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The Effect of Fatty Alcohols on the Dodecane-Water and the Dodecane-SDS Solution Interfaces

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Synopsis. The effects of fatty alcohols ($C_mH_{2m+1}OH$, $m=1$—12) at the dodecane–water and the dodecane–sodium dodecyl sulfate (SDS)-solution interfaces has been investigated by measuring the interfacial tension and by observing the stability of the emulsion. The following results have been obtained: the addition of lower alcohols ($m=1$—3) increases the interfacial tension at the dodecane–SDS-solution interface, and they are considered as emulsion breakers. With regard to middle and higher alcohols, though, the interfacial tension decreases with the increase in the carbon number. They can thus be used as emulsion stabilizers.

The effects of additives on spontaneous emulsification and on the stability of emulsion have been investigated by many investigators.[1—5] We[6] ourselves have previously reported that 1-dodecanol in dodecane and sodium dodecyl sulfate (SDS) in water form emulsions spontaneously in the presence of surfactants or alcohols above certain concentrations. Vold and Mittal[7] have reported that, in a Nujol–water–0.2% SDS emulsion, the stability of the emulsion increases with the addition of 1-dodecanol up to 56%, on the basis of SDS.

In this study, the effect of the carbon-chain length of fatty alcohols has been investigated at the dodecane–water and the dodecane–SDS-solution interfaces.

Experimental

Materials. *Surfactant*: The sodium dodecyl sulfate (SDS) was supplied by Wako Pure Chemical Ind. Ltd., and was extracted with ether and recrystallized from ethanol.

Fatty Alcohols: The methanol, 1-dodecanol (Wako Pure Chemical Ind. Ltd.,), ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, and 1-undecanol (Tokyo Kasei Ind. Ltd.,) were of a reagent grade and were used without further purification.

Water and Oil: The distilled water and dodecane (Nikko Petrochemical Co.,) were of a commercial grade and were used without purification.

Apparatus. The interfacial tension and its variation with the time were measured at 30 °C with a Wilhelmy tensiometer, Shimadzu ST-1.

Procedure. Dodecane (8.0 ml) was used as an oil phase. Distilled water (8.0 ml) and 8×10^{-3} M† SDS solution (8.0 ml) were used as a water phase. After the equilibrium of the oil–water interface has been established, fatty alcohol was added to the oil phase with a syringe, and the change in the interfacial tension with the course of time was measured.

The dodecane, fatty alcohols, and 2×10^{-2} M SDS solution were emulsified by stirring. These emulsions were observed and photographed.

Results and Discussion

The Behavior of Fatty Alcohols at the Dodecane–Water Interface. In Fig. 1, the solid line shows the effect of fatty alcohols on the interfacial tension at the dodecane–water interface. The interfacial tension is lowered by the addition of alcohols, the extent of which is the largest in the case of 1-butanol.

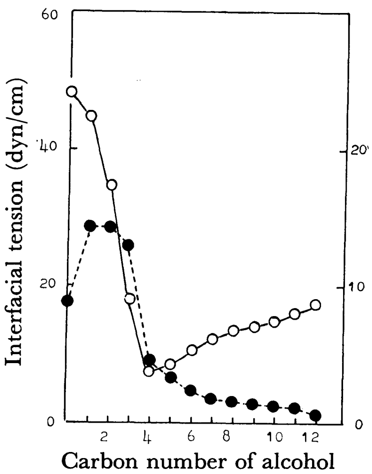

Fig. 1. The effect of carbon number of fatty alcohol on the interfacial tension at the dodecane-water interface. Oil phase : dodecane 8.0 ml, water phase : solid line-distilled water 8.0 ml; ○, dotted line-SDS soln. 8.0 ml; ●, additives : fatty alcohols ($m=1$—12) 0.8 ml.

We tried to calculate the HLB number of alcohols by the Davies method, and the concentration ratio of alcohol in the water phase and the oil phase (C_w/C_o), by means of the following equations:

$$\Delta G_{o\to w} = 800n - \Delta G_{o\to w}(\text{hydrophilic groups}) \quad (1)$$

$$C_w/C_o = \exp(-\Delta G_{o\to w}/RT) \quad (2)$$

where $\Delta G_{o\to w}$ is the free energy when alcohol is transferred from the oil phase to the water phase, n is the number of $-CH_2-$ groups in an alcohol, the increment of

Table 1. Hydrophilic and lipophilic properties of fatty alcohols

m[a)]	H.L.B.	$\Delta G_{o\to w}$ / cal mol^{-1}	C_w/C_o
1	8.4	−2400	53.9
2	8.0	−1600	14.3
3	7.5	− 800	3.7
4	7.0	0	1.0
5	6.5	800	0.26
6	6.1	1600	7.0×10^{-2}
7	5.6	2400	1.8×10^{-2}
8	5.1	3200	4.9×10^{-3}
9	4.6	4000	1.3×10^{-3}
10	4.2	4800	3.4×10^{-4}
11	3.7	5600	9.1×10^{-5}
12	3.2	6400	2.4×10^{-5}

a) m is the carbon number of fatty alcohol.

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

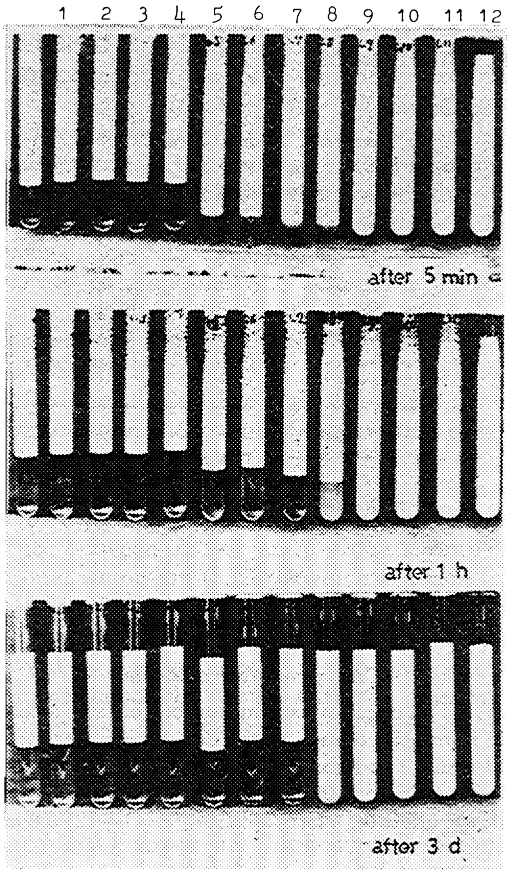

Fig. 2. The observation ofdo decane–water–SDS–fatty alcohol emulsions.
Oil phase : dodecane 3.0 ml, water phase : 2×10^{-2} M SDS soln. 3.0 ml, additives : fatty alcohols (m=1—12) 0.1 M in emulsion.

$\Delta G_{o\to w}$ per $-CH_2-$ groups is 800 cal/mol, and $\Delta G_{o\to w}$ (–OH group) is −3200 cal/mol.[1] C denotes the concentration of alcohol, and the subscripts o and w refer to oil and water. The results are shown in Table 1.

The results of calculation and Fig. 1 suggest that 1-butanol is well balanced in hydrophilic and lipophilic properties, and that lower alcohols (m=1—3) become more hydrophilic, while alcohols which have more than 4 carbon atoms become more lipophilic.

The Effect of Fatty Alcohols at the Dodecane–SDS-solution Interface. In Fig. 1, the dotted line shows the effect of alcohol on the interfacial tension at the dodecane–SDS-solution interface (right ordinate). From this results, it is considered that lower alcohols (m=1—3) have an emulsion-breaking effect, as is shown in Fig. 2. In the cases of the other higher alcohols, the reason for the decrease in the interfacial tension is considered to be as follows. It is well known that a complex is formed by the van der Waals force and a polar force between higher alcohol and the SDS molecule.[8] Thus, the adsorption of alcohol and the SDS molecule at the dodecane–water interface is further increased, and the interfacial tension decreases. Therefore, it may be considered that the stabilizing power of SDS is increased in the presence of alcohols which have a long chain. Figure 2 shows photographs of emulsions which are composed of dodecane, alcohols, SDS, and water. The emulsion without alcohol is at the far left of the photographs. From the left to the right of the photographs, the carbon numbers of the alcohols added increase. We ascertained by the dilution method that these emulsions were of the oil-in-water type. As can be seen from Fig. 2, it is clear that lower alcohols act as emulsion-breakers, while higher alcohols act as emulsion-stabilizers.

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