160. *Adsorption from Binary Systems of Limited Concentration Range: Application of Some Fundamental Concepts.*

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The adsorption on carbon blacks of stearic acid from four organic solvents has been examined. The isotherms have been considered in the light of concepts previously applied to adsorption from completely miscible liquids.

At very low concentrations the composite isotherm is a close approximation to the isotherm for adsorption of the solute, but the two curves diverge with increasing concentration. The extent of adsorption of stearic acid on Spheron 6 varies markedly according to the solvent and is much less than a monolayer at the highest available concentrations. On carbon blacks which have been heated to high temperatures, a complete monolayer is formed at high relative concentrations. The stearic acid molecules are adsorbed with the major axis parallel to the surface.

The individual isotherms obey the Langmuir equation, but the equation cannot be used to calculate monolayer values. Consequently, this type of adsorption does not provide a primary method of determining specific surface areas of solids. Before it is so used, it is necessary to know whether the solute forms a complete monolayer on that type of solid, and what molecular orientation is adopted.

IN early investigations of adsorption from solution by solids, for example those made by Freundlich and summarised in his book,[1] no distinction was made between systems of limited miscibility or solubility (*e.g.*, aqueous solutions of phenol or benzoic acid) and those of complete miscibility (*e.g.*, aqueous solutions of acetone or acetic acid). Attention was usually confined to dilute solutions, the isotherm was assumed to represent the adsorption of the " solute," and it was usually represented by the so-called Freundlich equation. Later the Langmuir equation was used in a form thought to be appropriate for adsorption from solutions, the pressure terms being replaced by concentration terms. This led to the use of adsorption from solution for evaluating surface areas of solids, although no justification was given for this application of the Langmuir equation to a type of system for which it has not been derived.

More recently it has been shown that these assumptions give a quite inadequate description of adsorption from completely miscible pairs of liquids. Both components are normally adsorbed, and the experimentally determined isotherm is a measure of the net effect on the concentration of the solution. This " adsorption " is comparable with " surface excess " (as defined according to the $\Gamma^{(N)}$ convention) as applied to the liquid–vapour interface.[2] When the complete isotherm is investigated, it can never be represented by the Freundlich or the Langmuir equation. Moreover, although methods have been suggested for determining the isotherms for the individual adsorption of each component, they cannot in general be described by a Freundlich or a Langmuir equation.[3] The use of such isotherms for determining specific surface areas of solids thus has in general no firm theoretical foundation.

In view of these findings, it is important to re-examine adsorption from systems of limited concentration range. This is the first of a series of investigations of adsorption from such solutions by solids of known specific surface area. At present the systems are confined to two-component mixtures.

EXPERIMENTAL

Adsorbents. The two main adsorbents, Spheron 6 and Graphon, were carbon blacks chosen because they are believed to be non-porous. Spheron 6 is a medium-processing channel black

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

[2] Kipling, Proc. Third Intern. Congress of Surface Activity, Verlag der Universitätsdruckerei, Mainz, 1961, Vol. II, p. 77.

[3] Kipling and Tester, *J.*, 1952, 4123.

with a relatively high uniformity in particle size; [4] the arithmetic mean diameter is 250 Å. Its specific surface area is known from measurements of adsorption of nitrogen which have been confirmed by electron microscopy. The surface areas of the other carbons were also known from one or both of these measurements, most of which had been made by the manufacturers and are given in the Table.

	Specific surface area (m.^{2} per g.) from:	
	N_2 adsorption	electron microscopy
Spheron 6	115	106
Graphon	84	
Carbolac I (2400°)	237	210
Monarch 74 (2000°)	194	150
Sterling MT (2700°)	7—10	8·4

Graphon could alternatively be designated as Spheron 6 (2700°), as it is made by heating Spheron 6 to 2700°. This results in removal of oxygen and hydrogen, and in partial graphitisation.[5] The temperatures in parentheses are those to which the carbon blacks have been heated after their original preparation.

Adsorbates. Lauric acid (m. p. 44·2°) and stearic acid (m. p. 69·5°) were used as supplied; the purities, determined by vapour-phase chromatography of their methyl esters, were 99·95% and 99·99%, respectively. Malonic acid was recrystallised from benzene–ether containing 5% of light petroleum. Purification of the solvents has been described previously.[3, 6]

Procedure. Adsorption was carried out at 20°. Solutions of stearic acid were analysed by titration with aqueous sodium hydroxide in the presence of warm neutral ethyl alcohol. Solutions of lauric acid and malonic acid were analysed by interferometry.

RESULTS AND DISCUSSION

1. *True and Apparent Adsorption.*—The " surface excess " given by the composite isotherm is related to the actual concentration of each component at the surface by the equation:

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

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. Equation 1 is based simply on a material balance between the bulk liquid and the adsorbed phase and must, as a matter of algebraic necessity, apply to adsorption from any solution, and over all ranges of concentration. The composite (or " surface excess ") isotherm is therefore not identical with that which shows the true adsorption of the solute. For some solutions, however, the former is a good approximation to the latter. This is so when the solubility limit occurs at a low mole fraction. In equation 1, x is then so small that $n_2^s x$ is negligible, and $(1 - x)$ is close to unity, so that $n_0.\Delta x/m \approx n_1^s$. Equation 1 can still be used to calculate n_2^s, which is bound to be considerable at the lowest values of x. The results for a typical case are shown in Fig. 1; the further assumptions made in the calculation are explained below (Section 5). For systems with an appreciably lower solubility limit (*e.g.*, stearic acid in any simple organic solvent at room temperature), the individual isotherm would be indistinguishable from the composite isotherm within the limits of experimental error (Table 1).

For higher solubility limits with a given solvent, the values of $n_0.\Delta x/m$ and n_1^s would diverge further. The concentration at which divergence becomes serious does, however, partly depend on the solvent. It tends to be lower for aqueous systems, as is illustrated by Fig. 2.

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[4] Smith in " Encyclopedia of Chemical Technology," ed. Kirk and Othmer, Interscience, New York, 1949, Vol. III, p. 34.

[5] Schaeffer, Smith, and Polley, *Ind. Eng. Chem.*, 1953, **45**, 1721.

[6] Blackburn and Kipling, *J.*, 1954, 3819; Blackburn, Kipling, and Tester, *J.*, 1957, 2373.

TABLE 1.

Adsorption from solutions of stearic acid in cyclohexane by carbon black at 20° (mmoles of dimeric acid/g.).

Graphon				Spheron 6			
x	$n_0.\Delta x/m$	n_1^s	n_2^s	x	$n_0.\Delta x/m$	n_1^s	n_2^s
0·0000	0·000	0·000	0·290	0·00000	0·000	0·000	0·40
0·0001	0·052	0·052	0·048	0·00013	0·021	0·021	0·30
0·0005	0·062	0·062	0·000	0·00038	0·030	0·030	0·26
0·0010	0·062	0·062	0·000	0·00075	0·037	0·037	0·23
0·0015	0·062	0·062	0·000	0·00125	0·042	0·042	0·20
0·0020	0·066	0·066	0·000	0·00188	0·047	0·048	0·17

2. *Use of the Langmuir Equation.*—When the Langmuir equation has been applied to adsorption from solution, it has been assumed that the adsorbed phase is confined to a thickness of one molecule, and that the limiting value of the isotherm corresponds to the formation of a complete layer of solute molecules on the solid surface. Fig. 3 shows the adsorption of stearic acid from various solvents by Spheron 6. The individual isotherms for adsorption of stearic acid follow the corresponding composite isotherms closely and can all be fitted by equations of the Langmuir type. The extent of adsorption, however, clearly varies considerably with the nature of the solvent. A possible interpretation would be that the orientation of the stearic acid molecules at the surface varied according to the solvent from which it was adsorbed. This seems unlikely to explain as many levels of adsorption as we have found, and it is simpler to conclude that the adsorbed layer is a mixed layer containing solvent molecules as well as solute molecules. This is rarely emphasised for this type of system, even when the determination of specific surface areas is discussed (*e.g.*, recently, ref. 7).

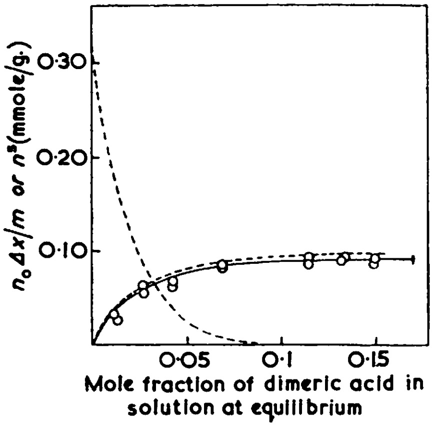

FIG. 1. Adsorption on Graphon from solutions of lauric acid in carbon tetrachloride: full line, composite isotherm; broken lines, individual isotherms.

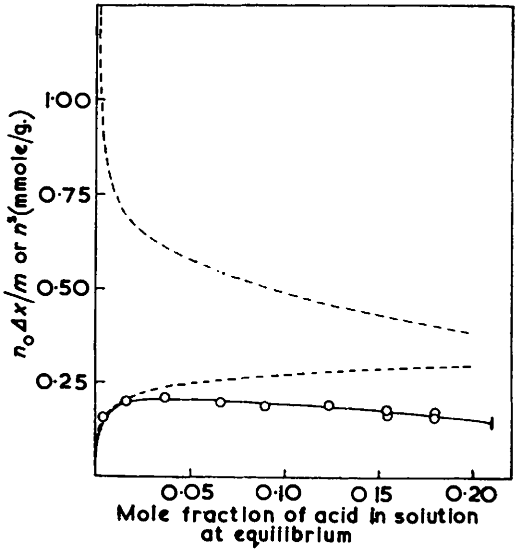

FIG. 2. Adsorption on Graphon from aqueous solutions of malonic acid: full line, composite isotherm; broken lines, individual isotherms.

3. *Orientation at the Surface.*—In adsorption on Graphon, the isotherms come to a plateau whose height is almost the same for adsorption from the four solvents which we have investigated (Fig. 4). This might, therefore, represent complete coverage of the surface by stearic acid molecules. The area available to each monomeric stearic acid molecule would then be 114 Å². The extent of adsorption, however, has often been

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[7] Dunicz, *J. Chem. Educ.*, 1961, **38**, 357.

judged in relation to the value of about 20·5 Å^2 for long-chain fatty acids in condensed films on aqueous substrates,[8] corresponding to an orientation of the molecules with the long axis perpendicular to the surface. We believe this comparison to be inappropriate in the present case. If the molecules were adsorbed with the long axis parallel to the surface, and close-packed as shown diagrammatically in Fig. 5, each monomeric molecule would occupy 114 Å^2. It is reasonable to suppose that such an orientation would be adopted on a Graphon surface. In most of the solvents used, the stearic acid is present essentially in dimeric form at most concentrations. The double hydrogen-bonding between the carboxyl groups is only likely to be broken if the monomers so formed can form fresh hydrogen bonds with the surface. This can readily happen on the surface of water, but cannot happen at all on the surface of Graphon. We therefore conclude that from solutions of high relative concentration, a complete monolayer of stearic acid is formed on Graphon.

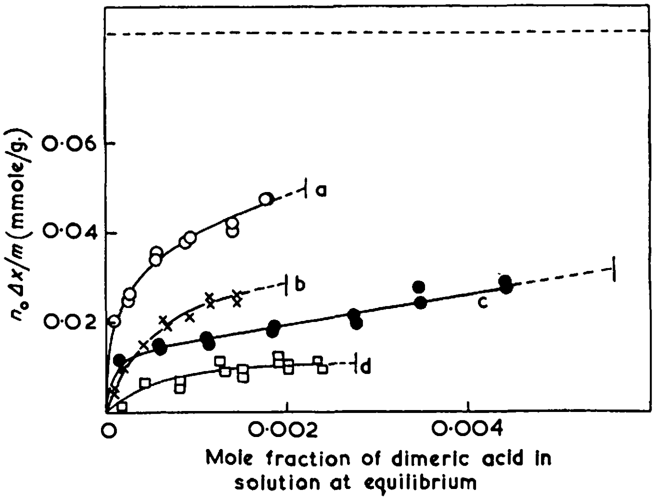

FIG. 3. Adsorption (composite isotherms) on Spheron 6 from solutions of stearic acid in: (a) cyclohexane, (b) ethyl alcohol, (c) carbon tetrachloride, (d) benzene. The top broken line shows the calculated value for a complete monolayer.

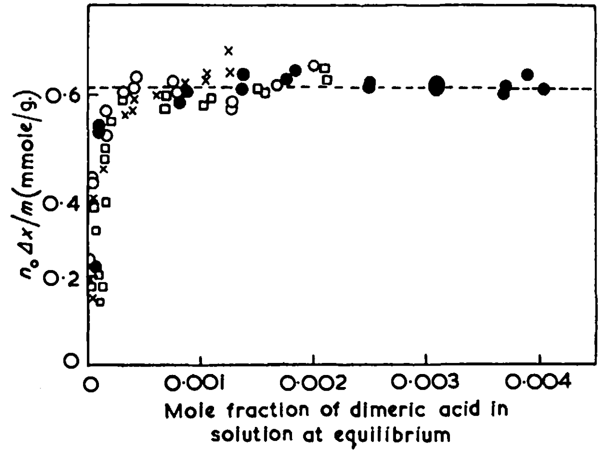

FIG. 4. Adsorption (composite isotherms) on Graphon from solutions of stearic acid in: ○ cyclohexane, × ethyl alcohol, ● carbon tetrachloride, □ benzene. The broken line shows the calculated value for a complete monolayer.

Similar behaviour is found in adsorption on other carbon blacks which have been heated to high temperatures (Fig. 6).

4. *The Nature of the Solid Surface.*—From the molecular area of 114 Å^2, the adsorption on Spheron 6 corresponding to a complete monolayer of stearic acid can be calculated.

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[8] Adam, " Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd edn., 1941.

This is shown in Fig. 3. It is higher than the level reached by any of the isotherms. We conclude, therefore, that the oxygen groups present on the surface of Spheron 6 are sufficiently polar to attract the solvent molecules appreciably, but are not sufficiently polar to bring about disruption of the dimeric stearic acid molecules and their subsequent orientation perpendicular to the surface.

Monarch 74 (2000°) and Carbolac 1 (2400°) give isotherms much closer to those shown by Graphon. For Monarch 74 (2000°), however, the isotherm rises slightly in the region of concentration over which the isotherm for Graphon shows a " plateau." Both show a more pronounced rise at high relative concentrations than does the isotherm for Graphon. The temperatures at which the carbons were treated were high enough for the original hydrogen and oxygen to have been removed. The residual differences in the isotherms therefore seem to be attributable to varying degrees of graphitisation.

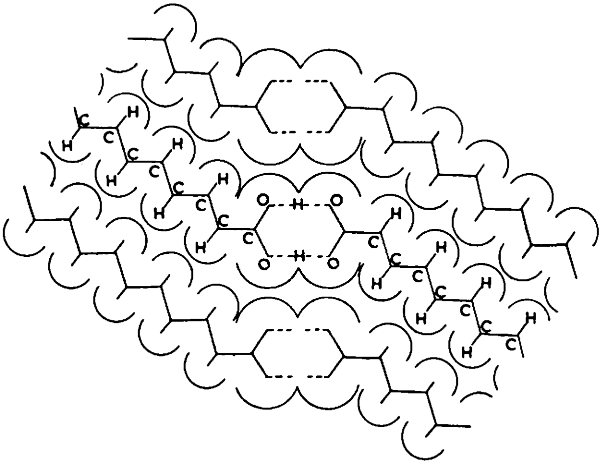

FIG. 5. Arrangement of stearic acid molecules in the adsorbed state; projection on to plane forming surface of adsorbent.

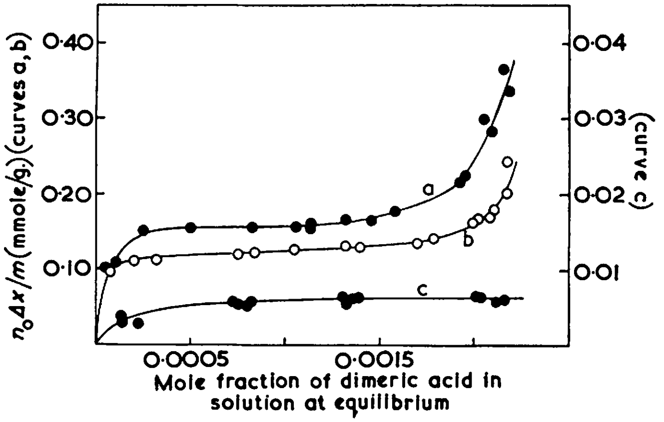

FIG. 6. Adsorption (composite isotherms) for the adsorption of stearic acid from solutions in cyclohexane on: (a) Carbolac 1 (2400°), (b) Monarch 74 (2000°), (c) Sterling MT (2700°).

5. *Individual Adsorption Isotherms.*—As it is reasonable to suppose that adsorption is confined to a single molecular layer, a further equation [3,9] can be used which has been valuable in the investigation of completely miscible systems:

$$n_1^s/(n_1^s)_m + n_2^s/(n_2^s)_m = 1, \qquad (2)$$

where $(n_1^s)_m$ and $(n_2^s)_m$ are the numbers of moles of components 1 and 2, respectively, which form a complete monolayer on 1 g. of solid. Equations (1) and (2) have been used

[9] Elton, *J.*, 1951, 2958.

together to calculate the isotherms for adsorption of the individual components shown in this paper.

6. *Systems with a High Solubility Limit.*—If a solute is adsorbed to the extent of a complete monolayer at a relatively low concentration, but has a much higher solubility limit, then between these concentrations n_1^s is constant and n_2^s is zero. The value of $n_0.\Delta x/m$ must therefore fall linearly with x in this region:

$$n_0.\Delta x/m = n_1^s(1 - x). \qquad (3)$$

This emphasises that the application of the Freundlich or Langmuir equations to the composite isotherm can only be justified on mathematical grounds as an approximation and at low concentrations.

The value of $n_0.\Delta x/m$ may decrease even if the solute is adsorbed to the extent of less than a complete monolayer, as is shown in Fig. 2.

7. *Adsorption at High Relative Concentrations.*—From a series of investigations of adsorption from partially miscible pairs of liquids (*e.g.*, adsorption by Spheron 6 from aqueous solutions of hexanoic acid [10]), it is clear that extensive multilayer adsorption of the " solute " frequently takes place. The inception of multilayer formation is observed at relatively low concentrations. By contrast, adsorption of solids seems generally to be confined to a monolayer except at high relative concentrations. Some, but not all, composite isotherms show a sharp rise from the plateau close to the solubility limit. Experimental difficulties limit the accuracy of determinations close to the solubility limit, but multilayer formation may occur here. For the liquid solute this may be regarded as incipient phase separation, but for the solid solute it may be regarded as incipient crystallisation.

One of us (E. H. M. W.) is indebted to the Sierra Leone Government for 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 black, and to Messrs. Price's (Bromborough) Ltd. for the gift of the purified fatty acids.

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[10] Hansen and Craig, *J. Phys. Chem.*, 1954, **58**, 211.