608. *Behaviour of Methyl Esters of Monocarboxylic Acids Adsorbed from Organic Solutions by Carbon Blacks: the Higher Members*

By E. H. M. Wright

Adsorption of methyl laurate, palmitate, and stearate from solutions of cyclohexane and carbon tetrachloride on to the carbon blacks Graphon and Spheron 6 has been studied. It appears that, for all the carbon tetrachloride systems, the adsorbed phase is confined to a monolayer, that at low concentrations various amounts of the two components are present in the adsorbed phase, and that the amount of ester in this phase increases as the bulk concentration increases, and tends in the limiting case to complete monolayer coverage by ester molecules.

For the cyclohexane systems, if it is assumed that the ester molecules adopt the same orientation as for the carbon tetrachloride systems, then the adsorbed phase appears to be multimolecular, extending to some three layers in each case. On the other hand, it is possible that the adsorbed phase is essentially unimolecular, but that the hydrocarbon chains of the esters are partly on the surface and partly turned into the bulk solution phase.

MUCH effort is being directed towards a fuller understanding of the factors which influence adsorption from solution at the solid–solution interface, and towards the development of a comprehensive theory of adsorption from solution. It has been recognised that there are many factors which influence adsorption from solution, but the more important seem to be adsorbate–adsorbent interactions, interactions between different molecules of the solution at the surface and in the bulk solution, and the general properties of the solution itself.

In a recent study of the adsorption of the homologous series of monocarboxylic acids from organic solutions on to carbon blacks [1,2] the series did not show a uniform type of adsorption behaviour. What promises to be a useful theory of adsorption from solution is being developed [3] and, to further this development, investigations are being carried out to obtain adsorption data and other values for various systems.

It was decided to investigate the pattern of adsorption for a series of methyl esters, and the results for the higher members of the series are given in this Paper; those for the lower members have been presented already.[4]

[1] Kipling and Wright, *J.*, 1962, 855.
[2] Kipling and Wright, *J.*, 1963, 3382.
[3] Everett, *Trans. Faraday Soc.*, 1964, **60**, 1803.
[4] Wright, *Trans. Faraday Soc.*, 1964, **60**, 1814.

EXPERIMENTAL

Adsorbents.—The carbon blacks, Spheron 6 and Graphon have been described previously.[1] The specific areas of the adsorbents measured by nitrogen adsorption are Spheron 6, 115 m.^{2}/g., and Graphon, 84 m.^{2}/g.

Solvents.—The purification of the solvents cyclohexane and carbon tetrachloride has been described.[5,6]

Methyl Esters.—The methyl esters of lauric, palmitic, and stearic acids were prepared as described by Markley.[7] Methyl palmitate and stearate were purified by repeated disillation in a molecular still, and methyl laurate by repeated distillation under reduced pressure.

Analysis of the methyl esters by vapour-phase chromatography showed them to be at least 99·9% pure and Table 1 gives the values of their respective refractive indices at 45°.

TABLE 1

Refractive indices of methyl esters at 45°

Methyl ester	n_D^{45} (expt.)	n_D^{45} (lit.[8])
Laurate	1·4218	1·4220
Palmitate	1·4317	1·4317
Stearate	1·4344	1·4346

Procedure.—Adsorption was carried out at 30°, and solutions of the esters were analysed interferometrically.

Monolayer Values.—The quantities of the adsorbates required to form a complete monolayer on the surface of the adsorbents are given in Table 2. Those for the solvents were calculated from adsorption of the vapour by use of the B.E.T. equation, and those for the esters calculated on the assumption that in the adsorbed phase the molecules lie with major axes parallel to the surface.

It has been shown [9] that the methyl esters of acetic, butyric, and octanoic acids adsorbed from the vapour phase on Graphon and Spheron 6 assume a " parallel " orientation, and it is assumed that the same kind of orientation is adopted by the higher esters.

TABLE 2

Monolayer values in mmoles/g.

	Spheron 6	Graphon	Calculated area/molecule (Å^2)
Cyclohexane	0·37	0·28	—
Carbon tetrachloride	0·42	0·32	—
Methyl stearate	0·147	0·107	130·0
Methyl palmitate	0·160	0·117	119·0
Methyl laurate	0·198	0·145	96·5

RESULTS AND DISCUSSION

The results are shown in Figures 1—5. These isotherms show the surface excess of the esters in the adsorbed layer, $n_0\ \Delta x/m$. The surface excess given by these isotherms is related to the actual concentration of each component at the surface by the equation:

$$n_0(\Delta x/m) = n_1^s \,.\, (1 - x_1^L) - n_2^s \,.\, x_1^L \qquad (1)$$

where Δx is the change in mole fraction of component 1 in the bulk liquid, which occurs when m grams of adsorbent are brought into contact with n_0 moles of liquid, x_1^L 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 gram of solid. Equation (1) is based simply on a material balance between the bulk liquid and the adsorbed phase, and applies to adsorption from any solution over all concentration ranges.

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

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

[7] Markley, " Fatty Acids," Interscience, New York, 1947.

[8] Wyman and Barkenbus, *Ind. Eng. Chem., Analyt.*, 1940, **12**, 658.

[9] Wright, *J.*, 1964, 2267.

The composite adsorption isotherms (Figures 1—5) show that the methyl esters are, in general, preferentially adsorbed over the whole concentration range, but some assumptions have to be made in order to gain an insight into the nature of the adsorbed phase. It has been shown [2] that, when the corresponding monocarboxylic acids are adsorbed from organic solutions on Graphon and Spheron,[6] the adsorbed phase is generally confined to a single layer, and it is useful to see how far the assumption of a single-layer adsorbed phase is justified for the esters.

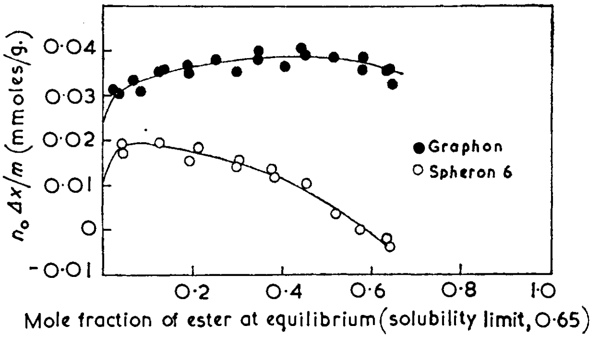


FIGURE 1. Adsorption by Spheron 6 and Graphon from mixtures of methyl stearate and carbon tetrachloride at 30°

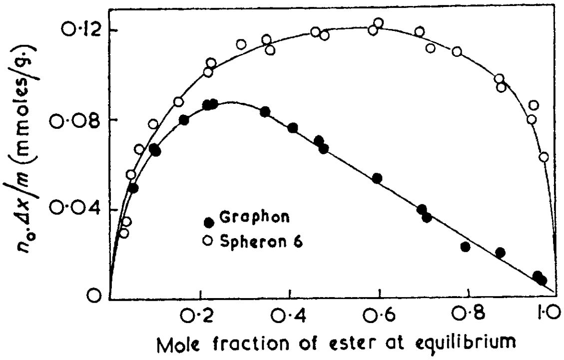


FIGURE 2. Adsorption by Spheron 6 and Graphon from solutions of methyl palmitate and carbon tetrachloride at 30°

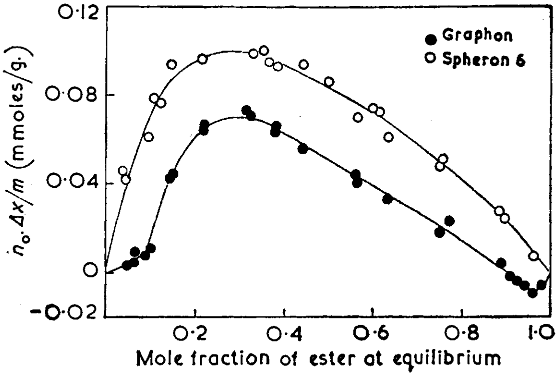


FIGURE 3. Adsorption by Spheron 6 and Graphon from solutions of methyl laurate and carbon tetrachloride at 30°

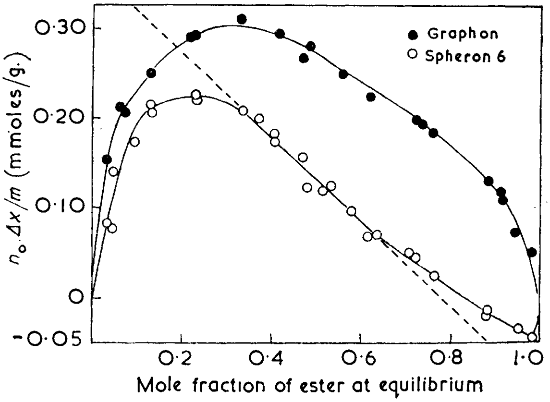
The problem resolves itself to calculating suitable values for n_1^s and n_2^s, and this can be done by combining equation (1) with the following equation:

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

where $(n_1^s)_m$ and $(n_2^s)_m$ are the numbers of moles of components 1 and 2, respectively, required to form a complete monolayer on one gram of adsorbent. Equation (2) involves the assumptions that the surface of the adsorbent is completely covered by the adsorbates at all concentrations, and that the adsorbed phase is of unimolecular thickness.[5,6]

The Carbon Tetrachloride Systems.—The individual isotherms for the esters and carbon tetrachloride for Graphon and Spheron 6 are given in Figures 6—11. These isotherms reveal that the solvent offers some competition for the surface but, in general, the esters are preferentially adsorbed. On Graphon, the limiting adsorption (n_1^s) for methyl stearate and palmitate corresponds approximately to the monolayer values expected on the assumption of a " parallel " orientation of the esters on the surface. This is in accord with the behaviour of the corresponding acids.[2]

FIGURE 4. Adsorption by Spheron 6 and Graphon from solutions of methyl palmitate and cyclohexane at 30°. The dotted lines indicate the Nagy–Schay extrapolation



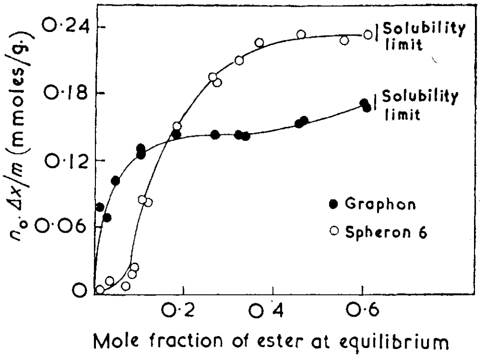


FIGURE 5. Adsorption by Spheron 6 and Graphon from solutions of methyl stearate and cyclohexane at 30°

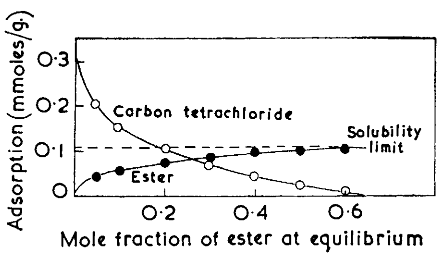


FIGURE 6. Individual isotherms for adsorption on Graphon from solutions of methyl stearate and carbon tetrachloride at 30°. The broken line indicates the monolayer level for the ester

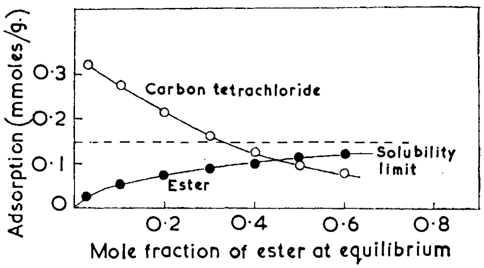


FIGURE 7. Individual isotherms for adsorption on Spheron 6 from solutions of methyl stearate and carbon tetrachloride at 30°. The broken line indicates the monolayer level for the ester

For methyl laurate, however, there is an initial reluctance of the ester to be adsorbed on the Graphon surface, but this is eventually overcome, although the limiting plateau of the n_1^s isotherm is slightly lower than the expected monolayer value. This is not surprising, and can be understood in terms of the shorter chain length of methyl laurate

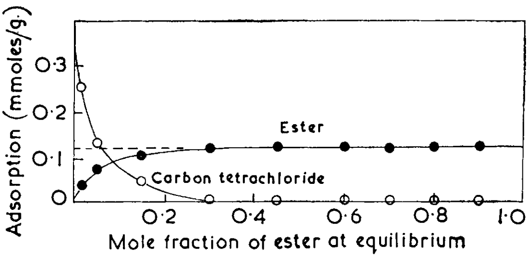
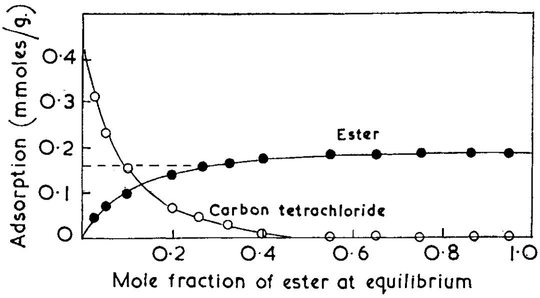


FIGURE 8. Individual isotherms for the adsorption on Graphon from solutions of methyl palmitate and carbon tetrachloride at 30°. The broken line indicates the monolayer level for the ester

FIGURE 9. Individual isotherms for adsorption on Spheron 6 from solutions of methyl palmitate and carbon tetrachloride at 30°. The broken line indicates the monolayer for the ester



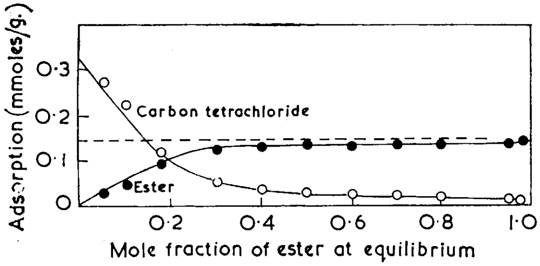
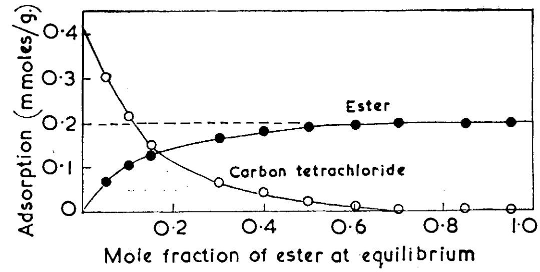


FIGURE 10. Individual isotherms for adsorption on Graphon from solutions of methyl laurate and carbon tetrachloride at 30°. The broken line indicates the monolayer level for the ester

FIGURE 11. Individual isotherms for adsorption on Spheron 6 from solutions of methyl laurate and carbon tetrachloride at 30°. The broken line indicates the monolayer level for the ester



(and hence a lower heat of adsorption, since the esters appear to assume a parallel orientation on these adsorbents), and the competition of carbon tetrachloride molecules for the surface.

This is similar to results for adsorption studies with alkylbenzenes—n-heptane—Graphon systems[10] where it was shown that there was increasing preferential adsorption of the alkylbenzene with chain length; in this work, monolayer adsorption of alkylbenzene with parallel orientation was obtained only for the highest member studied, *viz.*, octadecylbenzene.

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[10] Parfitt and Willis, *J. Phys. Chem.*, 1964, **68**, 1780.

On Spheron 6, the limiting adsorption for methyl laurate and palmitate corresponds approximately to the expected monolayer values. For methyl stearate, however, the limiting adsorption tends to, but does not attain even on to the solubility limit, the expected monolayer value. It has been shown [11] that, for the long-chain acids and for the long-chain hydrocarbons,[12] the adsorption on Spheron 6 does not in general attain the monolayer value, even though it might for adsorption on Graphon. This can be understood in terms of the nature of the adsorbent surfaces. On the " clean " carbon and relatively " inert " surface [4] of Graphon, a close-packed monolayer of long-chain molecules may be readily formed, the ease with which this is accomplished increasing with chain length. By contrast, a complete monolayer of ester may not be formed on Spheron 6, an adsorbent whose surface is covered with chemisorbed oxygen,[13] aldehyde and carbonyl groups,[14] as well as quinonoid and lactone types of structures.[15]

It would appear that the polar groups present on Spheron 6 are capable of polarising the molecules of the solvent more than the paraffin chains which form the major part of the higher esters. Competition from the solvent for the surface is therefore more effective, and the resultant effect seems to be the inability of the ester to attain complete monolayer coverage.

The Cyclohexane Systems.—The adsorption of methyl palmitate and stearate, but not of the laurate, from cyclohexane solution have been studied. This is because the closeness of the values for the refractive indices of the laurate and of cyclohexane, make the interferometric method of analysis inadequate.

From the composite isotherms (Figures 4 and 5), it does not seem as if the adsorbed phase is confined to a monolayer of ester molecules oriented parallel to the surface. The highest values of $n_0 \,.\, \Delta x/m$ for each of these systems is greater than the corresponding $(n_1^{\mathrm{s}})_{\mathrm{m}}$ value (given in Table 2) and, since from equation (1) $n_0 \,.\, \Delta x/m$ cannot be greater than n_1^{s} (since n_1^{s} and n_2^{s} are always positive or zero), the assumption of an adsorbed phase confined to a monolayer cannot be satisfactory.

The alternative of a unimolecular adsorbed phase with the ester molecules perpendicularly oriented is not very likely in view of what is known about the behaviour of similar molecules adsorbed on carbon blacks.[1,2,12]

It is possible that basically the ester molecules lie parallel to the adsorbent surface, but that the hydrocarbon chains turn partly away into the bulk solution. This would considerably increase the maximum uptake of ester molecules held essentially in a unimolecular adsorbed phase.

A useful method of gaining an insight into the nature of the adsorbed phase was first proposed by Nagy *et al.*,[16] and developed by Cornford *et al.*[11] In this treatment it was shown that, in certain circumstances, the thickness of the adsorbed phase could be ascertained if the compositie isotherm had a reasonably long linear section with a negative gradient. Extrapolation of the linear section of the isotherm gives intercepts on the ordinates through $x_1^{\mathrm{L}} = 0$ and $x_1^{\mathrm{L}} = 1$ of $(n_1^{\mathrm{s}})_{\mathrm{c}}$ and $-(n_2^{\mathrm{s}})_{\mathrm{c}}$, respectively, which define the composition of the adsorbed phase for this section of the isotherm. If monolayer values are assumed for the two components, it follows that

$$(n_1^{\mathrm{s}})_{\mathrm{c}}/(n_1^{\mathrm{s}})_{\mathrm{m}} + (n_2^{\mathrm{s}})_{\mathrm{c}}/(n_2^{\mathrm{s}})_{\mathrm{m}} = t \qquad (3)$$

where t is the mean molecular thickness of the adsorbed layer. If this treatment is applied to the composite isotherm for methyl palmitate on Spheron 6, it follows that

$$t = 0{\cdot}3675/0{\cdot}160 + 0{\cdot}100/0{\cdot}37 = 2{\cdot}57,$$

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[11] Cornford, Kipling, and Wright, *Trans. Faraday Soc.*, 1962, **58**, 74.

[12] Davidson, Ph.D. Thesis, Hull Univ., 1962.

[13] Beebe, Biscoe, Smith, and Wendell, *J. Amer. Chem. Soc.*, 1947, **69**, 95.

[14] Smith and Schaeffer, Proc. Rubber Tech. Conf., London, 1948.

[15] Garten, Weiss, and Willis, *Austral. J. Chem.*, 1957, **10**, 295.

[16] Nagy and Schay, *Magyar Kém. Folóirat*, 1960, **66**, 31; Schay, Nagy, and Szekrenyesy, *Periodica Polytech.*, 1960, **4**, 95.

that is, the adsorbed phase extends essentially to some three layers, if the ester molecules were oriented parallel to the surface. A similar assumption for the behaviour of methyl palmitate on Graphon would account for the relevant composite isotherm.

For methyl stearate, the limiting value for $n_0 \,.\, \Delta x/m$ is 0·235 mmole/g. of Spheron 6; on Graphon the limiting plateau occurs at $n_0 \,.\, \Delta x/m = 0{\cdot}144$ mmole. If it is assumed that the adsorbed phase consists of three layers of molecules, and that the ester molecules are oriented parallel to the surface, then the actual value of $(n_1^{\mathrm{s}})_{\mathrm{m}}$ in this case would be three times the value given in Table 2, *viz.*, 0·441 on Spheron 6. If a value of n_1^{s} is calculated by using equations 1 and 2 on this assumption, the value at $x_1^{\mathrm{L}} = 0{\cdot}6$ for Spheron 6 would be 0·47, which is approximately the value for three parallel layers of molecules on the surface.

Thermodynamic data are not available for these binary mixtures, but from the behaviour of the lower members in this series,[4] it appears as if the forces of interaction between ester and cyclohexane are much weaker than between ester and carbon tetrachloride. This is likely to be a major factor in determining the difference of behaviour of the carbon tetrachloride and cyclohexane systems; indeed, the adsorption results reveal that the tendency of cyclohexane to separate from the environment of ester molecules is much higher than for the corresponding carbon tetrachloride systems.

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