[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Soap Micelles that Solubilize Dimethyl Phthalate, a Liquid Insoluble in Water and in Hydrocarbon

BY JAMES W. McBAIN AND HARRIETTE McHAN[1]

It has commonly been supposed that solubilization by aqueous soap solution is somehow concerned with similarity to or solubility in the hydrocarbon portion of the soap molecule. Hartley suggested that it might even be mere solution[1a] in the hydrocarbon tails of the detergent. However, the original German[2] X-ray studies, from which a typical diagram is taken in Fig. 1, have indicated that usually much of the solubilization occurs in layers within the lamellar X-ray micelles.

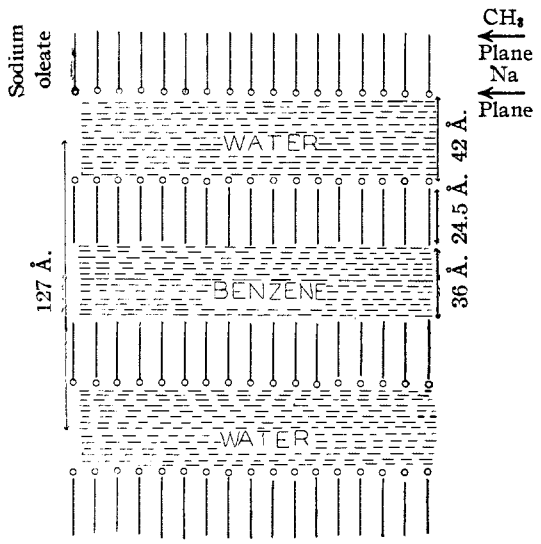

Fig. 1.—Schematic diagram of a micelle in 9.12 wt. % sodium oleate solution with 0.791 g. benzene/g. oleate.

Hughes, Sawyer and Vinograd[3] were able to show from the effect upon the intensity of the long spacing corresponding to the total thickness of the micelles, that the solubilizing material occupied a middle layer between the two layers of soap, just as in Fig. 1. By suitable alteration of the solubilized material they could enhance the intensity of the long spacing, leave its intensity almost unchanged, while its length was increased, as in Fig. 1, or even reduce the intensity through zero and bring it back again with further excess of solubilized material. This would appear to be conclusive proof of that interpretation and to negative the more recent suggestion of Mattoon, Stearns and Harkins[4] that the long spacing has nothing to do with the structure of the micelle but is purely intermicellar and not intramicellar. Their previous work endorsed the interpretation of the German pioneers in this field.

For the present purpose it was of importance to find a substance insoluble in water and insoluble in hydrocarbon which yet had a sufficiently low molecular weight to be freely solubilized by a soap such as potassium laurate. Dimethyl phthalate is such a substance. Its solubility is 0.42 g. in 100 cc. of water. It is soluble to the extent of only 3.70 g. in 100 cc. of pure *n*-dodecane at 25° (and 3.6 g. in *n*-decane). Hence, if it is readily solubilized, this cannot be attributed to solubility in hydrocarbon.

In 0.1 *N* potassium laurate, dimethyl phthalate (Eastman Kodak Company) is soluble to the extent of 1.99 g. in 100 cc. of the soap solution. Corrected for the solubility in water this leaves no less than 1.57 g. solubilized in 100 cc. of aqueous soap.

Considering these data on a mole to mole basis it is seen that the solubility of dimethyl phthalate in dodecane is only 0.042 mole to 1 mole dodecane, whereas it is 0.80 mole per mole of potassium laurate (with the same number of carbon atoms), an increase of nineteen times the solubility in the hydrocarbon. Hence it is impossible for the dimethyl phthalate to be solubilized by dissolving in the hydrocarbon. If reckoned upon pure dry soap, 100 g. of potassium laurate solubilized 66 g. of phthalate.

Solubilization is at a maximum for a concentration of 0.1 *N*, the variation with concentration for 100 cc. of solution being 0.46 g. in 0.04 *N* potassium laurate, 1.57 in 0.1 *N* and 3.02 g. in 0.25 *N*; or on a mole to mole basis, 0.59, 0.80 and 0.63, respectively.

Now the question remains as to where this solubilized dimethyl phthalate is situated. One way of testing this is to measure the solubility in the corresponding polar liquid with the same number of carbon atoms; namely, pure *n*-dodecyl alcohol, and it is found that its solubility is 32.5 g. of dimethyl phthalate in 100 cc. of the lauryl alcohol, or 0.37 mole per mole. Hence the solubility is evidently due to the polar groups and may well be due to hydrogen bonding. Therefore, if the dimethyl phthalate is solubilized in lamellar micelles it must be attached to the external or polar groups of the soap molecules.

However, it is well known that solubilization is not quantitatively proportional to[3,5] the expansion of X-ray micelles, but that some solubilization

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(1a) Hartley, *J. Chem. Soc.*, 1868 (1938).

(2) Hess and Gundermann, *Ber.*, **70**, 1800 (1937); Hess, Kiessig and Philippoff, *Naturwiss.*, **26**, 184 (1938); Kiessig and Philippoff, *ibid.*, **27**, 593 (1939); Hess, Philippoff and Kiessig, *Koll. Z.*, **88**, 40 (1939); Stauff, *ibid.*, **89**, 224 (1939); Kiessig, *ibid.*, **96**, 252 (1941); Stauff, *ibid.*, **96**, 244 (1941); Philippoff, *ibid.*, **96**, 255 (1941).

(3) Hughes, Sawyer and Vinograd, *J. Chem. Phys.*, **13**, 131 (1945).

(4) Mattoon, Stearns and Harkins, *ibid.*, **15**, 209 (1947).

(5) Harkins, Mattoon and Corrin, *J. Coll. Sci.*, **1**, 105 (1946).

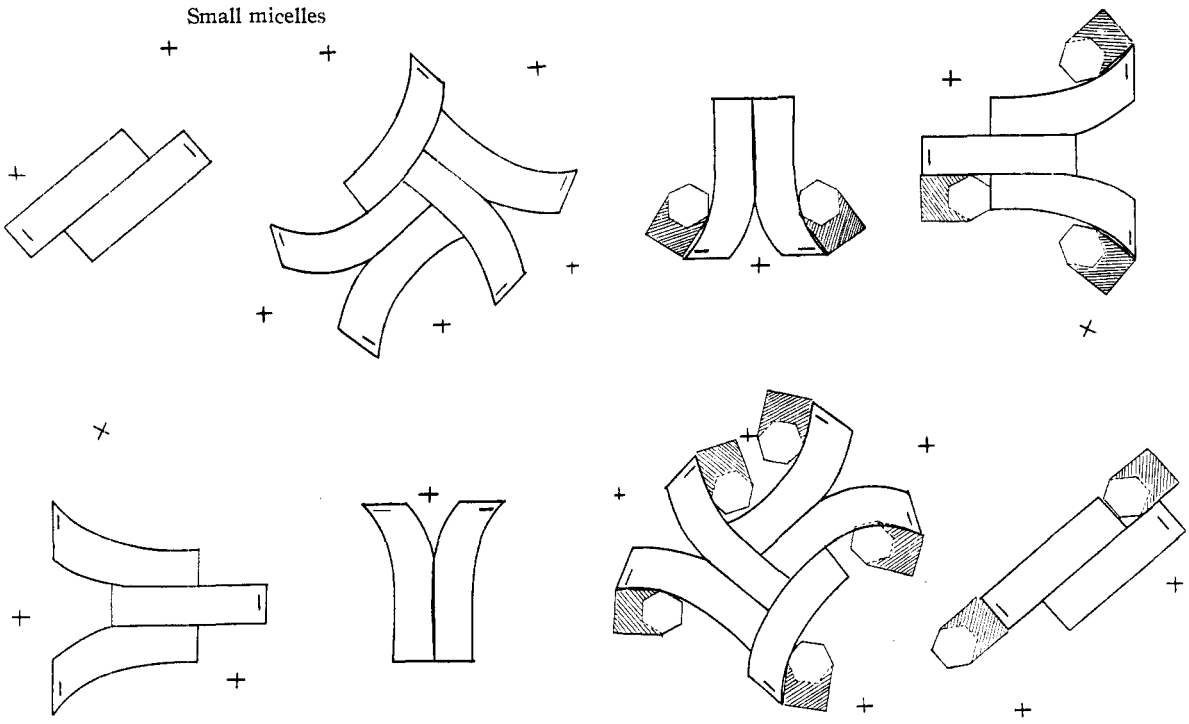

Fig. 2a. Fig. 2b.

Fig. 2(a).—Type of smaller micelles probably existing in less concentrated solutions of colloidal electrolytes, precursors of the lamellar micelles that predominate in more concentration solution. (Fig. 2(b)) Scale diagram of solubilization of dimethyl phthalate molecules by polar groups of small micelles.

must be by other micelles that escape X-ray examination. Dilute solutions contain small micelles of various shapes and sizes, whereas lamellar micelles become predominant in more concentrated solutions. We may suggest that the small micelles and the spherical micelles of McBain and others could solubilize dimethyl phthalate in the manner indicated in Fig. 2 where the polar groups are brought into contact with each other and are simultaneously hydrated.

X-Ray examination of these solutions by O. A. Hoffman[6] in this Laboratory, show that the *intensity* of the lines corresponding to the long spacings of lamellar micelles is much reduced by the presence of dimethyl phthalate, although the *spacing* remains sharp and almost constant, indicating that they are being replaced by other micelles, presumably those characteristic of more dilute solutions. The long spacing in 1.47 N potassium laurate is reduced from 47.58 to 45.79 Å. Mrs. Ann Cushman in this Laboratory finds by the Beckmann freezing point method that the osmotic coefficient of potassium laurate is altered from 0.406, 0.188 and 0.151 to 0.434, 0.210 and 0.173 for 0.1, 0.26 and 1.0 molal potassium laurate after correcting for the solubility of dimethyl phthalate in water. This is a uniform increase of 0.02 in osmotic coefficient in each case, again indicating the formation of more numerous smaller micelles.

(6) McBain and Hoffman, presented at the 22nd Colloid Symposium, M. I. T., June, 1948.

Similarly Mrs. Cushman found for conductivity that this increases from 47.47 and 45.88 to 53.00 and 50.42 for 0.1 N and 0.26 N potassium laurate, respectively, although in 0.74 N solution the change is in the opposite direction from 51.95 to 46.20 and in 1.0 N from 50.31 to 42.88. For 0.5 N the change is from 49.20 to 47.70. The viscosity of potassium laurate solution is markedly increased by the addition of dimethyl phthalate for 0.1 N solution, this being a change from 0.01059 to 0.01221 poise. This may account for the reversal of sign in the change of conductivity in the more concentrated solution.

Finally, and very significantly, we find that the solubilization of dimethyl phthalate by potassium laurate is lowered by the addition of potassium chloride. The mole ratio of solubilized dimethyl phthalate to potassium laurate in 0.1 N solution, 0.80, decreases to 0.60 in the presence of 1 N potassium chloride, since potassium chloride favors formation of lamellar micelles.

McBain and Richards[7] found that although hydrocarbons and many other related substances are solubilized much more strongly in the presence of salts, salts greatly depressed the solubilization of the polar compounds, octyl alcohol and benzaldehyde. Quite probably similar mechanisms are responsible in all these cases. Hydrocarbons are definitely solubilized at least partly between the hydrocarbon layers of the detergent but these

(7) Richards and McBain, THIS JOURNAL, **70**, 1338 (1948).

polar compounds must be associated with the polar groups of the detergent.

The non-ionic detergent Triton X-100 in 0.1 *N* solution also solubilized dimethyl phthalate, with a mole ratio of 0.6, which again decreases very rapidly upon the addition of potassium chloride, to 0.14 with 1 *N* potassium chloride, and yields no X-ray evidence for the presence of lamellar micelles after the addition of phthalate (S. S. Marsden, Jr.). However, the phthalate and isopropylbenzene are miscible in all proportions, which may account for this ratio of solubility due to similarity of structure. A cation active detergent, laurylpyridinium chloride, in 0.02954 *N* solution, yielded a mole ratio of 0.76.

To sum up, dimethyl phthalate, with very low solubility in water and in hydrocarbon, is freely solubilized by aqueous potassium laurate, showing that it is not dissolved or solubilized by the hydrocarbon part of the detergent. Dimethyl phthalate is, however, freely soluble in dodecyl alcohol, which shows that the solubilization is a function of the polar groups of the detergent molecule. Furthermore, the solubilization is depressed by the addition of salts, whereas that of hydrocarbons and other organic liquids is increased by salts. The solubilization of dimethyl phthalate is therefore ascribable to the small micelles characteristic of dilute solutions, such as the ionic micelle of McBain, and not to the lamellar micelles favored by addition of salts and predominant in more concentrated solutions. The disparity in size of the phthalate molecule and the detergent, and the necessity of keeping the polar groups together practically precludes the possibility of interpenetration, as is clear from Fig. 2(b).

Summary

Potassium laurate in decinormal solution solubilizes twenty times as much dimethyl phthalate as could be dissolved in the same weight of hydrocarbon. This therefore cannot be attributed to solubility in the hydrocarbon tails of the soap, nor in the hydrocarbon interior of spherical micelles. However, the phthalate is fairly soluble in polar compounds. Its solubility is therefore ascribed to adsorption on *exterior* polar groups of the small micelles. This is supported by X-ray evidence, the depressing influence of added salts (which normally promote formation of lamellar micelles), and the much lower relative solubilization in higher concentrations of soap. Some detergents do not form lamellar micelles in any concentration, others do in more concentrated solutions, whereas in more dilute solutions, small micelles preponderate, such as the McBain ionic micelles or fragments or nuclei of lamellar micelles, and it is these that solubilize dimethyl phthalate.

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The Quantitative Determination of C^{14} Activity in Biological Systems by Direct Plating[1]

BY JOHN R. HOGNESS, LLOYD J. ROTH, EDGAR LEIFER AND WRIGHT H. LANGHAM

With the increased use of C^{14} tagged compounds in biological tracer studies a direct method for rapid and quantitative determination of radioactivity in biological fluids becomes important.

One useful but tedious method involves combustion of the organic material in such fluids as blood, plasma and urine, collection of the carbon dioxide and the precipitation on suitable plates as barium carbonate according to the method described by Yankwich.[1a] This method implies that the C^{14} containing compound under study be similarly assayed by combustion and counting as barium carbonate.

A more rapid method involves the direct plating of aliquots of the biological fluids themselves onto suitable counting discs and subsequent determination of radioactivity with a thin mica window G.M. tube. Such a method becomes most useful when large numbers of samples of urine and other biological fluids are to be analyzed. This report describes a method that has been used in some of the studies of the metabolism of nicotinic acid and related compounds in this Laboratory.[2,3] It became apparent, however, that for valid interpretation of the measured activity obtained in this manner suitable calibration is essential. Calibration curves must be made for different biological fluids used as well as for all radioactive isotopes employed as tracer substances. Obviously the method is applicable only to solids with low vapor pressures at 100°, *e. g.* 25–50% of radioactive urea is lost during the direct plating of a water solution.

Method

The method of direct plating described in this paper is essentially that used at the Donner Laboratory of the University of California for determining activity in organic solvents.[4] We have found the method satisfactory for the

(1) This document is based on work performed under Contract Number W-7405-eng-36 for the Atomic Energy Commission.

(1a) Peter E. Yankwich, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **19**, 439–441 (1947).

(2) L. J. Roth, E. Leifer, J. R. Hogness and W. Langham, *J. Biol. Chem.*, **176**, 249 (1948).

(3) E. Leifer, J. R. Hogness, L. J. Roth and W. Langham, THIS JOURNAL, **70**, 2908 (1948).

(4) Melvin Calvin, University of California, Berkeley, Calif., private communication.