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ORIGINAL CONTRIBUTION

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An origin of a middle surfactant phase (Dp): A critical double end point in a water/polyoxyethylene alkyl ether/propanol/heptane system

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Abstract Phase behavior of water/hexaethyleneglycol dodecyl ether ($C_{12}EO_6$)/propanol/heptane system was investigated in a composition–temperature space (25–30 °C) at atmospheric pressure. A cone-like three-phase body consisting of aqueous (W), surfactant (Dp), and oil (O) phases is formed in the two-phase body of Wm (aqueous micellar phase) + O at 30.0 °C. With decreasing temperature the three-phase body becomes thinner and finally disappears at a critical double end point (CDEP) where the two critical end points of W and Dp phases are merged. The CDEP exists at about 26.2 °C (T_{CDEP}). The hydrophile–lipophile balance (HLB) of the mixed amphiphile changes towards lipophilic on addition of propanol. As a result, the Wm phase separates into two phases W + Dp above the T_{CDEP}. Further addition reduces the lipophobicity of aqueous media (or the solvophobicity of the mixed amphiphile), and the W and Dp phases are merged again. Below T_{CDEP}, since $C_{12}EO_6$ becomes much hydrophilic, the change of HLB lurks and a middle phase (Dp) cannot be observed.

Key words Critical double end point – cone-like three-phase body – hydrophile – lipophile balance – solvophobicity

Introduction

Amphiphiles can self-associate in a polar or an apolar solvent, and form aggregates of different shapes according to the given conditions. Various kinds of surfactant phases and their phase behavior have been described [1–13]. A noticeable feature is the appearance of a three-phase region where a bicontinuous microemulsion (or D) phase coexists with excess water (W) and oil (O) phases [2, 4]. The schematic three-phase behavior [4, 14–16] is shown in Fig. 1a. The composition of the D phase (α) shifts from the water-rich to the oil-rich region ($K_c \rightarrow \alpha \rightarrow L_c$) when the surfactant changes from hydrophilic to lipophilic. The change of temperature and/or the mixing ratio of lipophilic surfactant to hydrophilic surfactant induces the HLB change of the system. The D phase merges with the W phase at a critical end point (CEP) K_c and with the O phase at another CEP L_c. Between two critical tielines, K_c-β' and L_c-γ', a three-phase region is present. In the three-phase region, the surfactant exhibits the maximum solubilization capacity and the ultralow interfacial tension between the coexisting W and O phases is attained [8]. This three-phase behavior evolves from a tricritical point (TCP) [15–17], where K_c and L_c coincide with each other as shown in Fig. 1a.

We have recently reported [13] another type of three-phase behavior in water/polyoxyethylene mono-alkyl ether (CmEOn)/propanol/oil systems at constant temperature and pressure. This is schematically represented in Fig. 1b. A closed-loop coexistence curve (K_c'-α-K_c-γ-K_c') for the middle surfactant (Dp) and the aqueous (W) phases

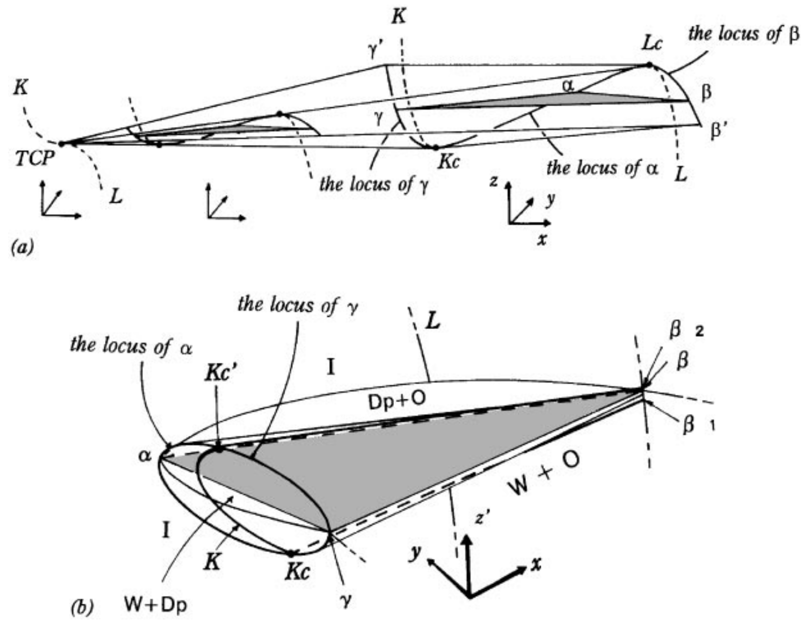


Fig. 1 (a) Schematic representation of three-phase behavior of surfactant (D), excess water (W), and excess oil (O) phases. The gray triangle indicates a tie triangle. K and L are critical curves of W–D and D–O. K_c and L_c are the critical end points. K_c-β' and L_c-γ' are the critical tie lines. The x-, y- and z-directions denote the weight fractions of oil/(water + oil), surfactant/system, and the change in hydrophile–lipophile balance, respectively. α, β, and γ denote the compositions of D, O, and W phases, respectively. The three-phase body is concentrated to a tricritical point (TCP) when an appropriate variable is introduced. (b) Schematic representation of the three-phase behavior of the Dp phase, the aqueous phase (W), and the oil phase (O). α, β, and γ denote the compositions of Dp, O, and W phases, respectively. K and L are critical curves of Dp–W and Dp (or Wm)–O, respectively. K_c and K_c' are the critical end points of Dp–W. K_c-β_1 and K_c'-β_2 are the critical tie lines. The z'-direction denotes the weight fraction of propanol/system. I indicates one-phase region

is formed in the presence of propanol. As a result, a cone-like three-phase body is formed in the two-phase body of Wm (aqueous micellar phase) + O inside the four-component composition tetrahedron. However, the origin of the Dp phase corresponding to the TCP for the D phase has not been clarified. Such a point would offer more information on the formation of the middle surfactant phase and functions of propanol. Propanol has great potential to form microemulsions, e.g., in lecithin systems [18–21].

In this context, we studied the effect of temperature on the three-phase behavior in a water/$C_{12}EO_6$/propanol/heptane system. This paper is especially focused on the origin of a cone-like three-phase body in the lower temperature side and the first of a series of studies on a whole series of three-phase bodies which disappear at a TCP (72.5 °C) [22].

Experimental section

Materials

Homogeneous hexaethyleneglycol dodecyl ether ($C_{12}EO_6$) was obtained from Nikko Chemicals Co., Ltd. Extra-pure-grade propanol and heptane were obtained from Tokyo Kasei Kogyo Co., Ltd. All the chemicals were used without further purification. Water was distilled twice after being ion-exchanged.

Procedures

Determination of the phase boundaries and identification of each phase were performed in the same manner as described in the previous paper [13].

Results

Three-phase behavior of water/$C_{12}EO_6$/propanol/heptane system at 30.0 °C

Phase diagrams of a water/$C_{12}EO_6$/propanol/heptane system at 30.0 °C and atmospheric pressure are shown in Fig. 2. Figure 2 is part of the section through the composition tetrahedron having the water/$C_{12}EO_6$/heptane triangle as the base. The weight ratios of water/oil, $R_{w/o}$, are 50/50 (a) and 10/90 (b). The three-phase region does not touch a one-phase region and is surrounded by a two-phase

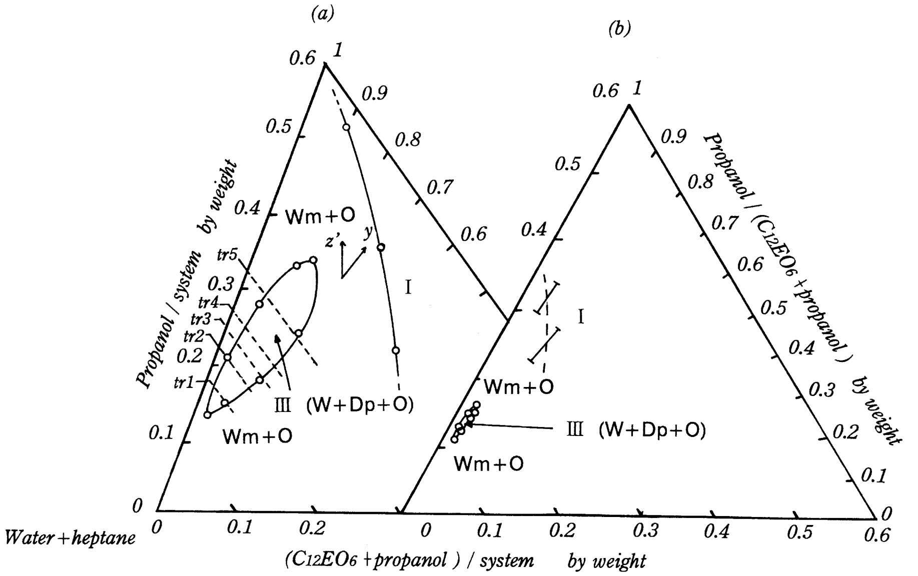


Fig. 2 Phase diagrams of water/$C_{12}EO_6$/ propanol/ heptane system at 30.0 °C and 1 atm. The $R_{w/o}$'s are: (a) 50/50 and (b) 10/90. The y- and z'-directions correspond to those in Fig. 1b. III denotes three-phase region. (a) is from Ref. [13]

region. This means that the phase sequence with the increase of propanol demonstrates Wm + O → three-phase coexistence → Wm + O. In addition, the three-phase region at $R_{w/o} = 10/90$ is narrower than that at $R_{w/o} = 50/50$. The three-phase region is a section of a cone-like three-phase body shown in Fig. 1b [13].

The critical line K_c–K'_c

When all p phases become identical (pth order critical point [23]) in a c-component system, the number of degrees of freedom for the point, $f_{\mathrm{crt}}^{(p)}$, is given by the following equation [23, 24]:

$$f_{\mathrm{crt}}^{(p)} = c - 2p + 3 \ . \tag{1}$$

In a four-component system, $f_{\mathrm{crt}}^{(2)}$ is 3. At constant temperature and pressure, one can obtain a critical line on the two-phase surface. In fact, a critical line ascending on the surface of the two-phase body (W + Dp) is seen in a section of constant propanol/$C_{12}EO_6$ of the composition tetrahedron (Fig. 3). In Fig. 3, the position of critical line is shown by the arrow, which was determined by the change in volume fractions of each phase: the Dp phase disappears on the amphiphile-dilute side, whereas the W phase on the amphiphile-rich side.

Change in the three-phase behavior with temperature

To investigate the effect of temperature on the three-phase behavior, the phase diagrams as a function of temperature are shown at various wt%'s of propanol + $C_{12}EO_6$ in the system (Fig. 4). These exhibit the phase change on the transversals across the three-phase region at constant $R_{w/o}$'s, e.g., broken lines tr1–tr5 in Fig. 2. The three-phase region becomes narrower with decreasing temperature and finally disappears at 26.2 °C at all $R_{w/o}$ ranges (50/50–93/7). At $R_{w/o} = 50/50$, the three-phase region at 22.5–27.5 wt% remains at 26.3 °C, whereas at 18.0 and 32.5 wt% it disappears at higher temperatures. This suggests that the three-phase region should not touch the one-phase region at $R_{w/o} = 50/50$.

The disappearance of the three-phase body is elucidated by a series of phase diagrams with changing temperature (Fig. 5). The three-phase region becomes thinner with decreasing temperature and disappears in the Wm + O region at 26.2 °C. It does not touch a one-phase region at $R_{w/o} = 50/50$, as suggested above. This means that the W and Dp phases remain in the water-rich region and the O phase in the oil-rich region. This behavior differs from that of a tricritical point (TCP) [15–17]. In the TCP case, the loci of the three coexisting phases are connected in one curve, which lies from end to end of the three-phase region (γ'-K_c-α-L_c-β') and is concentrated to the TCP, as seen in Fig. 1a. The three-phase region is in contact with a one-phase region in any section of constant $R_{w/o}$.

The movement of critical tie lines and critical end points

To understand the mechanism of disappearance of the three-phase body, the movement of the critical tie lines was investigated. The change in volume fractions of each phase along the lines *l*1–*l*6 (Fig. 4) is shown in Fig. 6. The position

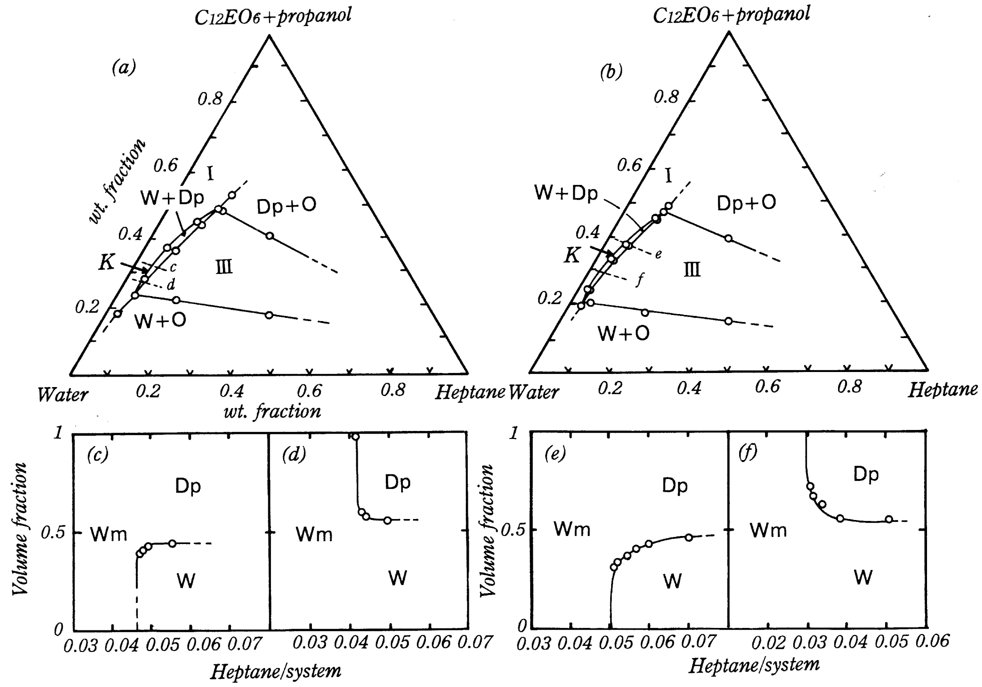


Fig. 3 Phase diagrams at 30.0 °C and 1 atm with constant weight ratios of propanol/$C_{12}EO_6$: (a) 80/20 (b) 85/15, and the change in volume fractions along the broken lines c–f. The weight ratios of ($C_{12}EO_6$ + propanol)/water are: (c) 0.330/0.670 (d) 0.275/0.725 (e) 0.40/0.60 (f) 0.30/0.70

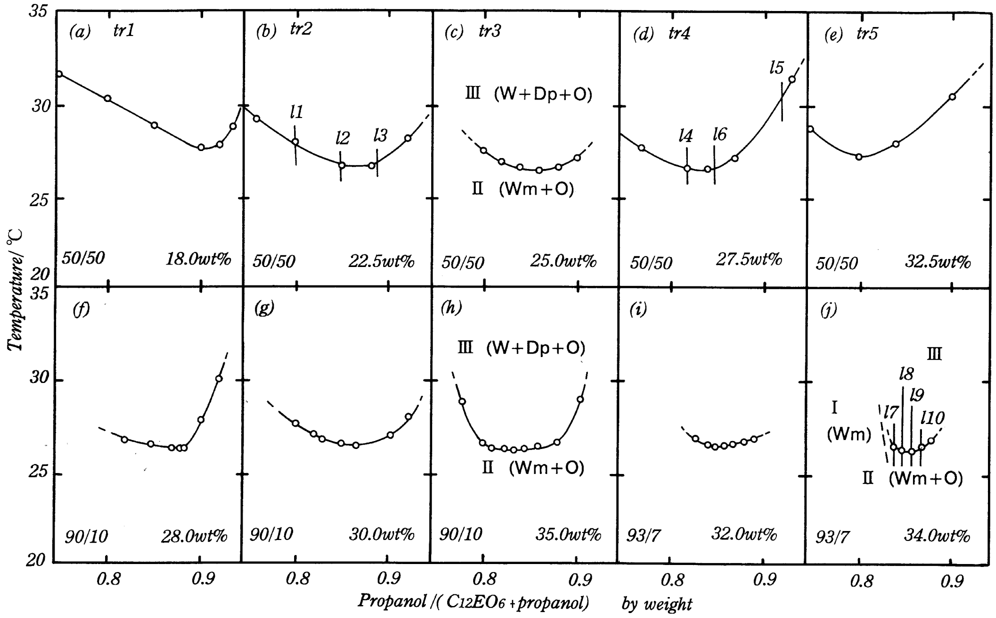


Fig. 4 The phase diagrams at constant wt% of ($C_{12}EO_6$ + propanol) in system as a function of temperature. The wt% of total amphiphile is indicated in the figure. The $R_{w/o}$'s are 50/50 (a)–(e), 90/10 (f)–(h), and 93/7 (i)–(j). Figures (a)–(e) are the diagrams on tr1-tr5 in Fig. 2, respectively

of the critical tie line K_c-β_1 (Fig. 1) at $R_{w/o} = 50/50$ is shown by Fig. 6a, b, and d: *l*1, 2 and 4 are on the propanol-less side of the three-phase region. As is obvious in Fig. 6a, the W phase disappears at 28.5 °C. K_c-β_1 lies at a lower wt% of total amphiphile than 22.5 wt% at 28.5 °C. On the contrary, the Dp phase disappears at 26.7 °C in Fig. 6b. K_c-β_1 shifts onto the higher side of the concentration than 22.5 wt% as the temperature decreases. Besides, the W phase disappears at 27.5 wt% (Fig. 6d). K_c-β_1 remains on the lower side than 27.5 wt% at 26.3 °C. K_c-β_1 lies between 22.5 and 27.5 wt% at 26.3 °C. In the same manner, K'_c-β_2 (Fig. 1) shifts to the lower side of the concentration, as temperature decreases (Fig. 6c, e, f). The line of K'_c-β_2 is also located between 22.5 and 27.5 wt% at $R_{w/o} = 50/50$ at 26.3 °C. It is probably concluded that K_c-β_1 and K'_c-β_2 approach each other in both *y*- and

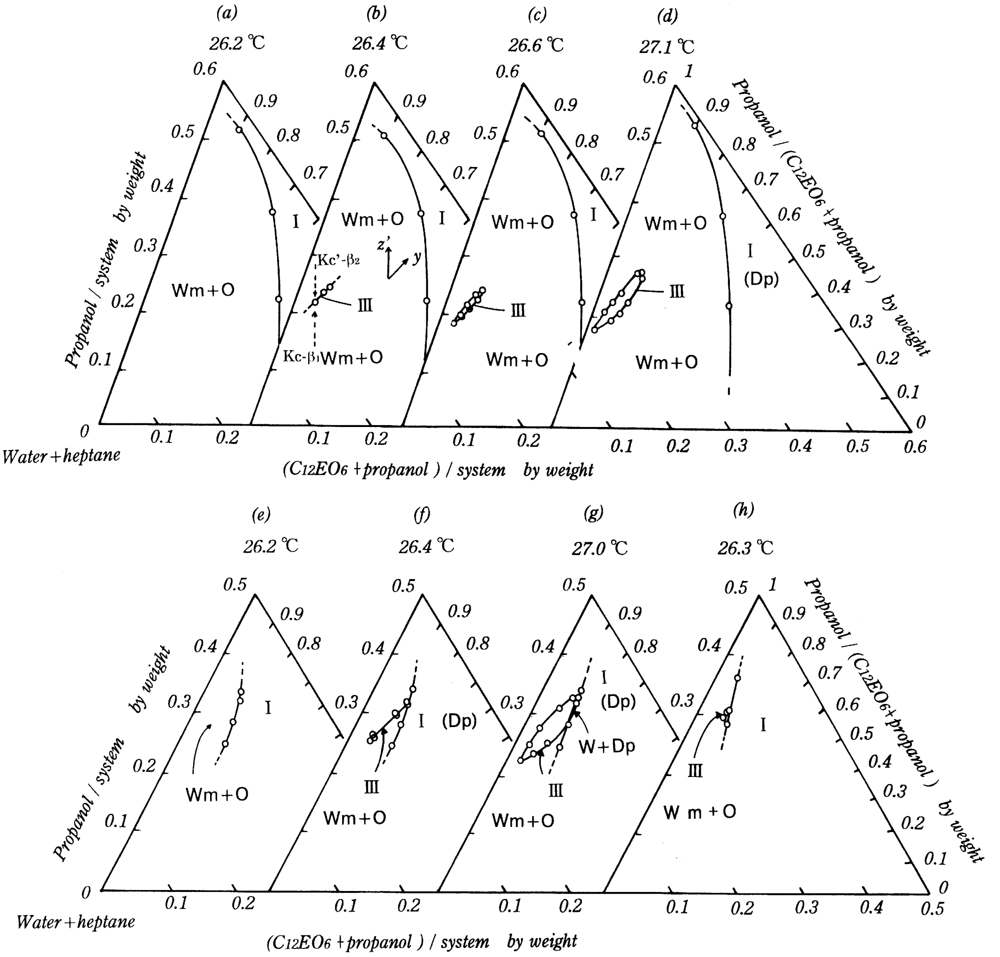


Fig. 5 Phase diagrams of water/$C_{12}EO_6$/propanol/heptane system at constant temperatures. Each one is a part of a section through the composition tetrahedron. The $R_{\mathrm{w/o}}$'s are 50/50 (a)–(d), 90/10 (e)–(g), and 93/7 (h). The y- and z'-directions correspond to those in Fig. 1b. The broken arrows show the movement of K_c-β_1 and K_c'-β_2 with decreasing temperature

z'-directions as shown by the broken arrows in Fig. 5b, since the three-phase region gets thinner (Fig. 5).

The positions of K_c and K_c' were determined near 26.3 °C. The critical tie line coincides with the contacting point (or X-point [16]) of one-phase and three-phase regions at the CEP [13]. Both critical tie lines extend beyond $R_{\mathrm{w/o}} = 90/10$, because the three-phase region touches the one-phase region of Dp phase (Fig. 5f). Thus, with temperature the change of volume fractions for each phase was measured around the X-points at $R_{\mathrm{w/o}} = 93/7$ (Fig. 5h), i.e. along the lines $l7$–$l10$ (Fig. 4j). The results are shown in Fig. 6g–j. The Dp phase disappears in Fig. 6h–j. This shows both critical tie lines lie at a higher concentration of amphiphile than 34.0 wt% or do not reach $R_{\mathrm{w/o}} = 93/7$. However, the volume fraction of each phase remains almost constant very close to the three-phase boundary and slightly bluish color or critical opalescence was observed in W and Dp phases. K_c and K_c' are close to the respective X-point at $R_{\mathrm{w/o}} = 93/7$. Due to the coincidence of the two X-points, K_c and K_c' are located close to each other.

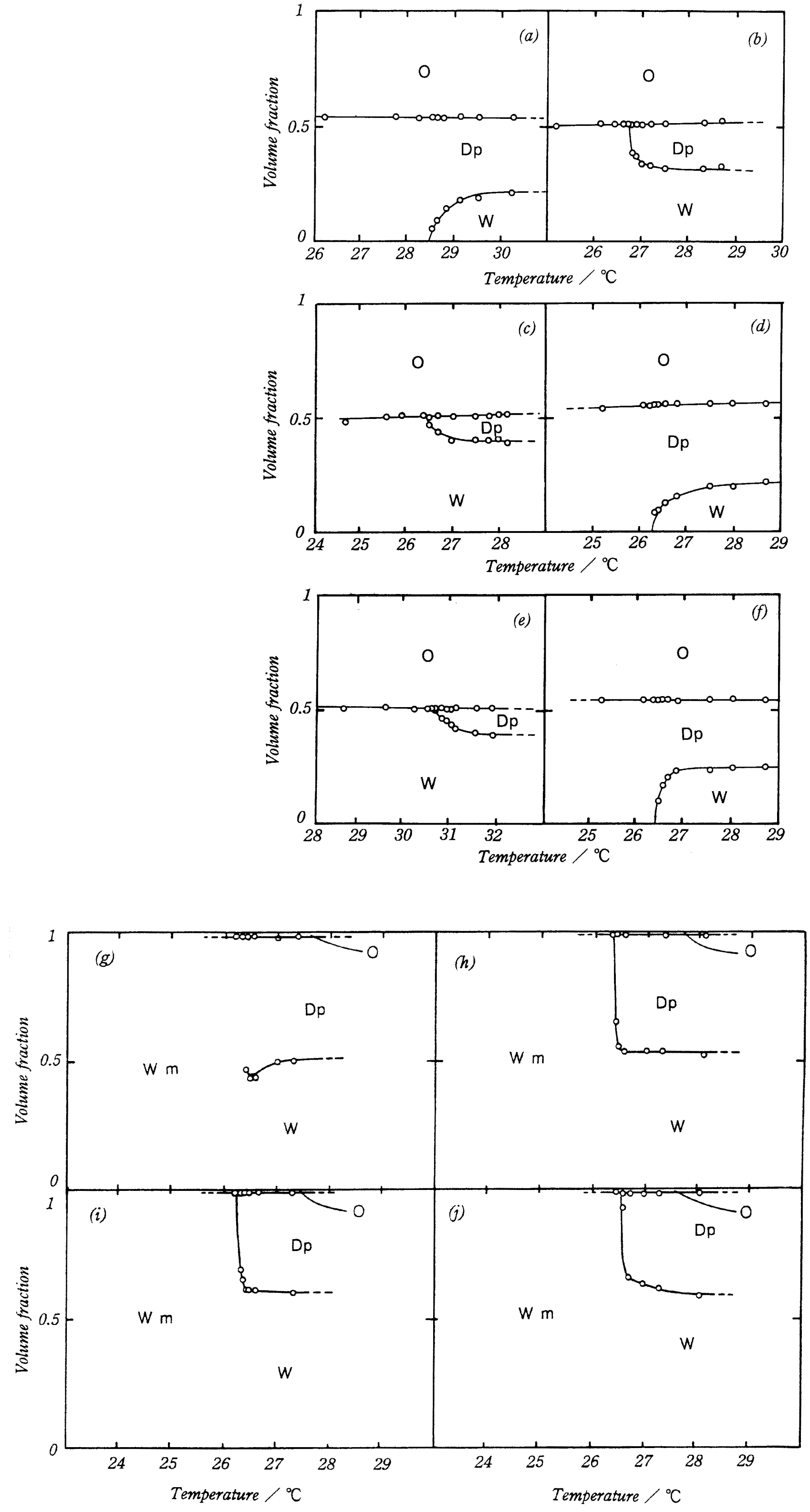
The disappearance phenomenon of the cone-like three-phase body is illustrated in Fig. 7. The three-phase body becomes thinner with decreasing temperature, and finally disappears when the critical tie lines are superimposed. K_c and K_c' merge at one end of the superimposed critical tie line. We call this point the critical double end point (CDEP). The critical line K disappears, simultaneously.

Critical double point and critical double end point

Closed-loop coexistence curves with upper and lower critical points have been observed at constant pressure in binary systems [5, 15, 26–28]. If the critical points coalesce at a particular point, the point should be called the critical double point (CDP). One can obtain such points by changing pressure [28] or adding a third appropriate component [15]. The number of degrees of freedom for a CDP, f_{CDP}, in a c-component system is given by,

$$f_{\mathrm{CDP}} = f_{\mathrm{crt}}^{(2)} - 1 = c - 4 + 3 - 1 = c - 2 \,. \qquad (2)$$

Fig. 6 The change in volume fractions of each phase along the lines *l*1-*l*10 in Fig. 4: (a) *l*1, (b) *l*2, (c) *l*3, (d) *l*4, (e) *l*5, (f) *l*6, (g) *l*7, (h) *l*8, (i) *l*9, and (j) *l*10



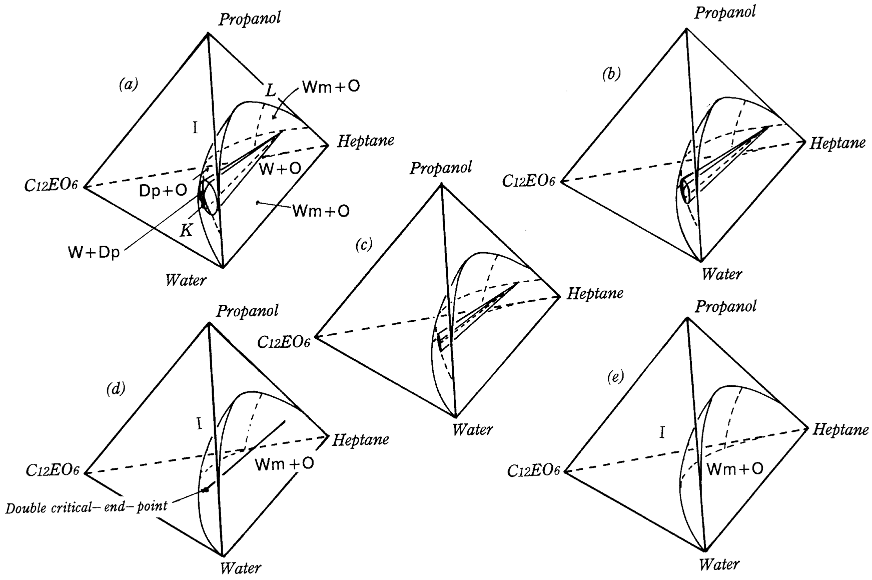


Fig. 7 The schematic representation of the change of a cone-like three-phase body with decreasing temperature. The temperature decreases in the order, (a) → (b) → (c) → (d) → (e). The lateral broken curves on a two-phase surface are the intersections with the plane including a tie triangle with the surface. The broken curves L are critical curves of Wm (or Dp)–O. The $C_{12}EO_6$-concentrated region is not drawn here. The two-phase region on propanol–water–heptane plane is referred to Ref. [25]

In a four-component system, f_{CDP} becomes 2. This means a CDP exists on the critical curve K in a composition tetrahedron. On the other hand, our result definitely demonstrates the CDEP is uniquely determined in a composition-T space of a four-component system at a fixed pressure. The number of degrees of freedom for a CDEP should be expressed by the following equation:

$$f_{\mathrm{CDEP}} = f_{\mathrm{CDP}} - 1 = c - 3 \ . \qquad (3)$$

Subtracting 1 means a third and ordinary phase coexists with the critical phases. The CDEP is a CDP. A CDEP was called the critical double point in the previous paper [29].

Discussion

Formation of Dp phase and properties of amphiphile and aqueous solvent

On the basis of our results, the effects of temperature and the addition of propanol on the closed-loop coexistence curve are schematically represented in Fig. 8. The consolution curves of W and Dp phases are represented by the loci of K_c and K'_c. The change of hydrophile–lipophile property of CmEOn with temperature and the changes of properties of amphiphile aggregates and the aqueous solvent with propanol concentration are also shown beside the axes. The term "lipophobic" of aqueous solvent [30] means the property that the aqueous solvent excludes the apolar portions or the apolar molecules. This reflects all the solvent properties such as polarity, hydrogen bonding, and so on. With the term "hydrophobicity" or "solvophobicity", we describe the property of the amphiphile aggregates that the aggregates do not dissolve in the water or solvents, irrespective of the solubility of water or solvent in the surfactant phase. As propanol acts as a water-soluble cosolvent as well as a lipophilic cosurfactant in the condition [13], it considerably dissolves in water when the middle (Dp) phase is present (Fig. 3).

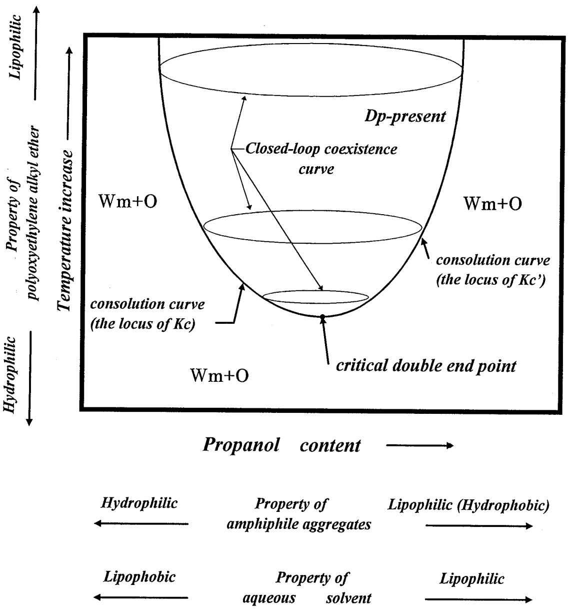


Fig. 8 A schematic representation of the Dp-present region. The consolution curves for W–Dp are represented as the loci of K_c and K'_c

When CmEOn is moderately hydrophilic at higher temperature, the addition of propanol shifts the HLB of the mixed amphiphile towards lipophilic and induces the formation of the Dp phase. Further, the addition of propanol decreases the lipophobicity of the aqueous solvent. The solvophobicity of amphiphile aggregate is relatively reduced. The W and Dp phases merge again. Consequently, the closed-loop coexistence curve for W and Dp phases or the cone-like three-phase body is formed between the two consolute curves [13]. As CmEOn becomes more hydrophilic with decreasing temperature, the amount of propanol required for the phase separation increases. However, the amount of propanol required for the consolution (K_c') decreases as shown by Fig. 4. The two consolution curves meet at the CDEP at a particular temperature (the CDEP temperature, T_{CDEP}) (Fig. 8). Below the T_{CDEP}, since CmEOn becomes still more hydrophilic, the solvophobicity of the aggregate is decreased. The change of HLB is not remarkable and thus the middle phase cannot be observed.

Our interpretation is consistent with the CDP in a ternary water/C_4EO_1/C_4EO_2 system [15]. A closed-loop miscibility gap is formed in water/C_4EO_1 system when the temperature changes at a constant pressure. Kahlweit et al. could obtain the CDP by the addition of C_4EO_2 to the two-phase system and has pointed out that C_4EO_2 increases the hydrophilicity of the (mixed) amphiphile [15]. It is noteworthy that the effects of temperature and the addition of C_4EO_2 corresponds to the effects of the addition of propanol and temperature in the present system, respectively.

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