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MUTUAL SOLUBILITY IN MIXED MICELLES OF FLUOROCARBON AND HYDROCARBON SURFACTANTS FROM SURFACE TENSION DATA

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The mutual solubility in mixed micelles of fluorocarbon and hydrocarbon surfactants was determined by surface tension measurements, as convincing evidence for the partial miscibility postulated by Mukerjee and Yang.

Micelle-forming surfactants were completely miscible in mixed micelles for all systems reported until 1976, when Mukerjee and Yang found abnormal relations between the critical micellization concentration (cmc) and the monomeric composition and between the differential electric conductance and surfactant concentration, and explained the data in terms of the partial misciblity in mixed micelles of fluorocarbon and hydrocarbon surfactants.[1)]

The surface tension of aqueous solutions of Neos Ftergent (NF),[2)] a fluorocarbon surfactant, and sodium tetradecyl sulfate (STS),[3)] a hydrocarbon surfactant, was measured in the presence of 50 mM sodium chloride[4)] at 30°C, while the molar ratio of the two surfactants was kept constant. The solid circles in Figs. 1 and 2 show plots of cmc and surface tension against the monomeric mole fraction of STS, respectively. These values were taken from the break in the surface tension vs. surfactant concentration curve. In the presence of 50 mM sodium chloride, the surface tension of pure NF and STS remained constant within, at least, ten fold concentration over the cmc, whereas the values for their mixtures decreased with increasing concentration.

The method used to determine the composition of mixed micelles is similar to that already reported for oily mixtures[5)] and the details will be published elsewhere.[6)] This method assumes that the surface tension of pure surfactants remains constant above the cmc and that the mole fractions of monomers and micelles composed of two surfactants are a function of surface tension alone above the cmc.

From the material balance of STS in solutions above the cmc, one can derive

$$x_{mSTS} = (C_t \cdot x_{STS} - cmc \cdot x_{bSTS})/(C_t - cmc) \quad (1)$$

Here C_t is the total surfactant concentration and x_{mSTS}, x_{STS}, and x_{bSTS} are the micellar, overall, and monomeric mole fractions of STS, respectively. We measured the surface tension of a solution at an overall mole fraction x_{STS} and at about ten fold concentration over the cmc. Then, one can read the monomeric mole fraction x_{bSTS} corresponding to this measured surface tension value from the surface tension vs. x_{bSTS} curve in Fig. 2, and also the cmc value corresponding to this x_{bSTS} value from the cmc vs. x_{bSTS} curve in Fig. 1. Thus, a mole fraction of micelles coexisting in the solution can be calculated by substituting these values of C_t, x_{STS}, cmc, and x_{bSTS} into Eq. 1.

The micellar mole fraction thus obtained is shown by the open circles in Figs. 1 and 2. In Fig. 2, the surface tension remains constant at 18.61 dynes/cm regardless of the micellar mole fraction within 0.056 and 0.722. These limits, A and B in Figs. 1 and 2, represent the mutual solubility in the mixed micelles: the solubility of STS in the NF micelle is 0.056, whereas that of NF in the STS micelle is 0.722. A similar procedure has been applied to determine the mutual

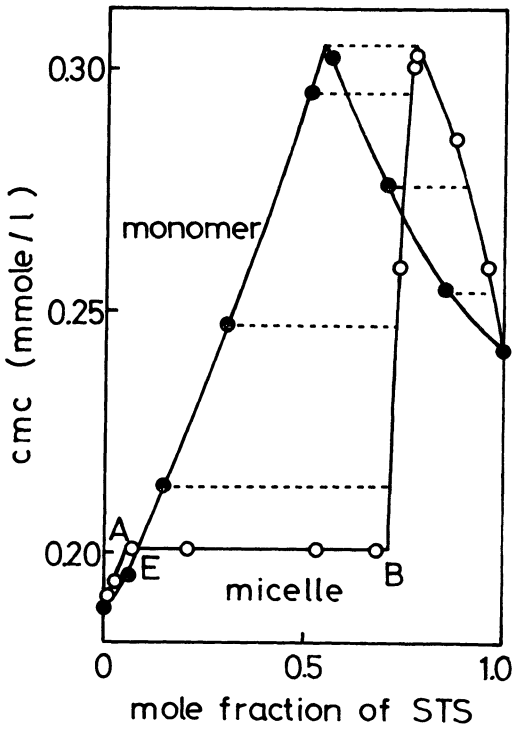

Fig. 1. Cmc.

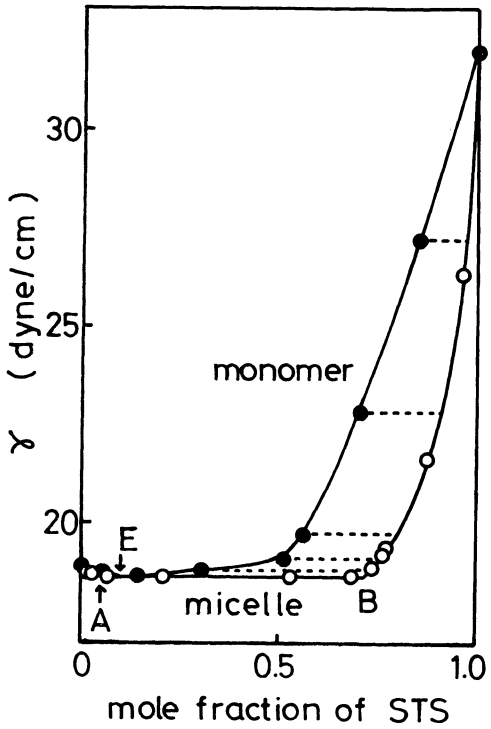

Fig. 2. Surface tension.

solubility in mixed monolayers at the air-water interface.[7)]

The dashed lines in Figs. 1 and 2 illustrate some tie lines, the ends of which represent the mole fractions of coexisting monomers and micelles. In solutions at overall mole fractions within x_A and x_B, one kind of mixed micelles forms at low concentrations whereas two kinds of mixed micelles coexist at higher concentrations.

Thus, NF and STS are partially miscible in the mixed micelles and the mutual solubility could be determined by surface tension measurements.

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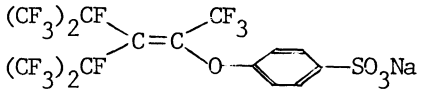
REFERENCES AND NOTES

1) P. Mukerjee and A. Y. S. Yang, J. Phys. Chem., 80, 1388 (1976).

2) NF from Neos Company has the chemical structure as follows:



and was used after recrystallization twice from ethanol and once from acetone.

3) STS was synthesized by neutralizing the reactant of 1-tetradecanol with concentrated sulfuric acid and recrystallized three times from ethanol after extraction with diethyl ether.

4) Merck sodium chloride was purified by the active charcoal treatment after extraction with diethyl ether.

5) N. Funasaki and S. Hada, Bull. Chem. Soc. Jpn., 49, 2899 (1976).

6) N. Funasaki and S. Hada, Presented at the ACS/CSJ Chemical Congress, Hawaii, April 1-6, 1979; J. Phys. Chem., submitted for publication.

7) R. E. Pagano and N. L. Gershfeld, J. Phys. Chem., 76, 1238 (1972); M. Nakagaki and N. Funasaki, Bull. Chem. Soc. Jpn., 47, 2094, 2482 (1974).

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