

Structure of Soap Micelles as Indicated by X-Rays and Interpreted by the Theory of Molecular Orientation II. The Solubilization of Hydrocarbons and Other Oils in Aqueous Soap Solutions

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several cases, particularly methane, acetylene, benzene, and ethylene, the applications involve symmetry types of isotopic molecules of different total symmetry. Perhaps one reason that such applications are not more common is the chemical problem of preparing the isotopic molecules. Because of the equivalence of various members of a point set, many chemical reactions exchange all of them, thus retaining the symmetry of the original molecule. This is particularly true if a relatively pure deuterated product is desired.*

¹ W. F. Edgell, J. Chem. Phys. 13, 337 (1945).

² Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 231.

³ Langseth and Lord, Kgl. Danske Vid. Sels. Math.-Fys. Medd. 16, No. 6 (1938).

⁴ Hibben, *The Raman Effect and its Chemical Applications* (Reinhold Publishing Corporation, New York, 1939), p. 117. Some of this portion was written by E. Teller.

⁵ M. de Hemptinne, Jungers, and Delfosse, J. Chem. Phys. 6, 319 (1938).

⁶ Halverson, "The Use of Deuterium in the Analysis of Molecular Spectra" (Dissertation, The Johns Hopkins University, 1943). A condensed version in the form of a review paper covering all deuterated polyatomic molecules studied spectroscopically up to 1945 is to be submitted for publication in the near future.

* The earliest application of the product rule in this manner known by the author is in a paper by Redlich and Stricks, *Monats.* 68, 374 (1936), on some deuterated benzenes.

Structure of Soap Micelles as Indicated by X-Rays and Interpreted by the Theory of Molecular Orientation

II. The Solubilization of Hydrocarbons and Other Oils in Aqueous Soap Solutions

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October 15, 1945

IN emulsion polymerization the principal locus for the formation of polymer particle nuclei is initially in the monomer oil layers of the soap micelles¹ present in the aqueous phase. Thus, it is of interest to consider the relations and the structure of these oil layers.

The long or layer spacing (d) of the micelles as determined by x-ray measurements may be represented by either a linear (1) or a logarithmic Eq. (2), as follows:

$$d = b - ac, \quad (1)$$

$$d = k_1 + k_2 \log (1/c), \quad (2)$$

where c is the weight fraction of soap in the solution.

When a soap solution is shaken with a water-insoluble oil, the layer spacing (d) is increased by an amount (Δd) presumably caused by the inclusion of a thin layer of oil (Fig. 1) between the hydrocarbon ends of the soap molecules and a resulting expansion of the micelle in a direction perpendicular to the layers. At present the following relations are exhibited.

1. For ethyl benzene in saturated solutions at room temperature Δd is constant at 14.9 Å within the limits of error of the x-ray measurements over a concentration range of from 7 to 23 percent aqueous potassium laurate.

2. For undersaturated solutions Δd (and τ introduced later) is linear with respect to the amount of oil dissolved,

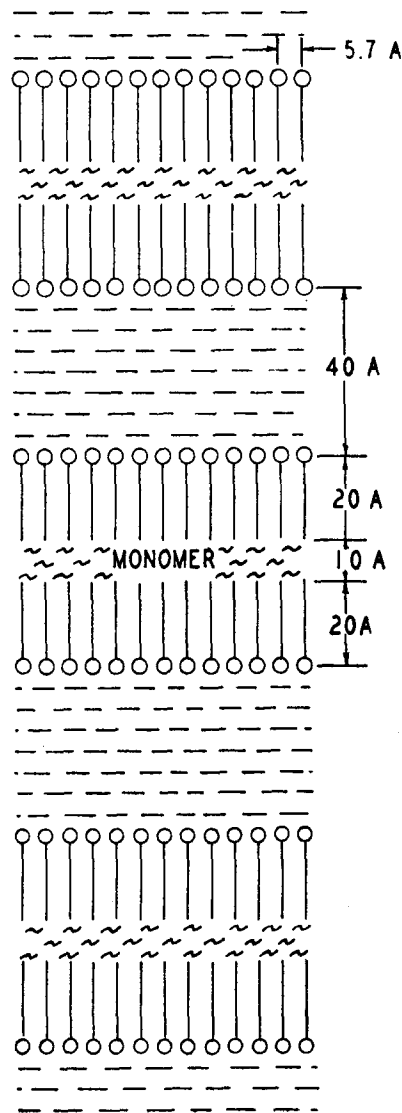


FIG. 1. Highly idealized structure of a soap micelle. Dashes represent aqueous layers.

or $\Delta d = kW$ where W is the weight of oil per 100 g of soap solution. For ethyl benzene k is 3.5 and for n -heptane 3.82.

3. The value of Δd for saturated solutions of normal hydrocarbons in 15 to 25 percent aqueous potassium laurate at 25°C decreases from 15.5 Å for n -hexane (6 C) to 8.0 for dodecane (12 C). Thus, the value of Δd at saturation decreases rapidly with the length of the molecule.

The chain-to-chain distance in micelles of pure soaps as calculated from the Bragg spacing varies from 4.6 to 4.7 Å. Since this distance is not increased, within the accuracy of the measurements, by the presence of styrene, ethyl benzene, isoprene, n -heptane, etc., little, if any, of the oil lies between the chains. In this direction the area per chain for close packing is 27 sq. Å, but the mean area per chain

is greater than this, since the structure is that of a liquid in the direction of the chain-to-chain spacing. The apparent density of the solubilized oil, mostly in these thin oil layers, differs but little from the bulk density of the oil. Thus, *n*-heptane has a bulk density of 0.67981₆ g/cc at 25°C; this is equal to its apparent density in its saturated solution in 25 percent potassium laurate solution. With only a tenth as much heptane present the apparent density is only very slightly higher (0.68843₄ g/cc).

An important question now arises: is the mean thickness (τ) of the oil layer equal to the x-ray layer spacing increment (Δd)?

The apparent mean thickness, τ , is calculated by dividing the volume of oil present by the total area of the double soap layers of the micelles (Σ). This area (Σ) is the product of the area per soap molecule (30 sq. Å) and $N/2$ where N is the number of soap molecules in micelles. The following relations emerge:

1. The ratio of $\tau/\Delta d$ for saturated solutions of ethyl benzene in aqueous potassium laurate increases linearly from 0.60 to 8.8 percent soap to 0.87 at 23.0 percent soap.

2. In 25 percent aqueous potassium laurate $\tau/\Delta d$ is 0.83 for ethyl benzene; 0.60 for styrene; 0.41 for *n*-heptane; and even smaller for lauryl mercaptan.

The wide divergence between τ and Δd may be attributed to several causes. Thus, it is not improbable that the activity of both the soap and the aqueous phase is changed by the addition of an oil with a consequent thickening of the micelle water layer. The molecular area of soap in the double layer is known to remain unchanged on the addition of many oils, such as hydrocarbons, etc. It is, however, affected by certain other oils such as lead tetrethyl and carbon tetrachloride, but these also give anomalous effects with respect to the layer spacing.

¹ W. D. Harkins, J. Chem. Phys. 13, 381 (1945).

A First-Order Change which Involves the Vaporization in Two Dimensions of *N*-Heptane on the Surface of Silver*

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October 4, 1945

IN an extensive investigation of the behavior of films on *n*-heptane on the surfaces of metals a reversible first-order vaporization-condensation has been found on silver. This is of interest because changes of this order not only have never before been found on the surface of a solid, but also because many experts in the field of adsorption have doubted that such changes can occur. In most phase changes in films on solids, as well as on water, there is no heat of transformation; i.e., the changes are of the second order. Vaporization in two dimensions of oil films on the surface of water commonly involve such a heat (first order) but under certain conditions may exhibit no heat of transformation (second order). The order of such

changes has been considered by Dervichian¹ and by Harkins.²

The first-order change occurs on silver at a pressure of 0.019 mm and a temperature of $14.90 \pm 0.05^\circ\text{C}$. However, it is not found at 25°C , so this must be above the critical temperature for the change. The relations are exhibited in Fig. 1 with volume (v) and three-dimensional vapor pressure (p) as variables, and in Fig. 2 in terms of film

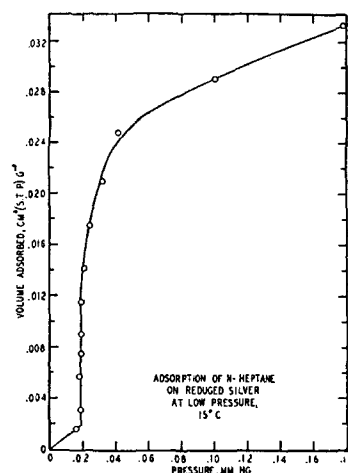


FIG. 1. The adsorption isotherm in the low pressure region of *n*-heptane on silver at 14.90°C . The first-order transition is represented by the vertical line at a pressure of 0.019 mm Hg.

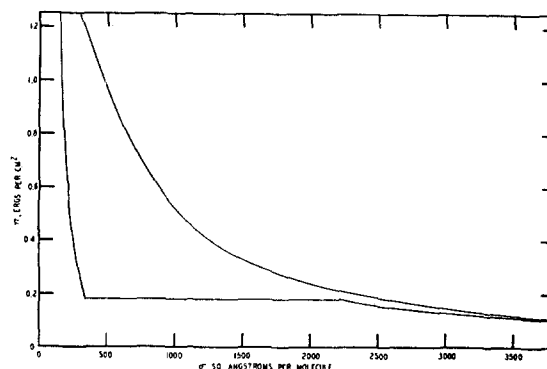


FIG. 2. The pressure-molecular area (π - σ) isotherms of the film of *n*-heptane on silver at 14.90° and 25.00°C . The latter is above the critical temperature of the first-order transition.

pressure (π) and molecular area (σ). The volume adsorbed varies from 0.00194 to 0.01380 cm³ g⁻¹, while the area per molecule varies from 310 to 2200 Å² at a film pressure of 0.18 dyne cm⁻¹.

These relations are much the same as those found in the two-dimensional vaporization on the surface of water of a film of oil in which the liquid expanded phase changes into vapor. While the critical constants for the change on silver have not been determined, the following relations