Types and Mechanisms of Solubilization

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The solubility of various compounds such as hydrocarbons, dyes, long chain alcohols, fatty acids, and insoluble soaps in water is increased by the addition of soluble soaps and other detergents. This phenomenon is usually designated as solubilization. A considerable number of investigators have studied the solubilization of compounds of varying polarity, size, charge, etc., with quite inconsistent results. An attempt is made here to show relationships between these various, seemingly conflicting, data and to add some new data from this laboratory which increases the validity of these correlations.

Some typical solubilization data are shown in Fig. 1, where MR (moles of material solubilized per mole soap) is plotted as a function of soap concentration. Two main types of solubilization occur depending on the compound solubilized.

The first group is exemplified by hydrocarbons. For example, Curve A shows the solubilization of ethyl benzene in potassium laurate solutions which is typical of systems in which MR increases at all soap concentrations, up to almost 1.0 M, above the critical micelle concentration (CMC). The initial decrease in solubility below the CMC is probably a salting out effect, and a minimum is reached at the CMC. Further examples of this type are the solubilization of benzene by cetyl pyridinium chloride as determined by Hartley (2), of propylene and other vapors by potassium oleate reported by McBain and O'Connor (3), and of liquid hydrocarbons such as n-decane and benzene solubilized by potassium laurate and by potassium myristate (4).

Curve B in Fig. 1 is taken from McBain and Green (5) and shows the solubilization of Orange OT (1-octylazo-2-naphthol) in potassium laurate solutions. A constant MR at a concentration above 0.15 M potassium laurate is typical of compounds such as dyes, fatty acids, and long chain alcohols. Another example of this second type is shown by McBain, Merrill, and Vinograd for the solubilization of Yellow AB (phenylazo-p-naphthylamine) in aqueous sodium desoxycholate solutions and also in lauryl sulfonic acid solutions (6). A relatively unrecognized case of this type of solubilization is the increase in solubility of insoluble calcium dodecyl sulfonate and calcium dodecyl sulfate in solutions of their corresponding sodium salts (7). Soap mixtures such as potassium laurate and potassium palmitate, and sodium laurate and sodium palmitate (8) should be also included in this group for the palmitate should be considered to be solubilized by the laurate.

These two sets of data indicate that solubilization begins in the region of the CMC. Below this concentration, the soap acts like an electrolyte causing a decrease in solubility of the hydrocarbon or the polar compound, such as another soap, below that in water due to a salting out effect. This has been shown to occur in the case of ethylbenzene in the presence of potassium laurate (1) and in the decrease in solubility of calcium dodecyl sulfonate in solutions of sodium dodecyl sulfonate below the CMC of the latter soap (7). It might be supposed that solubilization begins below the CMC as observed in the appearance of color in insoluble dye-soap below the CMC mixture (9). However, these amounts dissolved are so small, often only a few per cent more than is soluble

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Summary

Extensive analyses have been made of American and Australian woolwaxes. Combined hydroxy acids have been shown to be the most characteristic and important components of these waxes. Both contained considerable amounts (about 91.5% in the case of the American wax and 31.7% in the Australian sample) of diestolidic esters of the alcohol of the unsaponifiable fraction. This conclusion is supported by calculations of composition, by observations of viscosity and emulsifying properties, and by determinations of mean molecular weight by the Prahl method.

REFERENCES

1. E. S. Lowen, Landw. (woolwax) 1946.

Fig. 1. Solubilization of ethyl benzene (A) and Orange OT (B) in potassium laurate solutions (25°C.).
in water, that the individual dye molecule must be considered to be bound, at first, either by electro-static or van der Waals type of attractive forces, with an individual soap molecule.

The curves in Fig. 1 indicate that colloidal properties of potassium laurate start just above the CMC, 0.025 M, and that this soap in the presence of hydrocarbons reaches full colloidal form at about 0.15 M. It is probable that, in the region between the CMC and 0.15 M where the change in MR per unit soap concentration is greatest, both the size and number of solubilizing soap aggregates, probably micelles, increases. Above the concentration where the soap reaches its full colloidal form, there is probably no change in micelle size, considering only the soap molecules and not the solubilized materials, but only a change in number of micelles. Indirect evidence for this is obtained from the fact that the number of polymer particles formed in emulsion polymerization is directly a function of the amount of micellar soap used as emulsifier (10). The interpretation of this increase in solubilization of simple hydrocarbons, where MR increases with increasing soap concentration, is that there is more soap in micellar form at higher soap concentrations, and that the area and/or volume available per mole of a soap for solubilization of hydrocarbons is larger than that for polar compounds, as will be shown below. This follows the findings of Hartley (2) that the micelle concentration increases more rapidly than the total concentration, in which case some of the single long chain electrolyte ions present are incorporated into the micelles along with those added.

**Hydrocarbons**

The addition of hydrocarbons such as benzene and n-heptane to soap solutions is accompanied by an increase in the long spacing as determined by X-ray measurements (11-20). Kiessig and Philippoff have shown that the long spacing of a 9.12% solution of sodium oleate changes from 91 Å to 127 Å upon the addition of 0.791 gm. benzene per gm. oleate (14). Hughes, Sawyer, and Vinograd have reported that the increase in double layer thickness in potassium laurate solutions is a linear function of the molar volume of the liquid additive (18). The slope of this line is larger in the case of normal straight chain hydrocarbons than for substituted benzenes. Various authors assume a lamellar type of micelle with their long axes lying approximately parallel to the long spacing, in the case of soap-micelle solutions, as observed in the case of soap mixtures (12-16, 19). The equivalent change in spacing could be explained if the idea of the spherical micelle as advanced by Hartley (21) or of the double layer disc or oblate spheroid micelle is considered (22). These changes in spacing are shown in Fig. 2 for the case of 0.63 N potassium laurate saturated with ethyl benzene for two of the proposed structures (19). This increase in X-ray spacing has been reported only upon the addition of simple hydrocarbons such as benzene, n-heptane, etc. In this type of solubilization, the MR is always found to increase with increasing soap concentration above the CMC up to at least 1.0 M.

**Polar Compounds**

In the second type of solubilization where the MR is constant above the concentration where the soap reaches its full colloidal form, there should be no increase in the distance between adjacent layers upon the addition of a dye, a long chain fatty acid, a long chain alcohol, or another soap. The X-ray data of Mattoon have shown that the long spacings of mixtures of soap solutions are linear functions of the mole ratios of the two soaps (23). If this type of solubilization involved the closure of the material being solubilized in the hydrocarbon-like central region of the micelle, then one would expect an increase in spacing, in the case of the soap mixtures, which would at all times be larger than the reported linear variation of the long layer spacings. X-ray studies on mixed soap-fatty acid crystals show that the cell dimensions of the mixtures are equivalent to those of the pure soap (24). In addition, the critical concentration for the formation of micelles of soap mixtures lies between the CMC of the pure soaps (25). Preliminary reports of soap-fatty acid and soap-long chain alcohols indicate that there is no change in the long X-ray spacings of these mixtures (26, 27) as one would expect from the case of the soap-soap mixtures.

Thus, it appears that solubilization of this type involves the incorporation of the solubilized molecules with their long axes lying approximately parallel to those of the soap molecules. This can be exemplified further by considering the observed change in spacing in the case of soap mixtures (23). This change in long spacing is a linear function of the mole ratio of the mixtures. When two anionic detergents having the same anion but different cations as in the case where calcium and sodium dodecyl sulfate are mixed, no differences in spacing should be observed in solutions of each detergent alone and in solutions of their mixtures. Similarly, there should be no change in spacing for solutions of soap-fatty acid mixtures, and soap-long chain alcohol systems. According to this in-

![Fig. 2. Highly idealized schematic diagram of 0.63 N potassium laurate solutions showing effect of added ethyl benzene. Lamellar micelle of McBain and spherical micelle as pictured by Hartley are shown.](image-url)