

PHASE BEHAVIOR AND SOLUBILIZATION OF 1-HEXANOL IN THE WATER-CONTINUOUS PHASES CONTAINING SURFACE-ACTIVE COMPOUNDS

Seong-Geun OH*, Jin-Gu KIM and Jong-Duk KIM**

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, P.O.Box 131, Chungryang, Seoul, Korea

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Abstract—For ternary systems of 1-hexanol, water, and surface-active compounds, the phase diagrams and the solubilizations of alcohol in the micellar water-continuous phases were determined by chromatographic analysis and by measuring conductivities and turbidities. Near the region of the water-1-hexanol binary system, a narrow three-phase region including two water-continuous phases appeared as surfactant added. Depending on the levels of surfactant concentration, the transition of the micelles to the liquid crystallines occurred in the first order type or in the continuous type. The maxima of the electrical conductivities and the onset of the turbidities were consistent with the approximated phase boundaries. The change of the solubilities of alcohol in the aqueous micellar solutions indicated that on or near the phase transition regions there might exist cylindrically-organized flexible micelles, having high conductivities and high turbidities but small solubilization efficiencies of alcohol in the amphiphilic layer.

INTRODUCTION

Multicomponent mixtures containing surface-active compounds have been used in the various industries including fine chemicals, drugs, foods, energy, materials and surface treatments, where the ability of hydrophilic and hydrophobic balance for amphiphile compounds is known to be important in controlling microstructures, properties, and molecular alignments [1-4]. In most applications, however, the optimum conditions for the complicated and microbalanced molecular alignments and the thermodynamically stable microstructures, are not yet satisfactorily established, and the estimation techniques for the size and shape and the dynamic nature of microstructures are immature [5].

Among the various phases of such ternary systems consisting of surface-active compounds and/or of aqueous soaps with alcohols, an isotropic aqueous liquid phase (L_1), another isotropic liquid phase continuous to the alcohol or nonaqueous region of reversed micelles (L_2), and several liquid crystalline phases with different lattice structures were generally identified [6-9], and a theory of intermicellar equilibria, R-theory, has been proposed within the experimental evidence

[6,7]. In addition to the micelle phases, the intermediate structures of Winsor's type III systems [6,7], have not been identified in spite of the several microstructural models, including hard oil and water globules [10], lamellar structure [11,12], randomly arranged polyhedra [13], dog-boned bicontinuous structure [14,15], random curvature [16], and droplets in coacervation or cosolubilization [17,18] and, in recent, flexible interfaces with varying size and shape [19]. Above the critical micellization concentration (CMC), in fact, such a transition of phases and microstructures depends on the chemical compositions of each compound in the phase diagrams as well as on the resulting configurations of molecular interactions [8,9]. However, the formation and transition of microstructures, and the nature of intermolecular and interstructural forces have not been fully explained despite of the thermodynamic descriptions of molecular aggregates [20-23]. Meanwhile, the determination of phase diagrams containing several compounds, though tailed long time in experiments, has been carried out to understand the interrelations of microstructures and the continuity of the related phases [24]. In fact, the interrelations of the microstructures, the properties, and the phase diagrams are among the most important parts of information for material system design.

In this report, when 1-hexanol is solubilized in

* Present address, Pacific R & D Center, LTD

** To whom all corresponds should be addressed.

aqueous solutions of surfactants, the ternary phase diagrams and the solubility change of alcohol were investigated for the association colloid-water systems in the range of the water-continuous phases by liquid chromatographie, electrical conductivities and turbidities.

EXPERIMENTS

1. Materials and preparations

The sample solutions were made of deionized and doubly distilled water (55 μ Mhos in electrical conductivity) with 1-hexanol (Merck Co.) and sodium dodecyl sulfate (SDS) and cetyl trimethylammonium bromide (CTAB) (Tokyo Kasei Co.) and all the chemicals were used as purchased.

The phase boundaries were determined by two different methods, chromatographic and titration methods [25]. After taking the amounts of alcohol by volume and surfactant by weight (± 0.0001 g), the 10 cc samples, were mixed prudently or sonicated, and incubated in the 15 cc glass samplers with Teflon-taped caps at 30°C and 45°C for two months. Some of the samples were centrifuged at 4000 rpm for 10 min to remove the bubbles formed during mixing. Another series of samples was prepared by titrating with alcohol along the paths of the fixed amount of the aqueous surfactant solutions, and the changes of the solution properties were monitored by measuring electrical conductivities and turbidities.

2. Measurements

Chromatographic analysis and phase textures

The concentrations of the equilibrated samples were determined by liquid chromatographie with RI detector (Waters Co.). The column was 30 cm long and 1/4 inch tube packed with μ -porasil and the mobile phase was methanol. The maximum resolution was obtained at the flow rate of 0.7 cc/min and the column temperature 19°C. On the other hand, the textures of the equilibrated phases were observed by the cross polarizer.

Electrical conductivity and turbidity

The conductivities of the samples, prepared by the titration method after agitated completely with a magnetic stirrer in the thermostatic, were determined by conductivity bridge YSL-32, of which the cell constant was equal to 1.0 cm^{-1} , and the transient turbidities after sonicated, were determined by Turner photospectroscopy in the range of 450 to 500 nm. Also, the equilibrium turbidities of the separated phases were determined after 2 months, when the number of phases and the texture were not subjected to change.

RESULTS AND DISCUSSIONS

1. Phase equilibria

After the samples were incubated for two months, the solutions at the low concentrations of surfactants were separated into the micellar solution (L_1), the inverted micellar solution (L_2), and the liquid crystalline phase (D) [6-9]. Under the cross polarizer, the texture of liquid crystalline phases appeared with the marbled local domains, scattering the polarized light, while the isotropic phases completely blocked the transmitting light.

In table 1, and figure 1, the concentrations determined by chromatographie and the phase textures of SDS-1-hexanol-water systems were presented and in table 2 and figure 2 for CTAB-1-hexanol-water systems. In figures, the concentrations of the phases were given by the circles (•) and the tie lines by lines. As temperature

Table 1. Concentrations of sodium dodecylsulfate - 1-hexanol - water mixtures determined by liquid chromatographie and phase textures identified by cross polarizer. All numbers are weight percentages.

SDS	1-hexanol	water	state	SDS	1-hexanol	water	state
at 30°C							
0.0	97.1	2.9	L_2	0.0	0.7	99.3	L_1
2.6	94.0	3.4	L_2	0.5	2.5	97.0	L_1
7.6	88.0	4.4	L_2	4.0	6.0	90.0	D*
					2.0	3.0	95.0
9.7	84.3	6.0	L_2	7.0	8.0	85.0	D
12.9	79.0	8.1	L_2	9.8	16.9	73.3	D
16.6	71.4	12.0	L_2	11.6	20.4	68.0	D
19.0	65.0	16.0	L_2	18.7	26.0	55.3	D
22.3	57.8	19.9	L_2	18.8	28.2	53.0	D
22.8	52.5	24.7	L_2	21.2	28.4	50.4	D
at 45°C							
0.0	95.0	5.0	L_2	0.0	0.8	99.2	L_1
7.7	84.5	7.8	L_2	0.4	1.3	98.3	L_1
16.2	68.8	15.0	L_2	1.0	4.1	94.9	D
17.5	65.4	17.1	L_2	2.7	4.8	92.5	D
20.5	56.6	22.9	L_2	3.4	13.9	82.7	D
21.8	45.4	32.8	L_2	8.2	23.2	68.6	D

*Water-continuous liquid crystalline phase appeared in the three-phase systems.

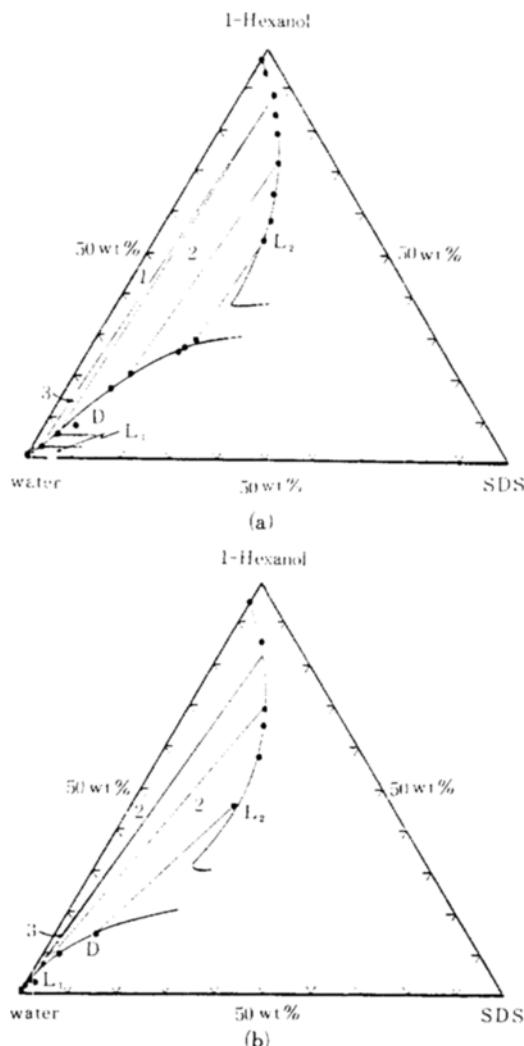


Fig. 1. Phase diagram of sodium dodecylsulfate (SDS)-1-hexanol-water mixtures at (a) 30°C and (b) 45°C.

The circles (●) represent the concentrations of equilibrated phases. L_1 represents the water-continuous phase containing micelles, L_2 for the alcoholic solution containing inverted micelles and D for liquid crystalline lamellae phases.

increased, the two-phase regions for both cationic and anionic surfactant systems were significantly reduced, but the general shapes were consistent with the results of Mustafa et al. [26] and Ekwell et al. [8,9] except that the three-phase region appeared near the surfactant-lean conditions for both systems. In the works of Mustafa et al. [26], the three-phase region was not reported probably because of their titration method. Even in our

Table 2. Concentrations of cetyltrimethylammonium bromide-1-hexanol-water mixtures determined by liquid chromatography and phase textures identified by cross polarizer. All numbers are weight percentages.

CTAB	1-hexanol	water	state	CTAB	1-hexanol	water	state
at 30°C							
0.0	97.1	2.9	L_2	0.0	0.7	99.3	L_1
5.5	91.0	3.5	L_2	1.0	2.3	96.7	L_1
6.6	88.0	5.4	L_2	2.3	5.6	92.1	L_1
10.0	82.0	8.0	L_2	5.0	7.0	88.0	D
11.0	76.0	13.0	L_2	7.0	10.0	83.0	D
13.0	69.0	18.0	L_2	10.0	13.0	77.0	D
18.0	60.0	22.0	L_2	16.0	18.0	66.0	D
22.0	32.0	46.0	L_2	17.7	19.4	62.9	D
19.0	28.0	53.0	L_2	22.0	24.0	54.0	D
at 45°C							
0.0	95.0	5.0	L_2	0.0	0.8	99.0	L_1
7.4	81.0	11.6	L_2	1.6	2.2	96.2	L_1
9.5	78.9	11.6	L_2	2.1	3.7	94.2	L_1
11.8	72.7	15.5	L_2	5.0	7.0	88.0	D
17.0	60.0	23.0	L_2	7.6	12.1	80.3	D
19.0	50.0	31.0	L_2	9.0	19.0	72.0	D
19.0	40.0	41.0	L_2	13.0	16.5	70.5	D
17.0	30.0	53.0	L_2	20.0	20.0	60.0	D

titration measurements, the three-phase region was missed since it was so narrow and appeared slowly.

The three-phase region consisted of an aqueous phase (L_1), an alcohol rich phase (L_2), and a surfactant-rich phase in water-continuous medium (D). The L_1 phase is continuous to the water phase and the L_2 phase to the alcohol, while the surfactant-rich phase D is continuous to the crystalline phase. In general, since the three-phase region should be bounded on three two-phase regions, the region could be terminated either at the binary systems, or at a critical point (plait point). In order to confirm the behavior, the phase diagram near the three-phase region was re-examined after the additional experiments and shown in figure 3 for water-continuous phase at 45°C. One of the two-phase regions, which consisted of water-continuous phase (L_1) and surfactant-rich phase (D), were found to be terminated at the critical point or extended along a narrow

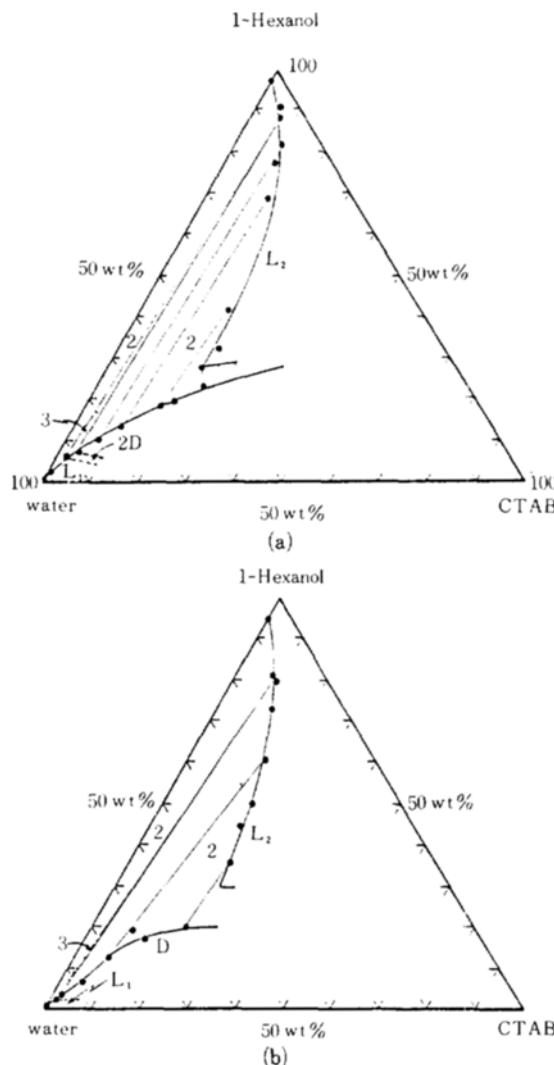


Fig. 2. Phase diagrams of cetyl trimethylammonium bromide(CTAB)-1-hexanol-water mixtures at (a) 30°C and (b) 45°C.

All symbols shown in Fig. 1.

channel where two phases coexisted. Further, in figures the transitions from the isotropic micellar solution to the anisotropic crystalline phase were identified by two pathways, the supercritical transitions above the critical point at relatively high surfactant concentrations, and the first-order type transitions near the three-phase region.

In figures 1 and 2, if the hydrophile-lipophile balance (HLB) and CMC's were compared [2], the L_1 phase of sodium dodecyl sulfate (SDS), which is strongly hydrophilic and has the value of 40, appeared in the broader range than that of less hydrophilic CTAB whose

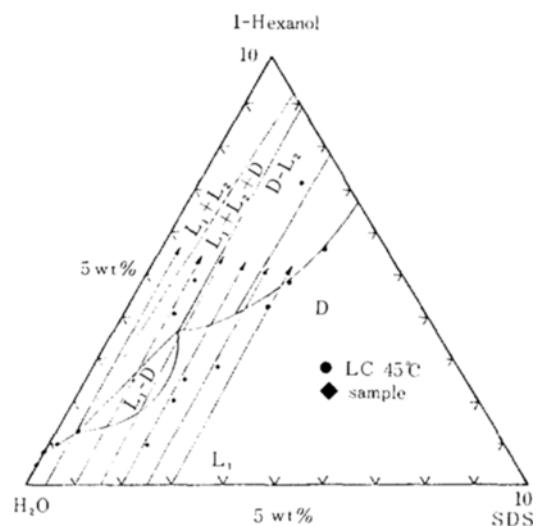


Fig. 3. Enlarged phase diagrams of sodium dodecyl sulfate (SDS)-1-hexanol-water mixtures for the regions of water-continuous phase (L_1) at 45°C.

The titration paths shown by arrows and the concentrations of equilibrated samples chromatographed shown by circles (●) and cross-checked at the positions of diamonds (◆).

HLB number is 8.8. Further, the micellar solutions of SDS were stabilized in the broader range of alcohol, since the CMC's of SDS and CTAB in water were 8.08 and 0.92 m mole/l respectively [24].

2. Conductivity and turbidity

In the previous figures, it was shown that the phase transition of either the first order or the higher order occurred, when the amount of 1-hexanol increased. Following the transition path in figure 3, the electrical conductivities and the phase turbidities were observed to determine the phase boundaries and partly to envisage the microstructural transition. In figure 4, a typical example of conductivity behavior for SDS systems was given at 45°C. For the given path of a fixed amount of surfactant, the conductivities increased up to a certain point, where the phase separation occurred, and then decreased indicating that the conductivities of the liquid crystalline phases were lower than those near the two-phase boundaries. Though the conductivity maxima appeared in all paths, one could find that the detailed internal phenomena be significantly different when compared with the phase diagrams. Below the concentration of surfactant where three phases appeared, the decrease in the conductivities could be attributed to the phase separation of L_1 and L_2 , but beyond

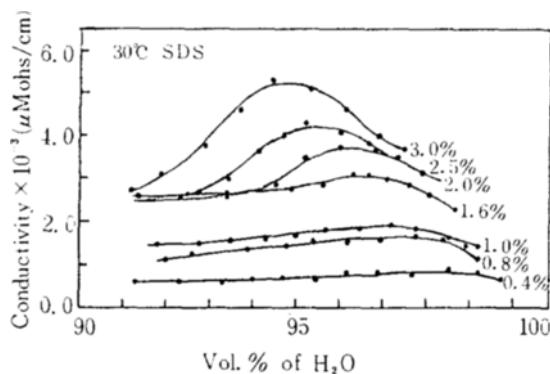


Fig. 4. Electrical conductivities of the water-continuous phases at 30°C along the paths shown in Fig. 3.

the concentration to the phase transition from the L₁ to D phases. For such behaviors, there exist several theories, including percolation theory [27], electron hopping model [28] and scattering model [29], all related to the critical theories. In fact, the well-aligned liquid crystalline phases were less conductive than the intermediate states, having smaller order parameters and highest conductivities.

The turbidities of mixtures along the same paths in spectroscopic measurements provided more significant clue for the phase transition [6-10], in fact, the microstructural transition. In figure 5, the intensities of transmitted light for a selected path at 35°C showed two minima near the phase boundaries of the first-order transition, where the turbidities remained long time. Under the cross polarizer, it was also recognized that small fragments of the second phase floated in the mother phase, and that a local maximum of turbidities at the middle of the two-phase region was accompanied by the rapid phase segregation.

3. Solubilization of 1-hexanol in water-continuous phase

In figure 6, the maximum conductivities in figure 4 were plotted along the concentrations where the phase turbidity appeared in the single phase. The closed symbols (●, ■) are represented for the conductivities of the binary surfactant solutions and the arrows for the experimental paths along the alcohol titration. Up to a certain concentration of surfactant, there existed a region of straight line like that of the binary surfactant solutions, representing that the added alcohol was incorporated into the micelles, but not in the bulk phase, since the molecular solubilities of 1-hexanol in the bulk phase were small and limited.

In figure 7, the molar ratio of alcohol to surfactant obtained from the conductivity curves of figure 6, was shown indicating that the solubilization efficiency of sur-

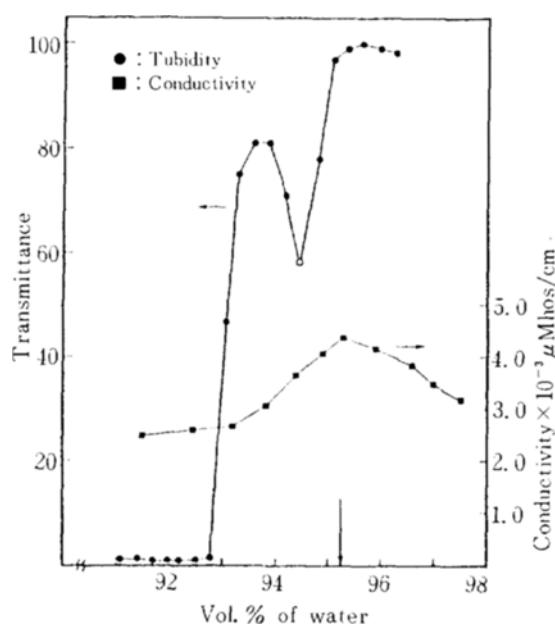


Fig. 5. Turbidity and conductivity curves along the paths in Fig. 3 for initial 2.5 wt% SDS solution.

The vertical arrow indicates the concentration of separating the liquid crystalline phase.

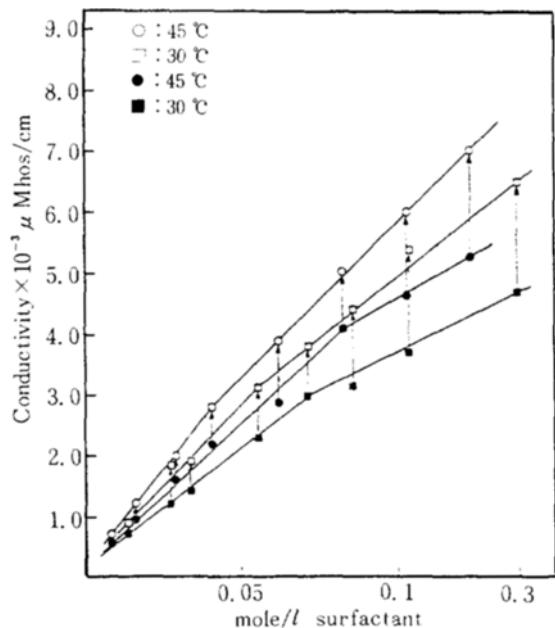


Fig. 6. Conductivities of sodium dodecyl sulfate-1-hexanol-water systems along the phase boundaries at various amounts of surfactant.

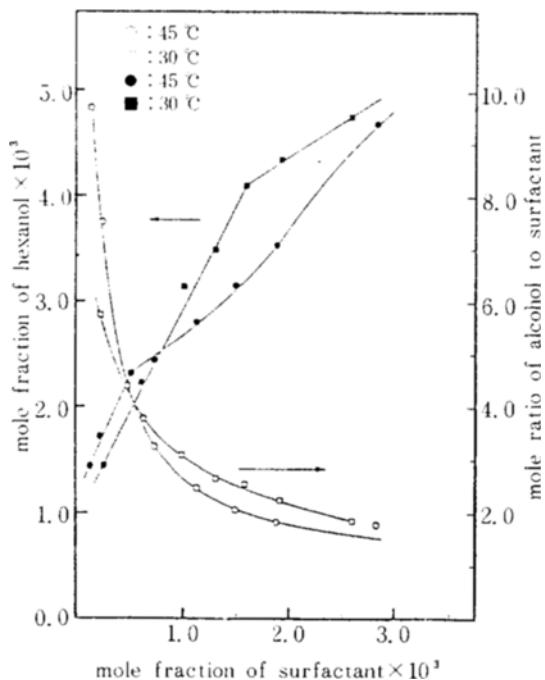


Fig. 7. Solubility limits and alcohol/surfactant ratio of sodium dodecyl sulfate-1-hexanol-water systems in the water-continuous phase at 30°C and 45°C.

factant was significantly reduced as surfactant added. If the partitioning of alcohol into the micellar side did not increase and if the amount of alcohol solubilized in the continuous phase was fixed, the concentrations of alcohol must increase linearly as it was at the low concentrations of surfactant. As surfactant added, however, the solubilities significantly shifted, because the micelles overcrowded and interacted each other deforming the balanced structures.

As temperature increased from 30°C to 45°C, the ratios of amounts of alcohol to surfactant increased at low concentrations of surfactant, while decreased at higher concentrations of surfactant. It was because the solubilities of alcohol in the bulk phase were large at 45°C and because the large amount of solubilized alcohol was incorporated into the bulk phase. At the region of the high concentrations of surfactant, the associations of the surfactant molecules were rather enhanced because of the hydrophobic interaction, resulting in the formation of micelles from the solutions [9]. The results were consistent with the fact that the phase separation of the surfactant phase was often observed at elevated temperature for the binary systems [8,9]. Therefore, the alcoholic phases would be separated out forming inverted micellar or liquid

crystalline phases.

In fact, the solubilizations of alcohol in the water-continuous phases depended on the nature of the solute, for example, hydrophilic or hydrophobic or both. The solute would be incorporated into the inner core of micelles, along the palisade layer of amphiphile, or adsorbed on the layer surface [2,3]. In cases of 1-hexanol, though soluble in water or slightly soluble even without amphiphiles, the alcohol molecules would be mainly incorporated in modifying the micellar structures. The decrease in CMC as adding alcohol supported the incorporation of alcohol in forming the micelle [1,2]. On the other hand, it was also instructive for less soluble solutes like xylene which was incorporated inside the micelles of sodium caprylate systems [8].

If the additionally solubilized alcohol was only incorporated into the palisade layer and if the core volumes were constant, the solubility change would be attributed to the microstructural transition, and be given inversely proportional to the surface area change. In forming a cylindrical micelle from n spherical micelles, the ratio of the surface area of n spherical micelles to that of the cylindrical micelles is $3n/(2n + 1)$. Then, the solubilities of alcohol in the cylindrical micelles can be much smaller than those of the spherical micelles. If n approaches to infinite, the ratio falls on 1.5, and then the solubilities of cylindrical micelles drop to 2/3 of those of spherical micelles. Further, in the continuous deformation of spherical micelles to the lamellar phases, since the morphological structure of the micelles would be flexible [19], the scattering of the locally accumulated charge density [29] could result in the increase of the conductivity. Therefore, it is our conjecture that the cylindrically organized intermediate microstructure, having high conductivity and high turbidity, instantaneously appears in the course of the phase transition, and that it is related to the critical phenomena between micellar and liquid crystalline phases.

CONCLUSIONS

The phase diagrams of ternary systems including surface-active compounds were determined by the chromatographic measurements of concentrations, and the solubilization of alcohol in the water-continuous phases by phase textures under a cross polarizer, electrical conductivities, and phase turbidities.

Among three phases near the water-alcohol binary system, liquid crystalline phase was water-continuous, and birefringent. The coexistence region of the micellar phase and the liquid crystalline phase was very narrow or would be terminated at the critical point between these phases at 45°C. Sodium dodecyl sulfate having high HLB number, stabilized the L_1 phase in the broader

ranges than cetyl trimethylammonium bromide did.

The extremum concentrations of the electrical conductivities and the phase turbidities were consistent with the phase boundaries and the transition of the microstructures indicating that there might exist some internal adjustments for a new phase or microstructure.

As surfactant added, the ability of solubilizing alcohol in the water-continuous phases significantly decreased due to the structural change, probably from spherical micelles to cylindrical micelles.

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