Phase Behavior of 2-Butoxyethanols/Water/Oil Systems

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Synopsis. Phase diagrams of 2-isobutoxyethanol (D)/water (W)/decane (O) system were studied at 2.0, 8.2, 15.0, 19.0, and 19.8 °C. The addition of O lowers the critical solution temperature of the D–W system from 26.2 to 2.0 °C, at which temperature the critical solution curve ends with the lower critical end point (Kc). On the other hand, the addition of W raises the critical solution temperature of the O–D system to 19.8 °C at which the critical solution curve ends with another critical end point (Lc). A three-phase region consisting of O, D, and W phases appears in a temperature range between the two critical end temperatures.

Recently, similarity of phase behavior has been reported among some amphiphilic compound systems, such as an ionic surfactant/brine/(cosurfactant)/oil,[1,2] short-chain alcohol/brine/oil,[3] and nonionic surfactant/water/oil systems.[4] In these systems, an amphiphile changes from water-soluble (hydrophilic) to oil-soluble (lipophilic) with the increase in salt content or changing in temperature. In the transition range of phase behavior, there is a three-phase region in which an amphiphile phase coexists with a water phase and an oil phase in equilibrium.

In this paper, phase behavior of 2-isobutoxyethanol/water/oil system has been investigated around the temperatures of the three-phase region in order to compare with long-chain surfactant systems.

Experimental

Materials. Extra-pure-grade 2-isobutoxyethanol, 2-butoxyethanol, diethylene glycol hexyl ether, and hydrocarbons were obtained from Tokyo Kasei Kogyo Co. and were used with out further purifications.

Procedures for the determination of phase boundaries are described elsewhere.[5]

Results and Discussion

Phase Diagram of 2-Isobutoxyethanol/Water/Decane System. If temperature is taken as an axis perpendicular to a composition plane at constant pressure, the three-dimensional shape of a ternary system is a triangular prism and a horizontal section is the isobaric, isothermal section of the system, *i.e.*, the phase diagram of a three-component system. The phase diagrams of 2-isobutoxyethanol/water/decane system were determined at 2.0, 8.2, 15.0, 19.0, and 19.8 °C, and are shown in Figs. 1(a)—(e). The compositions are given in weight fractions. W, D, and O denote the water, 2-isobutoxyethanol, and oil phases, respectively.

The lower critical solution temperature of the binary

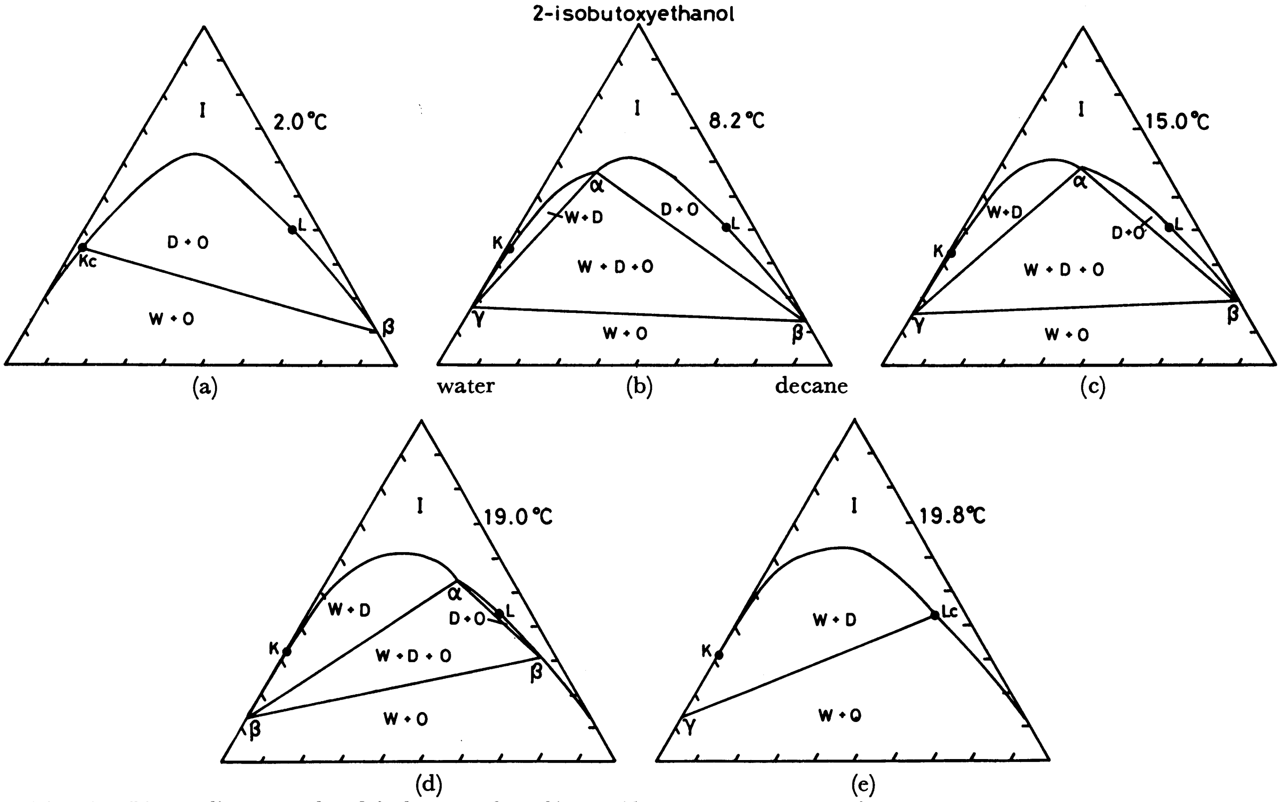

Fig. 1. Phase diagrams for 2-isobutoxyethanol/water/decane system at various temperatures.
O: an oil phase, W: a water phase, D: a 2-isobutoxyethanol phase, α, β, and γ: invariant points, K and L: plait points, Kc: the lower critical end point of W-D, Lc: the upper critical end point of O-D, I: one-phase region.

system of D–W is 26.2 °C, below which there are complete miscibilities in the binary systems of D–W and O–D. But, a large miscibility gap exists in the ternary system due to the poor mutual solubility of O and W. Plait points of the D–W and O–D phases in the three-component system are indicated by K and L. The locus of K in the triangular prism, *i.e.*, in the space of temperature and compositions, ends with the lower critical end point, Kc (water, 62.8 wt%; 2-isobutoxyethanol, 34.8 wt%; decane, 2.4 wt%) at 2.0 °C. On the other hand, the locus of L in the triangular prism ends at the upper critical end point Lc (water, 8 wt%; 2-isobutoxyethanol, 43 wt%; decane, 49 wt%) at 19.8 °C as is shown in Fig. 1(e). At the temperatures between the two critical end temperatures, a three-phase region consisting of O, D, and W phases appears due to the superposition of three-miscibility gaps; O+D, D+W, and O+W regions. The compositions of three coexisting liquid phases are invariant at constant temperature and pressure, and these points are indicated by α, β, and γ in Fig. 1. At the lower critical end temperature (LCET), W and D phases become identical on the line Kc-β, as is shown in Fig. 1(a). On the other hand, O and D phases merge on the line Lc-γ at the upper critical end temperature (UCET), as is shown in Fig. 1(e). The plait point K reaches the D–W axis at 26.2 °C, above which there is no plait point in the phase diagram.

The vertical section of the phase diagrams in Fig. 1 is shown in Fig. 2. The water/oil ratio is unity and the concentration of 2-isobutoxyethanol is plotted horizontally. Similar vertical sections of 2-butoxyethanol water/decane, diethylene glycol hexyl ether/water/decane and triethylene glycol octyl ether/water/decane[4] systems are also shown in Fig. 2. A three-phase region moves toward a water-oilaxis (left-hand axis) with the increase in the molecular size of an amphiphile. On the other hand, the temperature range of the three-phase region is little affected by the molecular size of an amphiphile, because the hydrophile-lipophile property

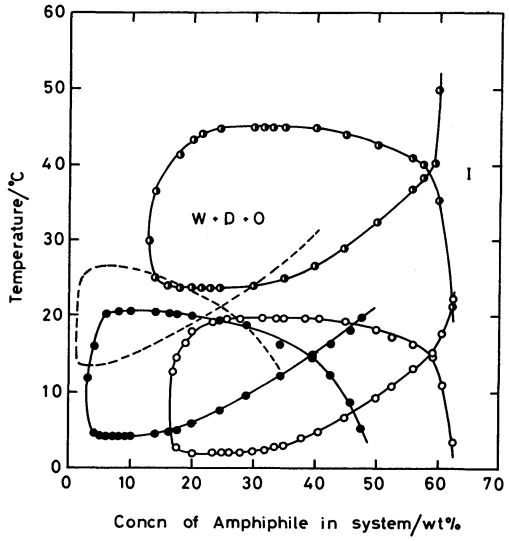

Fig. 2. The effect of the concentrations of an amphiphilic conpound on the equi-weight mixture of water and decane.
-○-: 2-Isobutoxyethanol system, -◑-: 2-butoxyethanol system. -●-: diethylene glycol hexyl ether system, ------: triethylene glycol octyl ether system.

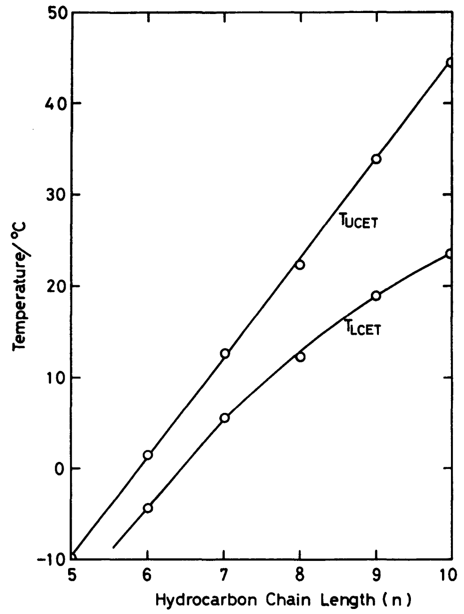

Fig. 3. The effect of hydrocarbon chain length of oil (C_nH_{2n+2}) on the critical end temperatures in the 2-butoxyethanol/water/oil systems.

of a nonionic amphiphile is related to the ratio of the hydrophilic and lipophilic portions.[6]

The Effect of Oil Size on the Difference in LCET and UCET. If three components are fixed, LCET and UCET are invariant at constant pressure. The lower and upper limits of a three-phase region in Fig. 2 correspond to LCET and UCET respectively. LCETs and UCETs in various 2-butoxyethanol/water/oil systems are shown in Fig. 3. With an decrease in the hydrocarbon chain-length of oil, the difference in LCET and UCET becomes smaller. If the two critical end temperatures coincide strictly, a tricritical phenomenon may be observed.[7] The degree of freedom (f) at a pth order critical point (p=3 at a tricritical point) is determined by the following equation;[8]

$$f = c - 2p + 3,$$

where c is the number of components. In a three-component system, f=0 holds at a tricritical pont, which is an invariant point in the space of temperature, pressure and compositions. Therefore, in order to observe a tricritical phenomenon, the pressure in a ternary system has to be changed.

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