

683. *The Adsorption of Stearic Acid from Solution by Oxide Adsorbents.*

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In adsorption from solutions in cyclohexane, stearic acid is adsorbed with the major axis of the molecule parallel to the surface of silica, but perpendicular to the surfaces of alumina and titania. On silica there is close-packing of (probably dimeric) molecules, physically adsorbed. On alumina and titania monomeric molecules are adsorbed at specific sites, in some cases at spacings which preclude close-packing. The results are compared with those for adsorption on aqueous substrates.

There is some evidence that stearic acid is slowly chemisorbed by alumina.

STEARIC ACID is adsorbed from solution on homogeneous carbon surfaces with the major axis of the molecules parallel to the surface; the adsorbed molecules are probably dimeric.^{1,2} This is in contrast to the perpendicular orientation of stearic acid molecules in close-packed films on aqueous substrates,³ in which the molecules are monomeric. The difference in orientation is almost certainly due to the difference in polarity of the two substrates. The monomeric fatty acid molecules can form hydrogen bonds with water, but not with the almost non-polar carbon surfaces. In many organic solutions, stearic acid molecules are already hydrogen-bonded to form dimers, and the hydrogen-bonding is likely to remain in

¹ Kipling and Wright, *J.*, 1962, 855.

² Kipling and Wright, *J.*, 1963, 3382.

³ Adam, "The Physics and Chemistry of Surfaces," Clarendon Press, Oxford, 3rd edn., 1941.

the adsorbed molecules. The dimeric stearic acid molecule is very large and can therefore compete very effectively with the solvent for positions on the surface of a non-polar adsorbent. As there is good evidence that stearic acid is adsorbed by hydrated alumina in the perpendicular orientation,⁴ it is interesting to examine the orientation on solids intermediate in polarity between carbon and alumina.

The range of solids chosen is described in Table I. All were regarded as essentially

TABLE I.

Sample	Description	Nature of surface	Specific surface area (m. ² /g.)
Cab-O-Sil ^a	Flame silica	Almost free from -OH groups	190 ± 15 (N ₂)
Microsil ^b	Precipitated silica	Complete coverage of -OH groups	120 ± 10 (N ₂)
Alcoa C730 ^c ...	γ-Al ₂ O ₃ .3H ₂ O *	Close-packed surface of -OH groups	21.8
Alcoa D50 ^c	γ-Al ₂ O ₃ .H ₂ O *	Alternate =O and -OH groups	22.4
Alon C ^d	Flame alumina—mainly anhydrous γ-alumina	About 90% coverage by -OH groups	90 ± 5 (N ₂)
Alon (1200°) ^d ...	α-Al ₂ O ₃	Almost free from -OH groups	9.1 ± 0.5
TiO ₂ ^a	Flame titania: 95% anatase, 5% rutile	About 70% hydrated	45
TiO ₂ (1200°) ...		Almost free from -OH groups	0.34 (Kr)

^a Information from manufacturer. ^b Result provided by Dr. J. N. Sherwood. ^c Ref. 4.

^d Result provided by Dr. N. R. Thompson.

* The nomenclature varies; we have used the same designation as in Kipling and Peakall, *J.*, 1957, 834.

non-porous solids. Cyclohexane was used as the solvent to minimise the interaction between solvent and adsorbent.

RESULTS AND DISCUSSION

Orientation.—The adsorption isotherms are shown in Figs. 1—3. These are composite isotherms, but we have shown¹ that for these dilute solutions they approximate very closely to the individual isotherms for the adsorption of stearic acid. From each it is possible to obtain a limiting value of adsorption (Table 2), either from an obvious plateau in the isotherm, or by extrapolating the isotherm to the limit of solubility for the system. These

TABLE 2.

Adsorbent	Calc. monolayer value (millimoles of monomer per g.)		Limiting obs. value	Ratio of obs. to calc. value
	Perpendicular orientation	Parallel orientation		
	Cab-O-Sil	—		
Microsil	—	0.18	0.21	1.2
Alcoa C730 (1 day's contact)	0.18	—	0.19	1.1
Alcoa C730 (7 days' contact)	0.18	—	0.21	1.2
Alcoa D50	0.18	—	0.085	0.47
Alon C	0.73	—	0.70	1.0
Alon C (1200°)	0.074	—	0.075	1.0
TiO ₂	0.37	—	0.25	0.68
TiO ₂ (1200°)	0.0028	—	0.0035	1.25

limiting values are compared with calculated monolayer values based on the two orientations for stearic acid, with molecular areas (expressed in terms of the monomeric molecules) of 114 Å² for the parallel orientation,¹ and 20.5 Å² for the perpendicular orientation. As these molecular areas differ by a factor of approximately five, there is little difficulty in deciding which orientation is adopted on each solid.

⁴ Russell and Cochran, *Ind. Eng. Chem.*, 1950, **42**, 1332.

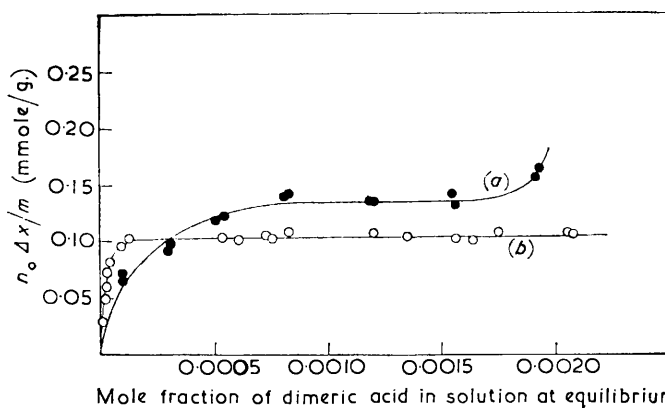


FIG. 1. Adsorption of stearic acid from solutions in cyclohexane (a) on Cab-O-Sil and (b) on Microsil.

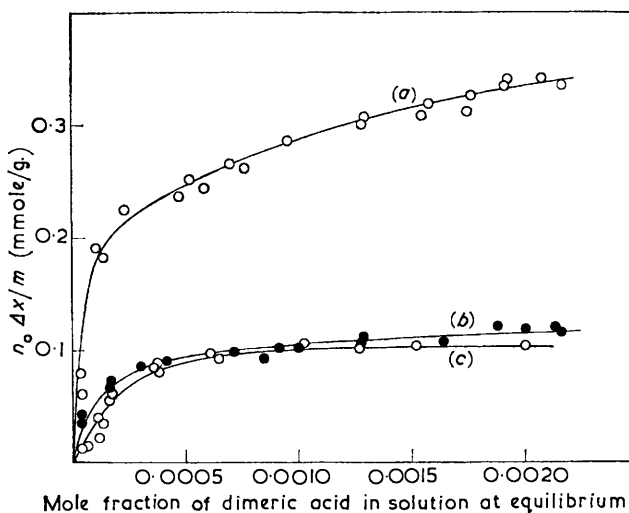


FIG. 2. Adsorption of stearic acid from solutions in cyclohexane (a) on Alon C, (b) on titania, (c) on Alcoa C730.

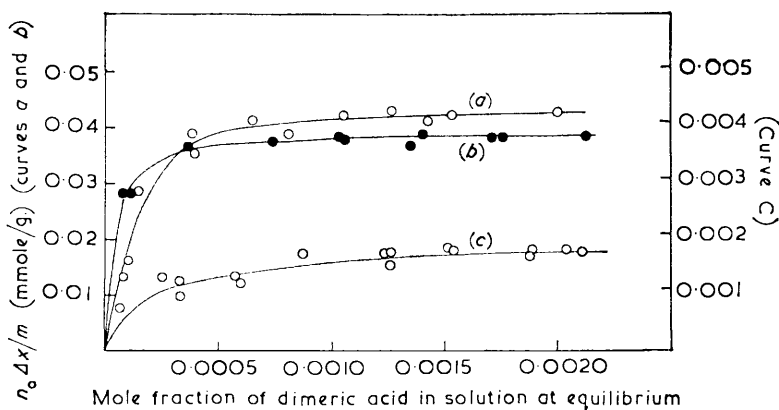


FIG. 3. Adsorption of stearic acid from solutions in cyclohexane (a) on Alcoa D50, (b) on Alon C (1200°), and (c) on TiO₂ (1200°).

(i) *Silica*. For both samples of silica, the results show that the stearic acid molecules are adsorbed in the parallel orientation, as on Graphon.

(ii) *Alumina*. For all except one sample, it is clear that the perpendicular orientation is adopted. The adsorption on Alcoa D50 is too great to correspond to the parallel orientation, but the limiting value is much less than for a close-packed monolayer in the perpendicular orientation.

(iii) *Titania*. The original sample of titania also forms less than a close-packed monolayer in the perpendicular orientation. The specific surface area of TiO_2 (1200°) is so small that it is reasonable to conclude only that the perpendicular orientation is adopted.

Adsorption at Specific Sites.—Adsorption to give less than a close-packed monolayer is unlikely to be due to competition from the solvent if the solute is so strongly attracted to the surface that it adopts the perpendicular orientation. It is more likely that the monomeric molecules are adsorbed, by hydrogen-bonding or even by chemisorption (see below), at specific sites on the surface, so that the closeness of packing in the adsorbed layer is determined by the spacings of the sites.

It happens that stearic acid can be adsorbed on a surface of close-packed oxide or hydroxide ions so as to leave very little space between the molecules. This explains the complete coverage of anhydrous alumina and of the trihydrate.* The arrangement is shown in Fig. 4, which is to scale. The outline of the stearic acid molecule corresponds to the projection first drawn in this form by Vold.⁶ It shows the outline of the zig-zag methylene chain, and the projecting (carbonyl) oxygen atom of the carbonyl group. The radius of the oxygen ion is taken⁷ as 1.25 Å, as in $\alpha\text{-Al}_2\text{O}_3$, though it may be slightly larger in other crystals,⁸ as may the radius of the hydroxide ion. de Boer *et al.*⁹ suggest that one molecule of lauric acid can be adsorbed for every four surface oxygen atoms. Fig. 4 represents this more specifically than did his diagram. Alumina monohydrate* has a layer structure,¹⁰ and stearic acid molecules cannot be adsorbed as closely. Fig. 5 shows a possible arrangement on the *a* plane, the ions being drawn with a radius of 1.4 Å. This arrangement gives an apparent surface coverage of 46%. The corresponding values for the *b* and *c* planes are 49 and 59%, respectively. Thus if the three planes present in equal proportions at the surface of the adsorbent, the average apparent surface coverage would be 51%, which is close to the value found experimentally (47%).

Interpretation of the results for titania is more speculative. The surface of the original sample is partly hydrated, and it is difficult to know what structure should be assumed for the layer of hydrated material adhering to the anhydrous crystal. A calculation can be made on the assumption that the position of the titanium atoms¹¹ is not greatly disturbed by the process of hydration and that the spacing of the oxide or hydroxide centres on which the stearic acid molecules are attached is governed by that of the titanium atoms. On this basis an apparent surface coverage of 64% can be calculated. The close agreement with the experimental value (68%) is probably fortuitous, but a less close agreement would still have supported the supposition that stearic acid is adsorbed at specific sites on this surface.

Chemisorption.—The possibility of studying adsorption on a more basic oxide such as magnesia was considered, but continuous chemical reaction occurred which involved the whole of the solid in bulk. It was therefore relevant to investigate whether reaction leading to chemisorption might occur with alumina or titania.

* Alcoa C730 and Alcoa D50 contain traces of free alkali.⁵ Adsorption results for these two solids may therefore be slightly high.

⁵ Russell and Cochran, *Ind. Eng. Chem.*, 1950, **42**, 1336.

⁶ Vold, *J. Colloid Sci.*, 1952, **7**, 196.

⁷ Pauling and Hendricks, *J. Amer. Chem. Soc.*, 1925, **47**, 781.

⁸ Pauling, "The Nature of the Chemical Bond," 2nd edn., Cornell U.P., Ithaca, N.Y., 1948.

⁹ de Boer, Houben, Lippens, Meijs, and Walrave, *J. Catalysis*, 1962, **1**, 1.

¹⁰ Russell, "Alumina Properties," Technical Paper No. 10, Aluminum Company of America, Pittsburgh, 1953.

¹¹ Remy, "Treatise on Inorganic Chemistry," Vol. 2, p. 59, Elsevier, Amsterdam, 1956.

A first indication is given by results of desorption experiments (Table 3). Adsorbed stearic acid can be removed completely from silica and titania (as it can from Graphon and Spheron 6, results for which are not given in the Table). Recovery from alumina decreases

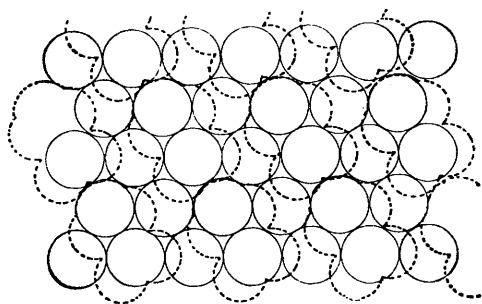


FIG. 4. Adsorption of stearic acid molecules on close-packed oxide or hydroxide ions.

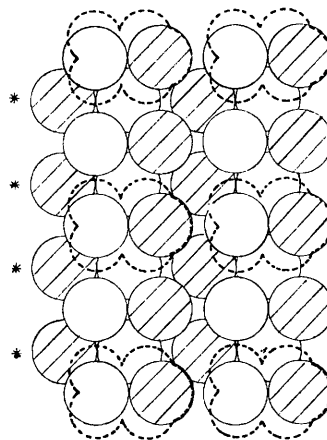


FIG. 5. Adsorption of stearic acid (dotted outline) on the a plane of gamma-alumina monohydrate. The shaded circles represent hydroxyl ions, the unshaded circles represent oxide ions. Rows marked * are at a slightly lower level than their neighbours.

as the contact time for initial adsorption increases. This suggests that, after initial physical adsorption, slow chemisorption follows.

This conclusion was supported by infrared analysis of the products of desorption. After adsorption for 1 day on alumina, the desorption product was entirely stearic acid. After 7 or 40 days' contact, however, the spectrum of the desorbate showed extra frequencies which suggested the presence of traces of aluminium monostearate. Our results therefore

TABLE 3.

Time allowed (A) for initial adsorption and (B) for desorption, and C the percentage of adsorbed acid remaining on adsorbent.

Adsorbent	A (days)	B (hours)	C	Adsorbent	A (days)	B (hours)	C
Microsil	10	72	0	Alcoa D50	1	72	0
TiO ₂	1	72	0		10	96	14
	10	72	0		40	96	20
	30	72	0	Alon C (1200°)	3	72	0
Alcoa C730	1	96	0		10	72	9
	7	96	27		40	96	15
	40	96	40				

agree with Schonhorn's conclusion¹² that a surface stearate can be formed by reaction between stearic acid and "sulfochromated" aluminium, which probably has a layer of oxide on the surface.

Nature of Substrate.—On the evidence available, it appears that stearic acid adopts a perpendicular orientation only on the oxides of the more electropositive elements (aluminium and titanium), and not on those of the more electronegative (silicon), even though this orientation is taken up on aqueous substrates. The question as to which orientation is adopted probably turns on quite small differences in energies of interaction. The heat of adsorption on the oxides is likely to increase with increasing electropositive character of the element concerned. As adsorption must occur at sites which prevent close-packing in

¹² Schonhorn, *J. Colloid Sci.*, 1963, **18**, 445.

the strict sense, the energy of lateral interaction, which must be appreciable in close-packing in the parallel orientation, is no longer available. By contrast, water is a mobile substrate which can adjust itself, under pressure, to allow close-packing of the hydrocarbon chains, with lateral interaction, while still permitting hydrogen-bonding between the carboxyl groups and the substrate.

Experimental.—The properties of the stearic acid and cyclohexane used have been described.^{1,2} The solutions were estimated by titration.¹ Adsorption was carried out at 20°. Desorption was carried out by placing the adsorbent in a column and passing a stream of cyclohexane through it continuously at 20°. The specific surface areas of the adsorbents were determined by low-temperature adsorption of nitrogen or krypton.

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