

The Mutual Solubilization of n-Decanol and n-Octane in Aqueous Sodium Octanoate Solutions

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The effect of n-decanol on the solubility of n-octane in the system sodium octanoate/n-decanol/water was investigated in the concentration range 1.51–3.85 molal sodium octanoate. In the formation of these oil-in-water microemulsions, the effect of the cosurfactant n-decanol was at least three times stronger than the effect of the surfactant sodium octanoate itself. It was concluded that most of the n-decanol was located in the surfaces of the aggregates in accordance with classical theory.

It is well known that cosurfactants such as paraffin chain alcohols participate in the micelle formation of association colloids in aqueous solutions. Many authors have investigated the effect of n-alcohols on premicellar association and on the CMC.¹ At higher concentrations, the situation is complicated. A transformation of spherical micelles into rods or discs on cosurfactant addition has been suggested.² These suggestions are based primarily on viscosity measurements. In the case of alkali soaps, however, the literature in only a very few cases reports any direct signs of anisotropy caused by addition of paraffin chain alcohols.^{3,4}

According to the simple classical theories, the long chain alcohols are solubilized primarily in the polar palisade layer of the micelles, whereas solubilized nonpolar hydrocarbons are located in the more lipophilic core of the aggregates. We have therefore found it of interest to try to elucidate in greater detail the mutual effects of n-paraffin alcohols and hydrocarbons on the solubilization in aqueous micellar L_1 phase. We have chosen to use the previously investigated model system water/sodium octanoate/n-decanol/n-octane.⁵

In connection with the studies of the phase equilibria in the system, we found that the most drastic changes in the mutual solubilization occur at very high concentrations, above 1.5 molal sodium octanoate. In this region, large amounts of both lipophilic additives are solubilized. These systems are often classified as oil-in-water microemulsions.

Experimental

The chemicals were the same as described earlier.⁵ The samples were prepared by adding different amounts of n-decanol and n-octane directly to glass ampoules containing sodium octanoate solutions of defined concentrations. After sealing, the ampoules were heated to 343 K and then shaken at 298 K until equilibrium was reached. The heterogeneity when lamellar liquid crystals (D phase) separated was easily confirmed by observing the probe between crossed Nicol prisms. Excess of liquid octane was detected optically or with a microscope as droplets or as a very unstable turbidity after shaking.

Results

In the investigated ternary system, water/sodium octanoate/n-decanol/n-octane, probably the most correct method to describe the phase equilibria is

Dedicated to Professor Per Ekwall on his 90th birthday.

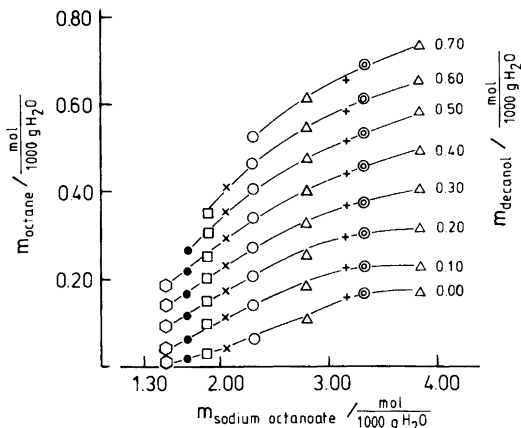


Fig. 1. The solubility of n-octane as a function of the molality of sodium octanoate at constant molalities of n-decanol at 298 K.

to use three-dimensional tetrahedral phase diagrams. However, in such diagrams, a plot of the mutual maximal solubility of n-decanol and n-octane in different concentrated aqueous sodium octanoate solutions would be a rather confusing curved surface. Under these circumstances, and since the samples were made by adding the solubilizes to aqueous sodium octanoate solutions of defined concentrations, we have chosen to describe our results with the aid of the plots used in Figs. 1-3. In these plots, all the concentrations of sodium octanoate, n-decanol and n-octane are given as molality. The curves in Fig. 1 illustrate the solubilization of n-octane at different concentrations of sodium octanoate. Each curve corresponds to a constant concentration of n-decanol. As is well known, the solubilization of n-octane begins at the CMC of sodium octanoate (about 0.1 molal sodium octanoate). On the scale of the y axis, this first solubilization is, however, not detectable. The curve for decanol-free sodium octanoate does not begin to rise until the concentration of sodium octanoate is 1.6 molal, which is rather close to the "third c.c." of sodium octanoate given by Ekwall.¹ From Fig. 1, we observe a rather strong enhancing influence of added n-decanol on the solubilization of n-octane. The different curves are, however, nearly parallel. As the solubility of n-decanol is limited at each sodium octanoate concentration, the curves for higher values of the parameter molal n-decanol

start at somewhat higher sodium octanoate concentrations. This effect is not noticeable until 0.4 molal n-decanol. The curves all end close to the concentration defined by the solubility of sodium octanoate, where E phase separates. In the regions to the left and above the curves, n-octane separates. The liquid crystalline phases solubilize very little n-octane, which, in excess, separates as droplets. The curves in Fig. 2 with molal n-octane on the y axis and molal n-decanol on the x axis describe more explicitly the influence of n-decanol on the solubilization of n-octane at constant concentrations of sodium octanoate. Again, at concentrations above 3.85 molal sodium octanoate, the system is in equilibrium with hexagonal E phase. n-octane is only sparingly soluble in the hexagonal phase E. To the right of the dotted curves in Fig. 2, the systems are in equilibrium with lamellar D phase and to the left of the solid curves n-octane separates. n-Octane is nearly insoluble also in the lamellar phase D. At each sodium octanoate concentration, the maximal solubility of n-decanol is very little influenced by addition of n-octane, as is shown by the dotted curves on the right. This small influence has not been investigated in detail here.

The linearity of the curves in Fig. 2 is very striking. The slope of the lines varies from 0.48 mol of n-octane per mole of n-decanol at the low-

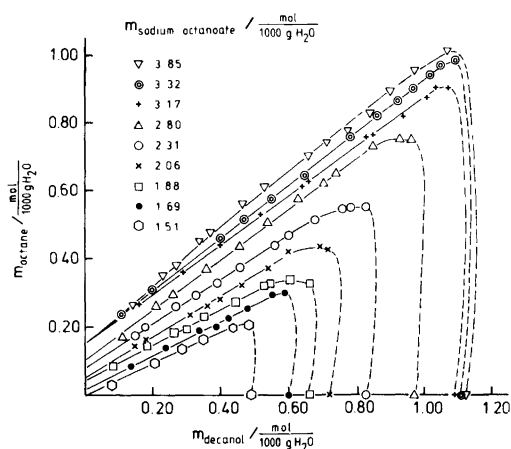


Fig. 2. The solubility of n-octane as a function of the molality of n-decanol at constant molalities of sodium octanoate at 298 K. The effect of n-octane on the solubility of n-decanol has not been studied in detail (the dotted lines).

est investigated sodium octanoate concentration (1.51 molal) to 0.81 mol n-octane per mole of n-decanol at the highest concentration, 3.85 molal sodium octanoate. The increasing solubilization of n-octane by addition of n-decanol reflects, of course, the strong influence of the cosurfactant on the association. In Fig. 3, the solubilization of n-decanol is described as a function of the sodium octanoate concentration. The parameter for the different curves is the n-octane concentration given on the right in the figure. The dotted curve gives the solubility of n-decanol in sodium octanoate solutions free of n-octane. The solubility of n-decanol is assumed to be uninfluenced by the addition of n-octane (compare the dotted lines in Fig. 1). The homogeneous solutions for different n-octane concentrations are thus found in the regions bordered on the left by the dotted curve and downwards by the descending solid curves. Below these solid curves, the systems do not contain enough cosurfactant (n-decanol) to solubilize all n-octane present. The curves in Fig. 3 again end at the solubility limit of sodium octanoate, where the hexagonal E phase separates.

Conclusions

A rough estimation of how much more effectively the cosurfactant n-decanol participates in the solubilization of n-octane than the surfactant sodium octanoate may be obtained starting with the following expression

$$m_{\text{octane}} = m_{\text{octane, aq}} + k_1 (m_{\text{surfactant}} + k_2 m_{\text{cosurfactant}}),$$

where m_{octane} is the total solubility of n-octane, $m_{\text{octane, aq}}$ is the solubility of n-octane in pure water and is negligible, and $m_{\text{cosurfactant}}$ is the concentration of n-decanol in the micelles. As the cosurfactant n-decanol is nearly insoluble in water, we include all n-decanol present in $m_{\text{cosurfactant}}$, whereas $m_{\text{surfactant}}$ includes here only the micellar sodium octanoate characterized by the extremely high solubilization power with respect to n-octane, i.e., the concentration region above 1.51 molal sodium octanoate studied here. As is seen from Fig. 1, the cosurfactant has a very strong influence on $m_{\text{surfactant}}$. The constant k_1 describes the solubilization of n-octane with respect to sodium octanoate. The solubilizing power of the cosurfactant in relation to that of the surfactant is given by k_2 .

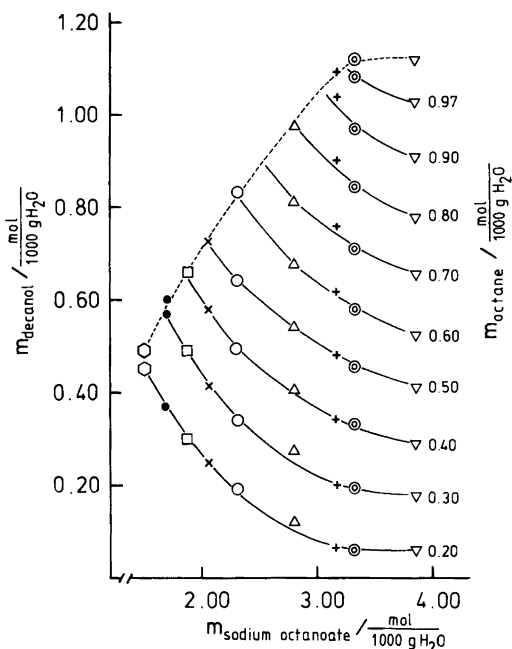


Fig. 3. The solubility areas at defined molalities of n-octane. Microemulsions form first at defined contents of n-decanol (full lines) and are stable to a content of n-decanol not studied in detail (dotted line).

The linear slopes of the curves in Fig. 2 give directly the value $k_1 k_2$, which varies between 0.48 and 0.81 mole n-octane per mole of n-decanol for increasing sodium octanoate concentrations. In the same manner, the slope k_1 is found from the curves in Fig. 1, where m_{decanol} is the parameter. Up to $m_{\text{surfactant}} \approx 3$ molal sodium octanoate, 0.15 mole n-octane per mole of sodium octanoate is a rather good mean value for k_1 . Especially at high sodium octanoate concentrations and low n-decanol contents, where the electrical forces between the charged groups of sodium octanoate predominate, lower slopes for k_1 are found.

Our conclusion is that, in the lowest investigated concentration region of sodium octanoate, the cosurfactant participates about $0.48/0.15 \approx 3$ times more effectively than the surfactant in the solubilization of n-octane. This is not surprising, since the n-decanol in the micelles, as is well known, lowers the repulsion between the charged groups of the sodium octanoate and thus increases the stability of the micellar system. These effects are still more pronounced at higher

sodium octanoate concentrations, as is seen from the increasing k_2 values. Our results may thus indicate that most of the paraffin chain alcohol is located on the micellar surface, as classical theory suggests, and not in the hydrophobic core of the micelles, as has been suggested lately.⁶

From our results, it was not possible to draw any definite conclusions about the micellar shape.

From Figs. 1 and 3, it is seen that the solubilizing power of sodium octanoate with respect to n-decanol is very little influenced by addition of n-octane.

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