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SHORT COMMUNICATION

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The transition of three types of three-phase behavior in a temperature-composition space of water/$C_{12}EO_6$/propanol/heptane system

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Abstract The change of three-phase behavior of a water/hexaethyleneglycol dodecyl ether ($C_{12}EO_6$)/propanol/heptane system was studied with increasing temperature (30.0–48.9 °C). A cone-like three-phase body consisting of aqueous (W), surfactant (D_p), and oil (O) phases is formed in the composition tetrahedron at lower temperatures. The body is expanded with increasing temperature, and touches the water–$C_{12}EO_6$–heptane triangle (the base) at 44.8 °C. At about 45.6 °C the loci of the D_p and O phases meet and cut off at a critical double end point and the three-phase body separates into two bodies: one has a chiral shape and the other is unclosed. The unclosed body is transformed with the change of shape of the tie triangle on the base as temperature increases and leaves from the base at 48.9 °C. A closed-loop miscibility gap between middle surfactant (D'_p) and O phases or a cone-like three-phase body is formed inside the composition tetrahedron at higher temperatures. The roles of $C_{12}EO_6$ and propanol are also discussed.

Key words CDEP – three phase behavior – surfactant phases

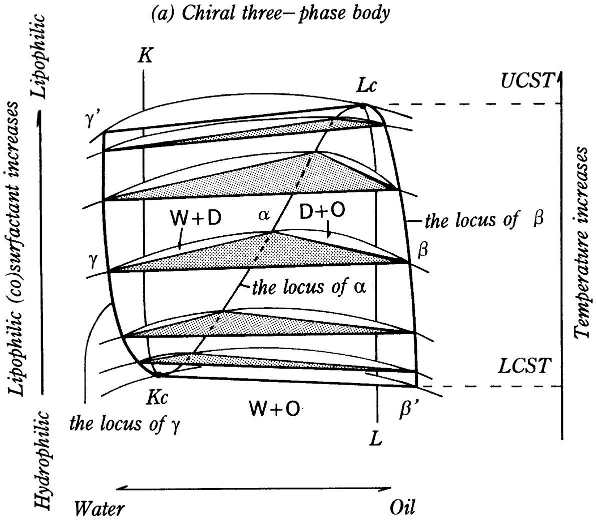
Introduction

It is well known that a middle microemulsion called D phase appears in a water/mixed surfactant/hydrocarbon system when the hydrophile–lipophile balance (HLB) is adjusted after changing the mixing ratio of surfactants [1–3]. The D phase changes from water-rich to oil-rich via both-rich between two critical end points (CEPs), K_c and L_c, as shown in Fig. 1a [3]. Thus a chiral [4] three-phase body is formed. Since the surfactant works most efficiently in a middle surfactant phase, the study of the behavior of the middle surfactant phase is interesting and important in research and application.

Middle- or long-chain monohydric alcohols have been used as a cosurfactant [5–8] to obtain a middle microemulsion. On the other hand, a considerable amount of methanol or ethanol prevents surfactants from forming micelles [9, 10]. Propanol exhibits characteristic properties [7, 8, 11–15]: it acts as hydrophilic [7, 8, 11] or lipophilic [13–15] cosurfactant and/or cosolvent(s) [11, 13–15] in microemulsion systems. We have recently reported [14, 15] another type of three-phase behavior in a water/polyethylene glycol alkyl ether (C_mEO_n)/propanol/hydrocarbon system (Fig. 1b). A middle surfactant phase called D_p phase forms a closed-loop coexistence curve with an aqueous (W) phase under the condition that C_mEO_n acts as a moderately hydrophilic surfactant. A cone-like three-phase body is formed in a two-phase body of aqueous surfactant (W_m) and oil (O) phases.

As is well known, C_mEO_n changes from hydrophilic to lipophilic with increasing temperature [2] and a chiral three-phase body is formed between the upper and lower critical solution temperatures (UCST and LCST) in

(a) Chiral three–phase body



(b) Cone– like three–phase body

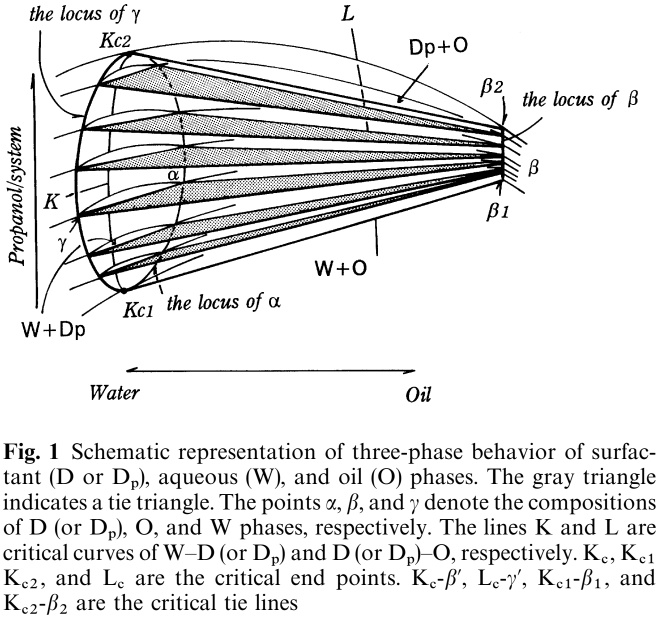


Fig. 1 Schematic representation of three-phase behavior of surfactant (D or D_p), aqueous (W), and oil (O) phases. The gray triangle indicates a tie triangle. The points α, β, and γ denote the compositions of D (or D_p), O, and W phases, respectively. The lines K and L are critical curves of W–D (or D_p) and D (or D_p)–O, respectively. K_c, K_{c1} K_{c2}, and L_c are the critical end points. K_c-β', L_c-γ', K_{c1}-β_1, and K_{c2}-β_2 are the critical tie lines

a water/C_mEO_n/hydrocarbon system (Fig. 1a) [16, 17]. Thus, in the previous study [15], the effect of decreasing temperature (30–26 °C) on the three-phase behavior of W–D_p–O was studied in a water/$C_{12}EO_6$/propanol/heptane system. The three-phase body gets thinner with decreasing temperature, and collapses into a superimposed critical tie line at 26.2 °C. K_{c1} and K_{c2} coincided with each other at the end of the line, a critical double end point. On the other hand, the effect of increasing temperature or making C_mEO_n lipophilic has not been reported. We studied the change of three-phase behavior of the same system with increasing temperature from 30.0 °C to 48.9 °C, and investigated the effect of HLB of C_mEO_n and the roles of propanol.

Experimental section

Materials and procedures

The same materials as those in the previous study [15] were used. Determination of the phase boundaries and identification of each phase were performed following the procedures described in the previous paper [14].

Results

Change of phase behavior of water/$C_{12}EO_6$/propanol/heptane system with temperature

Phase diagrams of water/$C_{12}EO_6$/propanol/heptane system at atmospheric pressure are shown in Fig. 2. Each diagram represents a part of the vertical section through the four-component composition tetrahedron at a constant temperature (30.0–48.9 °C). The weight ratio of water/heptane, $R_{w/o}$, is 50/50. The corresponding schematic three-phase behavior is illustrated in Fig. 3. A closed-loop three-phase region (IIIa) at 30.0 °C (Fig. 2a) is a section of a cone-like three-phase body consisting of aqueous (W), middle surfactant (D_p), and oil (O) phases (Fig. 3a) [14, 15].

As temperature increases, the three-phase region is widened (Figs. 2b and 3b) and touches the one-phase region of D_p phase at $R_{w/o} = 50/50$ (Fig. 2b–h). (Such a touching point as indicated by the arrow in Fig. 2b is called the X-point [18].) This means that the hydrophile–lipophile property of the mixed amphiphile ($C_{12}EO_6$ + propanol) at the X-point is just balanced [1]. The three-phase region touches the water–$C_{12}EO_6$– heptane triangle (the base) on the critical tie line (CTL) K_{c1}-β_1 at 44.8 °C, the LCST for water/$C_{12}EO_6$/heptane system (Figs. 2c and 3c). Since a D phase appears at the LCST in a water/C_mEO_n/hydrocarbon system, the D_p phase is essentially identical with the D phase. A three-phase tie triangle is formed on the base and the three-phase region is not closed inside the composition tetrahedron above 44.8 °C. As $C_{12}EO_6$ changes from hydrophilic to lipophilic with increasing temperature, the composition of surfactant phase (point α_1) on the base shifts towards the oil-rich side and the unclosed body is transformed (Fig. 3c–f).

Separation of a three-phase body at a critical double end point

The three-phase region bears constriction with increasing temperature (Fig. 2c and d) and finally separates into two (IIIb and IIId) at 45.6 °C (Figs. 2e, f and 3d). To investigate

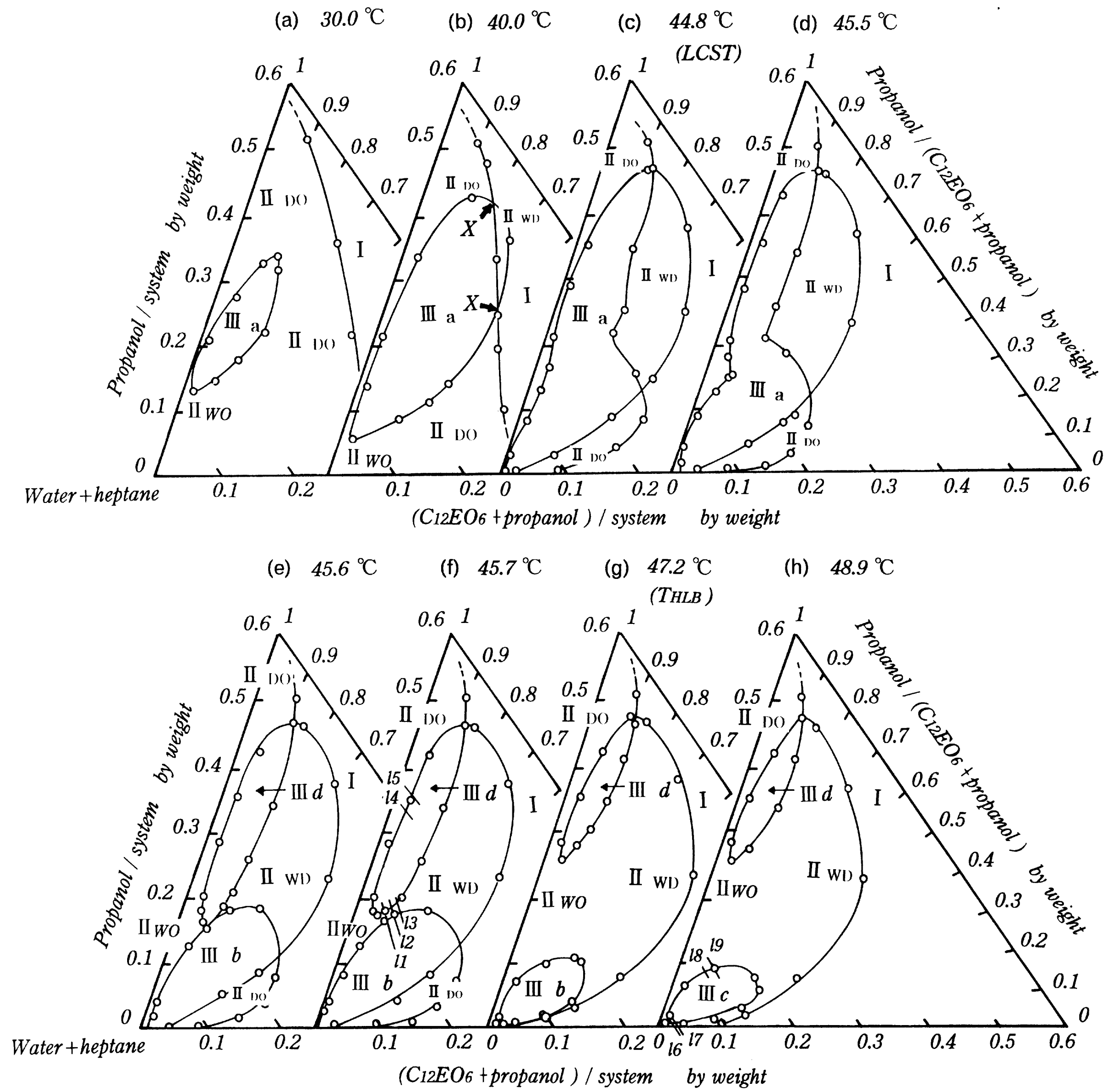


Fig. 2 Phase diagrams of water/$C_{12}EO_6$/propanol/heptane system at atmospheric pressure and $R_{w/o} = 50/50$. IIIa, IIIb, IIIc and IIId denote three-phase regions, and II_{WD}, II_{DO} and II_{WO} two-phase regions of W + D (or W + D'_p), D + O (or D_p + O), and W + O, respectively. The LCST and T_{HLB} are for the water/$C_{12}EO_6$/heptane system. The arrow with X indicates X-point

the mechanism of the separation and the respective three-phase behavior, the change in volume fractions of each phase along the lines *l*1–*l*5 (Fig. 2f) was measured (Fig. 4). The surfactant phase disappears on the surfactant-dilute side (*l*1 and *l*4), whereas the O or W phase does on the surfactant-concentrated side (*l*3 and *l*5). Two critical tie lines (CTL) of L_c-γ type (Fig. 1) lie between *l*1 and *l*3, and a CTL of K_c-β type (Fig. 1) between *l*4 and *l*5. The former two are closely located to each other. The phase equilibrium changes in the order (D + O →)III → W + O_m(D) → III → W_m(D) + O with increase of propanol, where W_m and O_m denote the aqueous and the oleic surfactant phases, respectively. The behavior of the surfactant phase in the IIId region is of D type (Fig. 1b). (The IIId region exists up to 72.5 °C and disappears at a tricritical point [19].) Since a four-phase region should appear when two different three-phase regions overlap [20, 21], this result proves again that the D_p phase is essentially identical with D phase.

The phase diagrams at $R_{w/o} = 85/15$ and 90/10 (45.7 °C) and the change in volume fractions of each phase along the lines *l*10–*l*13 are shown in Fig. 5. The CTLs of

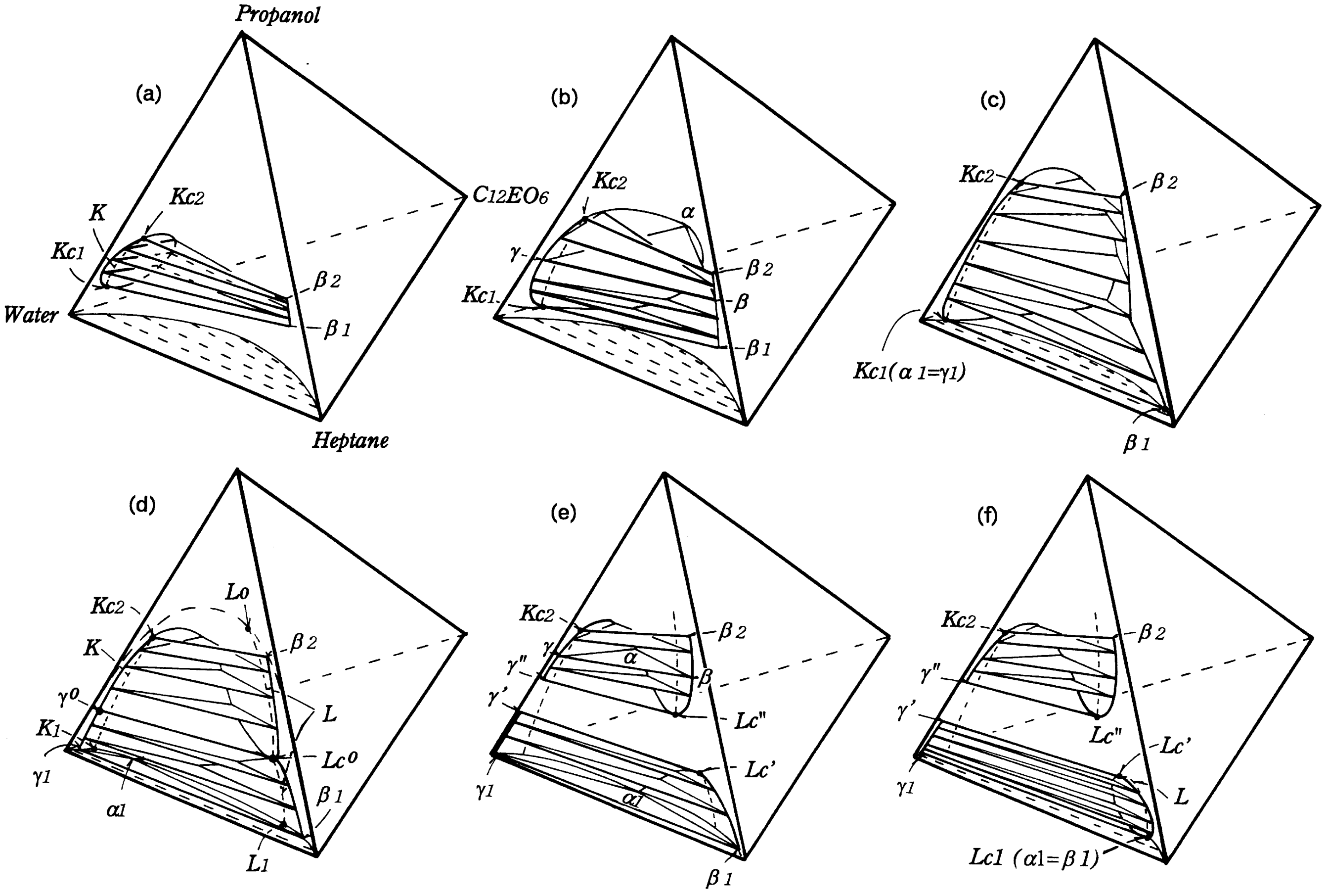


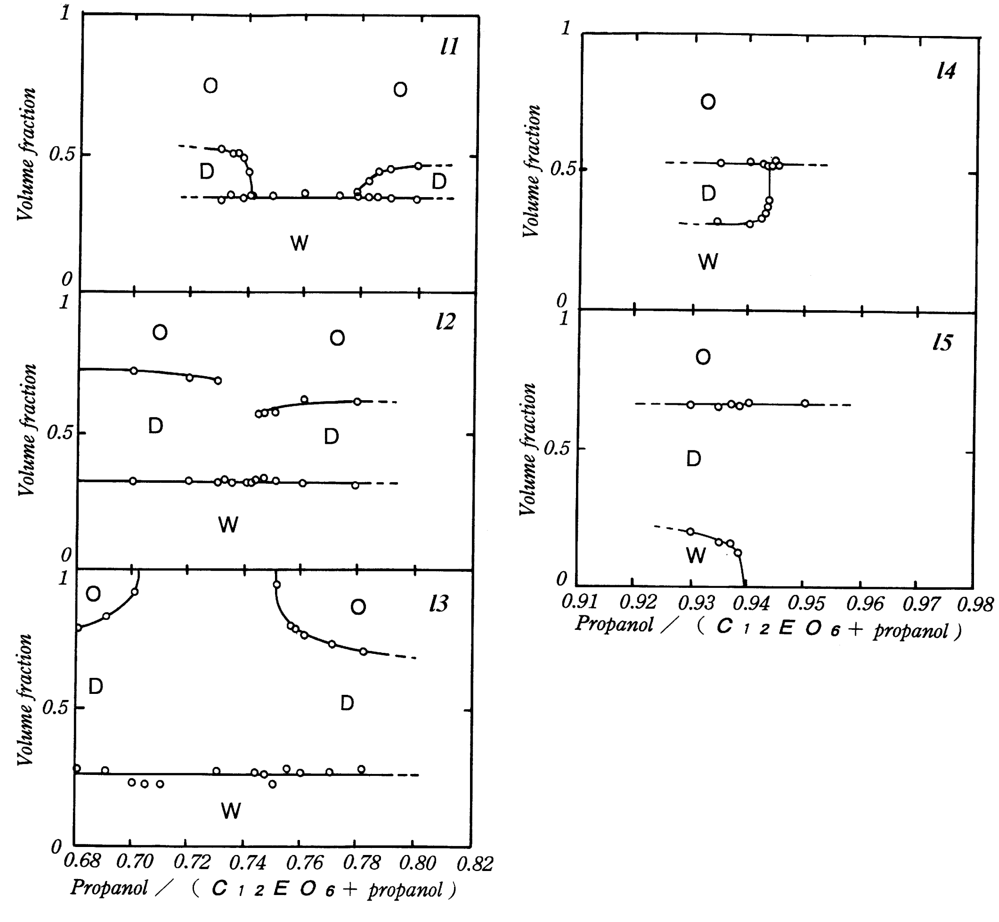
Fig. 3 Schematic three-phase behavior inside the composition tetrahedron: (a) corresponds to the phase behavior in Fig. 2a; (b) Fig. 2b; (c) Fig. 2c; (d) Fig. 2e–f; (e) Fig. 2g; (f) slightly below 48.9 °C. The behavior in the main miscibility gap on the base is also represented with some tie triangles and tie lines (broken lines). The points L_0 on the mutual solubility curve (broken curve) in (d) are the plait points for the propanol/water/heptane system, and L_1 and K_1 for the $C_{12}EO_6$/water/heptane system

L_c-γ type lie near $l11$, that is, they are closely located to each other at $R_{w/o} = 85/15$ as well. Therefore, it is concluded that the two CTLs are superimposed slightly below 45.7 °C. Further, the three-phase regions touch the one-phase region of oil phase at $R_{w/o} = 90/10$. Both CTLs terminate or the critical end points (CEP) exist between $R_{w/o} = 85/15$ and 90/10. Since a CEP is a particular X-point [14] and the two X-points approach each other near $R_{w/o} = 85/15$, it can be concluded that the two CEPs meet at one end (L_c^0 in Fig. 3d) of the superimposed CTL ($\gamma^0 - L_c^0$) slightly below 45.7 °C. This point is a different kind of critical double end point (CDEP) from the one previously reported [15]. The loci of surfactant and O phases and the critical curve L meet and are cut off respectively at the CDEP on the two-phase surface (Fig. 3d). Thus the three-phase body separates into two bodies at 45.6 °C. The two CTLs (γ'-L_c', γ''-L_c'' in Fig. 3e) originate in the superimposed CTL.

Formation of a cone-like three-phase body

The X-point of the IIIb region reaches the base of the diagram at 47.2 °C, the HLB temperature (T_{HLB}) of water/$C_{12}EO_6$/heptane system (Figs. 2g and 3e). The channel of W + D region is stretched to the very $C_{12}EO_6$-dilute region with increasing temperature and finally reaches the W + O region at the UCST for the water/$C_{12}EO_6$/heptane system. A closed-loop three-phase region (IIIc) is formed inside the tetrahedron (Fig. 2h) above the UCST. Figure 6 shows the change in volume fractions of each phase along the lines $l6$–$l9$ (Fig. 2h). The pattern of change is the one around the CTL of L_c-γ type. The IIIc region exists between two L_c-γ type CTLs. Since the IIIc region gets narrower as $R_{w/o}$ increases (Fig. 7), the three-phase body is a cone-like body. (This body shrinks with increasing temperature and collapses into a superimposed CTL at 51.7 °C [19].) The edge of the base is

Fig. 4 The change in volume fractions of each phase along the lines *l*1–*l*5 in Fig. 2f. The abscissa is represented by weight ratio



a closed-loop coexistence curve for the surfactant and the oil phases (Fig. 3f). We call the middle surfactant phase the D'_p phase. The D'_p phase is essentially identical with the D phase. To our knowledge, a closed-loop coexistence curve between surfactant and oil phases has not been reported.

Discussion

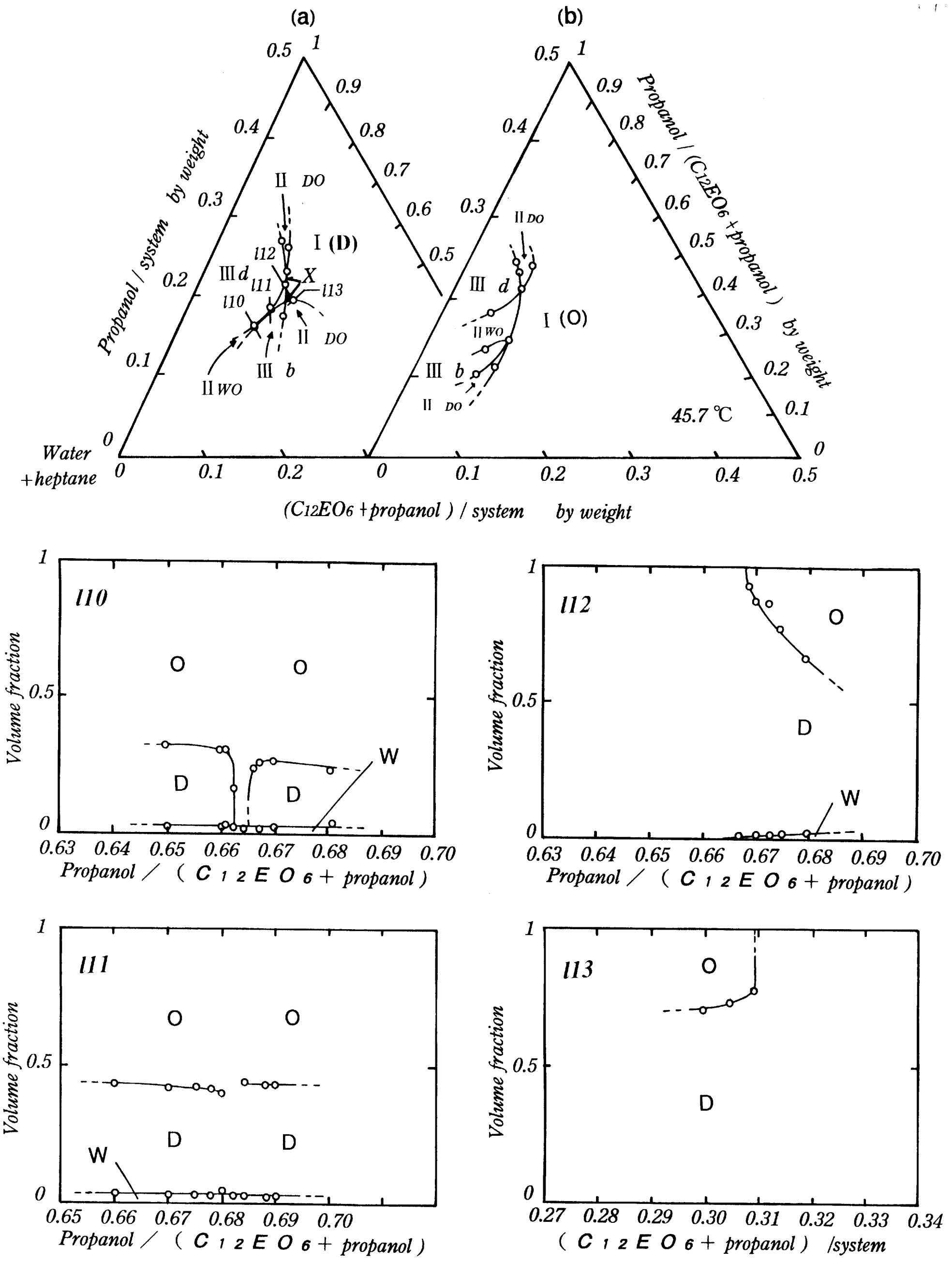
The roles of $C_{12}EO_6$ and propanol

At the lower temperatures, $C_{12}EO_6$ acts as a hydrophilic surfactant. The addition of propanol shifts the HLB of the mixed amphiphile towards lipophilic and reduces the lipophobicity of aqueous solvent [14, 15]. As a result, the closed-loop coexistence curve of W and D_p phases is formed above the CDEP [15].

As temperature increases, the hydrophilicity of $C_{12}EO_6$ is weakened and the balanced mixed amphiphile can be obtained by adding propanol. At 45.6 °C, slightly below the T_{HLB} for the water/$C_{12}EO_6$/heptane system, $C_{12}EO_6$ is a little hydrophilic. In fact, the D + O region is seen in a propanol-dilute region in Fig. 2f. On the other hand, one can find the phase sequence Wm(D) + O → III → W + D(Om) with an increase of $C_{12}EO_6$ in a region of propanol/system between 0.2 and 0.45. Here, based on the effects of adding propanol on the mutual solubilities between water and heptane (at 20 °C [22]) and the CMCs of several surfactants [23], we assume that a considerable amount of propanol as water-soluble or oil-soluble cosolvent reduces the lipophobicity of aqueous media or the hydrophobicity of oleic media, respectively. It can be interpreted that $C_{12}EO_6$ becomes lipophilic owing to the change in the nature of oleic media in the presence of propanol.

To analyze the roles of propanol rectangular phase diagrams at 45.7 °C are shown in Fig. 8. The ordinate is the weight fraction of propanol in (propanol + $C_{12}EO_6$), W_{surf}, or in (propanol + water + oil), W_{solv}. If propanol acts only as a cosurfactant, the CTL should be located on

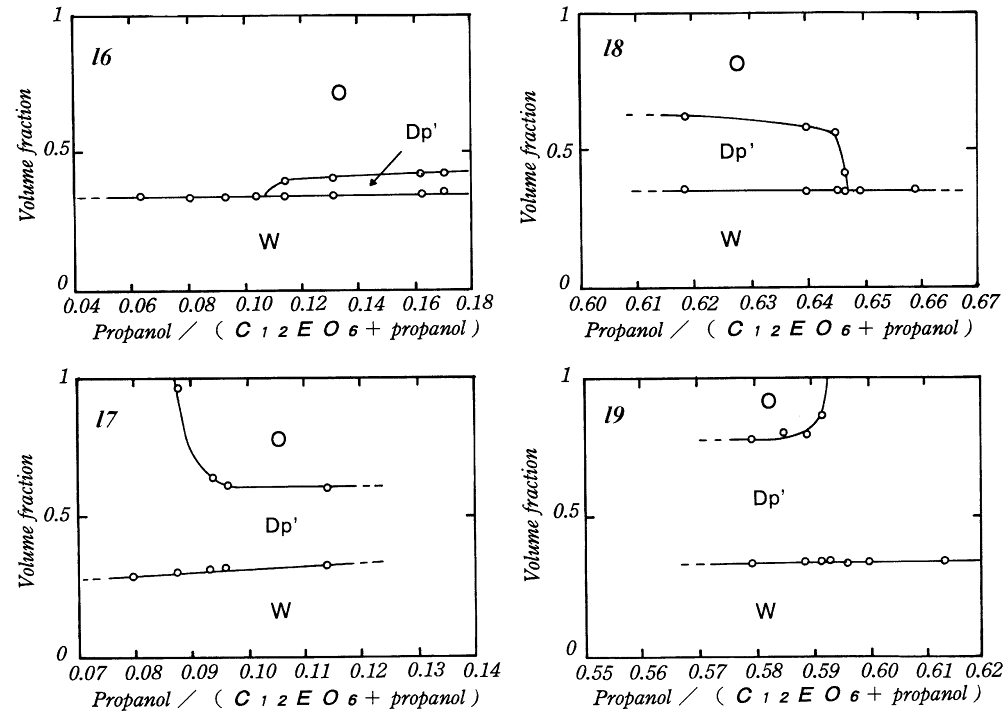
Fig. 5 Phase diagrams of water/$C_{12}EO_6$/propanol/heptane system at 45.7 °C and $R_{w/o}$ = 85/15 (a) and 90/10 (b) (top). The change in volume fractions of each phase along the lines *l*10–*l*13 (bottom). The abscissa is represented by the weight ratio



the top or bottom of the three-phase region when W_{surf} is changed. If propanol acts only as cosolvent, the CTL should be located on the top or bottom when W_{solv} is changed. $K_{c2} - \beta_2$ is located near the top of the IIId region in Fig. 8a, whereas the three-phase boundary at K_{c2}-β_2 is almost vertical in Fig. 8b. It can be concluded that propanol mainly acts as a hydrophilic cosurfactant around $K_{c2} - \beta_2$. On the contrary L_c'-γ' is not located at the top of the three-phase region either in Fig. 8a or in Fig. 8b. It can be interpreted that propanol acts as both cosurfactant and cosolvent(s) around L_c'-γ'. Propanol as an oil-soluble cosolvent induces the consolution of surfactant and O phases on L_c'-γ'. The phase separation on L_c''-γ'' is induced by the effect of propanol as a hydrophilic cosurfactant.

Above 48.9 °C, $C_{12}EO_6$ becomes lipophilic and the surfactant and oil phases dissolve each other in the

Fig. 6 The change in volume fractions of each phase along the lines *l*6–*l*9 in Fig. 2h. The abscissa is represented by the weight ratio



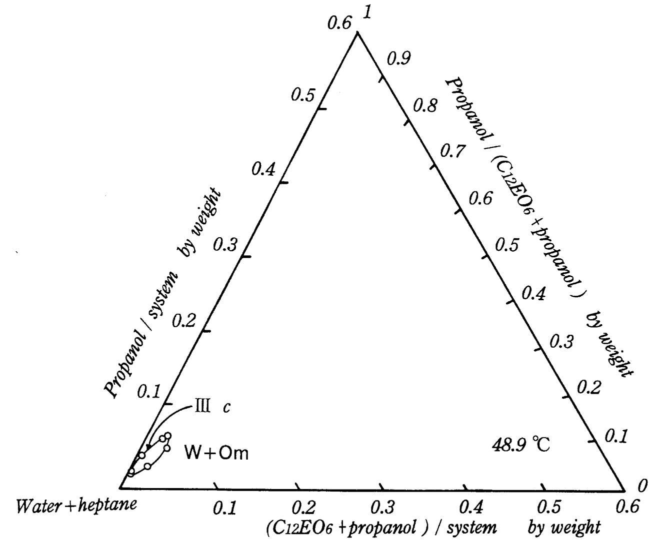
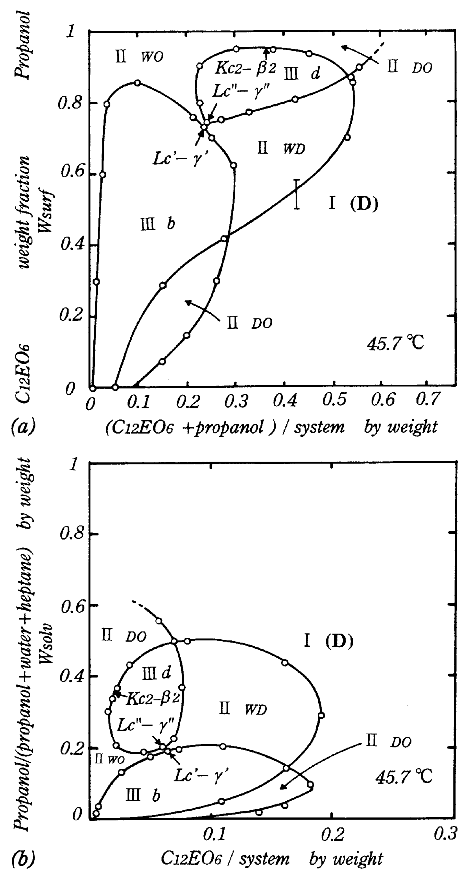


Fig. 7 Phase diagram of water/$C_{12}EO_6$/propanol/heptane system at 48.9 °C and $R_{w/o} = 90/10$. Only the three-phase region (IIIc) and two-phase region around it are depicted

Fig. 8 Rectangular phase diagrams of water/$C_{12}EO_6$/propanol/heptane system at 45.7 °C. These are variations of Fig. 2f. The position of CTL is indicated by the arrow with the corresponding mark in Fig. 3



water/$C_{12}EO_6$/heptane system. However, the separation of the Om phase occurs by adding a small amount of propanol. Propanol acts as a hydrophilic cosurfactant. (Since the composition of the coexisting W phase in the IIIc almost unchanged, the effect of aqueous media on the HLB of $C_{12}EO_6$ can be neglected.) When more propanol is added, the D'_p and the O phases dissolve each other again. The effect of propanol as an oil-soluble cosolvent becomes dominant. A closed-loop coexistence curve of D'_p and O phases or the cone-like three-phase body is formed. The two types of three-phase behavior (W–D_p–O and W–D'_p–O) are symmetrical to each other.

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