

186. *Measurement of Specific Surfaces of Calcined and Hydrated Alumina Powders by Adsorption of n-Heptoic Acid from Aqueous Solutions.*

By L. SAUNDERS.

The adsorption of *n*-heptoic acid from dilute aqueous solutions by calcined and hydrated alumina powders, the surfaces of which have been freed from soluble alkali, has been examined by means of the surface-tension balance.

The ratio of weight of acid adsorbed to weight of adsorbent is constant for considerable variation of experimental conditions, indicating the formation of an adsorbed layer of definite structure.

This being assumed to be a unimolecular, oriented, condensed layer, the minimum area per acid molecule is 20.5 sq. Å. From this, minimum values of the true specific surfaces of the powders can be calculated.

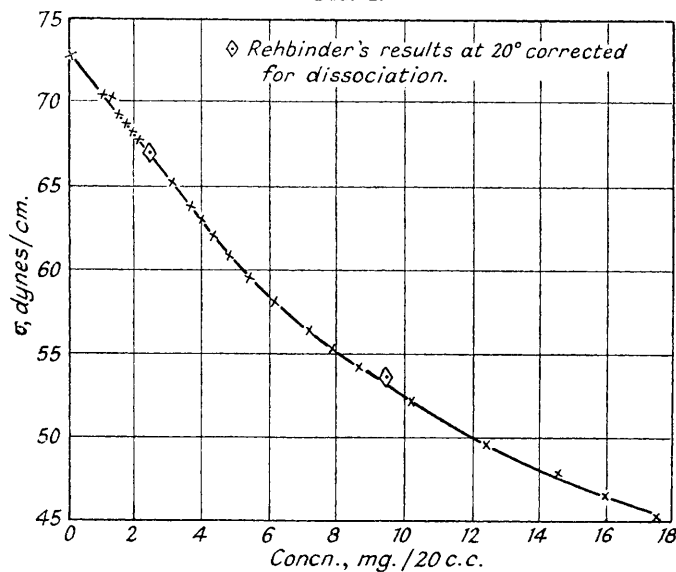
A LARGE number of adsorption methods for the determination of specific surfaces of fine powders have been developed. The disadvantage of many of these is that the adsorbate (*e.g.*, nitrogen, hydrocarbon vapours, dyes) has no particular surface activity, *i.e.*, shows no tendency to spread at an interface to form a unimolecular film. With such adsorbates, the transient formation of a unimolecular film has to be arbitrarily postulated. This difficulty can be overcome by the use of a surface-active adsorbate such as a higher fatty acid. If the carboxyl group affinity of the adsorbent is greater than that of the fluid containing the acid, an adsorbed film will be formed at the fluid-adsorbent interface in which the acid molecules will be oriented with their carboxyl groups towards the powder. In such an oriented film, the acid molecule is likely to occupy an area similar to that in a condensed, oriented film of fatty acid at an air-water interface, *i.e.*, 20.5 sq. Å.

Surface-active materials as adsorbates for the measurement of specific surface of powders have been used by Harkins and Gans (*J. Amer. Chem. Soc.*, 1931, **53**, 2804), Ewing (*ibid.*, 1939,

61, 1317), and Smith and Fuzek (*ibid.*, 1946, 68, 229). In each case non-aqueous solutions of the adsorbates were employed.

It seemed possible that a basic powder such as alumina might adsorb an oriented fatty-acid film from an aqueous solution of the acid. The author has found this to occur when calcined and hydrated alumina powders, the surfaces of which have been freed from soluble alkali, are shaken with dilute aqueous solutions of *n*-heptioic acid. The amount of acid adsorbed can be directly estimated by means of the surface-tension balance and is found to be dependent on the weight and fineness of the powder with which the solution is shaken. The ratio of weight of acid adsorbed to weight of adsorbent is independent of the time of contact of powder and solution provided complete mixing be obtained, it does not vary appreciably with temperature from 10° to 30°, and is independent of the initial concentration of acid solution over a considerable range. It is constant for considerable variation of weight of adsorbent, but decreases if too large a surface area of powder is added to very dilute acid solutions; under these conditions a condensed film of acid is probably not obtained. The constancy of this ratio indicates the formation of a stable adsorbed film of definite structure. It seems likely that this is an oriented, condensed film with an area per acid molecule of 20.5 sq. Å. If this is assumed,

FIG. 1.



Surface tension-concentration (corrected for dissociation): *n*-heptioic acid in water at 18°.

the absolute value of the specific surface of the powder can be calculated. It is possible that the area per molecule may have the higher value of 25 sq. Å., the limiting value for the slightly water-soluble, higher acids at the air-aqueous solution interface (Adam, "Physics and Chemistry of Surfaces", Oxford Univ. Press, 1941). However, following Harkins and Gans, and Smith and Fuzek, the lower value has been adopted. This gives minimum values for the true specific surfaces of the powders.

These minimum values agree moderately well with those obtained by the air permeability method of Lea and Nurse (*J. Soc. Chem. Ind.*, 1939, 58, 277) for coarser powders. With fine powders (> 1 sq. m. per g.), the adsorption method gives much higher results, probably owing to the fact that the very fine powders are considerably flocculated in air. The permeability method gives a specific surface corresponding to the mean particle size of the aggregates, whereas the adsorption method measures, in addition, the internal surface of the aggregates giving a specific surface corresponding to the ultimate particle size on which the chemical and catalytic activities of the powder depend.

The amount of heptioic acid adsorbed by alumina powders, free from soluble alkali on the surface, can be measured directly by means of the surface-tension balance. To determine a specific surface, varying weights of powder to produce total surfaces between 0.4 and 2.0 sq. m. are shaken with 20 c.c. of heptioic acid solution (concentration about 4.6 mg./20 c.c.), the mixture

is filtered, and the increase of surface tension ($\Delta\sigma$ dynes/cm.) due to adsorption of acid is found by balancing the filtrate against a sample of the original solution.

The surface tension-concentration curve for aqueous solutions of heptoic acid has been determined in detail at 18° by Sugden's maximum bubble pressure method (Fig. 1). The curve cuts the surface-tension axis at a point above the surface tension of water unless a correction for the dissociation of the acid is made. Using Dippy's value (*J.*, 1938, 1222) of the dissociation constant, 1.28×10^{-5} at 25°, the initial slope of the curve is only very slightly altered and it now cuts the surface-tension axis at $\sigma = 72.9$. The curve is linear for acid concentrations less than 5 mg./20 c.c. The slope of this initial portion is 2.49 dynes/cm. per mg./20 c.c. From Reh binder's results (*Z. physikal. Chem.*, 1924, 111, 447), corrected for dissociation, the following values of this initial slope have been calculated: at 0°, 10°, 20°, and 40°, 3.21, 2.75, 2.37, and 1.67 dynes/cm. per mg./20 c.c. The temperature coefficient in the vicinity of 18° is -0.04 per °c.

In a recent paper on the surface tension of aqueous solutions of the higher fatty acids, Douglas and Mackay (*Canadian J. Res.*, 1946, 24A, 8) describe measurements made by Ferguson and Hakes's modification of the capillary-rise method (*Proc. Physical Soc.*, 1929, 41, 214). They erroneously state that it is unnecessary to determine contact angles when this method is used. They also employ a Pyrex capillary which is far more likely to produce a contact angle with the acid solutions than a soda-glass tube. A plot of their results of lowering of surface tension of water by heptoic acid against concentration of acid (taking the I.C.T. value of 0.29% by weight as the saturation concentration of heptoic acid in water at 20°, as they express their concentrations as fractions of the saturation value) gives an irregular curve. These irregularities are due to the incidence of a contact angle between the heptoic acid solution and the Pyrex capillary. When a liquid does not completely wet the capillary, *i.e.*, has a contact angle on it, Ferguson and Hakes's method of measuring surface tension cannot be used, for the meniscus tends to stick in the capillary and its movement is not sensitive to small changes of pressure.

If $\Delta\sigma$ dynes/cm. is the increase of surface tension produced by shaking M g. of alumina powder with 20 c.c. acid solution (concentration < 5 mg./20 c.c.), we have

$$\text{Weight of acid adsorbed} = x = \frac{\Delta\sigma}{2.49 - 0.04t} \text{ mg.} \quad (1)$$

t is the amount by which the temperature of the solutions exceeds 18° at the time of balancing. (It is important that the two solutions should be at the same temperature when the balance point is determined.)

In a unimolecular, condensed film the acid occupies an area per molecule of 20.5×10^{-16} sq. cm., *i.e.*, 1 mg. of acid occupies 0.95 sq. m.

$$\text{Specific surface of powder} = 0.95 \times x/M \text{ sq. m./g.} \quad (2)$$

Thus the specific surface is simply related to the experimentally determined quantities $\Delta\sigma$ and M .

The accuracy of the specific surface determinations is considered to be $\pm 10\%$.

EXPERIMENTAL.

Before carrying out a specific surface determination, it is essential to remove soluble alkali from the powder surface, as this gives high results owing to neutralisation of the acid. The author has found that no further appreciable extraction of soluble alkali occurs after 4 hours' vigorous extraction of small samples of commercial alumina powders with boiling distilled water in a Soxhlet apparatus. The acid-insoluble, calcined alumina can be extracted with boiling, dilute hydrochloric acid. After extraction, the powders are dried at 110°. In some cases, the powders cake on drying, but this loose aggregation does not affect the value for specific surface found by this method.

n-Heptoic acid was obtained from B.D.H. On fractional distillation, nearly all the sample came over between 117° and 118°/13 mm. (cf. b. p. 117.5°/13 mm. from Pool and Ralston's results, *Ind. Eng. Chem.*, 1942, 34, 1104). This fraction had b. p. 222°/760 mm. (cf. Pool and Ralston, 223°). The surface tensions of aqueous solutions of the distilled acid showed no appreciable differences from those of the undistilled material.

The surface-tension balance is a modification of that described by Warren (*Phil. Mag.*, 1927, 4, 358). A Sugden maximum bubble pressure surface-tension apparatus (Adam, *op. cit.*), is joined by a Y-tube to a similar apparatus having identical tube tip dimensions, and to an air pressure line incorporating a water manometer. It is a great advantage to have an all-glass assembly as this eliminates clogging of the capillaries by crumbs and dust from rubber tubing. The wide bubbling tubes are of 3-mm. soda-glass; the identical capillaries are made by drawing out a piece of 3-mm. soda-glass tubing and cutting it carefully in the centre. The ease of operation and reliability of the balance depend entirely on the shape of the capillaries. They should taper continuously to the orifice with as short a constricted portion as possible, the wall at the tube tip should be thin, and the radius of the orifice should be about 0.1 mm. To obtain all these desirable properties in one pair of capillaries requires some practice.

The two apparatuses are calibrated separately with water and benzene, and the constants, A and B determined for the empirical equation relating surface tension σ (in dynes/cm.) of a liquid to the difference in maximum pressures required to blow bubbles on the narrow (h_n) and the wide (h_w) tube when they are immersed to the same depth in the liquid (of density d) :

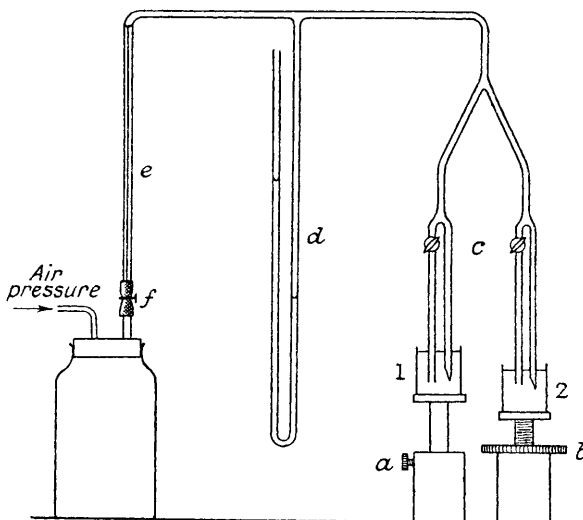
$$A(h_n - h_w + Bd) \dots \dots \dots (3)$$

h_n and h_w are pressures in cm. of water at 18°.

The value of B is mainly dependent on the radius of the wide tube and is small compared with ($h_n - h_w$). The identical tube tip dimensions are found to result in identical values of A and B .

To measure the difference of surface tensions of two heptoc acid solutions, they are placed in the beakers 1 and 2 as shown in Fig. 2. The taps to the wide tubes are closed and a rapid

FIG. 2.



Surface tension balance.

- 1, 2. Beakers containing solutions.
- a. Clamping screw for coarse adjustment of balance point.
- b. Milled wheel for fine adjustment.
- c. Taps to cut off wide tubes.
- d. Water manometer.
- e. Capillary tubing.
- f. Screw clip to adjust bubble rate.

stream of air is blown through the capillaries for several minutes; the stream is then reduced so that the capillaries bubble at a rate of about 1 per sec. The height of beaker 2 is adjusted until bubbles form alternately on the two capillaries. This balance point can be very sharply determined. At the balance point

$$\left. \begin{aligned} {}^1h_n &= {}^2h_n \\ \sigma_2 &= A({}^2h_n - {}^2h_w + B) \\ \sigma_1 &= A({}^1h_n - {}^1h_w + B) \end{aligned} \right\} \text{from equation (3) with } d = 1$$

$$\sigma_2 - \sigma_1 = A({}^1h_w - {}^2h_w)$$

$$\Delta\sigma = A \cdot \Delta h \dots \dots \dots (4)$$

The difference in surface tension is therefore proportional to the difference in maximum pressures required to blow bubbles on the two wide tubes at the balance point; 1h_w and 2h_w are measured on the water manometer by opening the taps separately.

If M g. of alumina powder are shaken with 20 c.c. of heptoc acid solution (concentration < 5 mg./20 c.c.) and the filtrate is balanced against the original solution, the two liquids being at the same temperature ($18^\circ + t^\circ$) at the time of balancing, then from equations (1), (2), and (4) :

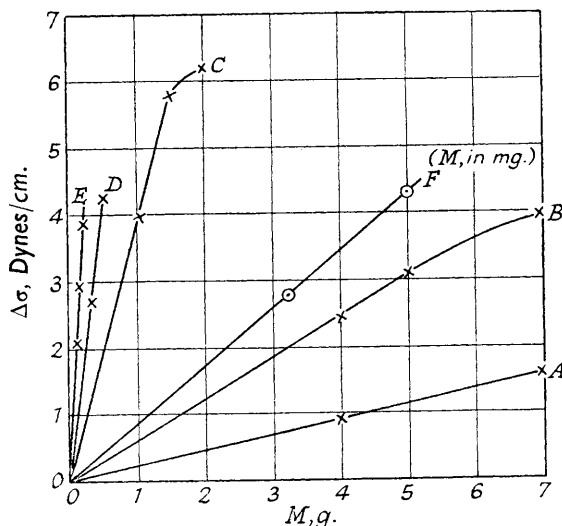
$$\text{Specific surface of powder} = \frac{0.95 A}{2.49 - 0.04t} \times \frac{\Delta h_w}{M} \text{ sq.m./g.}$$

In practice, the most suitable initial concentration of the heptoc acid solution has been found to be about 4.6 mg./20 c.c. (0.5 c.c. of acid to 2 l. of water). The weights of powder shaken with 20 c.c. of this solution should be such as to produce an adsorbing surface of 0.4—2.0 sq.m.

Grease-free distilled water of high surface tension was used for making up the solutions.

Fig. 3 shows values of $\Delta\sigma$ plotted against M for several alumina hydrate powders. The slopes of these curves are proportional to the specific surfaces of the powders. They indicate the relative inefficiency of ball milling for the production of alumina hydrate powders of high specific surface.

FIG. 3.



Increase of surface tension of heptico acid solution—weight of adsorbent (alumina hydrate) at 18°.

A. Through 200 B.S.S.	0.09 sq.m./g.
B. Milled 2 hrs.	0.24 sq.m./g.
C. Milled 8 hrs.	1.5 sq.m./g.
D. Milled 92 hrs.	3.4 sq.m./g.
E. } Specially prepared chemically to give large surface area	7.9 sq.m./g.
F. }	310.0 sq.m./g.

The following tables give further results of measurements.

Specific surface of alumina hydrate powders
(in sq. m./g.).

	Air permeability.	Adsorption.
A	0.09	0.09
B	0.18	0.19
C	1.00	1.51
D	1.05	310

Specific surface of calcined alumina powders.

	Air permeability.	Adsorption.
	0.53	0.76
	0.92	1.04
	0.81	1.64
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An X-ray pattern for powder D indicated a minimum specific surface of 250 sq. m./g.

Effect of variation of initial concentration of heptico acid.

Initial concn., mg./20 c.c.	Wt. of adsorbent, M, g.	$\Delta\sigma$, dynes/cm.	Wt. of acid adsorbed, x (mg.).	x/M , mg./g.
18.20 *	2.22	0.71	1.00	0.45
	4.15	0.94	1.25	0.30
	7.09	1.42	1.82	0.26
	9.89	1.71	2.18	0.22
9.10 *	1.59	0.59	0.42	0.26
	4.18	1.59	1.04	0.25
	7.71	2.77	1.82	0.24
	10.07	3.30	2.17	0.22
4.55	2.08	1.36	0.56	0.23
	4.21	2.89	1.18	0.26
	7.19	4.48	1.83	0.24
	9.67	5.66	2.31	0.23
2.27	1.94	1.30	0.53	0.27
	3.97	1.83	0.75	0.20
	7.66	2.65	1.13	0.15

* x is not directly proportional to $\Delta\sigma$ for solutions of concentration greater than 5 mg./20 c.c.

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