[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

The Dimensions of the Sodium Palmitate Molecule from a Study of the Surface Tensions of Dilute Aqueous Solutions

BY E. ROGER WASHBURN AND G. W. BERRY

Du Noüy[1] has made extensive studies of the surface activity of several biological and organic materials. From the results of his study with sodium oleate he calculated the dimensions of the sodium oleate molecule. The minima in the surface tension–concentration curve which are the basis for his calculation should be obtainable by the capillary rise method as well as by the ring method. The authors of this paper are not aware that the results of any such observations have been published; therefore it was decided to carry out such an investigation with the capillary rise method.

Apparatus

Capillarimeters of the closed type as used by Bigelow and Washburn[2] were constructed from selected pieces of uniform capillary tubing. The procedure of Bigelow and Washburn[2] was followed in measuring the bore of the capillary tubes and in cleaning the capillarimeters. The radius of capillarimeter A was 0.03260 ± 0.00002 cm., that of capillarimeter B, 0.01916 ± 0.00002 cm., that of capillarimeter D, 0.02700 ± 0.00002 cm.

A second type of capillarimeter was made as suggested by Quinn and Wernimont.[3] These were used only to check the results obtained by the closed capillarimeters.

A measuring microscope graduated to read to 0.001 cm. directly was employed in all measurements of capillary rise. The measurements were made at 25.00 ± 0.05°.

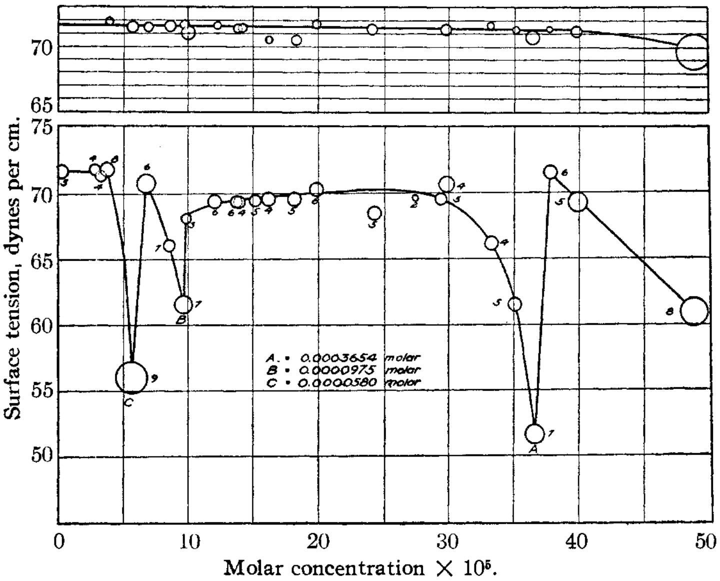
Materials

"Conductivity water" free from carbon dioxide was used. The sodium palmitate was prepared from metallic sodium and palmitic acid. The salt was crystallized three times from absolute alcohol and had a melting point of 272 ± 2°.

Saturated aqueous solutions of this salt were prepared at 60°. When cooled to 25° semi-solid gels were formed. The solutions were then filtered through a layer of this gel on a filter paper. The filtrate showed a very slight Tyndall cone.

The concentration of the filtrate was determined by evaporating a known amount to dryness and weighing the residue. Eight such determinations were made; the results varied from 0.0004875 to 0.0004884 molar, the average was 0.0004878 molar. These solutions served as stock solutions from which the less concentrated solutions were prepared by diluting with conductivity water. The air in the stock bottles and in the capillarimeters was displaced with carbon dioxide-free nitrogen before the solutions were added. Practically no palmitic acid separated from solutions protected in this manner.

Figures 1 and 2 were obtained by plotting the initial and equilibrium surface tensions, respectively, against the concentration. The circles indicating the points were drawn large enough to include all of the surface tension values that were obtained from solutions of any one concentration. In Fig. 2 the number of each circle represents the number of independent determinations of surface tension at the indicated concentration.



Figs. 1 and 2.

Du Noüy[1] assumed that adsorption takes place at the liquid–glass interface as well as at the liquid–vapor interface when an aqueous solution of a soap is in a glass container. The first minima in the equilibrium surface tension–concentration curve occur when the concentration is just sufficient to furnish enough solute molecules to form a monomolecular layer in the capillary meniscus and on the walls of the capillary tube below the meniscus. The solute molecules tend to orient

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[1] Du Noüy, "Surface Equilibria of Biological and Organic Colloids," A. C. S. Monograph, Chemical Catalog Company, New York, 1926.

[2] Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321–353 (1928).

[3] Quinn and Wernimont, THIS JOURNAL, **52**, 2723 (1930).

themselves in such a way that the surface energy of the system is at a minimum. This is the case when the solute molecules form a continuous monomolecular film over the surface, each molecule occupying such a position that it presents a minimum of surface to the interfacial areas. As the concentration of the solution is decreased the solute molecules orient themselves in such a way as to keep the surface energy as low as possible. They do this by pivoting about the carboxyl group until they present the next larger area to the interfacial surfaces. A third minimum value is found when further dilution causes the solute molecules to again pivot about the carboxyl group and thus present their maximum area to the interfacial surfaces.

If the following assumptions are made the dimensions of the molecules may be calculated.

1. A monomolecular film is formed at the surface when the concentrations are such that minimum surface tensions result, the molecules being oriented as described above.
2. The area on which adsorption, which determines the surface tension, occurs is constant at the different dilutions.
3. At these very low concentrations the adsorption from a constant volume in the vicinity of the meniscus is practically complete.
4. The volume of a molecule is constant and is equal to the product of its three dimensions and also to the molecular volume divided by Avogadro's number.
5. The specific gravity of the sodium palmitate in the film is the same as the density of the material in the solid bulk form.

We may set up the following equations for the number of molecules adsorbed at the different minima, and for the volume of a molecule:

$$\frac{A}{l_2 l_3} = VC_a \text{ at } A$$

$$\frac{A}{l_1 l_3} = VC_b \text{ at } B$$

$$\frac{A}{l_1 l_2} = VC_c \text{ at } C$$

$$l_1 l_2 l_3 = \frac{M}{6.06 \times 10^{23} \times d} = v$$

A = area on which adsorption takes place

V = volume from which adsorption takes place

C_a = concentration at A = 3.654×10^{-4} molar

C_b = concentration at B = 0.975×10^{-4} molar

C_d = concentration at C = 0.580×10^{-4} molar

$l_1 l_2 l_3$ = the three dimensions of the molecule, l_1 being the longest dimensions and l_3 the shortest

d = specific gravity of sodium palmitate = 0.854 at 25°

M = molecular weight of sodium palmitate = 278.25

v = molecular volume of sodium palmitate = 5.38×10^{-22} cc.

Solving the above equations for l_2, and then for l_1 and l_3 in terms of l_2, gives the following relations

$$l_2 = \sqrt[3]{\frac{C_b^2 v}{C_a C_c}} = 6.2 \times 10^{-8} \text{ cm.}$$

$$l_1 = l_2 C_a / C_b = 23 \times 10^{-8} \text{ cm.}$$

$$l_2 = l_2 C_c / C_b = 3.7 \times 10^{-8} \text{ cm.}$$

The cross section area and the length of the molecule was determined by an independent method, a study of surface films, as carried out by Langmuir.[4]

An alcoholic solution of sodium palmitate was allowed to spread on water and from the film of sodium palmitate (or of palmitic acid formed by hydrolysis) left after the alcohol had evaporated or dissolved in the water, the cross sectional area of the molecules was 20.8×10^{-16} sq. cm. The length of the molecules was found to be 25.9×10^{-8} cm. These results represent an average of about thirty different determinations. While these values do not agree exactly with the length and smallest cross sectional area calculated from the surface tension measurements, the difference is not great. Further work is being done on this phase of the problem in an attempt to find out whether the difference is significant.

The dimensions of the sodium oleate molecule as determined by du Noüy[1] are 12.30×10^{-8} cm. $\times$ 7.56×10^{-8} cm. $\times$ 6.64×10^{-8} cm. If the sodium oleate molecule is bent at the double bond it should be approximately half as long as the sodium palmitate molecule. One of the cross sectional dimensions should be very nearly double the corresponding dimension for sodium palmitate. The other short dimension should be approximately the same for both molecules; comparing the values found it is seen that such is the case.

It is interesting that the above dimensions bear approximately these relationships to each other. However, N. K. Adam[5] has pointed out that a similar interpretation offered by Langmuir[4] is not acceptable because he was comparing an expanded film of unsaturated acids with a condensed film of saturated acids.

Summary

1. The equilibrium surface tension–concentration curve for solutions of sodium palmitate have

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[4] Langmuir, THIS JOURNAL, **39**, 1848–1906 (1917).

[5] N. K. Adam, *J. Phys. Chem.*, **29**, 87–101 (1925).

been determined by the capillary rise method.

2. From the minima in this curve the dimensions of the sodium palmitate molecule were calculated to be 23 × 10^{-8} cm. × 6.2 × 10^{-8} cm. × 3.7 × 10^{-8} cm.

3. The smallest cross section area and the length of the molecule do not differ greatly from similar quantities measured by the Langmuir film method.

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[CONTRIBUTION FROM THE ESSO LABORATORIES, STANDARD OIL DEVELOPMENT COMPANY]

Preparation of Platinum Oxide Catalyst from Spent Material

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It has been the experience of this and other laboratories that a platinum hydrogenation catalyst prepared according to the method of Voorhees and Adams[1] generally exhibits low activity when any of the H_2PtCl_6 used has been recovered by the usual methods from spent catalyst. It is believed that this low activity is probably due to the presence of small amounts of impurities (catalytic poisons) introduced during the hydrogenation procedure.

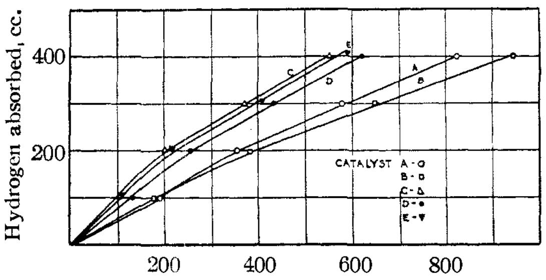

Fig. 1.—Hydrogenation of heptadecyl-*n*-butylphenylethylene.

Various recovery methods have therefore been studied in order to determine the best procedure for the preparation of an active catalyst from spent material. As a result of this work, a method is recommended which has given very satisfactory results and should be of interest to other laboratories engaged in similar work.

Experimental

The following impurities are generally found in the spent catalyst: (1) organic compounds left after hydrogenation and the filter papers used in separating the catalyst from the hydrogenated compounds; (2) inorganic constituents such as (a) copper and some of the other metals of the platinum group present as impurities in the original H_2PtCl_6 from scrap metal and small amounts of (b) iron, aluminum, calcium and magnesium introduced by ashing the filter paper.

A number of catalysts were prepared (according to the method of Voorhees and Adams) from H_2PtCl_6 obtained from spent material treated as follows.

(A) The spent catalyst was carefully separated by scraping from filter papers and the H_2PtCl_6 solution prepared according to the recovery method described in "Organic Syntheses."[2] This material therefore contained impurities listed in 1 and 2a, but very little of those listed in 2b.

(B) The material including the filter paper was ignited in a muffle furnace and the resulting ash treated as in A. The H_2PtCl_6 thus prepared contained only the inorganic impurities discussed under 2.

(C) The ignited material was purified by the procedure described by Wichers[3] except that only one ammonium chloride precipitation was carried out instead of three and that carbon monoxide was used as the reducing agent after ignition of the $(NH_4)_2PtCl_6$ precipitate. The method is briefly described below.

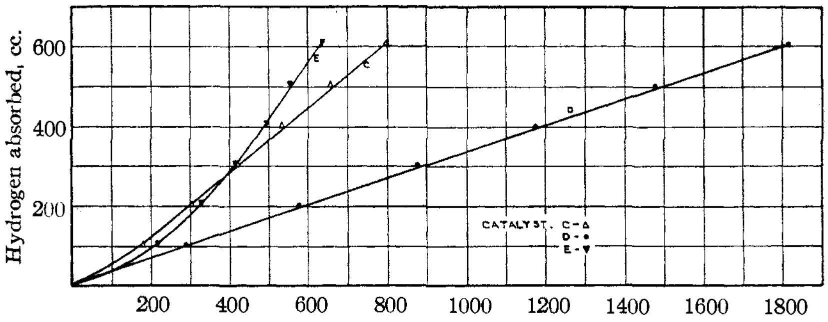

Fig. 2.—Hydrogenation of maleic acid.

Dissolve the ignited material in aqua regia, filter off any insoluble and evaporate the filtrate three times to

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[1] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

[2] "Organic Syntheses," John Wiley & Sons, Inc., New York, 1932, Coll. Vol. 1, p. 457.

[3] Wichers, THIS JOURNAL, **43**, 1268 (1921).