

A New Type of Micelle: Solubility by Film Penetration

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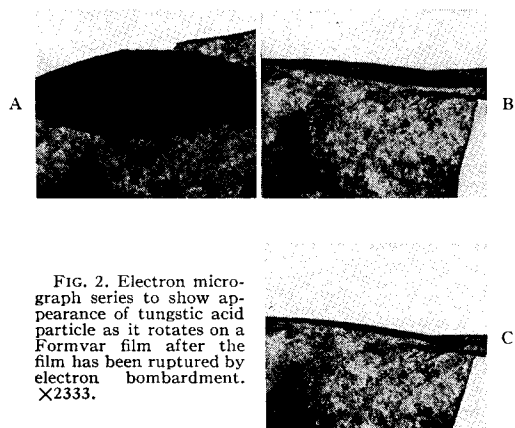


FIG. 2. Electron micrograph series to show appearance of tungstic acid particle as it rotates on a Formvar film after the film has been ruptured by electron bombardment. $\times 2333$.

minor axis, and thickness of the elliptical platelets (only one is shown) are 11.7, 4.05, and 0.15 microns, respectively, (ratio: 100:35:1.3). The mean dimensions of the length, width, and thickness of 21 rectangular crystals (taken from a differently treated suspension) of which a few are shown in Fig. 1B are 2.27, 0.75, and 0.044 microns, respectively, (ratio: 100:33:1.95). The results show that both types of particles are very thin. This follows for the particles of type *D* also directly from the fact that a small carbon particle adjacent to one of these crystals casts part of its shadow onto the crystal (arrow).

A decrease in the azimuth between the plane of the preparation and the direction of the beam of metal atoms improves the differentiation between particles of slightly different thicknesses, but it reduces the accuracy of absolute thickness determinations. Because of the very acute angle necessary in the above experiments, an attempt was made to work out a method for direct thickness determinations. The procedure adopted is as follows: The supporting film is subjected to a concentrated electron bombardment near the particle selected for thickness determinations. If the conditions are suitable, the film ruptures in a direction parallel to the longest axis of the particle and begins to curl up because of internal strain. When the particle adheres firmly to the film, the net result is a rotation of the particle about its longest axis, i.e., about an axis perpendicular to the electron beam. Figures 2A, B, and C show a particle of type *B*, just prior to rotation, after a rotation by 80° and after a rotation by 90° , respectively. The particle which is 14.6μ long and 5.0μ wide,



FIG. 3. Electron micrograph of a tungstic acid (oxide?) crystal curling up with Formvar film. $\times 2667$.

has, according to Fig. 2 and considering the end sections, a maximum thickness of 0.350μ . This leads to a dimensional ratio of 100:34:2.4. As regards the apparent thickening of the particle towards the center, in Fig. 2C, it is not possible at the present time to state whether this is real, i.e., whether it indicates a slightly elliptical shape perpendicular to the plane of the particles or is rather due to a deviation (by $\pm 2^\circ$) from 90° . A slight shortening of the shadow in Fig. 1A towards the end section is an argument in favor of the former possibility.

An application of this method to particles of type *D* failed, because, surprisingly, the thin crystals curled up together with the film (Fig. 3). The new method is therefore, in suitable cases, useful also for a rough comparison of the rigidity of colloiddally thin crystals.

Considering the fact that the particles of type *A* and *D*, illustrated in Figs. 1 and 2, were taken from suspensions of different original pH at different stages of aging with a resulting appreciable difference in their absolute dimensions,² it is interesting to note that the ratios length/thickness differ at the most by a factor of 2 and the ratios length/width differ by a factor of less than 0.1. Particularly noteworthy is the fact that the absolute mean thicknesses of the particles of type *A* considered above are of the same order of magnitude as the dimensions of the steps in the contours of such particles.¹

¹ J. H. L. Watson, W. Heller, and W. Wojtowicz, *J. Chem. Phys.* **16**, 997 (1948).

² W. Heller, W. Wojtowicz, and J. H. L. Watson, *J. Chem. Phys.* **16**, 998 (1948).

A New Type of Micelle: Solubility by Film Penetration*

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August 3, 1948

THE existence of a new type of soap micelle is demonstrated by earlier x-ray work¹ which proved that a *n*-long paraffin chain alcohol, amine, or another polar-non-polar molecule can penetrate the film of a soap micelle without increasing its thickness. In later work it has been found that with certain lengths of the paraffin chain of the detergent and the polar-non-polar compound the micelle even becomes a few angstroms thinner than that of the pure detergent.

This new phenomenon is entirely different from solubilization in which the micelle is thickened by as much as 12A or even more, since the solubilized hydrocarbon is located between the ends of the hydrocarbon chains, whereas the polar-non-polar molecules line up with the soap molecules with their polar groups toward the water.

It is obvious that if all of this is true the solubility relations exhibited in film penetration should be entirely different from and much more complicated than those in solubilization. That this is true has been shown by extensive work. It would be extremely unfortunate if such entirely different phenomena were to be designated by a single term. If the term film penetration is too lengthy, then *penetration* may be used.

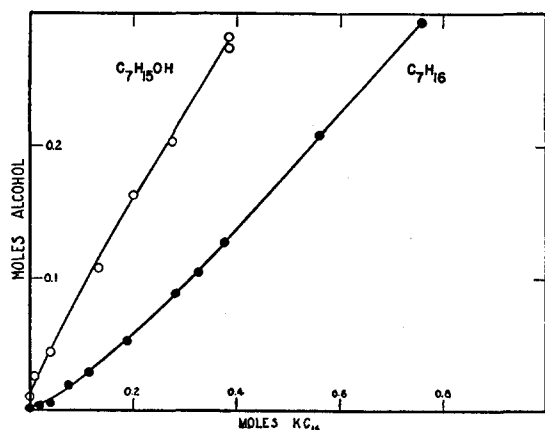


FIG. 1.

Thus we have solubility in micelles caused by *solubilization* and by *penetration*. That the latter may exhibit a greater effect is shown by Fig. 1 which in the lower curve gives the molal concentration of *heptane* (y axis) as a function of the concentration of potassium tetradecanoate. The solubility by penetration is from two to five times greater for the 7-carbon alcohol than by solubilization of the 7-carbon atom hydrocarbon. Also the curve for penetration is concave toward the soap concentration (x) axis, whereas that for solubilization is convex.

The great differences in solubility relations are illustrated in a striking way by Figs. 2 and 3. For example, in Fig. 2 the solubility by penetration of the 12-carbon atom alcohol (C_{12}) in the 12-carbon atom soap is shown to be from 2 to 3 times larger than in the 14-carbon atom (KC_{14}) soap, whereas the *solubilization* of the 12-C atom hydrocarbon is much larger in the 14 than in the 12-C atom soap.

However, the *penetration* of the 7, 10, and 12-C atom alcohols into the micelles of the 12-C atom soap follows the same rule as for solubilizations: i.e., the solubility decreases rapidly with the length of the hydrocarbon chain of the oil.

The complicated solubility relations which emerge in penetration are exhibited in Fig. 3. The solubility of the alcohols of 7, 8, and 9-C atoms increases rapidly, but not regularly, for any one alcohol as the length of the hydrocarbon chain of the soap increases from 8 to 14-C atoms. However, except for heptanol, the solubility of all of the alcohols up to 12-C atoms increases the most rapidly as the number of C atoms in the soap increases from 8 (the lowest investigated) up to 9. In general, the solubility is favored by an oddness in the number of C atoms in the soap. The increment of solubility per C atom decreases as the number of C atoms in the soap molecule increases up to 14.

This decrease in increment becomes most marked in the 12-C atom alcohol or amine which above the 13-C atom soap becomes a decrement so large that the 12-C atom amine or alcohol is much less soluble in the 14-C atom than in even the 9-C atom soap.

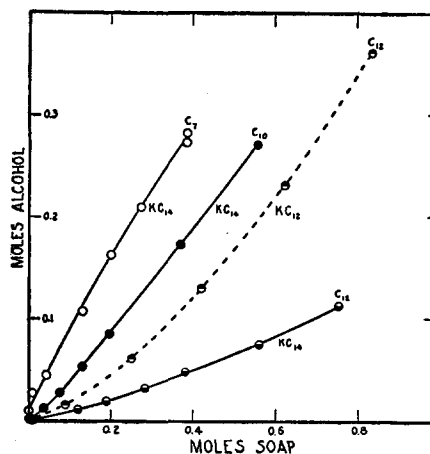


FIG. 2.

It should be noted that the solubility relations are much the same for the 10- and 12-C atom amines as for the corresponding alcohols.

The solubility by penetration of any one of the alcohols of from 7- to 12-C atoms is found to be from 10 to 30 percent higher in sodium dodecyl sulfate than in potassium dodecanoate. The amount of solubilization of a hydrocarbon in the sulfate is also higher.

In a 10 percent solution of potassium myristate, 28 grams of decyl alcohol became dissolved in 1000 grams of soap solution. The introduction of a second OH- group, at the other end of the hydrocarbon chain, gives decanediol (1, 10), a solid. Its solubility in the same soap solution is very low, less than 4.6 grams per 1000 grams of soap solution. The high insolubility of this alcohol is related to the occurrence of a polar -OH group at both ends of the molecule, so it is attracted more by the water, and the decrease in free energy on entering the hydrocarbon part of the micelles is less than when the group is present at only one end of the molecule.

The solubility relations which have been found in this laboratory exhibit the following relations (Table I).

1. In solubilization the relations are simple. The solubility *increases* with the length of the hydrocarbon chain of the colloidal electrolyte and decreases with the length of that of the hydrocarbon. This decrease is related to the decrease of activity of the hydrocarbon with chain length.

2. In film penetration the solubility decreases rapidly with the length of the hydrocarbon chain of the alcohol,

TABLE I. Effect of the nature of the polar group on the solubility of derivatives of dodecane by aqueous solutions of 0.3 mole of sodium lauryl sulfate per 1000 grams of detergent solution.

"Oil"	Grams "oil" (per 1000 grams of detergent solution)	Moles "oil"
Dodecane (solubilization)	<1.72	<0.01
Dodecylchloride	<1.82	<0.01
Dodecylmercaptan	6.55	0.03
Dodecylamine (penetration)	20.6	0.11
Dodecylalcohol (penetration)	22.8	0.12
Dodecyllic acid (penetration)	26.3	0.13

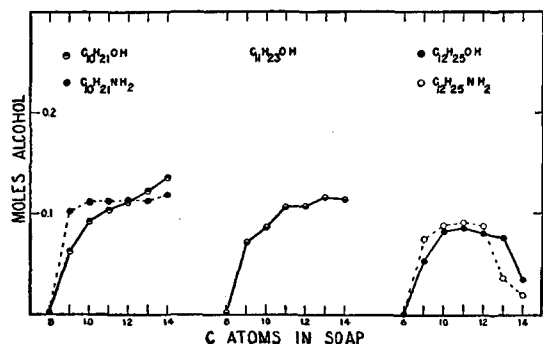


FIG. 3.

amine, etc., since in this case also the activity of the compound decreases rapidly with chain length. However, most of the relations are complex, and there is evidence that what may be described as molecular fitting enters, especially if the lengths of the soap chain and that of the polar-non-polar-non-ionic chain are not too different. For example, the solubility of the 11-C atom alcohol is in general higher than that which corresponds to the solubility of the 10- and 12-C atom alcohols.

Substances which enter the micelle by film penetration lower the critical micelle concentration. The rate of lowering with film concentration increases with extreme rapidity with the length of the molecule.² Substances which enter by solubilization have little effect upon the critical micelle concentration.

* 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.

¹ W. D. Harkins, R. W. Mattoon, and R. Mittelman, *J. Chem. Phys.* **15**, 763 (1947).

² M. L. Corrin and W. D. Harkins, *J. Chem. Phys.* **10**, 640 (1946), and later work with higher alcohols.

The Moment of Inertia of CF_3CH_3

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THE C—C bond distance in polyfluorinated compounds is a subject of much interest. On the basis of electron diffraction measurements Brockway, Secrist, and Lucht¹ reported a distance of 1.45 Å in C_2F_6 . On the other hand, nearly normal hydrocarbon bond distances for both the single and double bond in hexafluoropropene—namely, 1.52 and 1.31 Å, were found by Buck and Livingston² in their electron diffraction study. As an initial step in determining the bond distances and angles in CF_3CH_3 we have made a preliminary study of its microwave spectrum near 1.5-cm wave-length. The absorption cell was a five-foot section of standard 1.25-cm wave guide, used as a Hughes-Wilson³ Stark effect spectrometer.

Two lines were found. The first had a frequency of $20,741 \pm 2$ megacycles and had an absorption coefficient

of the order of $2 \times 10^{-6} \text{ cm}^{-1}$. It is due to the $J=1$ to $J=2$ transitions (for $K=0$ and $K=1$) in the ground state. Both linear and quadratic Stark effects were observed. The second line at $20,710 \pm 2$ megacycles appeared with an intensity of about half that of the first line, and is probably caused by the same rotational transition in a low lying, excited vibrational state. A second-order Stark effect was observed.

These data permit the calculation of the moment of inertia perpendicular to the threefold axis. Using Birge's⁴ values for the fundamental constants,

$$I_B = 161.80 \pm 0.07 \times 10^{-40} \text{ g cm}^2$$

in the ground state; for the unidentified excited state,

$$I_B = 162.04 \pm 0.07 \times 10^{-40} \text{ g cm}^2.$$

It is not possible to determine bond distances from these data alone, yet it is interesting to note several combinations which are in harmony with the observations. The electron diffraction measurements of Shand and Spurr⁵ yield $\text{C—C} = 1.52 \pm 0.02 \text{ Å}$, $\text{C—F} = 1.37 \pm 0.02 \text{ Å}$, $\angle \text{C—C—F} = 112^\circ 10' \pm 2^\circ$, $\angle \text{F—C—F} = 107^\circ 32' \pm 2^\circ$ when a tetrahedral methyl group with $\text{C—H} = 1.09 \text{ Å}$ was assumed. The moment of inertia⁶ calculated from these values, $I_B = 166.7 \pm 5.8 \times 10^{-40}$, while in agreement within the stated limits with the microwave value, does not represent the best choice of the distances and angles.

Before beginning the search for the microwave spectrum, a calculation of the microwave line positions was made with the following parameters: $\text{C—C} = 1.54 \text{ Å}$, $\text{C—F} = 1.33 \text{ Å}$, $\text{C—H} = 1.093 \text{ Å}$, $\text{F—F} = 2.16 \text{ Å}$, $\angle \text{H—C—H} = 109^\circ 28'$, $\text{H} = 1.008$, $\text{C} = 12.01$, $\text{F} = 19.00$, and $\text{N} = 6.0228 \times 10^{23}$. These lead to $I_B = 161.9 \times 10^{-40}$, the close agreement with experiment probably being fortuitous. A shorter C—C distance of 1.45 Å with all other distances and angles as listed immediately above gives $I_B = 154.7 \times 10^{-40}$. Such a distance requires compensation elsewhere; for example, $I_B = 161.7 \times 10^{-40}$ when $\text{C—C} = 1.45 \text{ Å}$ and $\text{C—F} = 1.38 \text{ Å}$, the other distances and all angles remaining as before.

If recent work^{2,6} may be interpreted as favoring the shorter C—F bond distance and angles which are nearly tetrahedral, the present results would favor a C—C distance in CF_3CH_3 more nearly like that in ethane than like that reported for C_2F_6 .¹

Work is planned on the preparation of isotopic molecules from which these distances may be determined unambiguously, within the limits imposed by zero-point vibration corrections.

The CF_3CH_3 used in this work was part of a sample furnished Professor Glockler by Dr. A. F. Benning, Jackson Laboratory, E. I. du Pont de Nemours Company. Thanks are due them for the loan of the material and to Mr. Donald A. Gilbert for assistance in the microwave measurements.

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⁶ H. J. Bernstein and G. Herzberg, *J. Chem. Phys.* **16**, 30 (1948).