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Studies of Spontaneous Emulsification. II. The Effect of Nonionic Surfactants

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At the oil/water interface, spontaneous emulsification occurs when oil containing certain oil–soluble substances such as cholesterol is allowed to stand in contact with aqueous nonionic surfactant solutions. In this study, the interfacial tension between oil and water phases was measured in the presence of various oil–soluble substances, such as cholesterol, 1-dodecanol, and *cis*-9-octadecene-1-ol, added as ingredients in oil and various nonionic and anionic surfactants added in water, this study ascertained their effects on the emulsification.

When oil and water phases are brought quietly into contact, spontaneous emulsification sometimes occurs on one or both sides of the interface without any external mechanical work. The spontaneous emulsification is considered to be a result of one or more of the following three reasons[1,2]: i) The instability of the interface due to a non-uniform diffusion of the components of the phases across the interface, which causes a kicking of the interface violent enough to break off droplets of the adjacent bulk phases. ii) An accompanying diffusion of oil and an additive into the water, which results in a dilution of the additive with the water, leaving oil droplets stranded and thus forming the emulsion. iii) The temporary appearance of a negative interfacial tension, which causes an enlargement of the interfacial area.

Schulman and Cockbain[3] have shown that, when a complex is formed between an oil-soluble substance and a water-soluble surfactant at the oil/water interface, spontaneous emulsification occurs, and that the molecular interaction at the interface is sensitively influenced by the stereochemical configuration and the kinds of the polar groups of the two interacting molecules. Davies and Haydon[4] have reported that hexadecanol in toluene and sodium decyl sulfate in water are spontaneously brought into emulsion in the presence of surfactant or alcohol at concentrations higher than certain levels. In this system, interfacial tension was measured at low concentrations of solutes, this tension was proved to be negative when extrapolated to the higher concentration range of the solutes. From this result, they have estimated that a negative interfacial tension is the cause of the spontaneous emulsification. In such a system, emulsification does not occur spontaneously below a certain concentration of the solutes. To clarify the cause of this emulsification, therefore, the detailed measurement of interfacial tension with various concentrations of solutes is essential.

The present investigation was undertaken to reveal the mechanism of the spontaneous emulsification by measuring the interfacial tension in a system including oil-soluble substances and nonionic surfactants at various concentrations; also, the molecular interaction at the Nujol/water interface was studied in relation to the kinds of additives and to the tendency of spontaneous emulsification.

Experimental

Materials. *Surfactants*: The anionic surfactant, sodium dodecyl sulfate (SDS), and various nonionic surfactants were obtained from the Nikko Chemical Co. The characteristic properties of the nonionic surfactants are shown in Table 1. The surface tension *vs.* concentration curves of these nonionic surfactants are shown in Fig. 1.

Oil-soluble Substances: Cholesterol, 1-dodecanol, and *cis*-9-octadecene-1-ol (oleyl alcohol) of an extra pure grade (Tokyo

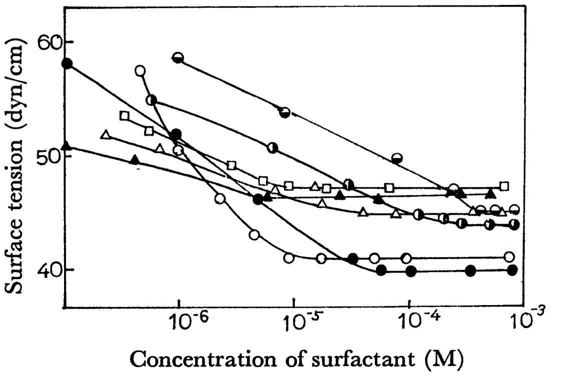

Fig. 1. Surface tension of aqueous solution of surfactants. ○ PCA-20; △ PCA-30; □ PCA-40; ● POA-20 ▲ POA-50; ◑ PS-40; ◒ POPA-30.

Table 1. Characteristic properties of used nonionic surfactants

Chemical composition	Abbr.	Number of ethylene oxide unit	HLB	CMC (mol/l)
Polyoxyethylene stearate	PS-40	40	17.4	2.45×10^{-4}
Polyoxyethylene hexadecyl ether	PCA-20	20	13.9	8.90×10^{-6}
Polyoxyethylene hexadecyl ether	PCA-30	30	16.0	3.21×10^{-5}
Polyoxyethylene hexadecyl ether	PCA-40	40	16.9	9.99×10^{-6}
Polyoxyethylene *cis*-9-octadecene-1-ol ether	POA-20	20	13.4	4.36×10^{-5}
Polyoxyethylene *cis*-9-octadecene-1-ol ether	POA-50	50	18.0	2.03×10^{-5}
Polyxyethylene *p*-hexadecylphenyl ether	POPA-30	30	16.9	3.28×10^{-4}

Kasei Co.) were adopted.

Water and Oil: Deionized and distilled water and liquid paraffin (commercial grade "Nujol") were used.

Apparatus. The interfacial tension and its time-course were measured by a Wilhelmy-type surface-tension meter (Shimadzu Surface Tensiometer ST-1).

Procedure. The oil-soluble substances and surfactants were dissolved in oil and water respectively, and the interfacial tension was measured at various concentrations of the solutes in each of the systems at 25 °C. These measurements were started 6 min (in the case of the anionic surfactants) 12 min (in the case of the nonionic surfactants) after the beginning of contact between the two phases, because the equilibria at these interfaces were reached after 5 min and 10 min respectively.

Results and Discussion

The Effects of Oil-soluble Substances. Figure 2 shows the effects of the oil-soluble substances on the interfacial tension in the Nujol/PCA-20 solution. In the figure, the dotted line shows the interfacial tension at which spontaneous emulsification occurs, while the arrow indicates the limit concentration of the component corresponding to the beginning of the emulsification, where the phases show a milky turbidity.

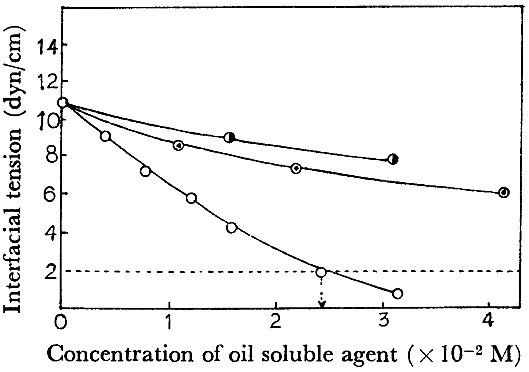

Fig. 2. Effect of oil soluble agents on the interfacial tension at Nujol/PCA-20 soln. interface.
Water phase; 2.7×10^{-3} M. PCA-20 soln.
○ Cholesterol; ◑ 1-dodecanol; ⊙ *cis*-9-octadecene-1-ol.

As shown in Fig. 2, it is clear that the interfacial tension is greatly lowered by the addition of oil-soluble substances; the degree of lowering is in the following order; cholesterol>*cis*-9-octadecene-1-ol>1-dodecanol. It is also clear that the most strongly effecting substance is cholesterol, suggesting that the interaction between cholesterol and a nonionic surfactant should be the strongest in these systems. In the system of cholesterol, spontaneous emulsification takes place at the level of 2.5×10^{-2} M; therefore, the interfacial tension is estimated to be about 2 dyn/cm. Unlike systems including SDS,$^{5)}$ *cis*-9-octadecene-1-ol has more effects than 1-dodecanol in the systems including nonionic surfactants.

The Effects of Surfactants. The Influence of the Structures of Surfactants: In systems in which cholesterol is included in the oil phase, surfactant molecules with various bond structures and nearly the same HLB were examined for their effects on the interfacial tension (Fig. 3). As is shown in Fig. 3, the interfacial tension between water containing the surfactants and Nujol including cholesterol is effected in this order; ether type>ester type>phenyl ether type. In these systems, spontaneous emulsification was observed for the ether-type at an interfacial tension of about 2 dyn/cm.

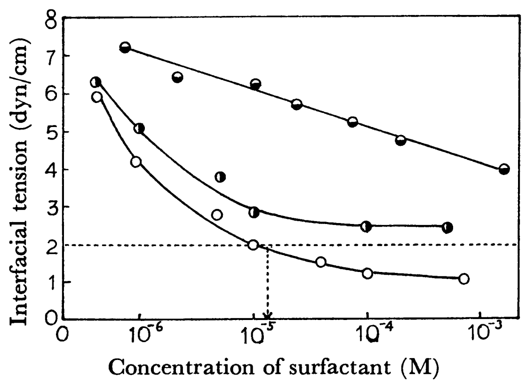

Fig. 3. Effect of surfactants on the interfacial tension at Nujol containing cholesterol/water interface.
Oil phase; 3 M/100 cholesterol soln.
○ PCA-40; ◑ PS-40; ◒ POPA-30.

The Influence of the Hydrophobic Group in Surfactants: Since ether-type nonionic surfactants are most effective in causing spontaneous emulsification, the influence of the hydrophobic group in the surfactants on the interfacial tension between Nujol containing cholesterol

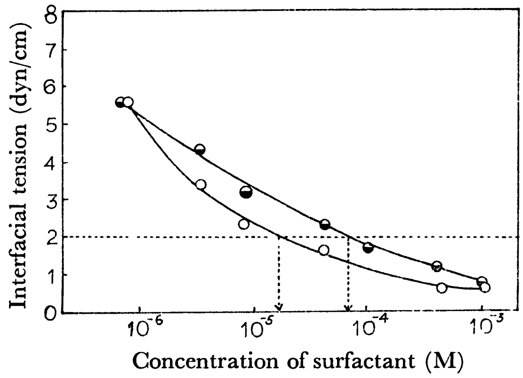

Fig. 4. Effect of surfactants on the interfacial tension at Nujol containing cholesterol/water interface.
Oil phase; 3M/100 cholesterol.
○ PCA-20; ◒ POA-20.

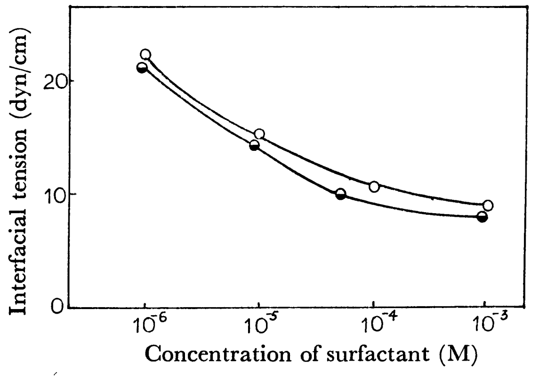

Fig. 5. Effect of surfactants on the interfacial tension at Nujol/water interface.
○ PCA-20; ◒ POA-20.

and water was studied; the results are plotted in Fig. 4. The surfactants consited of 20 units of ethylene oxide and had nearly equal HLB values. Figure 5 shows the equal intensity of the influence on the interfacial tension of the system in which the oil phase contains no oil-soluble substances. As can be seen in Fig. 5, cis-9-octadecene-1-ol ether-type nonionic surfactants lower the interfacial tension more intensively than do hexadecyl ether-type ones, in agreement with the results of Wrigley *et al.*[6] However, when the oil phase contains cholesterol, hexadecyl ether-type surfactants lower, the interfacial tension more than do *cis*-9-octadecene-1-ol ether-type ones, as is shown in Fig. 4. Therefore, it may be presumed that hexadecyl ether-type nonionic surfactants interact with cholesterol more strongly than do *cis*-9-octadecene-1-ol ether-type ones.

The Influence of Hydrophilic Chain Length in Surfactants, The relation between the hydrophilic chain length in surfactants and the effect on the interfacial tension at a Nujol-containing cholesterol/water interface was studied; the results are in Figs. 6 and 7. The hydrophobic group was the same in all kinds of surfactants. The interfacial tension was reduced to a larger extent by the surfactants with longer hydrophilic chains in the lower concentration range, but the degree of reduction is reversed in the higher concentration range of the surfactants, and in the case of *cis*-9-octadecene-1-ol ether-type nonionics, spontaneous emulsification was not observed with the surfactant containing 50 units of ethylene oxide groups. Therefore, it may be presumed that the interaction between the surfactants and cholesterol decreases with an increase in the hydrophilic chain length above 20 units of ethylene oxide groups.

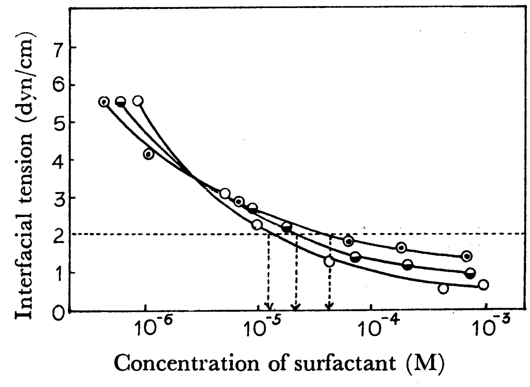

Fig. 6. Effect of surfactants on the interfacial tension at Nujol containing cholesterol/water interface.
Oil phase; 3M/100 cholesterol soln.
○ PCA-20; ◒ PCA-30; ⊙ PCA-40.

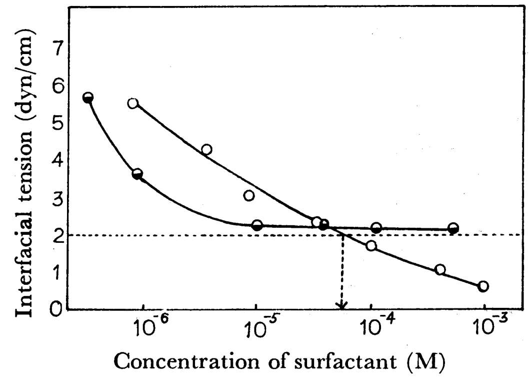

Fig. 7. Effect of surfactants on the interfacial tension at Nujol containing cholesterol/water interface.
Oil phase; 3M/100 cholesterol soln.
○ POA-20; ◒ POA-50.

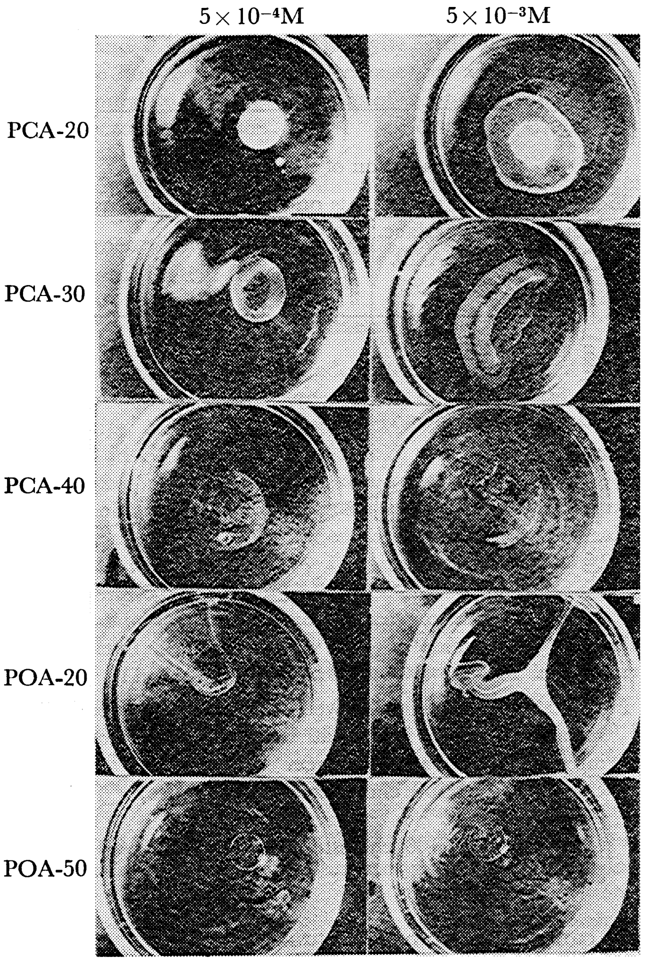

Fig. 8. Observation for emulsifying power in the system of Nujol with 3×10^{-2}M cholesterol/surfactant aqueous soln.

Figure 8 shows the appearance of spontaneous emulsification on the addition of a drop of oil containing 3×10^{-2} M cholesterol to aqueous solutions containing ether-type surfactants at 5×10^{-4} M and 5×10^{-3} M concentrations. The photograph shows the greater deformation of an oil drop and the higher turbidity, *i.e.*, the easier spontaneous emulsification. The emulsifying power of a surfactant decreases with an increase in the ethylene oxide chain length; that is, the interaction of nonionic surfactants with cholesterol decreases with the increase in the effect of hydrophilic groups in the surfactant. This agrees with the results shown in Figs. 6 and 7.

Further, the above results and the results for anionic surfactant systems, such as the cholesterol-sodium-dodecyl sulfate system, in which spontaneous emulsification occurs in the oil phase by means of the formation of a complex drawn up into the oil phase,[5] lead us to presume that a shorter length of the polyoxyethylene chain exhibits a greater likelihood of forming a complex

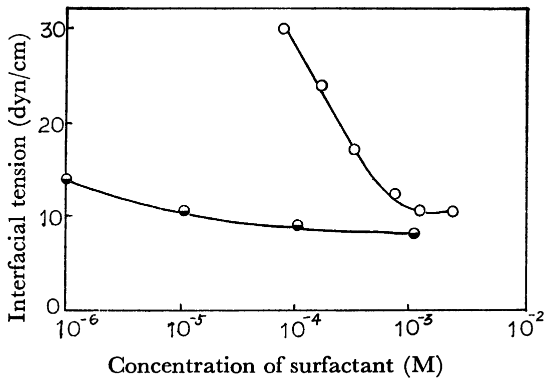

Fig. 9. Effect of surfactants on the interfacial tension at Nujol/water interface.
○ SDS; ◒ PCA-20.

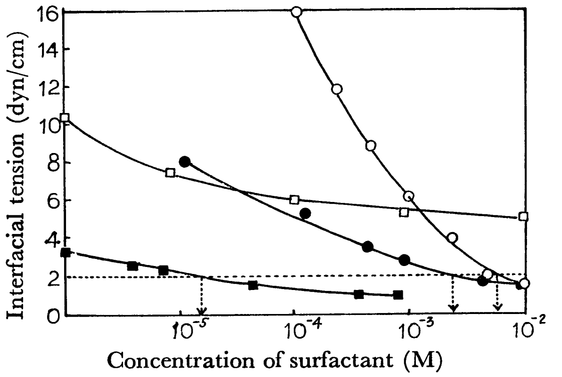

Fig. 10. Comparison between anionic and nonionic surfactants on the interfacial tension at Nujol containing cholesterol/water interface.
Oil phase: M/100 cholesterol–water phase; ○ SDS, □ PCA-20.
Oil phase: 3M/100 cholesterol–water phase; ● SDS, ■ PCA-20.

and causing spontaneous emulsification.

Comparison between Anionic and Nonionic Surfactants, Figures 9 and 10 show the effects of anionic and nonionic surfactants comparatively. When an oil phase contains no substances, the interfacial tension in the SDS system is 30 dyn/cm at the concentration of 5×10^{-4} M, as is shown in Fig. 9. That is, the interfacial tension of the PCA-20 system is lower than that of the SDS system at lower concentrations. On the other hand, as is shown in Fig. 10, when an oil phase contains 1×10^{-2} M cholesterol, the interfacial tension of the SDS system is lowered to a greater extent than that of the PCA-20 system above the surfactant concentration of 1.5×10^{-3} M, and spontaneous emulsification occurs above the concentration of 4.6×10^{-3} M. Therefore, it may be presumed that SDS interacts with cholesterol stronger than PCA-20.

Nevertheless, when an oil phase contains 3×10^{-2} M cholesterol, three times the above concentration, the interfacial tension *vs.* concentration curve shifts down turned and emulsification occurs at the level of 1.8×10^{-5} M in the case of PCA-20, while in the system of SDS emulsification occurs at 2.2×10^{-3} M. The case of SDS is not very different. That is, in the SDS system spontaneous emulsification occurs at a level about 100 times that in the PCA-20 system.

In a previous work[5] we found, with anionic surfactants containing different polar groups, that the oil-soluble cholesterol interacted in the following order: sodium dodecyl sulfate>sodium dodecanoate>sodium dodecylbenzene sulfonate.

From the above results, the molecular interaction between oil-soluble cholesterol and water-soluble surfactants may be thought to vary with the concentration of cholesterol in the oil phase, and its interaction with nonionic surfactants may be thought to be larger than that with anionic ones above a certain concentration of cholesterol in the oil phase.

Summary

In a Nujol/water system the oil phase of which contains both oil-soluble additives and water and the water phase contains oil and a surfactant, spontaneous emulsification scarcely occurs at all, while in systems composed of an oil phase containing a substance and of a water phase containing a surfactant, spontaneous emulsification is apt to take place, whereupon molecular interaction is presumed to occur to form a complex at the oil/water interface. This interaction is sensitive to the stereochemical configuration and polar groups of anionic surfactants molecules in the case of anionic surfactants and sensitive to bond structures, hydrophobic groups, and the polyoxyethylene chain length of nonionic surfactants.

Comparing anionic surfactants with nonionic ones, the former cause emulsification at lower concentrations than the latter in the presence of polar substances at low concentrations in the oil phase, but in the higher concentration range of the polar substances, on the contrary, nonionic surfactants interact with polar substances more strongly than do anionic ones, and spontaneous emulsification occurs at lower concentrations.

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