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Similarity in Phase Diagrams between Ionic and Nonionic Surfactant Solutions at Constant Temperature

The nonionic surfactants of the polyoxyethylene alkyl (aryl) ether type show hydrophilic properties at low temperatures gradually change to lipophilic properties at high temperatures. The reason for this is found in a reduced interaction between the hydrophilic moiety of nonionic surfactant and water with increased temperature. This means that the hydrophile-lipophile properties of nonionic surfactants will be balanced at a certain temperature for a given system. Above this temperature the surfactant is oleophilic and soluble in the given oil and below it hydrophilic and mainly soluble in water (1). Emulsion type changes from an O/W to a W/O type at this temperature. The temperature is called phase inversion temperature (PIT) in emulsion or HLB temperature, because the hydrophile-lipophile balance (HLB) of a nonionic surfactant in the given system just balances at this temperature (1). The solubilization of oil (or water) in aqueous (or nonaqueous) surfactant solution is large close to the PIT (1).

The effect of temperature rise on the solution behavior seems similar to the effect of a decrease in hydrophilic chain length of a nonionic surfactant. Actually a similar phase diagram has been obtained at constant temperature by changing the hydrophilic chain length of a series of nonionic surfactants instead of temperature (2).

Similar solution behavior may be observed as a function of the composition of a moderately hydrophilic ionic surfactant and a moderately lipophilic cosurfactant. In order to confirm this reasoning the phase diagrams of a four-component system composed of octylammonium chloride, octylamine, water, and *p*-xylene were studied and are shown in Figs. 1 and 2. Total surfactant concentration changes from 6 to 10 wt%/system from the left-hand side to the right-hand side in Fig. 1, whereas in Fig. 2 the system contains 10 wt%/system of octylammonium chloride + octylamine and 90 wt%/system of water + *p*-xylene. Realms I_w and I_o are the oil-swollen and water-swollen micellar solutions, respectively. Below the I_w realm excess oil separates from the aqueous micellar solution, i.e., the lower curve is the solubilization curve as a function of the composition of surfactant and cosurfactant. The dispersion type of this two-phase solution is an O/W type. A liquid crystal and an aqueous micellar solution coexist slightly above the I_w realm. In Fig. 1, L.C. denotes liquid-crystalline phase. There is a

narrow two-phase region consisting of L.C. and surfactant phases above the L.C. realm (3). Above this region (3) there is a very narrow surfactant phase, and then a two-phase solution, consisting of water and surfactant phases, is obtained and indicated by $D + W$ in Figs. 1 and 2. At the left-hand side of the phase diagram the amount of oil is small and we have a two-phase solution consisting of water and surfactant phases, $W + D$, but at the medium concentration the surfactant phase changes into a reversed micellar solution O_m . There is no clear boundary between the $D + W$ and $O_m + W$ realms.

A three-phase region (III), in which water, surfactant, and oil phases coexist, is observed between the I_w and I_o realms. Large amounts of water and oil are dissolved in the surfactant phase. The three-phase realm is narrow, because the volume fraction of the surfactant phase is large and water or oil phase will disappear owing to a small change in composition of surfactant and solvent. In a system which contains a total of 20 wt%/system of surfactants I_w

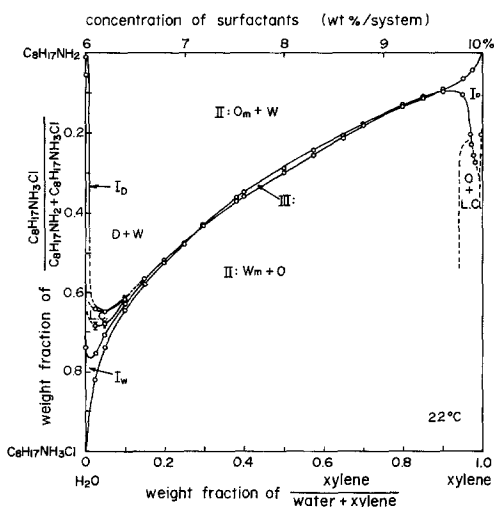


FIG. 1. Phase diagram of $\text{R}_8\text{NH}_3\text{Cl}$, R_8NH_2 , H_2O , and *p*-xylene at 22°C. Total surfactant concentration changes from 6 to 10 wt%/system from left-hand side to right-hand side. Ordinate is the weight fraction of $\text{R}_8\text{NH}_3\text{Cl}$ against a total surfactant. Abscissa is the weight fraction of *p*-xylene against total solvent.

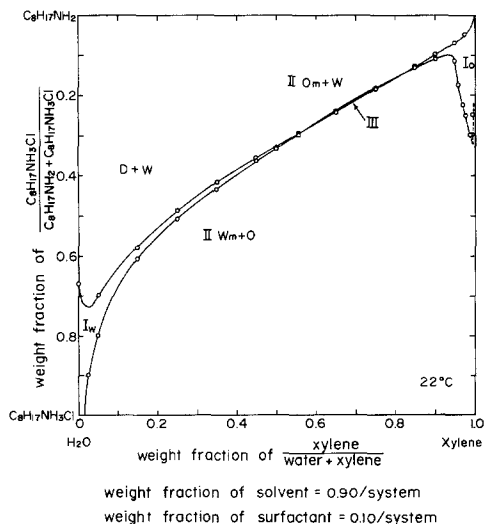


FIG. 2. Phase diagram of R_8NH_3Cl , R_8NH_2 , H_2O , and p -xylene at $22^\circ C$. $R_8NH_3Cl + R_8NH_2$, and $H_2O + p$ -xylene were kept 10 and 90 wt% of the system, respectively.

and I_o realms are stretched and a three-phase region is not observed (4), just as in a nonionic surfactant solution at higher concentration (2, Fig. 8). Although the oil-swollen micellar solution, I_w , the surfactant phase in realm III, and the water-swollen micellar solution, I_o , are different phases on the phase diagram, the changes in composition and structure of these phases are continuous. The structure of the surfactant phase on a submicroscopic scale may be envisioned as layers of the surfactant with thick solvated aqueous and oil layers. It should be observed that the surfactant phase is in equilibrium with a lamellar liquid-crystalline phase with a regularly layered structure. Above realm I_o excess water separates from a nonaqueous micellar solution, and the dispersion of the system is W/O type.

It is evident that the hydrophile-lipophile properties of the mixed surfactant monolayer at the oil-water interface just balances in III region in the figures and that the dissolution of oil (or water) in aqueous (or nonaqueous) solution markedly increases around this region. Since a part of octylamine dissolves in the oil phase, the apparent mole ratio for optimum HLB shifts to more octylamine-rich composition when the amount of oil against water increases, as seen in Figs. 1 and 2.

We estimate the HLB of octylamine is similar to $R_8(OCH_2CH_2)_3OH$ from the solution behavior of octylamine in water as a function of temperature.

With a more hydrophilic ionic surfactant such as $C_{12}H_{25}OSO_3Na$ and a more lipophilic cosurfactant such as $C_8H_{17}OH$, a similar phase diagram is not obtained (5). In order to obtain a similar phase diagram, 1 ~ 5 wt% NaCl aq. has to be added. The opposite tendency in phase diagrams as a function of temperature is observed in ionic and nonionic surfactant solutions (6).

CONCLUSIONS

The four-component phase diagram composed of ionic-surfactant (R_8NH_3Cl), cosurfactant (R_8NH_2), water, and p -xylene is similar to that of a hydrophilic nonionic surfactant, lipophilic surfactant, water, and hydrocarbon, or the phase diagram of nonionic surfactant, water, and hydrocarbon as a function of temperature. Combination of moderately hydrophilic ionic surfactant and moderately lipophilic co-surfactant seems an important choice (3). The opposite tendency in phase diagrams as a function of temperature is observed in ionic and nonionic surfactant solution (6).

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