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Studies on Spontaneous Emulsification. III. Molecular Interaction at the Oil–Water Interface

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Synopsis. At the oil-water interface, measurements of the interfacial tension were performed simultaneously with the observation of spontaneous emulsification. The effects of an oil-soluble alcohol (1-dodecanol) and a water-soluble surfactant (SDS) on the interfacial tension and on the spontaneous emulsification were studied.

In previous papers,[1,2] the molecular interactions at the Nujol–water interface were studied in relation to the kinds of additives and the tendency of spontaneous emulsification.

In this study, sodium dodecyl sulfate (SDS) was used as a water-soluble surfactant and dodecane containing 1-dodecanol as an oil phase. All have 12 carbon atoms in the hydrocarbon chains, and consequently this system is advantageous for studying the details of the interactions between the molecules causing the spontaneous emulsification.

The interfacial tension showed a minimum value when the 1-dodecanol molar fraction in the oil phase was approximately from 0.05 to 0.10 for all SDS concentrations in the water phase.

Spontaneous emulsification was not observed at the minimum interfacial tension, while it was observed when the molar fraction of 1-dodecanol in dodecane exceeded 0.10 and the concentration of SDS was 6×10^{-3} M*. Spontaneous emulsification with 1-dodecanol was also observed only above an SDS concentration of 4×10^{-3} M.

Experimental

Materials. SDS obtained from the Wako Pure Chemical Industries, Ltd., was purified by recrystallization from ethanol, and extracted with petroleum ehter. Dodecane was supplied from the Nikko Petrochemical Co., Ltd., and 1-dodecanol from the Wako Pure Chemical Industries, Ltd.

Apparatus. The interfacial tension was measured using a Shimadzu Seisakusho, Ltd., Wilhelmy-type Surface Tensiometer.

Procedure. Dodecane and 1-dodecanol were mixed in various proportions to prepare the oil phase, and SDS was dissolved in distilled water. The measurement of the interfacial tension was started 10 min after the beginning of the contact between oil and water phases. Spontaneous emulsification was observed with the unaided eye and was photographed. All measurements carried out at 25 °C.

Results and Discussion

Decrease in Interfacial Tension. The interfacial tension was measured for various compositions of the oil phase consisting of dodecane and 1-dodecanol, as well as for various concentrations of SDS in the water phase. From this the effects of these variations on the interfacial tension were derived.

Figure 1 shows the effect of the variation of the SDS concentration on the interfacial tension for each composition of the oil phase. It is apparent from Fig. 1 that the interfacial tension is lowered by the addition of 1-dodecanol in dodecane, and that the extent of the lowering is larger for smaller 1-dodecanol fractions in the oil phase. In this connection, the tension at the interface between the oil phase with a small molar fraction of 1-dodecanol and the water phase, including SDS, was measured. From Fig. 2, it is clear that the interfacial tension decreases greatly when the fraction of 1-dodecanol in the oil phase is in the range from 0.03 to 0.10. The interfacial tension was reduced to about 0.5 dyn**/cm for SDS concentrations

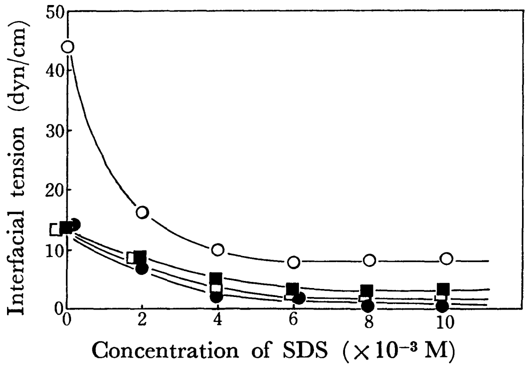

Fig. 1. The effect of concentration of SDS on the interfacial tension at the oil/SDS solution interface. Mole fraction of oil phase (dodecane : 1-dodecanol ○: (1.00 : 0.00), ●: (0.80 : 0.20), □: (0.60 : 0.40) ■: (0.00 : 1.00)

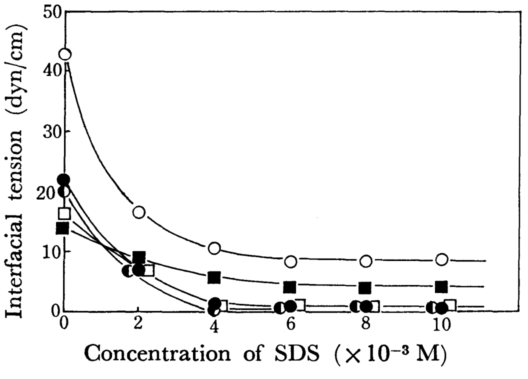

Fig. 2. The effect of concentration of SDS on the interfacial tension at the oil/SDS solution interface. Mole fraction of oil phase (dodecane : 1-dodecanol) ○: (1.00 : 0.00), ●: (0.97 : 0.03), ◐: (0.95 : 0.05) □: (0.90 : 0.10), ■: (0.00 : 1.00).

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* Throughout this paper 1 M=1 mol dm^{-3}.

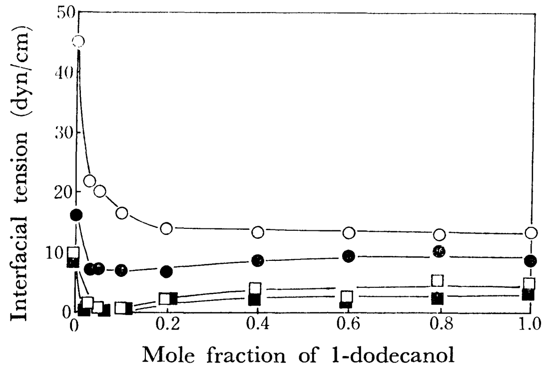

Fig. 3. The effect of composition of oil phase on the interfacial tension at the oil/SDS solution interface. Water phase ○: Water, ●: 2×10^{-3} M, □: 4×10^{-3} M, ■: 6×10^{-3} M.

above 6×10^{-3} M.

The relation between the composition of the oil phase and the interfacial tension is shown in Fig. 3. As is seen in the figure, the minimum value of the interfacial tension appears in the 1-dodecanol molar fraction range of 0.05 to 0.10 for concentrations of the SDS solution above 2×10^{-3} M. The minimum value of such a relation would be the result of molecular interaction between SDS and 1-dodecanol at the interface. When the concentration of 1-dodecanol in the oil phase is so low that no monolayer is formed, for example less than 0.05, and a solution including the other molecular species is injected, a variety of phenomena may occur.³⁾ If very small quantities of molecular species are present at the oil–water interface, they will eventually, by the processes of diffusion and convection, cause fluctuation, resulting in a large change in the interfacial tension.

Spontaneous Emulsification. The entire contour of the relation of the interfacial tension with the phase composition appearing separately in Figs. 1, 2, and 3 are shown together in Fig. 4. In this figure, the dotted line shows the critical SDS concentration at which spontaneous emulsification begins to occur, with the phases showing milky turbidity.

Figure 5 shows that spontaneous emulsification does not occur even for a SDS concentration in the water phase of 10×10^{-3} M, when the 1-dodecanol molar fraction in the oil phase is 0.05. However, this occurs for SDS concentrations above 6×10^{-3} M, when the 1-dodecanol molar fraction is 0.10 and 0.20. It is apparent that the limit of the appearance of spontaneous emulsification depends on the SDS concentration and the composition of the oil phase rather than on the value of the minimum interfacial tension.

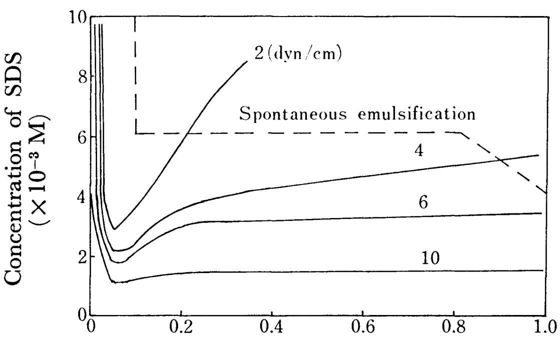

Fig. 4. The contour line of the infacial tension at the Dodecane & 1-dodecanol/SDS solution interface.

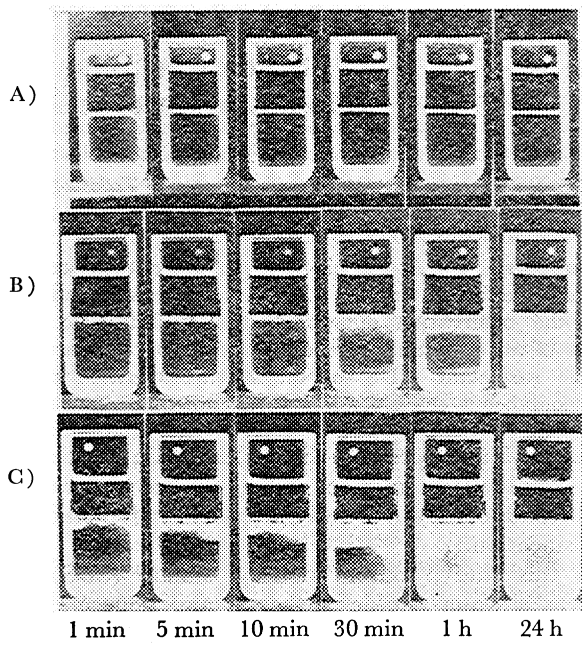

Fig. 5. Observation for spontaneous emulsification.
A) Oil phase dodecane: 1-dodecanol=0.95 : 0.05. Water phase 10×10^{-3} M SDS solution.
B) Oil phase dodecane: 1-dodecanol=0.90 : 0.10 Water phase 6×10^{-3} M SDS solution.
C) Oil phase dodecane: 1-dodecanol=0.80 : 0.20 Water phase 6×10^{-3} M SDS solution.

Schulman and Cockbain⁴⁾ have shown that spontaneous emulsification occurs when a complex is formed between an oil-soluble substance and a water-soluble surfactant at the oil–water interface. Mori *et al.*⁵⁾ have reported the existence of a complex between SDS and 1-dodecanol, and have shown the ratio of alcohol to sulfate to be 0.53—0.63.

In this work, no spontaneous emulsification was observed when the 1-dodecanol molar fraction was less than 0.05, although the interfacial tension showed a minimum. The amount of the complexes formed between the two components must be too small to be detectable with the unaided eye and, consequently, the visual change must be the change introduced by the complex formation.

References

1) K. Ogino and M. Ota, *Yukagaku*, **23,** 28 (1974).

2) K. Ogino and M. Ota, *Bull. Chem. Soc. Jpn.*, **49,** 1187 (1976).

3) J. H. Schulman and E. K. Rideal, *Proc. R. Soc. London, Ser. B*, **122,** 29, 46 (1937).

4) J. H. Schulman and E. G. Cockbain, *Trans. Faraday Soc.*, **36,** 651 (1940).

5) Y. Mori, K. Motomura, and R. Matsuura, *Bull. Chem. Soc. Jpn.*, **44,** 2078 (1971).

** Throughout this paper 1 dyn=10^{-5} N.