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Effects of the Oxyethylene Chain Length of Fluorocarbon Surfactants on Demixing of Micelles of Fluorocarbon and Hydrocarbon Surfactants

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Synopsis. The critical mole fraction of hydrocarbon surfactant decreases with an increase in the oxyethylene unit of either fluorocarbon surfactant or hydrocarbon surfactant. This tendency is explicable in terms of regular solution theory if the depth of water penetration into the micellar interior is assumed to increase with an increase in the oxyethylene unit.

Under certain conditions, fluorocarbon and hydrocarbon surfactants are partially miscible in their mixed micelles, forming two kinds of mixed micelles with different compositions.[1] We reported the effects of hydrophobic and hydrophilic groups of hydrocarbon surfactant on the critical solution points of such micellar systems.[2]

According to regular solution theory, the critical mole fraction x_{cH} of the binary liquid system consisting of the nonpolar compounds, F and H, can be written as[3]

$$x_{cH} = [1-(1-q+q^2)^{1/2}]/(1-q), \qquad (1)$$

where q is the ratio of molar volumes, *viz.* v_F/v_H. When we attempt to apply Eq. 1 to a mixed micelle, there is still an uncertainty as to volumes to be employed; the total molar volume or the molar volume of the hydrophobic group. To solve this problem, we investigate the effect of fluorocarbon surfactants on the critical solution points.

Experimental

The nonionic fluorocarbon surfactant, NFE7 ($[(CF_3)_2CF]_2C{=}C(CF_3)O(CH_2CH_2O)_nCH_3$, averaged $n=7$), was donated by Neos Company. This specimen is not homogeneous with respect to oxyethylene units. The nonionic hydrocarbon surfactant, heptaethylene glycol monododecyl ether (DE7), was obtained from Nikko Chemicals as at least 99% pure. The detail of surface tension measurements has been reported elsewhere.[2]

Results and Discussion

The surface tension method was used to determine the mutual solubility in micelles. In Fig. 1a, the surface tension of aqueous solutions of mixed NFE7 and DE7 is plotted against the mole fraction x_H of DE7 in the whole system. The total surfactant concentration is in a range of 1 to 1.3 mmol dm^{-3}, which is much higher than the critical micelle concentrations (cmc) of NFE7 and DE7, *viz.* 0.025 and 0.08 mmol dm^{-3}. These cmc values of NFE7 and DE7 decreased slightly with rising temperature. The cmc's of their mixtures are slightly larger than predictions from ideal mixing of these surfactants. Under these conditions, therefore, almost all of the surfactant molecules added form micelles and consequently the composition of the surfactants added is very close to that of micellized surfactants.

In the plateau region of the surface tension *vs.* composition curve, two kinds of mixed micelles coexist in a solution.[2] From two limits of this plateau region, we can determine mutual solubilities in the micelles. Further we can determine the solubility-temperature diagram for the NFE7 and DE7 system from Fig. 1a. This kind of diagram represents a coexistence curve for the co-micellar system similar to that of the binary liquid system. In Fig. 1b, the coexistence curve of mixed micelles of DE7 and NFE18 is included for comparison. From a coexistence curve and the locus of its midpoints, we can determine the critical composition x_{cH} and the critical solution temperature T_c. Thus, from Fig. 1b, we obtained the values of x_{cH} and T_c for the NFE18–DE7 and NEF7–DE7 systems. In Table 1, these values are shown together with those of other systems.[2]

In Table 1, NFE18 ($[(CF_3)_2CF]_2C{=}C(CF_3)O(CH_2CH_2O)_{18}CH_3$) and DE9 (nonaethylene glycol monododecyl ether) are not homogeneous samples with respect to oxyethylene units but DE5 (pentaethylene glycol monododecyl ether) is homogeneous (99%). The T_c value is found to decrease with an increase in the oxyethylene unit of either fluorocarbon surfactant or hydrocarbon surfactant (Table 1). Further, it is noted that this T_c decreasing (solubility increasing) ability of an oxyethylene unit of NFE is greater than that of DE. As is evident from comparison of the NFE7–DE7 and NFE18–DE7 systems, x_{cH} decreases with an increase in the oxyethylene unit of NFE.

From Eq. 1, we can calculate the critical mole fraction

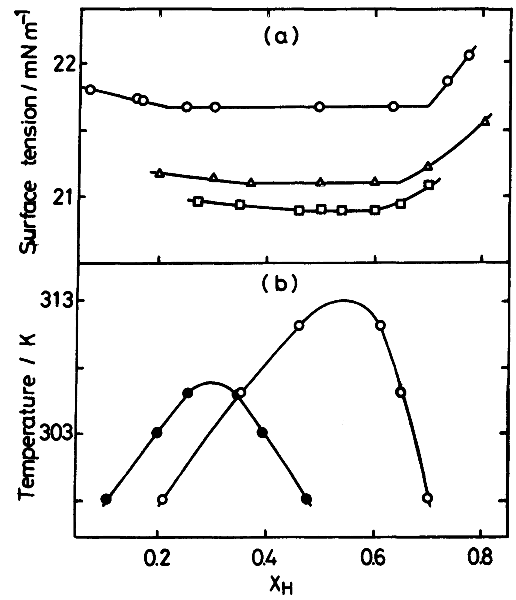

Fig. 1. (a) Surface tensions of aqueous solutions of mixed NFE7 and DE7 as a function of the mole fraction of DE7 at three temperatures (K): ○, 298.2; △, 303.2; □, 311.2. (b) Coexistence curves of two kinds of mixed micelles for the NFE7–DE7 (○) and NFE18–DE7 (●) systems.

TABLE 1. OBSERVED x_{cH} AND T_{c} AND CALCULATED x_{cH} BY USING DIFFERENT v'S

System	Observed		Calculated x_{cH}		
	x_{cH}	T_{c}/K	v_{t}	v_α	v_β
NFE7–DE7	0.550	313.3	0.530	0.527	0.499
NFE18–DE5	0.506	310.3	0.774	0.527	0.499
NFE18–DE7	0.300	307.0	0.731	0.527	0.499
NFE18–DE9	0.283	299.2	0.689	0.527	0.499

of hydrocarbon surfactant by employing the different molar volumes; v_{t}, v_α, and v_β. The v_{t} denotes the total molar volume of a surfactant. The demixing of micelles of fluorocarbon and hydrocarbon surfactants is ascribed mainly to the interaction of fluorocarbon and hydrocarbon chains in the micelle. Therefore, the molar volume of the hydrophobic group, v_{t}, may be used instead of v_α. However, water may penetrate into the micellar interior; the number of wet carbon atoms adjacent to a hydrophilic group may be zero,[4] one or two,[5] or several.[6] If water penetrates into the micellar interior up to the α-carbon atom of the hydrophobic group, then the molar volume of the dry hydrophobic group from β- through ω-carbon atoms, v_β, must be used for v_α. Molar volumes v_{t}, v_α, and v_β of NFE7 are estimated from the observed v_{t} values of NFE18, DE's, and related compounds at 298.2 K, as already made for NFE18 and DE's.[2] We used the following values (cm^3 mol^{-1}); $v_{\mathrm{t}}(\mathrm{DE5})=408.3$, $v_{\mathrm{t}}(\mathrm{DE7})=485.4$, $v_{\mathrm{t}}(\mathrm{DE9})=562.5$, $v_{\mathrm{t}}(\mathrm{NFE7})=526.3$, $v_{\mathrm{t}}(\mathrm{NFE18})=965.8$, $v_\alpha(\mathrm{DE5})=v_\alpha(\mathrm{DE7})=v_\alpha(\mathrm{DE9})=210.9$, $v_\alpha(\mathrm{NFE7})=v_\alpha(\mathrm{NFE18})=226.9$, $v_\beta(\mathrm{DE5})=v_\beta(\mathrm{DE7})=v_\beta(\mathrm{DE9})=194.7$, and $v_\beta(\mathrm{NFE7})=v_\beta(\mathrm{NFE18})=194.3$.

As the number of oxyethylene units of hydrocarbon surfactants increases, keeping the fluorocarbon surfactant (NFE18) constant, x_{cH} decreases. Apart from the direction, the magnitude in this change is inexplicable by using any of v_{t}, v_α, and v_β. Hence, we proposed a hypothesis which explains this discrepancy in x_{cH} between theory and experiment; we assumed a deeper penetration of water into the micellar interior with an increase in the oxyethylene unit.[2] The present data on the NFE7–DE7 system support this hypothesis. As is evident from Table 1, the x_{cH} value of the NFE18–DE7 system is smaller than that of the NFE7–DE7 system. This contradicts the theoretical results obtained by using any of v_{t}, v_α, and v_β. As the number of oxyethylene units increases, the surface area per surfactant molecule in the micelle increases and consequently water is likely to penetrate into the micellar interior more deeply. Therefore x_{cH} can decrease with an increase in the oxyethylene unit of fluorocarbon surfactants and this tendency is actually observed. This interpretation is also consistent with the fact that T_{c} decreases with an increase in the oxyethylene unit of either fluorocarbon surfactant or hydrocarbon surfactant.

Although the depth of water penetration into the micellar interior is still a matter of controversy,[4–6] the level of the α-carbon atom of dodecyl sulfates is most probable, as deduced from small angle neutron scattering.[7] The present results seem to support a shallow water penetration model in which the penetration depth depends on the number of oxyethylene units.

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