Critical Solution Temperatures in Co-micellar Systems

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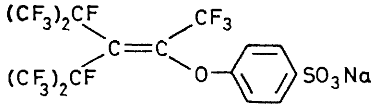
Summary As is seen in liquid fluorocarbon and hydrocarbon mixtures, a critical solution temperature (c.s.t.) existed in three co-micellar systems of fluorocarbon and hydrocarbon surfactants, and the c.s.t. and the micellar mole fraction of the fluorocarbon surfactant at the c.s.t. increased with an increase in the chain length of the hydrocarbon surfactants.

Micelles, which are formed by surfactants above the critical micellisation concentration (c.m.c.), may be regarded as a small system.[1] Recent studies suggested that some fluorocarbon and hydrocarbon surfactants are partially miscible in mixed micelles[2] and the mutual solubility has been determined from surface tension data.[3] Since micelles exhibit the properties of a liquid, a critical solution temperature (c.s.t.) is expected to exist for mixed fluorocarbon and hydrocarbon surfactants, as is seen in some liquid mixtures: the c.s.t. is defined as a temperature below which two micellar phases can co-exist and above which only one micellar phase is present.



NF

The surface tension of aqueous solutions of Neos Ftergent (NF), a fluorocarbon surfactant, and sodium alkyl sulphate (SAS), a hydrocarbon surfactant, was measured in the presence of 50 mol m^{-3} sodium chloride. Sodium dodecyl (SDS), tridecyl (STrS), and tetradecyl (STS) sulphates were used as the SAS. From the break in the curve of surface tension *vs.* surfactant concentration, the relation between the surface tension at the c.m.c. and the monomeric mole fraction of SAS, x_{bSAS}, and that between the c.m.c. and x_{bSAS} can be obtained. Using these relationships, the material balance of the surfactants, and surface tension data above the c.m.c., the relation of surface tension to the micellar mole fraction of SAS, x_{mSAS}, as already reported, can be determined.[3,4] In most experiments, the total surfactant concentration used to determine the micellar composition was about 10 fold over the c.m.c. for each mixture; the total concentrations employed for the NF–STS, NF–STrS, and NF–SDS systems were in the range 1·9—4·4, 1·9—12·8, and 1·9—17·0 mol m^{-3}, respectively, depending on the composition and the temperature It was demonstrated in the NF—STS and NF—STrS systems at 30 °C that the surface tension *vs* micellar composition curve does not depend on the total surfactant concentration used, in the range 5—10 fold concentration over the c m c

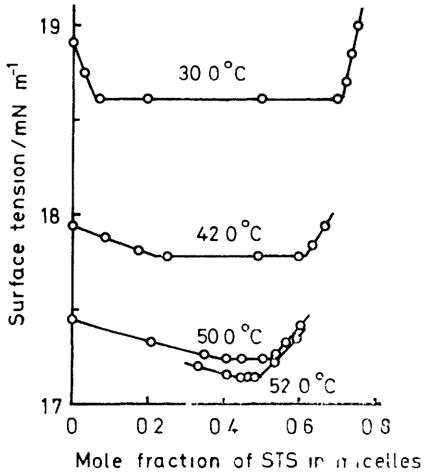


FIGURE 1 Surface tension *vs* micellar composition curves for the NF—STS system at different temperatures

In Figure 1, there are regions where the surface tension remains constant regardless of micellar compositions in these regions, two kinds of mixed micelles co-exist in equilibrium [3] As shown in Figure 1 the plateau regions became narrower with elevation in temperature

As shown in Figure 2, the mutual solubility, which was taken from the limits of the plateau regions in Figure 1, increased with elevation in temperature Similar measurements were made for the NF–SDS and NF–STrS systems, and are included in Figure 2 The point having a horizontal tangent in the solid line shown in Figure 2 gave the c s t and the micellar composition at the c s t for each system As the alkyl chain of the hydrocarbon surfactant is elongated, the c s t and the mole fraction of NF at the c s t increases, as is seen in liquid mixtures[5] such as fluorocarbon and hydrocarbon mixtures [6] Co-micellar systems which are composed of similarly charged fluorocarbon and hydrocarbon surfactants are likely to exhibit limited mutual solubilities in co-micelles at low temperatures [7]

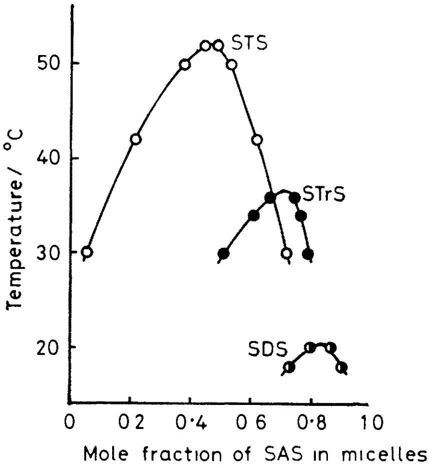


FIGURE 2 Temperature dependence of mutual solubility in mixed micelles for the three NF—SAS systems

The present work demonstrates that the c s t , as is observed in liquid fluorocarbon and hydrocarbon mixtures, is present in small systems such as micellar systems and that micelles have the character of a liquid phase These findings may lead to novel advances in solution chemistry and industrial applications of surfactants

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