

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

The Sorption of Vapors by Monolayers. II.¹ Organic Vapors on Stearic Acid Monolayers²

BY ROBERT B. DEAN AND FA-SI LI^{3,4}

Introduction.—The effect of vapors on the surface tension of liquids has been known for a long time. However Micheli,⁵ in 1927, was apparently the first to measure quantitatively the effect of organic vapors on the surface tension of clean water surfaces and to calculate the adsorption by means of the familiar Gibbs adsorption equation. Although it appears obvious by hindsight that organic vapors would also be adsorbed on organic monolayers, Washburn and his co-workers^{6,7,8} carried out a series of investigations of the spreading pressure of volatile organic liquids and found no detectable interference from adsorption of vapors at surface pressures greater than the spreading pressure of the liquid. In the first paper of this series,⁹ Dean and McBain reported qualitative observations which demonstrated that vapors of certain liquids are adsorbed on monolayers even above their spreading pressure. In this work we have measured quantitatively the change in surface pressure of stearic acid monolayers under saturated vapors of *n*-hexane, 2,3-dimethylbutane, benzene and carbon tetrachloride. Benzene and *n*-hexane have also been examined at various partial pressures below saturation; and, by making certain simplifying assumptions, we have been able to calculate the quantity of vapor adsorbed. The reason why adsorption of vapors did not interfere with Washburn's measurements is discussed.

Experimental

Materials.—Benzene was Baker and Adamson "B and A Quality," free from thiophene, and was redistilled collecting the fraction between 79.7 and 80°. It was tested and found to be free from surface active impurities.

n-Hexane and 2,3-dimethylbutane were of the "Pure Grade," Phillips Petroleum Company, with a 99 mole % minimum.

Carbon tetrachloride and toluene were of the "C. P. Baker Analyzed" grade.

1,2-Dichloroethane was practical grade for solvent purposes.

n-Octane and *n*-decane were of the white-labelled "Eastman" highest purity grade from the Eastman Kodak Company.

Benzene solutions of stearic acid were prepared by weighing the Eastman highest-purity stearic acid and dissolving with the redistilled benzene in a volumetric flask

at room temperature. Two concentrations, 0.00096 and 0.000500 mole/liter, were used.

Hydrochloric acid solution (0.01 *N*) was prepared from C. P. hydrochloric acid and was proved to have very low surface activity by surface tension measurement. All measurements were made on this substrate.

Nitrogen gas was washed by passing through wash bottles of water and the organic liquid before use.

Apparatus and Methods.—I. Qualitative confirmation of the adsorption of organic vapors on monolayers of stearic acid was carried out essentially as done by Dean and McBain⁹ but using a Cenco Hydrophil balance instead of the oil and thread piston. A stearic acid monolayer was set up over 0.01 *N* hydrochloric acid in the trough. A wire gauze rack was supported just above one end of the monolayer and a piece of filter paper was placed on the gauze. Organic liquid could then be dropped on the filter paper and the vapors would act on the monolayer. Suitable baffles prevented the vapor from reaching the float and the clean end of the trough.

II. Quantitative measurements of the effect of saturated and partially saturated vapors were carried out in the apparatus shown in Fig. 1. For this work, we abandoned the bulky Hydrophil balance and measured the surface tension instead of the surface pressure. The surface pressure was then obtained by subtraction. The monolayer was set up on a glass petri dish in a covered chamber inside a balance case. The ring was supported from a platinum wire hooked to one of the stirrups of a chain balance. The ring was a Cenco 70532 platinum-iridium ring with a mean circumference of 4.00 cm. \pm 0.1% and a radius ratio *R/r* of 40.1. The dish with the monolayer was supported on a leveling screw and was continuously adjusted in height as the chain was lowered to keep the index pointer at the zero position. In this way the ring remained in the same plane and the monolayer was pulled away from it. The surface tension reading was taken as the greatest force the ring would sustain before rupturing the surface. The corrections to the ring method of Zuidema and Waters¹⁰ were always applied. We found a value of 71.8 dyne/cm. for distilled water at 25°. Harkins and Jordan¹¹ report the slightly higher value of 71.97 as standard.

To prevent the creeping of liquids and possible contamination of the monolayer, the monolayer chamber was coated with G. E. Silicone Resin 9982¹² by baking at about 250°, rubbing with clean paper, and washing thoroughly with organic solvent and water. The molecular area of the stearic acid in the monolayer was calculated from the known amount of stearic acid solution in benzene (added by means of a micrometer-syringe buret) and the area of the dish, corrected for the estimated increase in area produced when the ring is pulling the surface up. The areas are believed to be accurate to \pm 1%. Organic vapors, together with water vapor, were carried into the monolayer chamber by a current of pure nitrogen. The saturator was a three chamber Geissler bulb immersed in a water thermostat. The relative pressure of the vapors could be controlled by varying the temperature of this thermostat. The temperature of the monolayer was held at 25 \pm 1° by manually regulating the room temperature, and was recorded to the nearest 0.1°. The surface pressure was calculated by subtracting the observed surface tension from the surface tension of pure water at that temperature. The surface pressure measurements are believed to be accurate to 0.5 dyne/cm.

(1) Paper I of this series appeared as reference (9).

(2) Presented at the 117th meeting of the American Chemical Society; Houston, Texas, March 26-30 (1950).

(3) This work is reported more extensively in the M.A. Thesis of Fa-Si Li, June, 1950, a copy of which has been deposited in the University of Oregon Library.

(4) Gates and Crellin Laboratory, California Institute of Technology, Pasadena, California.

(5) Micheli, *Phil. Mag.*, [7] **3**, 895 (1927).

(6) Washburn and Keim, *This Journal*, **62**, 1747 (1940).

(7) Transue, Washburn and Kahler, *ibid.*, **64**, 274 (1942).

(8) Washburn and Anderson, *J. Phys. Chem.*, **50**, 401 (1946).

(9) Dean and McBain, *J. Colloid Sci.*, **2**, 383 (1947).

(10) Zuidema and Waters, *Ind. Eng. Chem., Anal. Ed.*, **13**, 312 (1941).

(11) Harkins and Jordan, *This Journal*, **52**, 1751 (1930).

(12) Obtained through the courtesy of the General Electric Co.

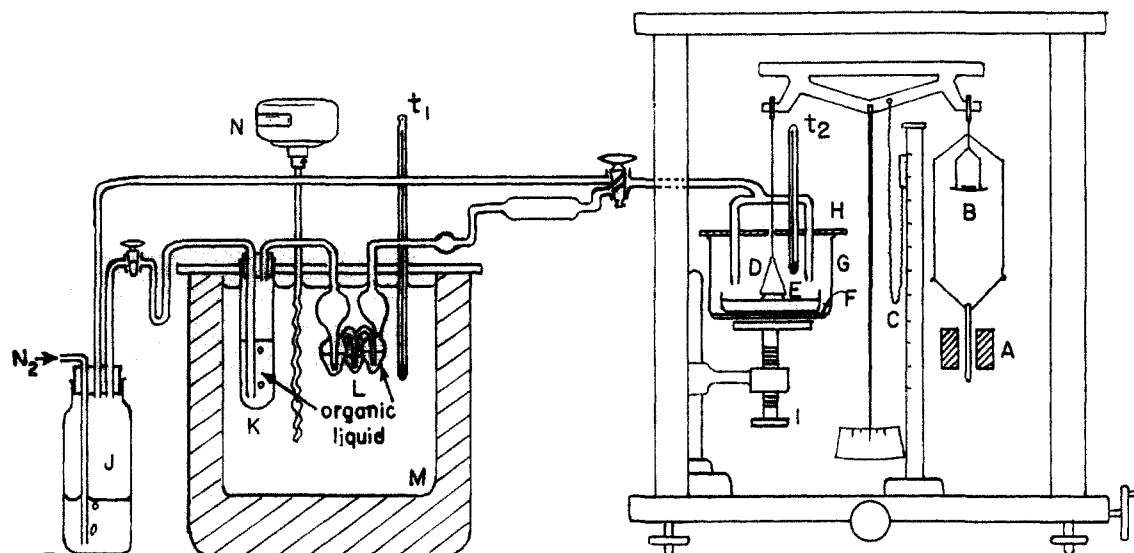


Fig. 1.—Essential features of Apparatus II: (a) tensiometer: A, magnetic damper; B, small weight pan; C, chain; D, platinum-iridium ring; I, leveling screw. (b) Monolayer chamber: E, glass petri dish containing the monolayer and substrate; F, absorbing filter paper; G, larger glass vessel; H, metallic cover; t_2 , thermometer at the monolayer temperature. (c) Saturator: J, gas washing bottle with water; K, presaturator tube; L, Geissler bulb; M, thermostat; N, stirrer; t_1 , thermometer at the saturator temperature.

Results.—I. Measurements with the surface balance showed in every case an expansion and an increase in the surface pressure of stearic acid monolayers on exposure to nearly saturated vapors. The increase is less at greater surface pressures, approaching zero asymptotically. There is no sharply defined critical surface pressure beyond which the vapor produces no expansion. In Table I the highest surface pressure which still is detectably increased (>0.2 dyne/cm.) by the action of saturated vapors is listed together with the initial spreading pressure of the liquid according to Harkins.^{13,14}

TABLE I

MAXIMUM SURFACE PRESSURE OF STEARIC ACID MONOLAYERS WHICH WILL BE DETECTABLY INCREASED BY ORGANIC VAPORS AT 20°

Vapor	Maximum surface pressure, dynes/cm.	Initial spreading pressure, dynes/cm.
<i>n</i> -Hexane	19	3.4
<i>n</i> -Octane	14	0.2
<i>n</i> -Decane	13	? (probably negative)
Benzene	16	9.8
Toluene	17	6.8

II. The effect of saturated vapors on the stearic acid monolayer is reported in Table II. Figure 2(a) shows the surface pressure π as a function of the area per molecule of the stearic acid in the monolayer, σ_2 . The insert (B) in Fig. 2 shows the same data plotted in terms of surface concentration of stearic acid, Γ_2 , using a reversed scale to

(13) Harkins and Feldman, *THIS JOURNAL*, **44**, 2665 (1922).

(14) Harkins, *Chem. Revs.*, **29**, 385 (1941).

TABLE II

SURFACE PRESSURE-AREA RELATIONS OF STEARIC ACID MONOLAYERS UNDER SATURATED ORGANIC VAPORS
Substrate, 0.01 *N* HCl; temperature, 25°

Molecular area of stearic acid, sq. Å./molecule	Surface pressure, π , dyne/cm.			
	<i>n</i> -Hexane	2,3-Dimethylbutane	Benzene	Carbon tetrachloride
∞	5.4	7.0	11.4	3.8
450	5.8	7.4	11.7	..
286	3.9
226	7.2	8.8	12.6	..
141	9.5	10.3	15.1	7.0
113	..	13.2
94	12.8	13.9	17.3	9.8
81	13.9
71	15.3	17.6	19.0	13.9
57	19.2	21.4	..	17.5
49	19.4
47	19.5	23.4	18.9	17.3
40	..	23.4	19.0	17.8
35	20.5
33	..	24.4
31	19.0	17.6
29.4	20.7
28.3	..	23.8	19.0	..
25.8	19.4	..
23.6	21.6

facilitate comparison with the main diagram. The value at infinite area, or zero surface concentration represents the effect of the organic vapor on the surface tension of pure water. It will be noted that even carbon tetrachloride (which is a non-spreading liquid¹⁴) is adsorbed on water to an equilibrium spreading pressure of +3.8 dynes/

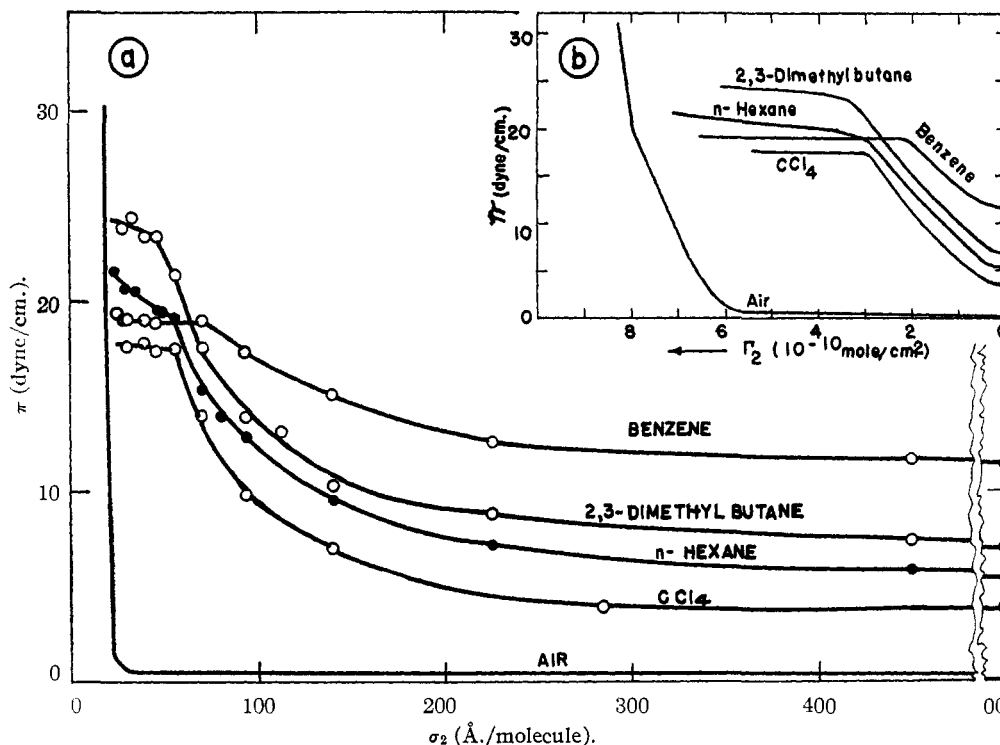


Fig. 2.—(a) The relation between the surface pressure, π , and the molecular area, σ_2 , of stearic acid monolayers under various saturated organic vapors. (b) The same data plotted in terms of surface concentration of stearic acid Γ_2 with a reversed scale (concentrations increase to the left). All temperatures are 25°.

cm. As the monolayer is compressed in the presence of a vapor, the surface pressure increases to a value of the order of 20 dynes/cm. at a surface area of about 60 sq. Å. per molecule of stearic acid. Further compression produces a relatively small increase in the surface pressure until the area per molecule is 25 sq. Å. At this point the surface pressure increases rapidly in the absence of the organic vapor and accurate measurements are impossible with our present apparatus. The π - σ_2 curve for stearic acid under an organic vapor resembles strongly the L_1 (liquid expanded) range and the L_1 - L_2 transition range of myristic acid at about 25°. ¹⁵

The effect of relative pressure, p_1/p_1^0 , of *n*-hexane and benzene vapors on the surface pressure of stearic acid monolayers at selected molecular areas σ_2 is shown in Fig. 3 and 4 together with Micheli's⁹ curves for the effect on clear water surfaces. The surface pressure increases in a sigmoidal fashion with the relative pressure.

Discussion

A rigorous thermodynamic analysis of this three-component system will be presented in a subsequent paper. Preliminary calculations show a surface excess of hexane corresponding to one hexane molecule to 25 to 30 sq. Å. The maximum adsorption of *n*-hexane vapor is not significantly

different on an expanded stearic acid monolayer ($\sigma_2 = 94$ sq. Å.) and on a compressed monolayer ($\sigma_2 = 29$ sq. Å.).

It is reasonable to suppose that the hydrocarbon chains of the stearic acid provide nuclei for the sorption of hexane molecules until approximately a monolayer of hexane has been sorbed. The π - σ_2 curve for stearic acid under saturated vapors strongly resembles the L_1 (liquid-expanded) range and the L_1 - L_2 transition range of a lower melting homolog. We may say that the organic vapor has plasticized the monolayer and enabled it to form a duplex film.

As the monolayer is compressed vapors will be squeezed out but the sorption of vapor per unit area remains nearly unchanged. We have not yet been able to obtain accurate data at high compression; but some adsorption of vapor is certain to occur on any organic monolayer because of the van der Waals forces between any pair of molecules. If there is adsorption, there must, by the Gibbs equation, be a lowering of the surface tension which means an increase in the surface pressure. The extent of the change in surface pressure will be small on condensed film with low compressibility. The values reported in Table I for detectable increases in surface pressure are close to the surface pressure for the transition to the two-dimensional solid phase of a stearic acid monolayer under air (about 20 dynes/cm.). ¹⁶ Above this

(15) Adam and Jessop, *Proc. Roy. Soc. (London)*, **A112**, 312 (1926).

(16) Adam, *ibid.*, **A99**, 336 (1921).

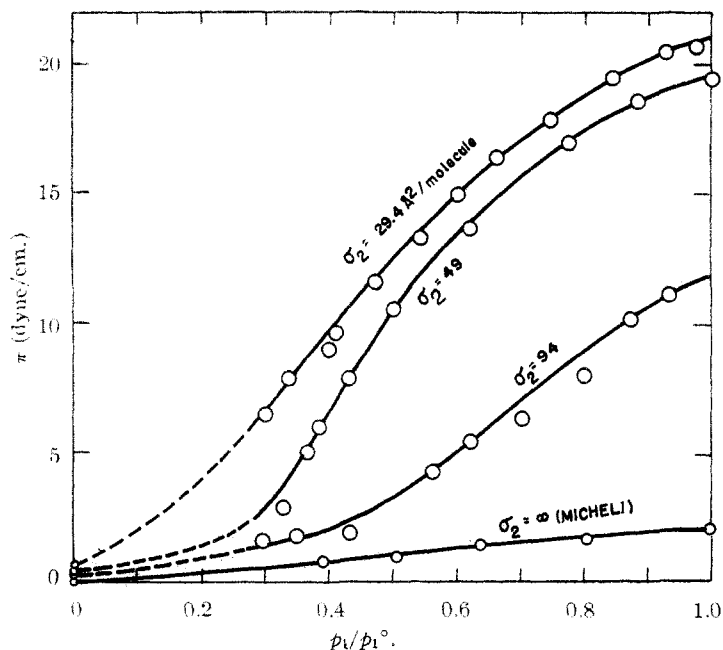


Fig. 3.—The relation between surface pressure, π , and relative pressure of *n*-hexane vapor at various molecular areas of the stearic acid monolayer, σ_2 .

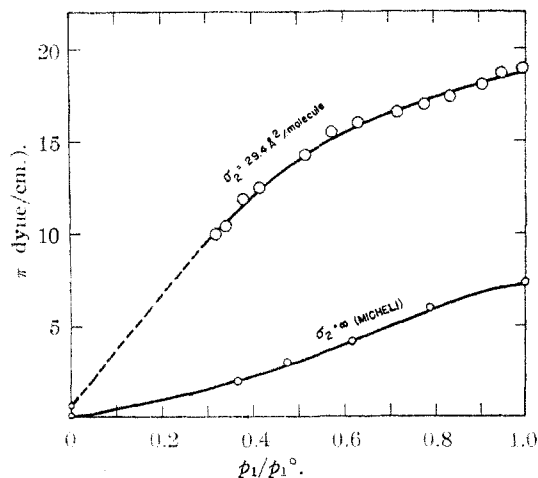


Fig. 4.—The relation between surface pressure, π , and relative pressure of benzene vapor at various molecular areas of the stearic acid monolayer, σ_2 .

pressure stearic acid films are nearly incompressible.

Washburn and co-workers^{6,7,8} measured the effect of drops of organic liquids on monolayers and found that the drop would spread and push back the monolayer if the surface pressure were less than the initial spreading pressure according to Harkins.^{13,14} If the surface pressure were greater than this value no expansion took place. Evidently in the experiments of Washburn, the area of the monolayer exposed to saturated vapors around the drop is too small to produce a detectable change in surface pressure. Otherwise we

would expect that even the vapors of non-spreading liquids, such as carbon tetrachloride, would be adsorbed on the film causing it to expand.

The strong adsorption of hexane on dilute monolayers of stearic acid suggested that the sorption of hexane on solid adsorbents might be similarly increased. A number of tests were run by Miss Doris May Chin, but no increase in the adsorption of hexane on various silica gels, alumina or cellulose was found. The solid adsorbents were treated with solutions of various anionic, cationic, and non-ionic surface active agents at concentrations from 0.001 to 5% of the weight of the adsorbent. The usual result was a reduction in adsorption which we attribute to the closing off of pores. It is quite likely that a mobile surface layer is necessary for enhanced adsorption of hexane.

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Summary

1. The increase in surface pressure of stearic acid monolayers upon exposure to saturated organic vapors has been measured. There is a small increase in pressure even at the highest available surface pressure indicating adsorption on the monolayer. In every case the monolayer is expanded at pressures considerably greater than the initial spreading pressure of the organic liquid.

2. At intermediate surface areas between 25 and about 60 sq. Å. per molecule of stearic acid, organic vapors increase the surface pressure to about 20 dynes/cm.; the exact value depends on the vapor used.

3. At still greater areas, the surface tension falls in a manner suggesting the L_1 (liquid-expanded) phase such as is shown by myristic acid at 25°.

4. The adsorption of hexane on stearic acid has been calculated from measurements at various relative pressures using the simplified Gibbs adsorption equation. Adsorption appears to be nearly constant at about one molecule of *n*-hexane per 28 sq. Å., over a wide range in molecular area of stearic acid.

No enhanced adsorption of hexane on porous solid adsorbents treated with surface active agents was found.