The Solubilization of Benzene in Aqueous Soap-Alcohol Solution

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One of the most outstanding properties of detergent solution is its ability to solubilize polar or non-polar oil above the critical micelle concentration[1,2]. Klevens[3,4] investigated the effect of added alcohols, salts and the other additives on the solubilization of *n*-heptane in potassium tetradecanoate solution and found a very marked increase in the solubilization of *n*-heptane.

The present paper reports the effect of added alcohols and salts on the solubilization of benzene in potassium dodecanoate solution at 25°C.

Experimental.—The solubilization end point was determined by transmission measurements with the same procedure described by Stearns et al.[1] Butanol, *iso*-pentanol, hexanol, cyclohexanol and octanol were purified materials[5]. Dodecanoic acid was purified by vacuum distillation. The solubilization of benzene in aqueous potassium dodecanoate was the same with that reported by Stearns et al.[1]

Results and Discussion.—*The Effect of Added Alcohols on the Solubilization.* The effect of added alcohols on the solubilization of benzene in aqueous potassium dodecanoate was plotted in Fig. 1.

It is evident that 1) the amount of benzene solubilized markedly increased by the addition of alcohols, 2) the longer chain alcohol is much more effective than shorter chain alcohol in promoting solubilization and 3) the effect of added alcohol is greater than that of corresponding fatty acid soaps. This suggests that the penetrated long-chain alcohol increases the micellar size and that by decreasing the electrical repulsive force of micelle-forming ion the aggregation number of micelle forming ion also increases, causing a marked increase in micellar size and solubilizing power. In the case of cyclo-hexanol and *iso*-pentanol the amount of benzene solubilized showed

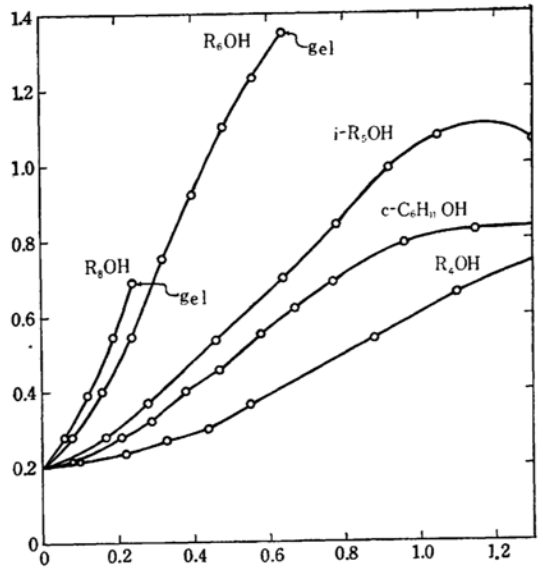

Fig. 1. The effect of added alcohols on the solubilization of benzene in potassium dodecanoate, 0.285 mole/l., solution ordinate: moles of benzene per 1000 cc. of solution.
R_4OH, butanol; i-R_5OH, *iso*-pentanol; R_6OH; hexanol; R_8OH, Octanol; C-$C_6H_{11}OH$, Cyclohexanol.

maximum and then gradual decrease. In the case of hexanol and octanol, gel formation occurred at a relatively low alcohol concentration, therefore the solubilization was determined only at the lower concentration.

Estimation of the Micellar Charge from the Solubilization Measurements. The effect of soap concentration on the solubilization of benzene per mole of micellar potassium dodecanoate was determined and plotted in Fig. 2[6]. The effect of potassium chloride on the solubilization of benzene in aqueous potassium dodecanoate, 0.192 mole/l., was also determined and plotted in Fig. 2.

It is supposed that the increase of solubilization of benzene per mole of soap is essentially the same phenomenon in both systems. Namely, the increase in the counter-ion concentration, due to the increase in soap concentration or added salts, decreases the electrical potential on the micelle surface and tends to increase

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1) R. S. Stearns, H. Oppenheimer, E. Simon and W. D. Harkins, *J. Chem. Phys.*, **15**, 496 (1947).

2) M. E.L. McBain and E. Hutchinson, "Solubilization", Academic Press Inc., New York, 1955.

3) H. B. Klevens, *J. Chem. Phys.*, **17**, 1004 (1949).

4) H. B. Klevens, *J. Am. Chem. Soc.*, **72**, 3581, 3780 (1950).

5) K. Shinoda, *J. Phys. Chem.*, **58**, 1136 (1954),

6) The concentration of micellar soap was calculated, subtracting the single ion concentration from the stoichiometric concentration. The solubility of benzene in water was subtracted from the total amount of benzene solubilized to calculate the actual amount of benzene solubilized in the micelle.

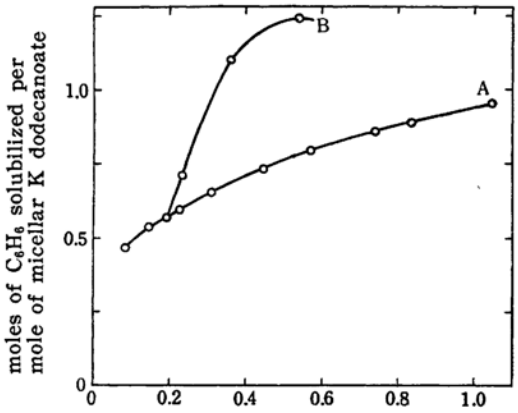

Fig. 2. A. the effect of soap concentration and B. the effect of counterion concentration on the solubilization of benzene in potassium dodecanoate solution at 25°C.

the aggregation number. If the micelles become larger, the amount of non-polar oil solubilized per micelle forming ion may increase. In a soap solution, the free counter-ion does not increase as expected from its stoichiometric concentration, since the counter-ion mostly adheres on the micelle surface. If we assume that the inter-micellar force is negligible, the amount of benzene solubilized per mole of micellar soap depends only on the concentration of counter-ion. From the comparison between curves A and B, we see that the amount of benzene solubilized per mole of micellar soap increases as slowly as about one-fifth times in curve A, therefore it can be concluded that about 80% of the counter-ion is fixed on the micelle surface, i.e., the degree of "ionization" of micelle is about 0.2 at about 0.2~0.3 mole/l. Recalculating Klevens's[4] and Stearn's[1] results with the same procedure, the degree of ionization of micelle was evaluated as 0.25 in the case of potassium tetradecanoate at about 0.5 mole/l.

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