

## A Cylindrical Model for the Small Soap Micelle

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We are also indebted to Mr. B. W. Bullock for valuable help in experimental matters. In conclusion we express our appreciation to Professor D. M. Dennison and Dr. E. O. Salant for their interest and many valuable discussions.

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<sup>1</sup> For an extensive bibliography, see Jean Lecomte, *Le Spectre Infrarouge* (Les Presses Universitaires de France, Paris, 1928), and A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman Hall Limited, London, 1942).

<sup>2</sup> E. K. Plyler, J. Opt. Soc. Am. **37**, 984A (1947).

<sup>3</sup> H. Rubens and E. Aschkinass, Wied. Ann. **64**, 584 (1898).

<sup>4</sup> W. E. Garner and C. H. Johnson, Phil. Mag. **3**, 97 (1927); C. R. Bailey and A. H. Lih, Trans. Faraday Soc. **25**, 29 (1929).

### A Cylindrical Model for the Small Soap Micelle\*

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December 16, 1947

THE model presented here (Fig. 1) is based on extensive papers on x-ray relations by Mattoon, Stearns, and Harkins,<sup>1</sup> and on a great deal of other work by Corrin, Oppenheimer, Mittelman, Herzfeld, Roginsky, and Lind.

A quotation from a Cambridge University Symposium<sup>2</sup> (1947) is as follows:

There are different schools of thought on these matters, for example McBain postulates two types of micelle, "ionic" and "neutral," Hartley only one, the "spherical" ionic micelle. The latter view is now generally accepted, and will be followed here.

McBain's views are expressed more accurately in his 1942 review.<sup>3</sup> His ionic micelle is spherical (adopted by Hartley) and his neutral micelle identical with Stauff's "Grossmizellen" or lamellar micelles.

Soap micelles are:

1. Small.

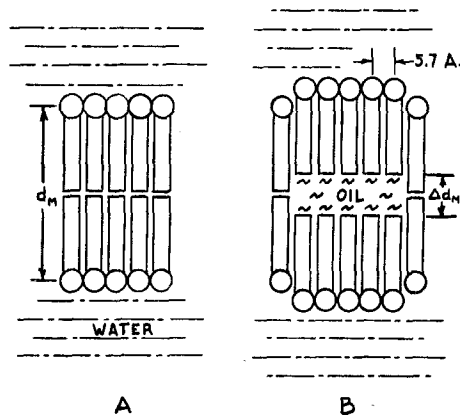


FIG. 1. Highly idealized cross section of a soap micelle. A. Without solubilized oil. B. With solubilized oil. The solubilization of an oil is found to increase the number of soap molecules in the micelle. Although a cylinder seems to represent most of the properties of the micelle as now known, it is imperfect in that it represents too large an interface at the side between hydrocarbon groups and water. Thus it seems not improbable that a model which lies between a cylinder and a cylindrical type of spheroid may be found to more perfectly represent the energy relationships. This would amount to a distortion of the side of the cylinder by means of which polar groups cover to some extent the non-polar hydrocarbon chains.

2. Not spherical and exhibit a thickness, as measured by a new x-ray *M*-band,<sup>4</sup> equal to the double length of the molecule.

3. This thickness is increased by the solubilization of a non-polar oil, but not by alcohols or amines.

4. When a salt is added the critical micelle concentration is decreased, the micelle size increased by increase in the diameter of the cylinder, and the principle of ionic strength and Debye-Hückel theory becomes invalid (Corrin and Harkins<sup>4</sup>).

5. The number of soap molecules per micelle is increased by solubilization of an oil and by long chain alcohols and amines.

By diffusion Hartley<sup>5</sup> found the cetyl pyridinium chloride micelle to be small and to contain about 70 molecules. Our x-ray work on different detergents indicates sizes of this order, but both smaller and considerably larger.

Our earlier x-ray work appeared to favor the lamellar model of McBain and German investigators,<sup>3b,c</sup> which consists of 5 or 6 large double layers of soap with interlayers of water of definite thickness ( $\tau$ ) as calculated from our data for potassium myristate.

After a long and intensive study, in an endeavor to find a mechanism which would control the interlayer or "bound" water in this way, the writer concluded that there is no such mechanism, and that these water layers are non-existent, but instead each double layer of molecules is a micelle and moves *freely* as a large "molecule" through the solution, until a second critical concentration (*ca.* 7 percent for potassium myristate) is reached. Above this concentration each double layer is a micelle, but the micelles now come closely enough together to restrict their motion (libration or rotation) so that above this concentration the x-ray *I*-band appears. This is related to the distance between the micelles.

Calculations of the thickness ( $\tau$ ) of the oil layer solubilized by the micelle, as made by the writer, proved incorrect the conception of this process as related to the lamellar model. Those who developed this model assumed (McBain's review, p. 124) that the increment ( $\Delta d_l$ ) in the long spacing due to the oil gives the thickness of the oil layer. The mean thickness ( $\tau$ ) should equal the volume of oil in the micelles divided by the area of the large double soap layers, which is known, since each pair of molecules occupies 28 sq.Å. In calculations for *n*-heptane, triptane, and ethyl benzene the mean thickness ( $\tau$ ) was found at all

Percent soap	Water layer thickness $\tau$ in Å
8	34
10	31.7
15	26.3
20	22.5
25	19.6
30	17.2
35	15.2

concentrations of the oils to be only 0.4 as large as  $\Delta d_l$ . For example, for 3.5 percent *n*-heptane in 25 percent potassium laurate  $\tau = 5.5\text{Å}$  but  $\Delta d_l = 13.6\text{Å}$  or 2.5 times larger than it should be. It was concluded that  $\Delta d_l$  is not the distance

between layers in a lamellar micelle, but the change in the intermicellar distance ( $d_I$ ).

With respect to solubilization, Corrin found that Hartley's spherical model gave much better agreement than this.

The cylindrical model is superior in that its height is measured by the  $M$ - or micelle thickness band, and it has a diameter which may be varied and can be calculated approximately at high concentrations from the  $I$ -band, or at low concentrations from light scattering (Debye).

In any model the energy relations make it essential to make the interface hydrocarbon chains-water as small as possible, which means that the cylinder may be somewhat distorted at the side to give coverage of the hydrocarbon chains by a few polar-ionic groups of the soap. However, the model is essentially a cylinder with these groups at the ends.

\* This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the government's synthetic rubber program.

<sup>1a</sup> R. W. Mattoon, R. S. Stearns, and W. D. Harkins, submitted for publication (September, 1947); <sup>b</sup> *ibid.* J. Chem. Phys. 15, 209 (1947); <sup>c</sup> W. D. Harkins, R. W. Mattoon, and R. Mittelman, *ibid.* 15, 763 (1947).

<sup>2</sup> A. E. Alexander, *Colloid Science, A Symposium* (Chemical Publishing Company, Inc., Brooklyn, 1947), p. 43. McBain now considers the "neutral" micelle to be the somewhat ionized "large lamellar micelle."

<sup>3a</sup> J. W. McBain, *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1942), edited by E. O. Kraemer, p. 124, for extensive references to work on the "large lamellar micelle" see; <sup>b</sup> W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Am. Chem. Soc. 68, 220 (1946), and <sup>c</sup> J. Colloid Sci. 1, 105 (1946).

<sup>4</sup> M. L. Corrin and W. D. Harkins, J. Am. Chem. Soc. 68, 679, 683 (1947).

<sup>5</sup> G. S. Hartley and D. M. Runnicles, Proc. Roy. Soc. A168, 420 (1938).

## The Solubility of Sodium Soap in Organic Solvents

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November 18, 1947

THE solubility of sodium palmitate and sodium stearate in organic solvents has been determined by several members of the Stanford Group.<sup>1-3</sup> These data seem rather difficult to correlate with each other or with other solubility data. The latter is usually most fruitful if the comparison is made on the basis of Hildebrand's relation:

$$\ln a_2 = -\frac{\Delta H_f}{R} \left( \frac{1}{T} - \frac{1}{T_f} \right),$$

where  $\Delta H_f$  the heat of fusion (or transition) and  $T_f$  the melting (or transition) temperature.<sup>4,5</sup>

In view of the fact that the sodium soaps exhibit not only a melting point but a series of transition points in the solid state, the ideal solubility curve changes its slope at as many points. The transition points and the transition heats have been determined by Vold.<sup>6</sup> It is therefore possible to construct the ideal solubility curve of these soaps. Such a curve for sodium palmitate is shown—marked "ideal"—on Fig. 1. The other curves on the same figure are the so-called  $T_i$  curves,<sup>7</sup> giving the temperature at which the isotropic melt changes into an anisotropic liquid crystal. The proximity of several curves to the Raoult's law curve is rather surprising, since one usually associates "ideality" with simpler physical behavior. It

should be noted that the slope of all solutions in hydroxylic compounds deviates in the low temperature (<180°C) region but little from the slope of the ideal curve, while the slope of the other solutions, particularly in hydrocarbons, is very much steeper. This suggests that the excess free energy of mixing with the alcohols consists of a negligible heat of mixing and a strongly negative entropy of mixing. The solution of soap in hydrocarbons requires on the other hand both rather large (negative) enthalpy and entropy changes. One would hardly have expected that the solubility of stearic acid in similar solvents deviates more from ideality than that of soap, as is evident from the data on Fig. 2. This applies particularly to alcoholic solutions.

In the high temperature region all solutions behave quite similarly in exhibiting solid solution phenomena, as is also apparent in visual observation of these systems. The effect of chemical structure of the solvent on the shape of the solubility curve is sometimes quite marked, as e.g., in the case of the cresols. The position of *p*-cresol solutions is given on the graph. The solubility curve of soap in *o*-cresol, on the other hand, is practically identical with that of cetyl alcohol and has, therefore, not been drawn in. In other cases there is little specificity as is exemplified by the solubility in cyclohexane and in low mole weight aromatic hydrocarbons, or cetane and white medicinal oil.

The humps in the solubility curves which are observed in soap solutions in cyclic (low molecular weight) hydrocarbons, in water, and in glycerol are somewhat reminiscent of the shape of solubility curves of systems forming two immiscible liquid phases in a certain temperature range. While presentation of the soap solubility data in the

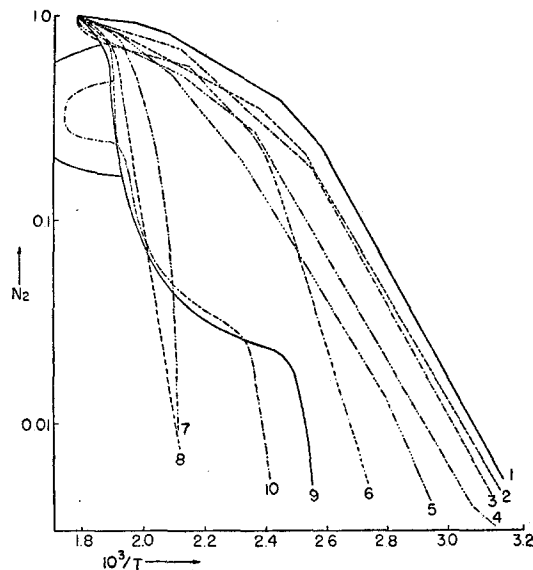


FIG. 1. Solubility of sodium palmitate in various organic solvents (from data of references 1, 2, 3) compared with ideal solubility curve (1).

- |                       |                                       |
|-----------------------|---------------------------------------|
| (1) Ideal solubility  | (6) <i>n</i> -butylamine              |
| (2) <i>p</i> -cresol  | (7) <i>n</i> -cetane                  |
| (3) Diethylene glycol | (8) Nujol                             |
| (4) Ethyl alcohol     | (9) Cyclohexane, sodium stearate in   |
| (5) Cetyl alcohol     | (10) Ethylbenzene, sodium stearate in |