The Tricritical Point in the n-$C_8H_{17}SO_3Na$/ n-$C_4H_9OH/H_2O/n$-$C_{14}H_{30}$ System

Hironobu KUNIEDA* and Tsutomu ARAI†
Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai 156, Hodogaya-ku, Yokohama 240
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Synopsis. The phase behavior of three coexisting liquid phases has been studied in the four-component system of n-$C_8H_{17}SO_3Na/n$-$C_4H_9OH/H_2O/n$-$C_{14}H_{30}$. With a rise in the temperature, the three-phase region shrinks to a tricritical point at which the three liquid phases become identical.

Since ultralow interfacial tensions are attained and a solubilizing power of a surfactant reaches its maximum around a three-phase region (water(W), surfactant(D), and oil(O) phases)[1,2] due to critical phenomena, it is very important to investigate the solution behavior of a surfactant around this region. In a three-liquid-phase system, two liquid phases (O-D or D-W phases) become identical in the presence of a third phase (W or O phase) at a critical end point which is located on the boundary between the two- and three-phase regions.[2] If the two critical end points of the O-D and D-W phases coincide with each other, the three coexisting phases become identical at a high-order critical point, the tricritical point.[3,4] This kind of critical phenomenon has been observed in some systems,[5] but not in a surfactant system.

We previously found a tricritical phenomenon in a bile-salt system.[4] In this paper, in order to find a tricritical point in an ordinary surfactant system, the phase behavior of the n-$C_8H_{17}SO_3Na/n$-$C_4H_9OH/H_2O/n$-$C_{14}H_{30}$ system has been investigated.

Experimental

Materials. Extra-pure-grade n-$C_8H_{17}SO_3Na$ and n-$C_{14}H_{30}$ were obtained from the Tokyo Kasei Kogyo Co., while extra-pure-grade n-C_4H_9OH was obtained from the Wako Chemicals Co. The procedures for the determination of the phase beoundaries have been described elsewhere.[4]

Results and Discussion

In the n-$C_4H_9OH/H_2O/n$-$C_{14}H_{30}$ system,[6] a three-phase region appears at a lower temperature in the absence of a surfactant, as is shown in Fig. 1 (●). In this case, a critical end point is an invariant point at a constant pressure (an atmospheric pressure).[2,7] By adding n-$C_8H_{17}SO_3Na$ to this three-component system, the maximum temperature of the three-phase region moves up to a higher temperature, as is also shown in Fig. 1 (○). This maximum temperature of a three-phase region is determined for a variety of over-all compositions; the maximum over all compositions of these maxima may be identified as the tricriti-

† Present address: Fuji Film Co., Nakanuma 210, Minamiashigara, Kanagawa 250-01.

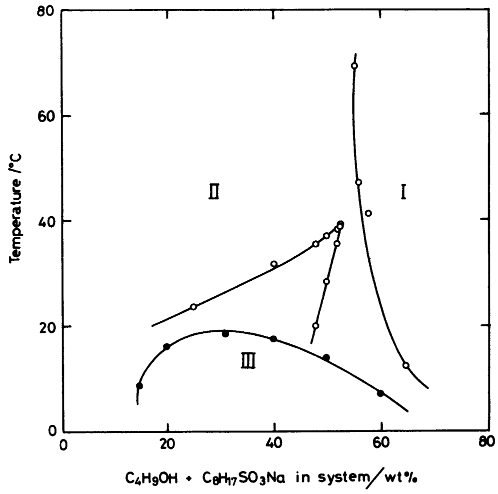

Fig. 1. Phase diagrams of equi-weight mixtures of H_2O-$C_{14}H_{30}$ containing C_4H_9OH (●) and 95 wt% C_4H_9OH+5 wt% $C_8H_{17}SO_3Na$ (○) as a function of temperature. I, II, and III denote one-, two-, and three-phase regions respectively.

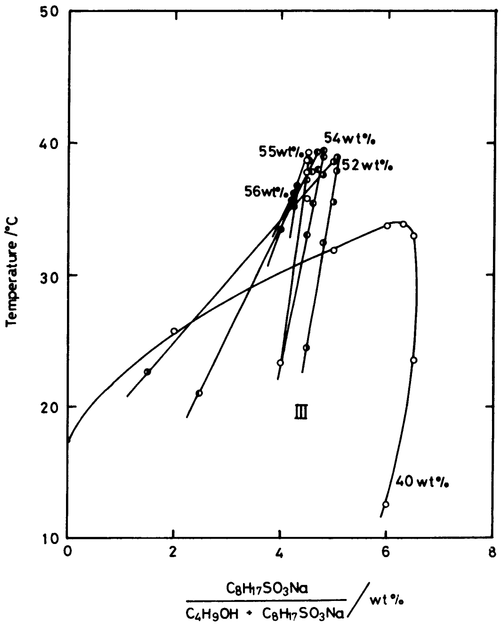

Fig. 2. The effect of concentration of $C_8H_{17}SO_3Na$ in $C_8H_{17}SO_3Na+C_4H_9OH$ on the three-phase region of equi-weight mixture of H_2O-$C_{14}H_{30}$ containing $C_8H_{17}SO_3Na+C_4H_9OH$. Numerical number in the Figure indicates the concentration of $C_8H_{17}SO_3Na+C_4H_9OH$ in system.

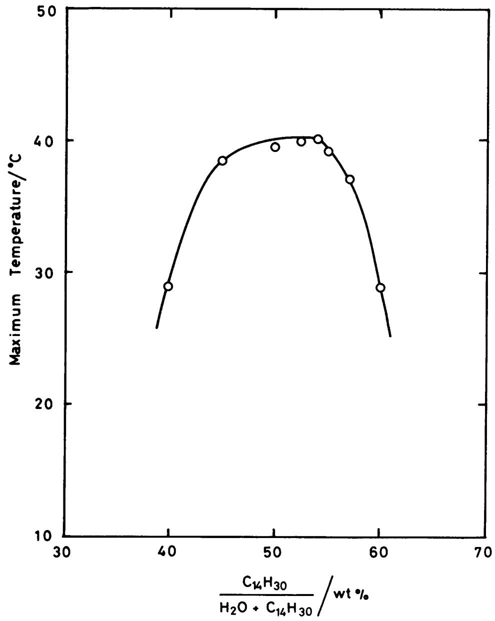

Fig. 3. The effect of $H_2O/C_{14}H_{30}$ ratio on the maximum temperature of the three-phase region.

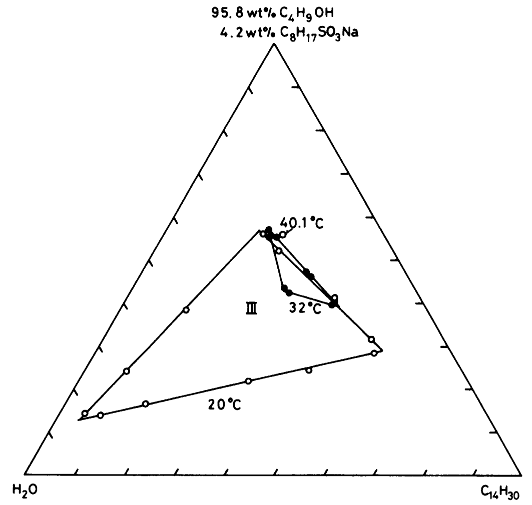

Fig. 4. The three-phase region of pseudo ternary system of (95.8 wt% $C_4H_9OH+C_8H_{17}SO_3Na$)/H_2O/$C_{14}H_{30}$. The three-phase region shrink to a tricritical point with the rise in temperature.

cal point.[3] This is because, in a four-component system, a line of critical end points exists in a certain space of temperature and compositions at a constant pressure, and the two critical end points of O-D and D-W exist at the respective temperatures as long as a three-phase region appears.[4] Since a three-phase region is a point in a composition tetrahedron at the maximum temperature, the two critical end points may coincide at this point, *i.e.*, the tricritical point. In Fig. 2, the three-phase region is determined as a function of n-$C_8H_{17}SO_3Na$/(n-$C_8H_{17}SO_3Na$+n-C_4H_9OH) and the weight fraction of oil/water is unity. In this case, the maximum temperature of the three-phase region appears at the 54 wt%/system of (n-$C_8H_{17}SO_3Na$+n-C_4H_9OH). Similar maximum temperatures are determined for a variety of water/oil ratios and are plotted in Fig. 3. The maximum temperature of these maxima is 40.1 °C (n-$C_8H_{17}SO_3Na$+n-C_4H_9OH, 56 wt%/system. n-$C_{14}H_{30}$/H_2O, 0.54/0.46 (W/W). n-$C_8H_{17}SO_3Na$/n-C_4H_9OH, 0.042/0.958 (W/W)).

Therefore, at this temperature, the three-phase region is a point in this four-component system and is identified as the tricritical point. In fact, the critical opalescence is observed in all phases in the vicinity of this point. The three-phase region in the pseudo-three-component system of 95.8 wt% n-C_4H_9OH+4.2 wt% n-$C_8H_{17}SO_3Na$)/H_2O/n-$C_{14}H_{30}$ is shown at 20, 32, and 40.1 °C in Fig. 4. The three-phase region shrinks to a point on approaching 40.1 °C.

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