The abscissa is ($R_{12}EO_8$ + propanol)/system and the ordinate is the ratio of propanol/($R_{12}EO_8$ + propanol). Figure 8(b): The abscissa is the weight fraction of $R_{12}EO_8$ in system and the ordinate is the weight fraction of propanol/(propanol + water + heptane). Water: heptane is kept 1 : 1 by weight. Temperature and preseure are kept at 45.0 °C and atmospheric pressure

mixture. On the other hand, temperature increase makes entropic effect on free energy stronger. The surfactants and water dissolve mutually again above the upper critical consolute temperature. Replacement of water by propanol may lead to reduction in polarity or hydrogen bonding in aqueous medium and then help entropic effect to dominate relatively. Solvophobicity is weakened. Raising temperature corresponds to the increase of propanol in aqueous medium. The addition of propanol in the present systems corresponds to the rise of temperature in the binary systems showing a closed-loop coexistence of water and surfactant phases.

Conclusion

Novel, cone-like three-phase bodies were found in composition tetrahedrons of water/propanol/polyethyleneglycol mono alkyl ether/oil systems. Forming the three-phase body attributes to an overlap of two miscibility gaps; one is a closed-loop miscibility gap between water and surfactant phases and the other is the main miscibility gap between surfactant aqueous phase and oil phase, the third coexisting phase. The two-phase region of water and surfactant phases exists solitarily with its sections showing also closed-loop, whereas the other two-phase regions are linked around the critical tie lines enveloping the three-phase body.

Propanol plays two major roles as a lipophilic cosurfactant and a water-soluble cosolvent. This means that the hydrophile-lipophile balance of an amphiphile is measured not by its solubilities in water and oil but by the function in amphiphile aggregates under a given condition.

Moreover, exclusive effect of solvents is required to keep amphiphile aggregates from dissolving into solvents.

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