Colloid Polym Sci 277:184–190 (1999)
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ORIGINAL CONTRIBUTION

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Origins of two surfactant phases (D and Dp′) in a temperature-composition space of water / $C_{12}EO_6$ / propanol / heptane system: tricritical point and critical double end point

Received: 9 July 1998
Accepted in revised form: 25 August 1998

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Abstract The origins of middle surfactant phases (D and Dp′) were investigated in the composition-temperature (49–73 °C) space of a water/hexaethyleneglycol dodecyl ether ($C_{12}EO_6$)/propanol/heptane system at atmospheric pressure. Two types of three-phase bodies exist in the dilute $C_{12}EO_6$ region of the four-component composition tetrahedron at 49.0 °C. A cone-like three-phase body consisting of aqueous (W), Dp′, and oil (O) phases becomes thinner with increasing temperature, and collapses into the superimposed critical tie lines (CTL) at 51.7 °C. One end of the superimposed CTL is a critical double end point where the closed-loop coexistence curve of the Dp′ and O phases disappears. The chiral three-phase body consisting of W, D, and O phases shrinks with increasing temperature, and finally vanishes at the tricritical point near 72.5 °C. The roles of $C_{12}EO_6$ and propanol are discussed and the conditions for the middle surfactant phases are discussed on the basis of the whole series of three-phase behavior.

Key words Critical double end point – Tricritical point – D phase – Dp′ phase

Introduction

It is known that a middle microemulsion phase, called the D phase, appears in a water/surfactant/oil system and forms a three-phase region with excess water (W) and oil (O) phases, when the hydrophile-lipophile (HL) property is balanced. The surfactant exhibits maximum solubilization capacity and highest ability to depress the interfacial tension between the coexisting W and O phases in this region [1, 2]. The shape of surfactant aggregates is drastically changed around the region [1]. The study of three-phase behavior in a surfactant system is important for basic research and practical applications.

Monohydric alcohols (carbon number ≥4) have been used as lipophilic cosurfactants to obtain a D phase in hydrophilic surfactant systems [3–7]. On the other hand, methanol and ethanol prevent surfactants from forming aggregates [8, 9]. Propanol exhibits characteristic properties in a surfactant system, according to the given conditions [5, 6, 10–16].

We have reported [13–15] three types of three-phase behavior for aqueous (W), middle surfactant (Dp, D, or Dp′), and O phases, and also their transitions in the composition-temperature (*T*) space (26.0–48.9 °C) of a water/hexaethyleneglycol dodecyl ether ($C_{12}EO_6$)/propanol/heptane system. The Dp phase emerges from an aqueous surfactant phase (Wm) at a critical double end point (CDEP) of 26.2 °C (T_{CDEP}). A closed-loop coexistence curve between Dp and W phases, i.e. a cone-like three-phase body, is formed in the composition tetrahedron above the T_{CDEP} [14]. The three-phase body is enlarged with increasing *T* and separates into two bodies at another CDEP [15]. One is a well-known chiral body [2, 15–21] where a D phase coexists with W and O phases [1, 2, 15–16]. The other is transformed with increasing *T*, and becomes another cone-like three-phase

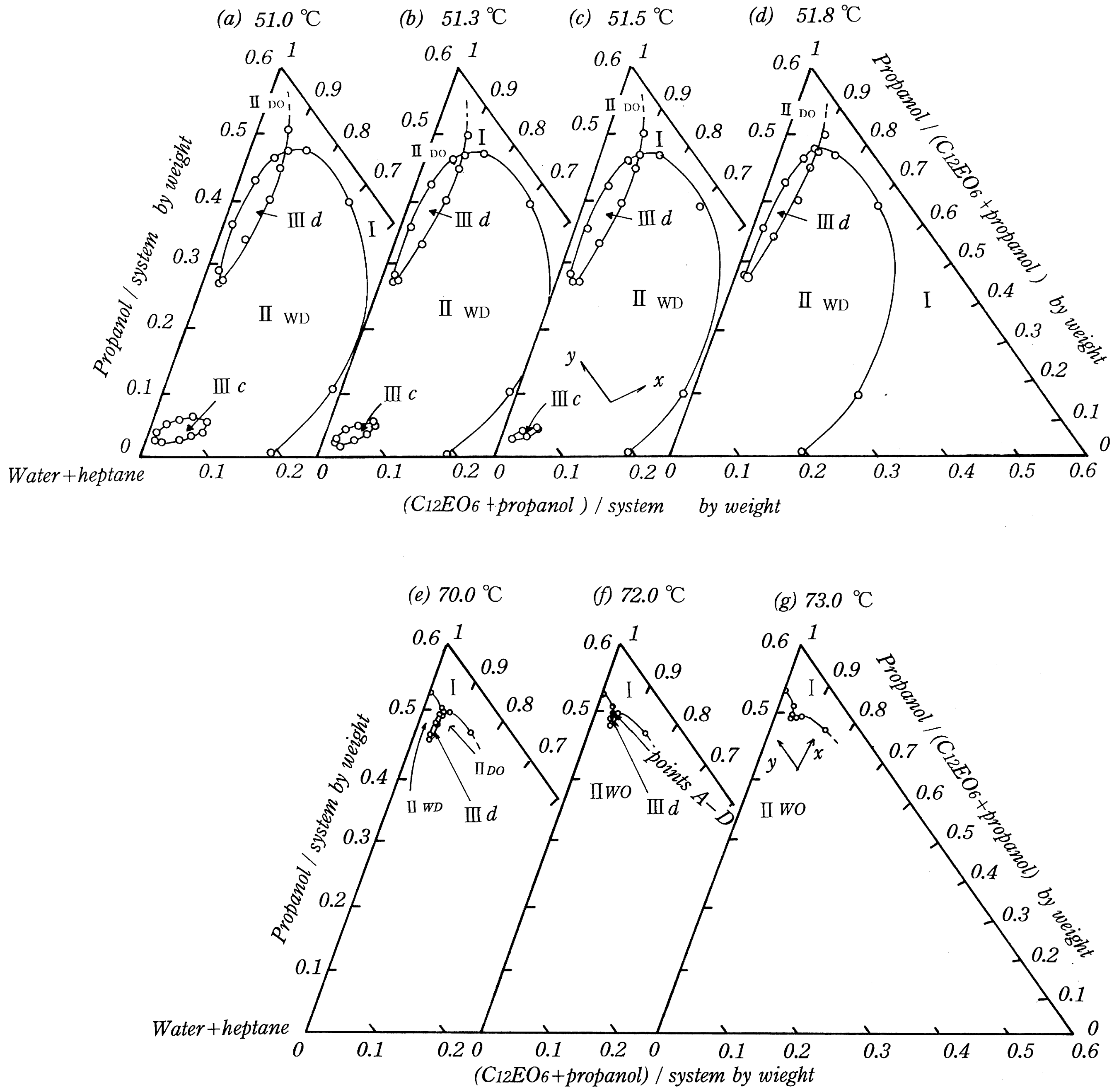


Fig. 1a–g Phase diagrams for the water/hexaethyleneglycol dodecyl ether ($C_{12}EO_6$)/propanol/heptane system at atmospheric pressure and $R_{w/o} = 50/50$. IIIc and IIId denote the three-phase regions, and IIWD, IIDO, and IIWO the two-phase regions of W–D (or W–Dp′), D–O, and W–O, respectively. The symbol I denotes a one-phase region. The sample points A–D for measuring volume fractions (Fig. 6) are indicated by the *closed circle* in **f**

body with W, Dp′, and O phases [15]. The Dp′ and the O phases form a closed-loop miscibility gap. The two types of three-phase behavior, W-Dp-O and W-Dp′-O, show symmetry with respect to the HL property and hydrophobicity-lipophobicity [14–15]. Since $C_{12}EO_6$ becomes more lipophilic with increasing T, it can be expected that the Dp′ phase would disappear at a CDEP of higher T.

However, it is known that a chiral three-phase body disappears at a tricritical point (TCP) [19–24]. If the CDEP and TCP are found for the water/$C_{12}EO_6$/propanol/heptane system, a whole series of three-phase bodies in the four-component system can be described. We studied the change in the three-phase behavior of the system with increasing T (51.0–73.0 °C), and discuss the effect of HL-property of $C_{12}EO_6$ and also the roles of propanol.

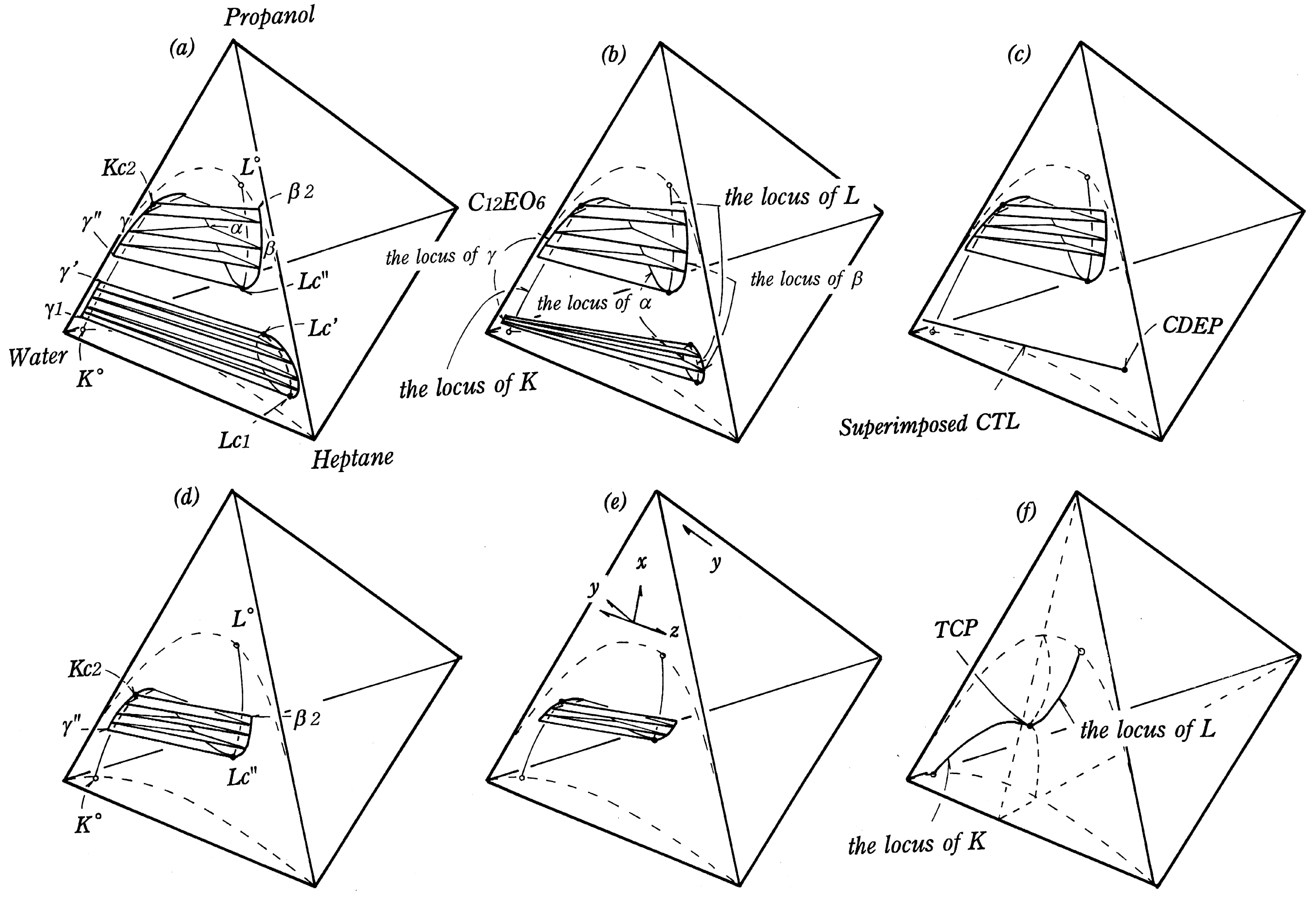


Fig. 2a–f Schematic of three-phase bahavior inside the composition tetrahedron. The main miscibility gaps on the propanol-water-heptane and the $C_{12}EO_6$-water-heptane triangles are also represented by *broken curves* with the plait points $L°$ and $K°$. K and L are the critical points of W-D (or -Dp′ or -Om) and D (or Dp′ or Wm-)O, respectively. The loci of K, L, and of each phase are on the surface of the two-phase body. *Kc2*, *Lc1*, *Lc′*, and *Lc″* are the critical end points (CEPs). *Lc1-γ1*, *Lc′-γ′*, *Lc″-γ″*, and *Kc2-β2* are the critical tie lines. The points α, β, and γ denote the compositions of D (or Dp′), O and W phases, respectively. T is as follows: T_{UCS} (≈48.9 °C) $< T_a < T_b < T_{CDEP}$ (≈51.7 °C) $= T_c < T_d < T_e < T_{TCP} = T_f$ (≈72.5 °C). T_{UCS} is the upper critical solution T for the water/$C_{12}EO_6$/heptane system and T_a is the T of **a**, etc

Experimental

Materials

The materials used were the same as in the previous study [14].

Procedures

Varying amounts of water, $C_{12}EO_6$, propanol, and heptane were weighed into each glass tube. The samples were flame-sealed and placed in a thermostated water bath (±0.01 °C). The phase boundaries were determined by visual observation of the samples after equilibration. Identification of each phase was performed on the basis of composition, phase volume change, continuity from identified phases, location in relation to the critical point or the critical tie line (CTL) in phase diagrams, and so on.

Results

Disappearance of the cone-like three-phase body of W–Dp′–O at a CDEP

Phase diagrams for a water/$C_{12}EO_6$/propanol/heptane system at atmospheric pressure are shown in Fig. 1. Each diagram represents part of the vertical section through the four-component composition tetrahedron at a constant T (51.0–73.0 °C). The weight ratio of water to heptane, $R_{w/o}$, is 50:50. The three-phase behavior is schematically represented in Fig. 2. The IIIc region is a section of a cone-like three-phase body consisting of W, Dp′, and O phases (Fig. 2a), which continues from

48.9 °C [15]. This region shrinks with increasing T, and disappears just below 51.8 °C. It does not touch the one-phase region at $R_{w/o} = 50/50$. This means that the respective composition points for the three coexisting phases remain in a water-rich or an oil-rich region when the three-phase body disappears. Figure 3 shows the change in volume fractions for each phase at $x = 5$ wt% and 13 wt%, where x is the concentration (wt%) of the mixed amphiphile in the system. These figures indicate the positions of CTLs at $R_{w/o} = 50/50$ as follows: Fig. 3a and b show Lc1-γ1 (Fig. 2a); Fig. 3c and d show Lc′-γ' (Fig. 2a). Lc1-γ1 shifts from the region where $x < 5$ wt% (48.9 °C) to a region where $x > 5$ wt% (50.8 °C) with increasing T. However, Lc′-γ' shifts from the region where $x > 13$ wt% (48.9 °C) to the region where $x < 13$ wt% (50.6 °C). Since the IIIc region becomes thinner in the y direction (Figs. 1c, 2e), the two CTLs approach each other as T increases. We also investigated the movement of the critical end points (CEPs). Figure 4 shows the phase diagrams for $R_{w/o} = 12/88$ and also the change in volume fractions for each phase along the lines $l1$–12. The CTLs lie near the lines $l2$ and $l5$ at 50.0 °C, and near $l9$ and $l12$ at 51.2 °C, respectively. The CEPs are located very close to the touching point of the IIIc region with the one-phase region [13]. The two CEPs approach each other with increasing T, as shown in Fig. 4c. It can be concluded that the cone-like three-phase body collapses into a superimposed CTL just below 51.8 °C (T_{CDEP}), as shown in Fig. 2c. One end of the superimposed CTL is a CDEP.

Disappearance of the chiral three-phase body at a TCP

The IIId region in Fig. 1 is a section of a chiral three-phase body [15]. This region shrinks in the x and y directions (Figs. 1, 2) with increasing T. The cusp of the one-phase region remains but the three-phase region is not found at 73.0 °C (Fig. 1g). To investigate the mechanism of the disappearance, the phase diagrams at various x values were obtained for $R_{w/o} = 50/50$ and for 70/30 (Fig. 5). The volume of the O phase is larger than that of the W phase at $R_{w/o} = 50/50$. The $R_{w/o}$ value of L° (Fig. 2) is 31/69 at 72.6 °C: (x_{water}, $x_{propanol}$, $x_{heptane}$) = (0.16, 0.48, 0.36) by weight. The IIId region is somewhat deviated to a water-rich region, as shown in Fig. 2e. Therefore, diagrams at $R_{w/o} = 70/30$ were also obtained.

The highest T for the three-phase region at each x is plotted in Fig. 6. (We have employed a similar procedure to the one Yoshida and Kunieda used [22].) Figure 7 shows the change in volume fractions for each phase at points A–D and along line E (Figs. 1f, 5d–e). Points A and C enter the W–O region via the IIId region with increasing T, whereas points B and D do not enter the IIId region. Thus, the curve with open circles in Fig. 6 indicates the minimum x value for the IIId region at this $R_{w/o}$. The curve with closed circles indicates the locus of point α (Fig. 2), or the maximum x value for the IIId region at this $R_{w/o}$. The region between the curves indicates the range of x where the three-phase region exists.

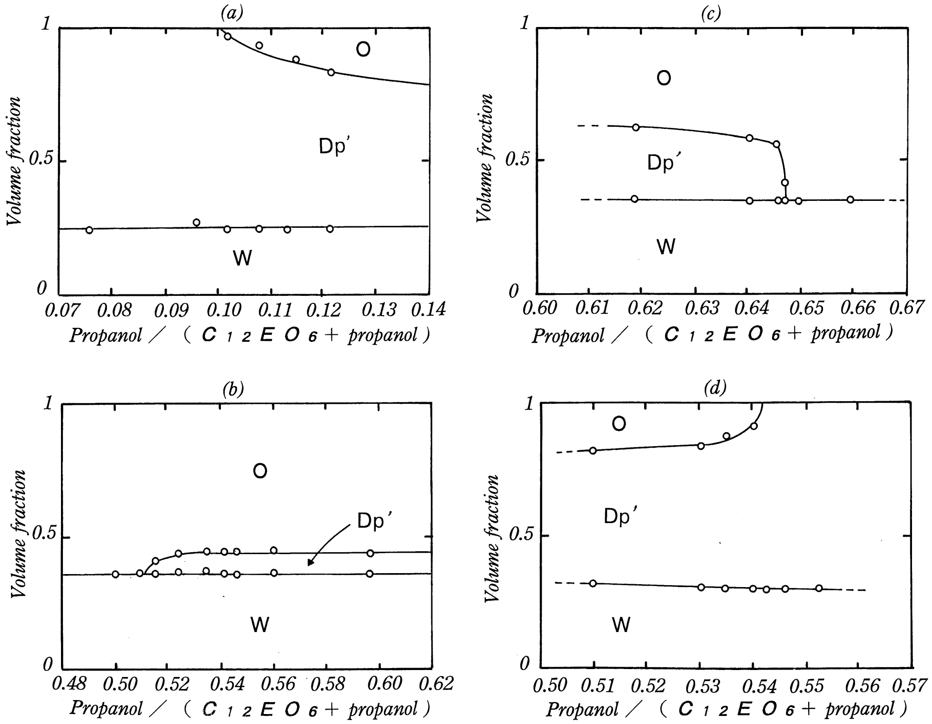


Fig. 3a–d The change in volume fractions for each phase. The *abscissa* represents the weight ratio: **a** $x = 5.0$ wt% 48.9 °C; **b** $x = 5.0$ wt% 50.8 °C; **c** $x = 13.0$ wt% 48.9 °C; **d** $x = 13.0$ wt% 50.6 °C

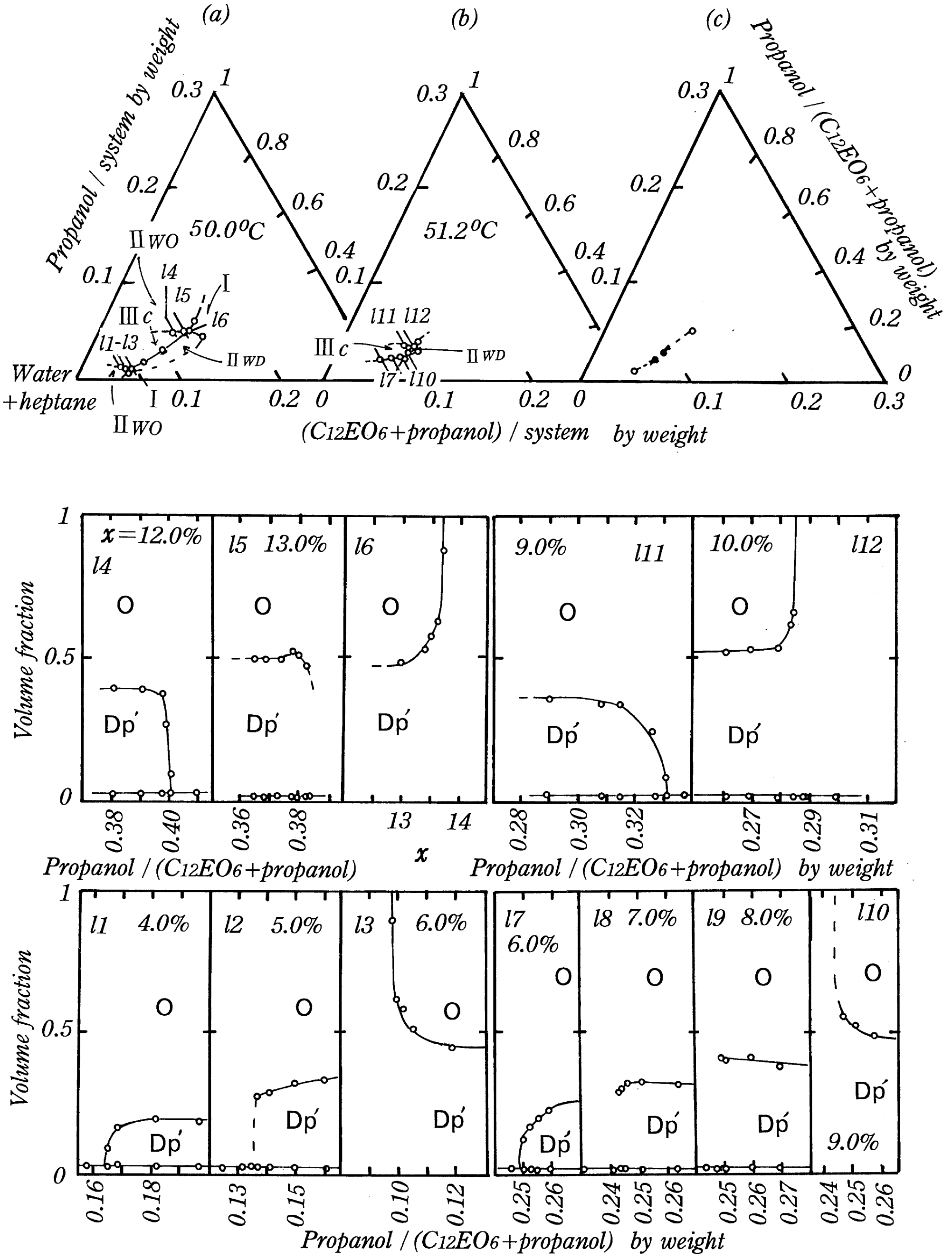


Fig. 4 Phase diagrams at 50.0 and 51.2 °C (**a**, **b**) and the movement of the CEPs (**c**). $R_{w/o}$ = 12/88. The symbol ○ in **c** indicates the CEP at 50.0 °C, and ● at 51.2 °C. The change in volume fractions for each phase along the lines *l*1–12 is shown in the lower part. The bottom phase is a W phase. Propanol/($C_{12}EO_6$ + propanol) = 0.365 on *l*6

The curves in Fig. 6 meet at about 72.5 °C for both values of $R_{w/o}$. This means that the three-phase region expands in the direction of the water-oil axis (*z* direction in Figs. 1, 2) just below 72.5 °C. It is known that a three-phase body shrinks first in the *x* and *y* directions and then in the *z* direction before disappearing at a TCP [20, 22, 23]. The present results are consistent with this order. The three-phase body, or the middle surfactant (D) phase, disappears at the TCP near 72.5 °C (T_{TCP}) (Fig. 2f).

Discussion

Formation of a Dp′ phase and properties of amphiphile and oil media

To explain the effect of *T* on the closed-loop coexistence curve of W–Dp′, we have drawn a conceptual diagram (Fig. 8) based on the present results. The effect of *T* on the HL property of $C_{12}EO_6$, the effects of adding propanol on the properties of amphiphile aggregates,

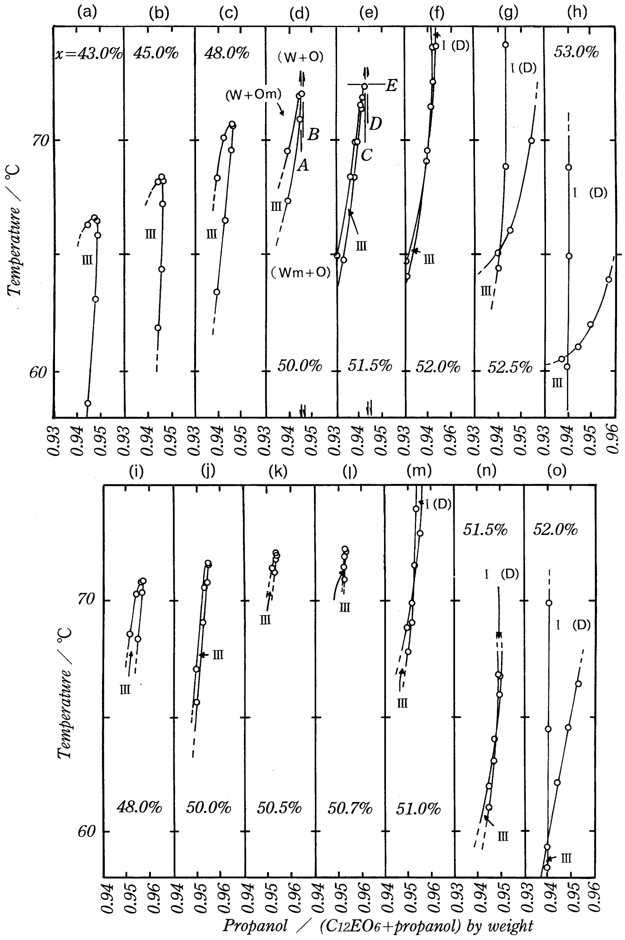


Fig. 5a–o Phase diagrams for water/$C_{12}EO_6$/propanol/heptane systems at various xs. $R_{w/o} = 50/50$ **(a–h)** and 70/30 **(i–o)**

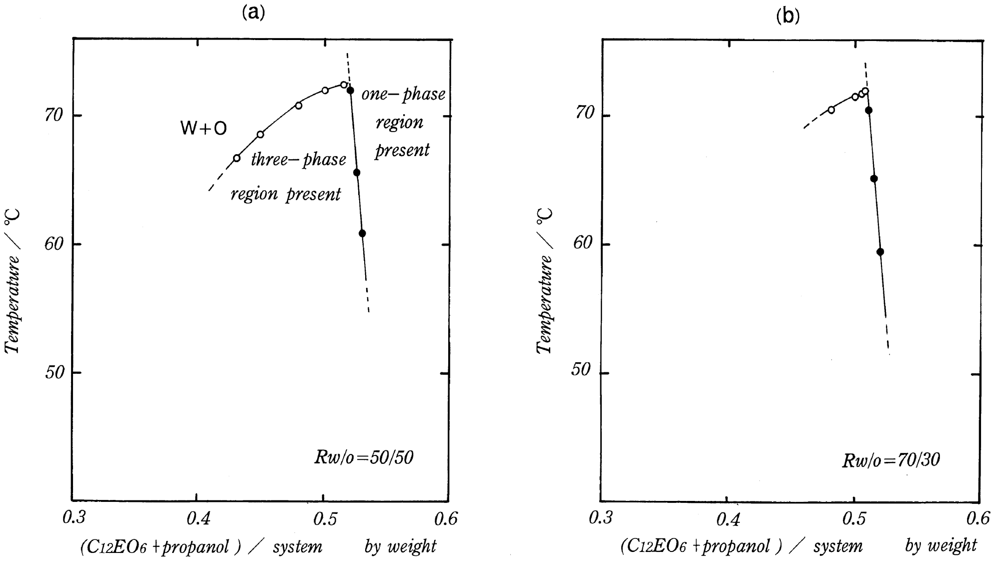
and the nature of the oleic solvent are also shown beside the axes. The term "hydrophobic" for an oleic solvent means that hydrated portions (or molecules) do not dissolve in oil. The term "lipophobicity" is used to show that the amphiphile aggregates do not dissolve in oil, in this paper irrespective of the solubility of oil in the surfactant phase. Propanol dissolves considerably in oil when the middle (Dp′) phase is present.

When $C_{12}EO_6$ is moderately lipophilic, the addition of propanol makes the HL property of the mixed amphiphile more hydrophilic [15] and induces phase separation into Dp′ and O phases. The addition of propanol also decreases the hydrophobicity of the oleic solvent and reduces the lipophobicity of amphiphile aggregates. The O and Dp′ phases then merge again. Consequently, closed-loop coexistence curves of Dp′-O or cone-like three-phase bodies are formed between the two consolution curves. As $C_{12}EO_6$ becomes more lipophilic with increasing T, the amount of propanol required for the phase separation (Lc1) increases. However, the amount of propanol required for the consolution (Lc′) decreases, as shown in Fig. 1. The two consolution curves meet at the CDEP at a particular T, T_{CDEP} (Fig. 4c). Above the T_{CDEP}, since $C_{12}EO_6$ becomes still more lipophilic, the surfactant aggregates cannot become lipophobic enough to coacervate out of the weakly hydrophobic solvent. Figure 8 in this paper and Fig. 8 in Ref. [14] are almost symmetrical with respect to the HL property and hydrophobicity-lipophobicity.

Disappearance of D phase and properties of amphiphile and both media

It is known that a D phase appears when the HL property of a surfactant is balanced. Assuming that this condition holds around the TCP, we can interpret the

Fig. 6a, b The three-phase coexisting region. The highest temperatures of the three-phase region in Fig. 5 are plotted



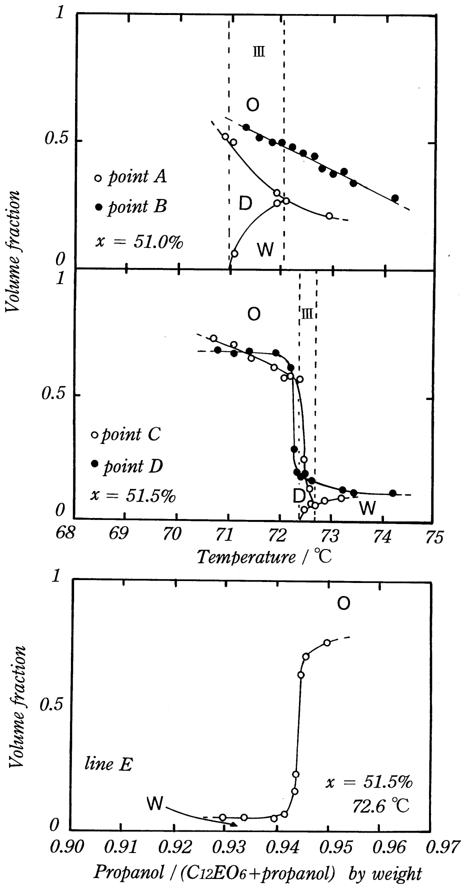


Fig. 7 The change in volume fractions for each phase at points A–D and along line E (x = 51.5 wt%, 72.5 °C) in Fig. 5. $R_{w/o} = 50/50$. The regions between broken lines are the three-phase regions (III) for points A and C

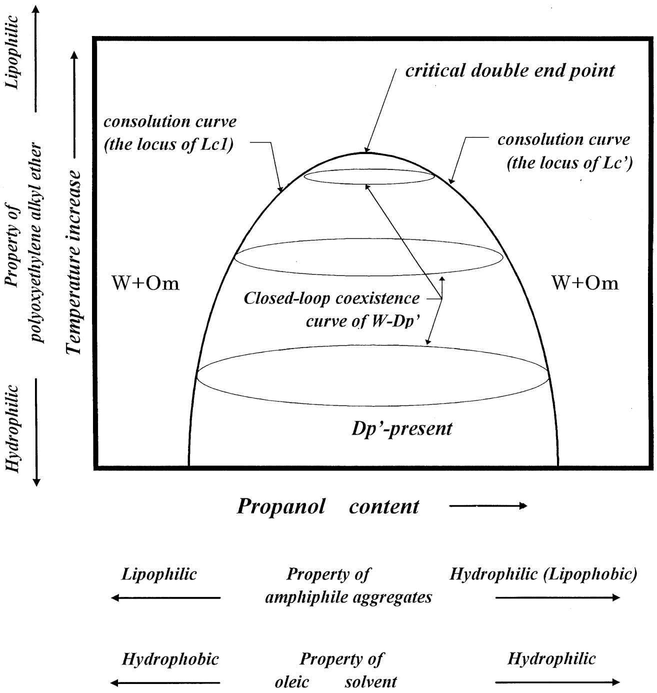


Fig. 8 A schematic representation of the Dp′ present region. The consolution curves for Dp′-O are represented as the loci of *Lc1* and *Lc′*

disappearance of the D phase at the TCP as follows. When the aqueous solvent is lipophobic and the oleic solvent is hydrophobic, the HL-balanced surfactant aggregate is amphiphobic [25] (both hydrophobic and lipophobic) and a middle surfactant phase is formed. The lipophobicity and hydrophobicity of these solvents are weakened by adding propanol and increasing the *T*. The increasing *T* decreases the free energy of mixing by multiplying the entropic effect. The exclusion of amphiphile (aggregates) by both solvents is reduced and the D-phase structure becomes disordered [22, 24]. Thus, beyond the TCP, the amphiphile, water, and heptane mutually dissolve at a balanced HL property and a middle surfactant phase does not emerge.

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