Effect of Mixed Surfactant upon Stability and Particle Size of Emulsion

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An effect of a mixed surfactant of SDS and homogeneous octaethylene glycol dodecyl ether (8ED) upon the stability and particle size of an octane-in-water emulsion was studied. The mixed surfactant solutions were found to exhibit equi-interfacial-tension over a wide concentration region of a mixed 8ED; the SDS concentrations were 6, 8, and 20 mmol dm^{-3}. The emulsion prepared by using mixed surfactant solution in such a concentration region showed a similar mean particle size. When SDS concentration was kept at 8 or 20 mmol dm^{-3}, the emulsions prepared by the mixed surfactant solutions had similar stability, independently of the mixed 8ED concentration. In the presence of 1 mmol dm^{-3} of SDS, the stability of the emulsions increased with the increasing concentration of mixed 8ED. In the case of SDS concentration of 6 mmol dm^{-3}, the emulsion was most stable at 1×10^{-3} mol dm^{-3} of mixed 8ED.

We have so far reported on the surface properties of mixed aqueous solutions containing SDS as an anionic surfactant and a series of polyethylene glycol dodecyl ethers ($C_{12}E_n$: n=1—8), having no distribution of poly(oxyethylene) chain lengths, as the nonionic surfactant.[1—3] We have found that an equi-surface-tension exists on the surface tension *vs.* the concentration curve over a wide concentration range of the nonionic surfactant in the presence of 6.3 mmol dm^{-3} of SDS, and also that the mixed micelle exists in the region. The existence of such a plateau region in the surface tension curve will also be expected to appear on the interfacial tension curve for the oil/water system consisting of a similar mixed surfactant solution and octane as the oil. The emulsion prepared by these surfactant solutions and octane will also be anticipated to become more stable over a wide concentration range of a nonionic surfactant.

Additives such as higher alcohols are often utilized as emulsion stabilizers,[4—12] since the emulsion becomes more stable by adding a small amount of a higher alcohol. This effect has so far been explained by formation of some more stable complex between alcohols and emulsifiers[5—7] due to the van der Waals interaction between the hydrocarbons or the ion-dipole interaction between the head groups.[13,14]

In this work, in order to confirm the emulsion stability for the octane-in-water emulsion system in the plateau region of the interfacial tension curve, the interfacial tensions were measured. These tensions are related to the stability of the emulsion produced from the corresponding individual and mixed surfactant solutions; the relation is also justified by the extent of drainage of the emulsion.

Experimental

Materials. The solium dodecyl sulfate (SDS) used here was obtained from Wako Pure Chemical Industries; it was purified by repeated crystallization from either ethanol or a mixture of 2-propanol and water. The purity was confirmed by the absence of any minimum in the surface tension *vs.* concentration curve. The octaethylene glycol dodecyl ether (8ED) supplied by Nikko Chemicals Co. has been confirmed to have a high purity and no distribution of poly(oxyethylene) chain lengths by GLC and TLC. The octane was a GR quality oil which was used without further purification. The water used for all experiments was purified by passing deionized water through a MILLI-Q Reagent-Grade Water System (MILLIPOR Ltd.) until its specific conductivity fell below 0.1 μS cm^{-1}.

Measurements. Interfacial tension was determined at 25 °C by a modified Wilhelmy type surface tensiometer, Shimadzu ST-1. Five ml of surfactant solution and of octane were poured slowly into a weighing bottle, and an octane/surfactant solution interface was formed. Then the bottle was stoppered, and left to stand for 40 min at the measurement temperature. This period was determined from the measurement of the time-dependence of the interfacial tension. After this period the interfacial tension was measured.

Emulsions were prepared as follows: Each mixture consisting of 20 ml of both surfactant solution and octane was emulsified with a Universal Homogenizer (Nihonseiki Kaisha) operated at 6000 min^{-1} for 5 min at room temperature. The emulsion thus prepared was transferred to sedimentation tubes, which had a stop cock, and left standing at 25 °C. The drainage of liquid from the emulsion (degree of separation; *DS*) was determined after 1 h, 2 h, and 24 h. The *DS* value is defined in the present work as follows:

$$DS \text{ value} = \frac{\text{volume of drained phase}}{\text{total volume of emulsion}} \times 100\,(\%)\,.$$

The mean particle size of the emulsions was determined immediately after preparation of each emulsion by a centrifugal particle size analyzer, Shimadzu CP-50.

Results and Discussion

Before discussing the stability of the octane-in-water emulsion system prepared using a surfactant mixture of SDS and 8ED, we must determine whether the properties of the interface of the octane/aqueous solution of each surfactant reflect the stability of the corresponding emulsion. The interfacial tension of 8ED solution against octane is shown in Fig. 1(a). The value decreased from 35 mN m^{-1} to 0.3 mN m^{-1} with the increase of 8ED concentration, and an apparent cmc (critical micelle concentration) was observed at about 1×10^{-3} mol dm^{-3}. Figure 2(a) shows the interfacial tension of SDS solution against octane. The cmc was observed at about 8 mmol dm^{-3}.

Figure 1(b) shows *DS* values of the emulsion which had been prepared with 8ED as an emulsifier. The emulsion began to be stable with increasing concen-

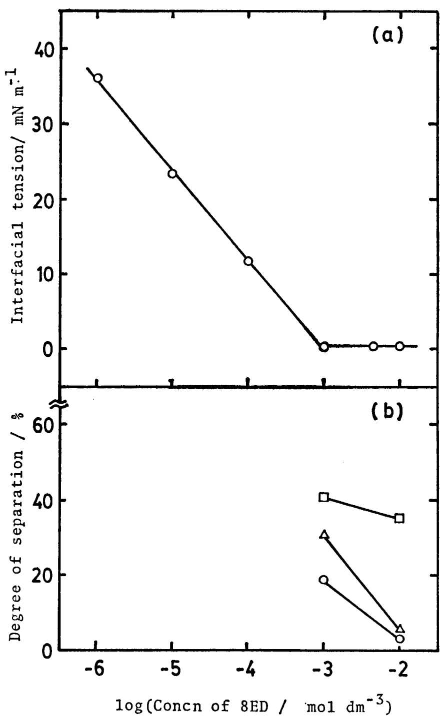

Fig. 1. (a) Interfacial tension of 8ED solution against octane.
(b) Degree of separation of octane emulsion prepared by 8ED, after 1 h (—○—), 2 h (—△—), and 24 h (—□—).

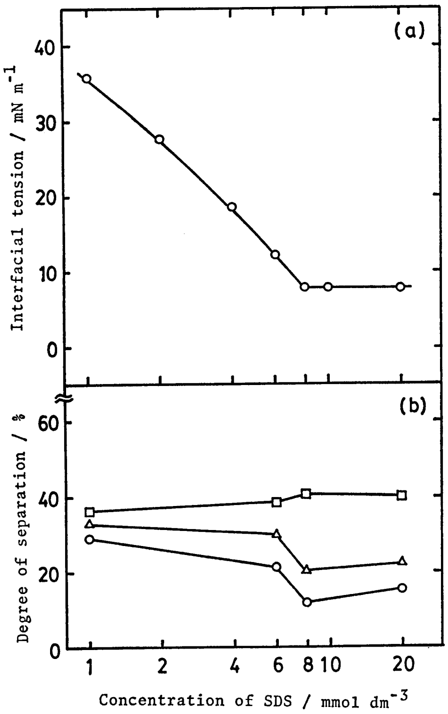

Fig. 2. (a) Interfacial tension of SDS solution against octane. (b) Degree of separation of octane emulsion prepared by SDS, after 1 h (—○—), 2 h (—△—), and 24 h (—□—).

tration above the apparent cmc of 8ED. Figure 2(b) also shows *DS* values of the emulsion prepared with SDS. The *DS* value became smaller as the SDS concentration increased; in the presence of 8 mmol dm^{-3} of SDS the *DS* value was smallest, in the measurement after one hour.

According to our previous data,[1] the surface tension *vs.* concentration curve for the mixed surfactant solution of SDS and homogeneous pentaethylene glycol dodecyl ether (5ED) showed a plateau region (equi-surface-tension region) over a wide concentration range of a mixed 5ED (from 3×10^{-6} to 1×10^{-3} mol dm^{-3}) in the presence of 6.3 mmol dm^{-3} of SDS. The existence of a mixed micelle between SDS and 5ED has been proved by the appearance of this plateau region.[1]

From these findings, such a mixed surfactant will be expected to show an equi-interfacial-tension region even in the interfacial tension curve. The interfacial tension of the mixed surfactant solution of SDS and 8ED against octane is shown in Fig. 3. In the presence of 6, 8, and 20 mmol dm^{-3} of SDS, each interfacial tension curve had an equi-interfacial-tension region.

If the O/W type emulsion of octane is prepared from the mixed surfactant solution which shows the plateau region in the interfacial tension *vs.* concentration curve, a homogeneous emulsion will be formed.

Table 1 indicates the mean particle size of the emulsion prepared from the mixed surfactant solution of SDS and 8ED. In the cases of SDS concentrations of 6, 8, and 20 mmol dm^{-3}, it was found that the mean particle sizes of the emulsions were almost the same for each SDS concentration, independently of the concentration of added 8ED. However, in the

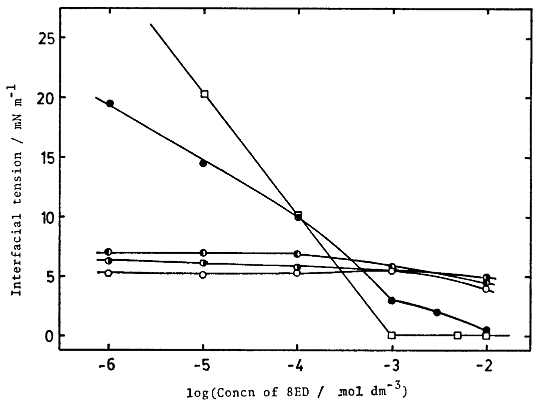

Fig. 3. Interfacial tension of 8ED against octane as a function of SDS additive concentration.
Additive concentration of SDS: 0 (—□—), 1 (—●—), 6 (—○—), 8 (—◑—), and 20 mmol dm^{-3} (—◐—).

Table 1. Mean particle size (μm) of the emulsion

8ED concn / mol dm^{-3}	SDS concn/mmol dm^{-3} 1	6	8	20
1×10^{-6}		9.5	8.8	9.9
1×10^{-5}	11.4	9.9	9.5	9.2
1×10^{-4}	10.1	9.5	9.1	9.2
1×10^{-3}	9.7	10.5	9.9	9.5
1×10^{-2}	8.9	10.0	9.2	9.0

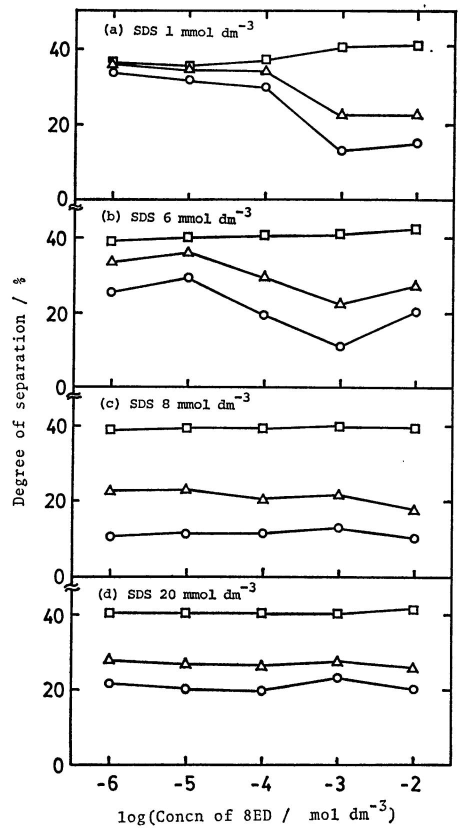

Fig. 4. (a), (b), (c), (d) Degree of separation of octane emulsion prepared by the mixed surfactant of SDS and 8ED, after 1 h (—○—), 2 h (—△—), and 24 h (—□—).

presence of 1 mmol dm^{-3} of SDS, the mean particle size of the emulsion decreased with the increasing concentration of added 8ED.

Figures 4(a), (b), (c), and (d) show the *DS* values of the emulsions prepared by the mixed surfactant solution of SDS and 8ED. At SDS concentration of 1 mmol dm^{-3} (Fig. 4(a)), the *DS* values of the emulsion after one hour began to become smaller at about 1×10^{-3} mol dm^{-3} of added 8ED. On the other hand, in the presence of 6 mmol dm^{-3} of SDS (Fig. 4(b)), in which the mixed surfactant solution gave an equi-interfacial-tension (see Fig. 3.), the *DS* value of the emulsion decreased with the increasing concentration of a mixed 8ED; the emulsion separation was smallest at 1×10^{-3} mol dm^{-3} of 8ED. In the cases of 8 and 20 mmol dm^{-3} (Figs. 4(c) and (d)), the *DS* value of the emulsion was almost constant at the respective SDS concentration, independently of the mixed 8ED concentration. In the presence of 8 mmol dm^{-3} of SDS, the smallest *DS* value in this series of the emulsion was observed after 1 h.

When an oil is emulsified by mixed surfactant solutions which have an equi-interfacial-tension, the emulsion can be expected to have a narrow distribution of emulsion particle sizes, and so the emulsion stability increases; The stability is also explained from the point of view of the properties of the adsorbed film at the oil/water interface. According to our previous data,[15] in the presence of 8 and 20 mmol dm^{-3} of SDS, the properties of the adsorbed layer of the mixed surfactant at octane/water interface are governed primarily by SDS. Thus these emulsions exhibit the same stability independent of the mixed 8ED concentration. However, in the presence of 6 mmol dm^{-3} of SDS, as the properties of the mixed adsorbed layer change from SDS-like properties to 8ED-like ones with increasing concentration of mixed 8ED, the emulsion stability may vary with the concentration of mixed 8ED.

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