The Effect of Alcohols on the Solubilization of Oleic Acid in the Aqueous Solution of Sodium Dodecyl Sulfate

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It may well be established that the solubilizing power of the detergent towards hydrocarbons, such as *n*-heptane[1] and benzene[2], increases by adding alcohols in the detergent solution, the more markedly the longer the hydrocarbon chains of the added alcohols are. The solubilization of polar materials in the presence of alcohols in the detergent solution, however, has not been known well. Kolthoff and Graydon[3] studied the effect of *n*-amyl alcohol and *n*-octyl alcohol on the solubilization of some dyes in the potassium soap solutions and found no such regular and simple relations as for nonpolar substances. Some other studies also reported the complicated nature of the solubilization of polar materials in the presence of additives[4]. In order to make the situation clearer we have investigated the effect of various alcohols on the solubilization of oleic acid in the aqueous solution of sodium dodecyl sulfate.

Experimental

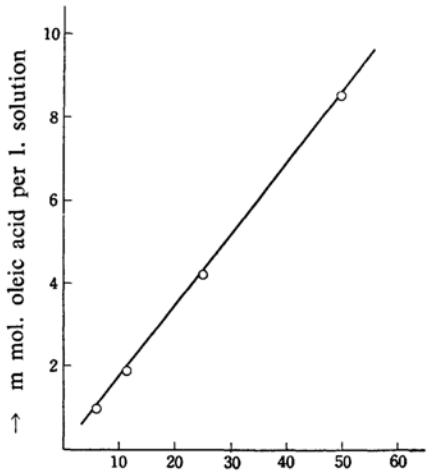
Materials.—Sodium dodecyl sulfate (SDS) used was synthesized from fractionally distilled *n*-dodecyl alcohol and purified by repeated ether extraction. Its purity was confirmed by elementary analysis and surface tension measurements. The alcohols used were purified by distillation and their boiling points were as follows: *n*-butyl alcohol (117°C), *n*-hexyl alcohol (157°C), *n*-amyl alcohol (137.5~138.5°C), *iso*-amyl alcohol (132°C), *n*-octyl alcohol (194°C), *n*-dodecyl alcohol (127°C/7 mmHg) and *n*-hexadecyl alcohol (190°C/15 mmHg). Oleic acid was obtained by distillation at 211°C/6 mmHg.

Method. — The solubilization end point was measured by the turbidity method using a Shimadzu AKA photoelectric nephelometer. The experiment was performed at a constant temperature of 25.0°C.

Results

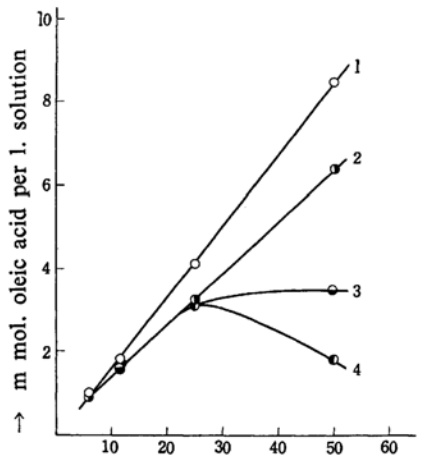
In Fig. 1 the amount of oleic acid solubilized in the aqueous solution of SDS is plotted against the concentration of the latter. An almost linear relationship has been obtained. When an alcohol is added to the detergent solution beforehand, the solubilization of oleic acid decreases as shown in Figs. 2, 3 and 4 for the case of *n*-butyl, *n*-hexyl and *n*-hexadecyl alcohol, respectively. In Fig. 5 the amount of oleic acid solubilized is plotted against the amount of alcohols added to the detergent solution of 0.05 mol./l. It is seen that the solubilization of oleic acid decreases monotonously as the amount of alcohols added increases and this effect of decreasing the solubilization of oleic acid increases as the chain length of the alcohol increases.

1) H. B. Klevens, *J. Am. Chem. Soc.*, **72**, 3780 (1950).
2) K. Shinoda and H. Akamatsu, This Bulletin, **31**, 497 (1958).
3) I. M. Kolthoff and W. F. Graydon, *J. Phys. Chem.*, **55**, 699 (1951).
4) M. E. L. McBain and E. Hutchinson, "Solubilization", Academic Press Inc., New York (1955), p. 85.



→ Concentration of SDS, m mol./l.

Fig. 1. The relation between the solubilized amount of oleic acid and the concentration of SDS.



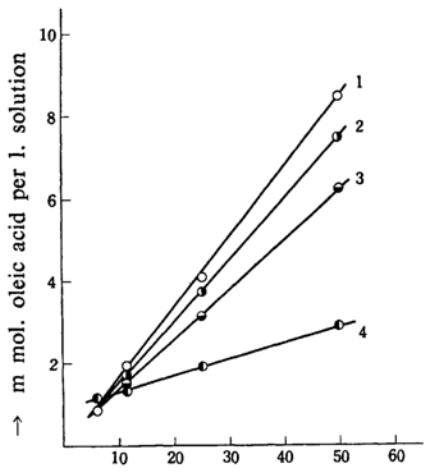
→ Concentration of SDS, m mol./l.

Fig. 2. The relation between the solubilized amount of oleic acid and the concentration of SDS containing *n*-butyl alcohol. Mol. SDS: mol. alcohol is 1, 1 : 0; 2, 1 : 1; 3, 1 : 2; 4, 1 : 3.

Discussion

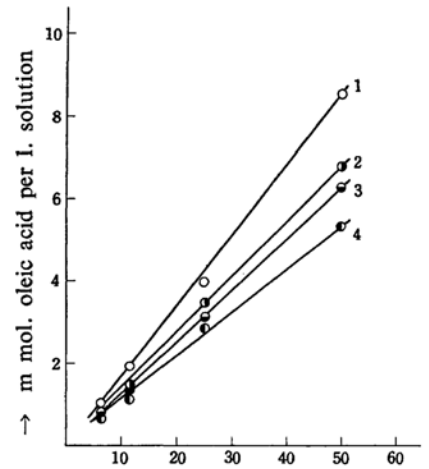
It may be a general agreement that alcohols added can cause a decrease in cmc of the detergent solution and an increase in micelle volume by penetration into the micelle surface. In the case of SDS solutions, Hutchinson et al.[5] measured the cmc in the presence of *n*-hexyl, *n*-heptyl and *n*-octyl alcohols and found that the cmc decreases as the amount of alcohols added increases. When hydrocarbon is solubilized in the detergent solution in the presence of alcohols, therefore, it is evident that its solubilization increases as the amount of alcohols added increases, since hydrocarbon is considered to dissolve in the micelle interior which has been made larger by the presence of alcohols. A typical example of the solubilization of hydrocarbon in the detergent solution in the presence of alcohols may be given by the result obtained by Klevens[1], which is reproduced in Fig. 6. This shows

5) E. Hutchinson, A. Inaba and L. G. Bailey, *Z. phys. Chem., N. F.*, 5, 344 (1955).



→ Concentration of SDS, m mol./l.

Fig. 3. The relation between the solubilized amount of oleic acid and the concentration of SDS containing *n*-hexyl alcohol. Mol. SDS: mol. alcohol is 1, 1 : 0; 2, 1 : 0.2; 3, 1 : 0.4; 4, 1 : 0.8.



→ Concentration of SDS, m mol./l.

Fig. 4. The relation between the solubilized amount of oleic acid and the concentration of SDS containing *n*-hexadecyl alcohol. Mol. SDS: mol. alcohol is 1, 1 : 0; 2, 1 : 0.0081; 3, 1 : 0.0168; 4, 1 : 0.0276.

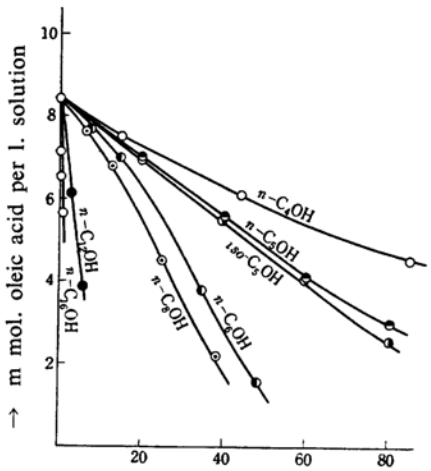


Fig. 5. The Effect of alcohols on the solubilization of oleic acid in 0.05 M SDS solution.

the effect of alcohols on the solubilization of *n*-heptane in the aqueous solution of potassium tetradecanoate. It is clearly seen that the solubilized amount of *n*-heptane increases as the amount of added alcohols increases and that the effect of alcohols to increase the solubilization of the hydrocarbon increases with the chain length of the alcohols. The result shown in Fig. 6 is quite contrary to the result obtained in the present experiment which is shown in Fig. 5. The solubilized amount of oleic acid decreases as the amount of alcohols added increases, the more markedly the longer the hydrocarbon chain of the alcohols is. It will be reasonable to ascribe this difference to the fact that hydrocarbon dissolves in the micelle interior, while polar materials, such as oleic acid in the present experiment, dissolve in the palisade layer of the micelle. Since alcohols also dissolve in the palisade layer, oleic acid will be hindered from dissolving in the same place by already existing alcohol molecules, the result being that the solubilization of oleic acid decreases as the amount of alcohols increases in the detergent solution, as shown in Fig. 5.

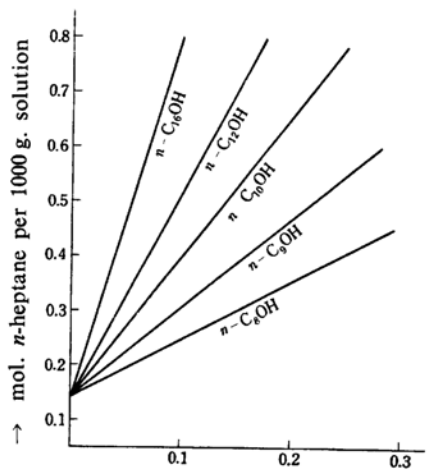


Fig. 6. The Effect of alcohols on the solubilization of *n*-heptane in 0.35 M K tetradecanoate solution (reproduced from Kleven's paper[1]).

In connection with the above explanation it may be interesting to note the effect of electrolytes on the solubilization of nonpolar and polar materials in the detergent solution. Klevens[6] studied the solubilization of *n*-heptane and *n*-octyl alcohol in the aqueous solution of potassium myristate in the presence of potassium chloride, potassium sulfate and potassium ferrocyanate. He found that the solubility of *n*-octyl alcohol decreases, while that of *n*-heptane increases, with the increasing electrolyte concentration in the detergent solution. Klevens explained this difference as follows. The increased aggregation of the micelles in the presence of electrolytes results in an increase in micelle interior volume which is available to a nonpolar solute, butre sults in a decrease in the micellar area which is available for penetration by a polar solute. Richards and McBain[7] also report that the presence of sodium chloride and potassium chloride decreases the solubilizing power of cetyl pyridinium chloride towards polar materials such as *n*-octyl alcohol and benzaldehyde, but increases that towards nonpolar materials such as benzene and *n*-octane. These results

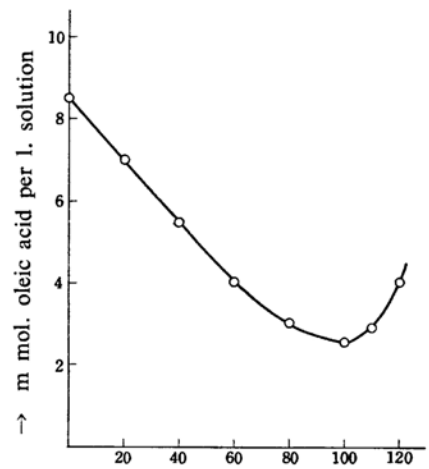


Fig. 7. The Effect of *n*-amyl alcohol on the solubilization of oleic acid in 0.05 M SDS solution.

6) H. B. Klevens, *J. Am. Chem. Soc.*, 72, 3780 (1950).
7) R. H. Richards and J. W. McBain, ibid., 70, 1338 (1948).

conform in their behaviors to the result obtained in the present experiment, the same explanation being applied, although the additives are electrolytes in the former and alcohols in the latter experiments.

It is to be noted that the concentration of alcohols in the detergent solution shown in Fig. 5 is not so great as that in Fig. 6. We found that, in the case of *n*-butyl and *n*-amyl alcohol, when the amount of alcohols in the detergent solution becomes greater than that shown in Fig. 5 the solubilization of oleic acid turns out to increase with the concentration of the alcohols in the detergent solution. The case of *n*-amyl alcohol is shown in Fig. 7. Since these alcohols are fairly soluble in water, the solvent property of water will alter as the amount of the alcohol in it becomes greater, the result being that the solubility of oleic acid in the solvent liquid will become appreciable. Also it may be probable that the micelle-forming property of the detergent is lessened by the presence of water soluble alcohols in fairly large concentrations, the result being that the solubilization of oleic acid in the detergent micelle will decrease. These two factors counteract each other in the determination of solubility of oleic acid in the detergent plus alcohol solutions. We see in Fig. 2 that the solubilization of oleic acid decreases when the concentration of the detergent containing *n*-butyl alcohol (mole ratio 1 : 3) exceeds a certain value. This may be attributed to the predomination of the factor of lessening the solubilization in the detergent micelle. On the contrary the result obtained in Fig. 7 may be attributed to the predomination of the factor of increasing the solubility of oleic acid in the water-alcohol mixture.

Summary

The solubilization of oleic acid in the aqueous solution of sodium dodecyl sulfate was studied in the presence of various kinds of alcohols in various concentrations. When the concentration of alcohols in the detergent solution is not so great, the solubility of oleic acid decreases as the amount of alcohols increases. This is explained by the solution of oleic acid and alcohols in the same place in the micelle, i. e., in the palisade layer. When the water soluble alcohols are used the solubilization of oleic acid turns out to increase at a certain concentration of the alcohols in the detergent solution. This is explained by the solution of oleic acid in the solvent liquid as well as in the detergent micelles.

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