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

The Sorption of Vapors by Monolayers. III. A Surface Balance for the Measurement of the Effect of Vapors on Monolayers[1]

BY ROBERT B. DEAN AND KENNETH E. HAYES

An apparatus for the study of monolayers under vapors is described. Surface pressure is measured with a vertical plate Wilhelmy-type surface balance. The chamber has a vapor volume of 1.5 liters and is controlled to 0.1°. Tolerances are approximately 0.05 dyne/cm. and 0.1 Gibbs (moles/cm.^{2} × 10^{10}).

Previous papers of this series[2,3] have demonstrated that vapors are adsorbed on monolayers. These papers represent preliminary observations which were obtained in apparatus with only crude thermal control. It was necessary to design a monolayer apparatus that could be saturated with vapors of organic liquids in a reasonable length of time and one which was thermostatically controlled. Previous apparatus for monolayer studies have all used large troughs with correspondingly large gas spaces above the trough.[4-6] Of the various designs previously published that of Anderson and the Stenhagens[6] would have been most suitable but even it has a chamber with a gross volume of 100 liters which would have to be saturated with vapors.

We have designed a small monolayer box with a gross volume of about 1.5 liters which is described in this paper. A floating barrier surface balance of the Langmuir–Adam–Harkins[4] type is unsuitable for monolayer work in the presence of vapors which will be adsorbed on the "clean" side of the barrier. Neither the ring method[3] nor the vertical Wilhelmy plate[5,6] require a clean reference surface and may be used for studies with vapors. We choose the Wilhelmy method because it permits the approach to equilibrium to be observed without disturbing the equilibrium by the final measurement. This has turned out to be of great importance when measuring spreading pressures since these sometimes require 24 hours to approach a limiting value.

The monolayer box is illustrated in Fig. 1. It consists of a hollow cube of cast aluminum 6" on a side with walls $^3/_4$ to 1 in. thick. The cube is cast in three pieces, I a flat top, II four walls cast as a unit and III the bottom containing the monolayer trough. The walls fit into a gutter around the trough. The top is machined flat and makes a sliding fit on the walls. There are two ports 2 in. in diameter glazed with double windows on opposite sides of the box.

The box is heated by two separate 2-ohm heating elements applied to the top and bottom between layers of asbestos and secured in place by brass plates screwed to the casting. Each element is heated by 6 volts a.c. and controlled by a thermoswitch in the casting. A complete heating and cooling cycle requires about one minute if the room temperature is at least 3° below that of the box. The original plans called for insulating the walls but not the top and bottom of the box. This has not proved to be necessary since temperatures measured in the casting, in the liquid, and in the vapor space are constant to 0.1° in both space and time. The trough is 10 cm. square with the upper edge just above the level of the bottom of the windows. The rim is about 3 mm. wide and the inside edges slope down to meet the bottom near the center to simplify cleaning. The entire surface of the monolayer trough is coated with Teflon[7] emulsion baked on at 350°. Teflon, $(CF_2{-}CF_2)_n$, has a high contact angle against water and has been recommended in the solid form for monolayer work.[8] It is even more useful in the emulsion form which can be baked on aluminum to give a strong surface film that is easy to clean and has a high contact angle with water and with organic liquids including acetone, hexane and benzene. Unlike paraffin and ferric stearate, Teflon is insoluble in all known solvents at room temperature. A sliding barrier coated with Teflon and operated by rods from outside the box is used to compress the surface films by as much as 30% of their initial area.

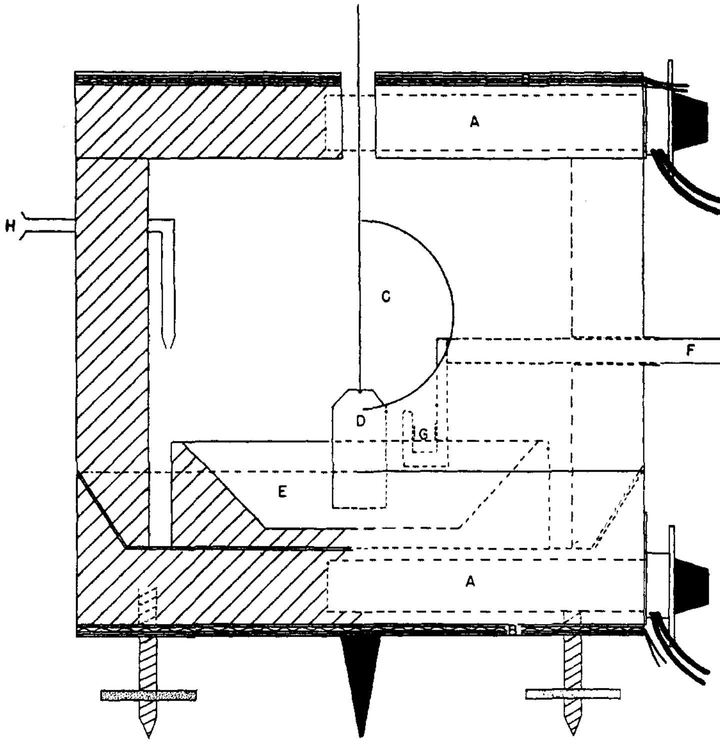

Fig. 1.—Detail of monolayer chamber: A, thermoregulator; B, heating coil; C, observation port; D, platinum plate; E, monolayer trough; F, barrier mechanism; G, barrier; H, vapor inlet.

Surface tension is measured by a Wilhelmy plate of roughened platinum.[9] This hangs on a light weight chain from one arm of an analytical chain-type balance which is supported on concrete blocks above the trough. The chain

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(1) Presented by Dr. A. H. Kunz at the 119th Meeting of the American Chemical Society, Colloid Division, Symposium on Instrumental Methods of Colloid Chemistry, Cleveland, Ohio, April, 1951. Supported by a grant from the Frederick Gardner Cottrell Fund of the Research Corporation.

(2) R. B. Dean and J. W. McBain, *J. Colloid Sci.*, **2**, 383 (1947).

(3) R. B. Dean and F.-S. Li, THIS JOURNAL, **72**, 3979 (1950).

(4) G. C. Nutting and W. D. Harkins, *ibid.*, **61**, 1780 (1939).

(5) D. G. Dervichian, *Ann. phys.*, [11] **8**, 361 (1937).

(6) K. J. I. Anderson, S. Ställberg-Stenhagen and E. Stenhagen, *The Svedberg*, 1884–1944, Stockholm, p. 11–32.

(7) Sold by the du Pont Company.

(8) H. W. Fox and W. A. Zisman, *Rev. Sci. Instruments*, **19**, 272 (1948).

(9) M. Abribat and A. Dognot, *Compt. rend.*, **208**, 1881 (1939).

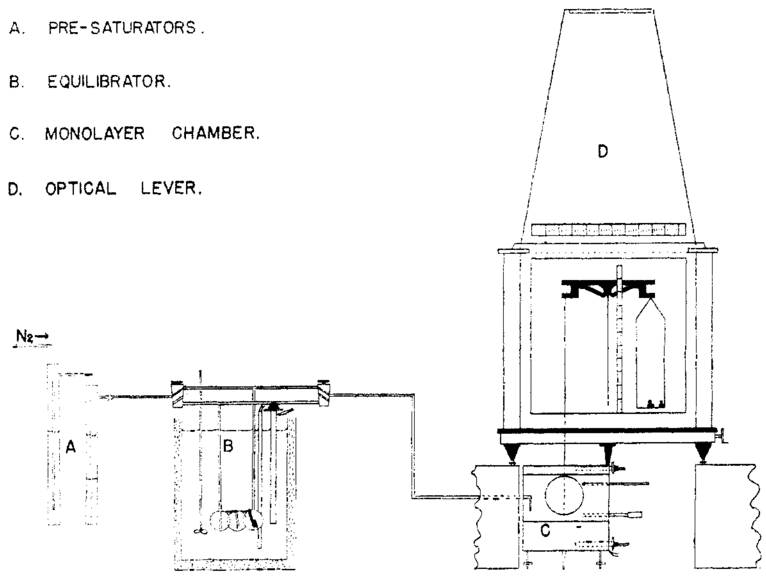

Fig. 2.—Complete assembly of adsorption apparatus.

passes through holes in the floor of the balance and the top casting. The position of the plate and the balance arm is read on a folded optical lever mounted above the balance. Light from a straight filament is reflected from a small mirror on the beam and focused on a translucent scale just above the balance case. A 1-mm. vertical movement of the plate displaces the image of the filament by 10 mm. Figure 2 shows a photograph of the complete assembly.

Hexane or other organic vapor is passed through the monolayer box in a stream of nitrogen that has been saturated with liquid hexane at a temperature corresponding to the desired vapor pressure as read from published tables. Water-pumped nitrogen flows at about 150 ml. per minute through a wash bottle full of water before going to the equilibrator. Two three-way stopcocks lubricated with an aqueous grease allow the equilibrator to be by-passed when necessary. The vapor line from the equilibrator to the monolayer chamber is wound with resistance wire so that it may be heated to prevent condensation of hexane in the line when operating at high relative vapor pressures. The stream of nitrogen and vapor is directed into the gutter surrounding the monolayer. Excess gas escapes through several holes in the box.

The trough is cleaned by rinsing it with acetone and then steaming it out over a specially constructed boiler that fits into the gutter of the inverted base. The barrier is also cleaned and wiped with acetone on a paper towel and rinsed with distilled water. The platinum slide is flamed before each run.

The trough is filled with subphase (0.01 *N* H_3PO_4) to a level 3 or 4 mm. above the edge and the surface is sucked off. This procedure is repeated several times and the liquid is finally adjusted to a level 1 to 2 mm. above the edge. The gutter is partially filled with distilled water and the wall casting, including the barrier mechanism, is put on. The platinum slide and chain are placed in the box and the chain is fished through the holes and hung on the balance hook when the box is assembled.

The optical indicator is brought to a convenient position by adjusting the balance chain. When the box comes up to temperature nitrogen gas is started and a true zero is recorded when equilibrium is reached. The surface is tested for cleanliness by advancing the barrier as far as possible. A clean surface will show no change in surface pressure on compression.

Stearic acid in benzene solution is delivered onto the surface of the trough from a micrometer-driven syringe with a long hollow needle which is inserted through a small hole in the front of the box. Evaporation of the benzene and spreading of the monolayer is observed through the window. The contact angle with the plate is also checked at this time. Since it is essential that this angle be zero, measurements can only be made under conditions such that the surface pressure rises as equilibrium is approached. Changes in surface pressure are recorded as changes in the position of the optical indicator on the scale. When the surface pressure under nitrogen has been recorded, the gas stream is directed through the equilibrator to saturate it with hexane and surface pressure is again recorded when the light spot stops moving.

We have been able to reproduce surface-pressure measurements to 0.05 dyne and surface concentrations to 0.1 Gibb ($= 0.1 \times 10^{-10}$ moles/cm.^{2}).[10] Equilibrium is usually reached in one-half hour at 30° using stearic acid and hexane vapor. Equilibrium values of surface pressures have been observed unchanged for 24 hours.

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(10) R. B. Dean, *J. Phys. Colloid Chem.*, **55**, in press (1951).

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The Sorption of Vapors by Monolayers. IV. Calculation of the Amount of Hexane Adsorbed on a Stearic Acid Monolayer[1]

BY KENNETH E. HAYES AND ROBERT B. DEAN[2]

A thermodynamic method for the calculation of the amount of organic vapor adsorbed on a long chain monolayer is presented, and the method applied to the system stearic acid–*n*-hexane. The thermodynamic standard state used in this computation is chosen as the surface concentration of stearic acid given by the spreading pressure of stearic acid under hexane vapor. The adsorption of hexane follows a type III isotherm at low stearic acid concentrations, but at high acid concentrations goes over to a type V with a limiting ratio of one molecule of hexane to one of stearic acid.

Stearic acid monolayers in the presence of organic vapors behave like expanded films of myristic acid. The amount of vapor adsorbed may be found by making use of the Gibbs adsorption equation.

Application of the Gibbs equation to the system: stearic acid, hexane, nitrogen and phosphoric acid solution (used as the liquid phase) leads to the result

$$-d\gamma = d\pi = S dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_N d\mu_N + \Gamma_A d\mu_A + \Gamma_W d\mu_W \quad (1)$$

where the subscripts 1, 2, N, A and W indicate, respectively, hexane, stearic acid, nitrogen, phosphoric acid and water. *S* denotes the surface density of the entropy, γ the surface tension and π the surface pressure. As we are dealing with a five-component system we need five independent

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(1) Presented by Dr. Myer G. Horowitz, at the 119th Meeting of the American Chemical Society, Colloid Division, Symposium on Surface Tension of Solutions, Boston, Mass., April, 1951.

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