627. *Adsorption on Carbon Black from Solutions of Monocarboxylic Acids: the Higher Members.*

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The adsorption on carbon blacks of the monocarboxylic acids (caprylic, lauric, palmitic, and stearic) from organic solvents is governed by three main factors. First, adsorption is greater on Graphon, which is free from surface complexes, than on Spheron, which is heavily covered; the three higher members of the series readily form a complete monolayer on the former, but not on the latter. Secondly, a given degree of adsorption occurs at a lower concentration the higher the molecular weight of the acid. Thirdly, the solvent competes with the solute to an extent which depends on the nature of the solid surface.

IN many of the classical studies of adsorption from solution the monocarboxylic acids were used,[1] and some attempt was made to consider adsorption in terms of the homologous series. These studies were limited, insofar as they were confined to aqueous solutions, both by the complexity of the solutions (that of acetic acid has been extensively investigated [2]) which makes interpretation difficult, and by the small number of acids which could be investigated. In some cases, moreover, difficulties in interpreting the results arose because the adsorbents, though known to be porous, had not been characterised further. This was particularly the case in examining the application of Traube's rule to adsorption by solids.

The adsorption of longer-chain fatty acids (notably stearic acid) from solution in organic solvents has also been studied. When non-porous adsorbents were used, it was possible to draw definite conclusions about the extent of adsorption and to suggest what orientation was adopted by the adsorbed acids. Experiments of this kind with carbon blacks have already been reported for stearic acid.[3] It was thought useful to extend the investigation to further selected members of the homologous series. It then became evident that no simple pattern of adsorption could be described for the series as a whole because a variety of factors was involved. The results for the higher members of the series are presented in this paper, and those for the lower members will be given later.

EXPERIMENTAL

Adsorbents.—The carbon blacks, Spheron 6 and Graphon, have been described previously.[3] Spheron 6 (1000°) is made by heating Spheron 6 to 1000° for 1 hr. with exclusion of air. Its surface area, determined by low-temperature adsorption of nitrogen, is 91 sq. m. per g. The thermal treatment removes almost all of the oxygen originally present as complexes on the surface of Spheron 6, and leaves about 0·4% by weight of hydrogen.

Fatty Acids.—Stearic (C_{18}), palmitic (C_{16}), and lauric (C_{12}) acids were supplied as pure samples by Messrs. Price's (Bromborough) Ltd. Analysis of the methyl esters by vapour-phase chromatography showed them to be, respectively, 99·99%, 99·99%, and 99·95% pure. M. p.s agreed with those quoted in the literature.[4]

Octanoic (caprylic) acid (C_8), from the same supplier, was fractionally distilled under reduced pressure. The fraction used had n_D^{20} 1·4281 (cf. the recorded value [5] of 1·4280).

The solubilities of the acids in the solvents used were, in general, taken from the literature.[6] Those for stearic acid were, however, re-determined when it was found impossible to prepare solutions corresponding to the values given. Our determination was based on analysis of the

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[1] Freundlich, " Colloid and Capillary Chemistry," Methuen, London, 1926.

[2] Fénéant-Eymard, *Mém. Services chim. État.*, 1952, **37**, 297.

[3] Kipling and Wright, *J.*, 1962, 855.

[4] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[5] Dorinson, MacCorkle, and Ralston, *J. Amer. Chem. Soc.*, 1942, **64**, 2739.

[6] Ralston and Hoerr, *J. Org. Chem.*, 1942, **7**, 546.

saturated solutions at 20° prepared from solutions initially above and below this temperature.[7] The results are given in Table 1.

TABLE 1.

Solubilities of stearic acid at 20°.

Solvent	Solubility (g. acid per 100 g. solvent): Ralston and Hoerr [6]	Present values
Benzene	2·46	1·91
Cyclohexane	2·40	1·51
Carbon tetrachloride	2·40	2·10

Octanoic acid is completely miscible at 20° with each of the solvents used.

Procedure.—In all cases, adsorption was carried out at 20°. The solvents used have been described previously.[3]

Solutions of stearic acid and palmitic acid were analysed by titration.[3] Solutions of lauric and of octanoic acid were analysed interferometrically. The analysis of the octanoic acid–carbon tetrachloride system at high mole fractions was less accurate than that for low mole fractions or for other systems.

Monolayer Values.—The quantities of the adsorbates required to form a complete monolayer on the surface of the adsorbents is given in Table 2. Those for the solvents were calculated, by use of the B.E.T. equation, from the isotherm for adsorption of the vapour. Those for the acids have been calculated on the assumption that the molecules are dimeric in the adsorbed state, and lie with the major axis parallel to the surface. A diagram illustrating this orientation is given in an earlier paper.[3] The calculated molecular areas for this orientation are also given in Table 2.

TABLE 2.

Monolayer values in millimoles/g.

	Calc. area per dimeric molecule (sq. Å)	Spheron 6	Spheron 6 (1000°)	Graphon
Benzene		0·45 *	0·35	0·32 †
Cyclohexane		0·40 *	0·30	0·29
Carbon tetrachloride		0·43	0·34	0·32
Stearic acid	228	0·084	0·067	0·062
Palmitic acid	204	0·094	0·074	0·069
Lauric acid	160	0·119	—	0·087
Octanoic acid	116	0·165	—	0·121

* Blackburn, Kipling, and Tester, *J.*, 1957, 2373. † Cf. Gasser and Kipling, Proc. Fourth Conference on Carbon, Pergamon Press, London, 1960, p. 55.

The results for the fatty acids are expressed in terms of the dimeric molecule in each case. The acids are thought to exist predominantly as dimeric molecules in these organic solvents over most of the range of concentration used,[8] except for solutions in ethyl alcohol. This was checked ebulliometrically for a solution containing 1·3 g. of stearic acid per 100 g. of cyclohexane. Results obtained by the transpiration method, though not of high accuracy, suggested that lauric acid is essentially dimeric when dissolved in cyclohexane, but monomeric in ethyl alcohol.

Desorption.—Stearic acid which had been adsorbed on either Spheron 6 or Graphon from cyclohexane, could be removed completely by washing the adsorbent with cold cyclohexane. A period of less than 72 hr. was required. This is evidence that stearic acid is not strongly adsorbed by these carbon blacks.

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[7] Vold and Vold in " Physical Methods of Organic Chemistry," ed. Weissberger, 2nd edn., Vol. I, Part I, p. 297, Interscience Publ., Inc., New York, 1949.

[8] Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755, 767.

RESULTS AND DISCUSSION

The experimental results are shown in Figs. 1—6. Those for adsorption of stearic acid on Spheron 6 and Graphon are given in a previous paper.[3]

These isotherms show the surface excess of the acids in the adsorbed layer, $n_0 . \Delta x/m$. To discuss the actual surface concentration, a distinction must be made between octanoic acid, which is miscible in all proportions with the " solvents," and the three higher acids which are solids forming solutions with a limited solubility. For adsorption from a system of two components:

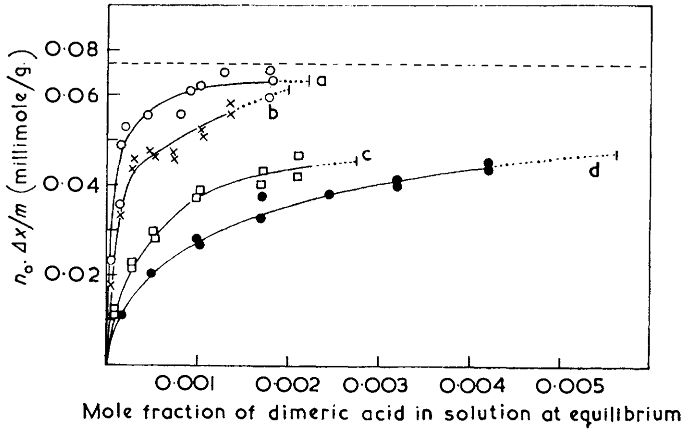

FIG. 1. Adsorption (composite isotherms) on Spheron 6 (1000°) from solutions of stearic acid in (a) cyclohexane, (b) ethyl alcohol, (c) benzene, (d) carbon tetrachloride. The broken line shows the calculated value for a complete monolayer. The vertical bar at the end of each isotherm shows the solubility limit.

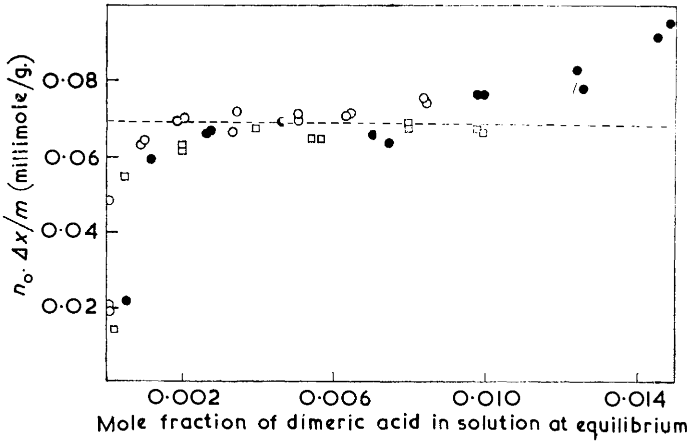

FIG. 2. Adsorption (composite isotherms) on Graphon from solutions of palmitic acid in: ○ cyclohexane, ● carbon tetrachloride, □ benzene. The broken line shows the value of $n_0 . \Delta x/m$ calculated for adsorption of a complete monolayer of palmitic acid.

$$n_0 . \Delta x/m = n_1^s . (1 - x) - n_2^s . x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Δx is the decrease in mole fraction of component 1 in the bulk liquid which occurs when m g. of adsorbent are brought into contact with n_0 moles of liquid, x is the mole fraction of component 1 in the bulk liquid at equilibrium, and n_1^s and n_2^s are the numbers of moles of components 1 and 2, respectively, adsorbed per g. of solid.

For the solutions of these solids, we have shown[3] that n_1^s differs very little from $n_0 . \Delta x/m$, even for high relative solubilities in the lauric acid systems.[3] For the octanoic acid systems, however, n_1^s and n_2^s must be calculated separately; this has been done by combining equation (1) with the following equation.

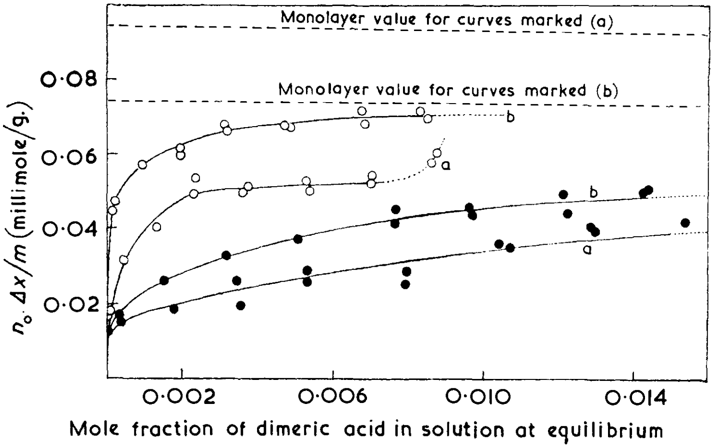

FIG. 3. Adsorption (composite isotherms) on Spheron 6 and Spheron 6 (1000°) from solutions of palmitic acid in: ○ cyclohexane, ● carbon tetrachloride; (a) adsorption on Spheron 6, (b) adsorption on Spheron 6 (1000°). The broken lines show the values of $n_0 . \Delta x/m$ for a complete monolayer of palmitic acid on Spheron 6 (upper curve) and on Spheron 6 (1000°) (lower curve). The vertical bar shows the solubility limit for the system concerned.

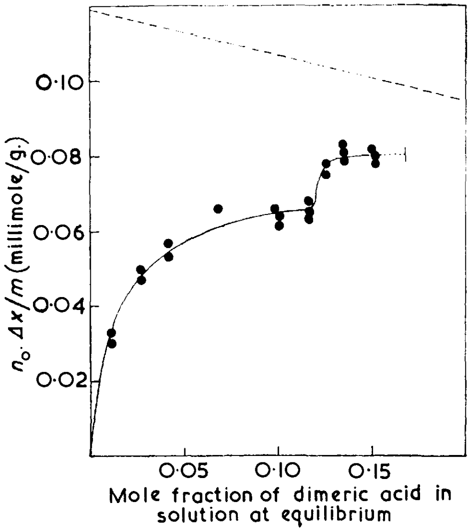

FIG. 4. Adsorption (composite isotherms) on Spheron 6 from solutions of lauric acid in carbon tetrachloride. The broken line shows the value of $n_0 . \Delta x/m$ calculated for adsorption of a complete monolayer of lauric acid. The vertical bar shows the solubility limit for the system concerned.

$$\frac{n_1^s}{(n_1^s)_m} + \frac{n_2^s}{(n_2^s)_m} = 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $(n_1^s)_m$ and $(n_2^s)_m$ are the numbers of moles of components 1 and 2, respectively, required to form a complete monolayer on the adsorbent. For the octanoic acid systems,

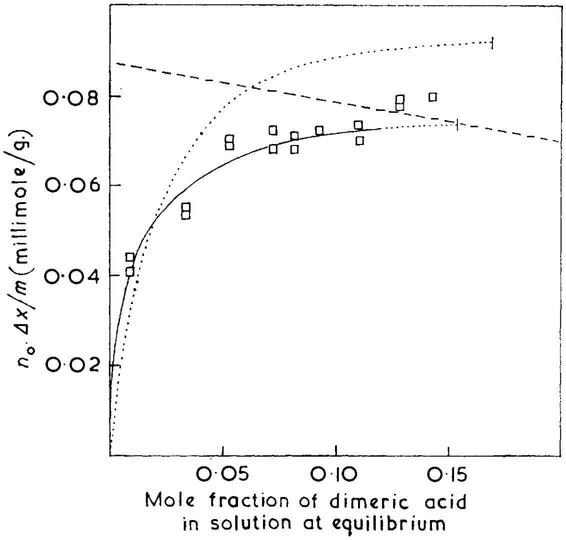

FIG. 5. Adsorption (composite isotherms) on Graphon from solutions of lauric acid in benzene. The dotted curve (reproduced from Fig. 1 of ref. 3) is the isotherm for adsorption from carbon tetrachloride. The broken line shows the value of $n_0 . \Delta x/m$ calculated for a complete monolayer of lauric acid.

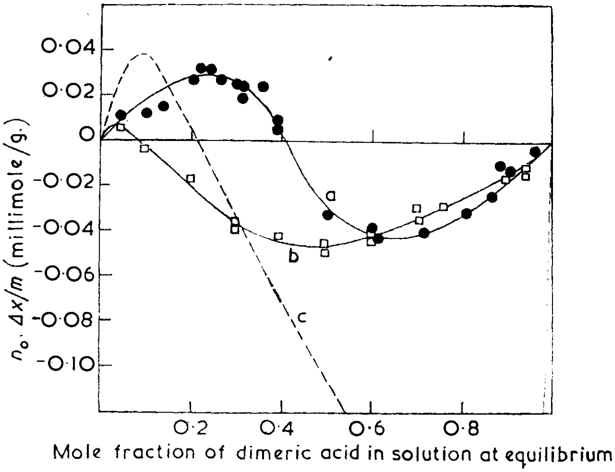

FIG. 6. Adsorption (composite isotherms) (a) on Graphon from solutions of octanoic acid in carbon tetrachloride, (b) on Graphon from solutions of octanoic acid in benzene, (c) on Spheron 6 from solutions of octanoic acid in carbon tetrachloride.

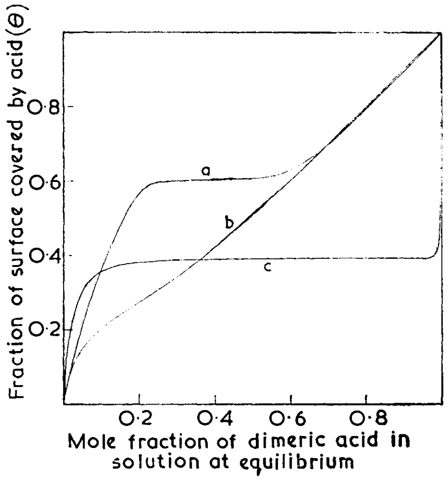

FIG. 7. Surface coverage by octanoic acid in adsorption (a) on Graphon from solutions in carbon tetrachloride, (b) on Graphon from solutions in benzene, (c) on Spheron 6 from solutions in carbon tetrachloride.

the composite isotherms are shown in Fig. 6. The individual isotherms (Fig. 7) have been plotted in terms of surface coverage (θ), to permit ready comparison of adsorption on the two adsorbents. Equation (2) was used in the expectation that the adsorbed layer would be no more than one molecule thick. The results are compatible with this view except at the higher concentrations for some systems.

Nature of the Solid Surface.—The isotherms for adsorption of palmitic and lauric acid on Spheron 6 (Figs. 3 and 4) and on Graphon (Figs. 2 and 5) are qualitatively similar to those for adsorption of stearic acid on the same adsorbents.[3] Adsorption on Graphon reaches approximately the value expected for a complete monolayer, the molecules of the acids being assumed to be adsorbed with the major axis parallel to the surface. As in a previous paper dealing with stearic acid,[3] the value of $n_0 \,.\, \Delta x/m$ corresponding to the formation of a complete monolayer is shown (Figs. 1—5) as a broken line. From equation (1) if there is no adsorption of solvent, we have:

$$n_0 \,.\, \Delta x/m = (n_1{}^{\mathrm{s}})_{\mathrm{m}} \,.\, (1 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Palmitic and lauric acid are more soluble than stearic acid in the solvents used, and the broken lines can be seen not to be parallel to the concentration axis; this is in accordance with equation (3). There is a tendency for the monolayer value to be slightly exceeded at the highest concentrations.

On the homogeneous and relatively inert surface of Graphon, there is little competition for the surface from the solvent, and a close-packed adsorbed layer is readily formed. Competition from the solvent increases as the chain-length of the acid decreases (as indicated by the increasing concentration needed for the formation of a complete monolayer of acid); this effect is already known for the adsorption of these acids from benzene on nickel powder.[9] For octanoic acid the completion of the monolayer is only attained from the pure acid. The same result can be expressed in terms of partition of the acids between the adsorbed layer and the bulk solution. The solubility of the acids increases as the chain-length decreases, *i.e.*, there is an increasing tendency for the acids to remain in the solution at the expense of the adsorbed layer.

By contrast, a complete monolayer of acid is not formed on Spheron 6 from any of the solutions investigated. The polar groups present on this carbon black are presumed to be capable of polarising the molecules of the solvents more than the paraffin chains which form the major part of the molecules of the higher fatty acids. Competition from the solvent for the surface is now much more effective, and the acid may be able to cover less of the surface than does the solvent.

The isotherms for adsorption on Spheron 6 (1000°) lie between those for untreated Spheron 6 and Graphon (Fig. 1). (For stearic acid, the isotherms shown in Fig. 1 should be compared with those in Figs. 3 and 4 of reference 3.) The formation of a complete monolayer is approached in the adsorption of stearic acid from cyclohexane and ethyl alcohol, and of palmitic acid from cyclohexane, but not from benzene or carbon tetrachloride (Fig. 3). The difference between the adsorptive properties of Spheron 6 and Spheron 6 (1000°) are probably due mainly to the absence of oxygen complexes on the surface of the latter. This would account for the reversal of order of the isotherms for benzene and carbon tetrachloride solutions as benzene is strongly held by oxide surfaces. The difference between Spheron 6 (1000°) and Graphon is probably due in part to the absence of hydrogen from the surface of Graphon, but it may also result from the greater degree of order of the carbon structure in Graphon.

The effect of surface on the extent of adsorption of stearic acid has been observed previously. Morris and Hollister[10] observed that surface coverage ranged from 5% to 19% for different carbon blacks when n-hexane was used as the solvent. These authors

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[9] Daniel, *Trans. Faraday Soc.*, 1951, **47**, 1345.

[10] Morris and Hollister, *Ind. Eng. Chem.*, 1948, **40**, 2325.

used a molecular area for the acid of 21 sq. Å, which implies orientation of monomeric molecules perpendicular to the surface. If, however, a parallel orientation is assumed, the surface coverage ranges from 27% to 103%, which corresponds to the range which we have observed.

The Effect of Chain-length.—The increasing readiness of the acids to form a complete monolayer on Graphon with increasing chain-length can be attributed to the simultaneous operation of two effects. Given that the molecules are adsorbed with the major axis parallel to the surface, the heat of adsorption per mole must increase with the number of methylene groups in the molecule. (It has been found for adsorption of glycine and its di-, tri-, and tetra-peptide on calcium montmorillonite from aqueous solution that the free energy of adsorption, $-\Delta G^*$, increases proportionately to the molecular weight.[11]) Correspondingly, the solubility in the solvents used decreases, *i.e.*, the acids show a decreasing tendency to remain in the liquid phase.

The same sequence is found for the adsorption on the other carbon blacks when adsorption is compared at a given mole fraction. This pattern may be expected to be followed by acids of longer chain-length than those investigated, but it will be shown in a subsequent paper that the lower fatty acids exhibit a more complex pattern.

The Effect of Solvent.—The solvent can have two effects, which do not necessarily operate in the same direction for different adsorbents. One is to compete with the solute for the solid surface; the other is, for a good solvent, to promote retention of the solute in the liquid phase at the expense of the adsorbed phase.

These two effects may not be easily separable in a given case, but their individual importance can be demonstrated. Thus stearic and palmitic acid form a complete monolayer on Graphon at relatively low concentrations from the solvents investigated, but do not form a complete monolayer on Spheron 6 from solutions of the highest available concentrations. This is attributable to the small attraction of the Graphon surface for any of the solvents, but a considerable attraction of the Spheron 6 surface, varying with the nature of the solvent. If the surface of Spheron 6 is regarded as consisting of hydrogen atoms (in aromatic or hydro-aromatic systems) and oxygen atoms present in various polar groups, the attraction for the solvents would decrease in the order ethyl alcohol, benzene, carbon tetrachloride, cyclohexane, and adsorption of the acids would increase in this order. For adsorption of stearic acid,[3] this order is observed except that ethyl alcohol is out of place, adsorption being greater than would correspond to this sequence. This may be due to two causes. Ethyl alcohol is very strongly held by the polar groups on the Spheron 6 surface and, when adsorbed, may present an " alkylated " surface [12] on which the fatty acids can subsequently be adsorbed quite readily. Further, the fatty acids tend to exist as monomers to a greater extent in ethyl alcohol than in the other solvents, and may thus be more readily attracted to the polar groups in the surface. The order for Spheron 6 (1000°), in the absence of oxygen groups, is carbon tetrachloride, benzene, ethyl alcohol, cyclohexane.

The effect of solubility is seen in the increasing mole fraction required to produce a complete monolayer on Graphon from a given solvent as the chain-length of the acid decreases and its solubility increases.

A further effect which may be dependent on the solvent used is shown in Fig. 4. A step occurs in the isotherm for adsorption of lauric acid on Spheron 6 from carbon tetrachloride. The step is relatively small, though quite definite, and could not easily be attributed to the formation of a second layer of adsorbate. It seems most likely to be due to a phase change in the adsorbed layer of lauric acid, though there is no indication why this should occur.

Individual Isotherms.—As we have shown previously,[3] the individual isotherms for

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[11] Greenland, Laby, and Quirk, *Trans. Faraday Soc.*, 1962, **58**, 829.

[12] Gasser and Kipling, Proc. Fourth Conference on Carbon, Pergamon Press, London, 1960, p. 55.

adsorption of the higher acids differ little from the composite isotherms, because the solubility is low. For the octanoic acid systems, however, this is not the case. The individual isotherms have been calculated on the assumption that the adsorbed phase is confined to a simple molecular layer and are shown in Fig. 7 in terms of the fraction of the surface covered (θ).

Two features are important. Even on Graphon, a complete monolayer of octanoic acid is not readily formed, by contrast with adsorption of the higher acids. This will be considered further when results for the lower acids are presented in a subsequent paper.

Secondly, each of the isotherms for adsorption from carbon tetrachloride (on Graphon and on Spheron 6, severally) passes through a prolonged plateau. This is analogous with the break in the adsorption of lauric acid from the same solvent on Spheron 6.

One of us (E. H. M. W.) is indebted to the Sierra Leone Government for the award of a research scholarship, during the tenure of which this work was carried out. We are grateful to the Cabot Corporation for the gift of the carbon blacks, and to Messrs. Price's (Bromborough) Ltd. for the gift of the purified fatty acids.

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