801. *Adsorption on Carbon Black from Solutions of Monocarboxylic Acids: the Lower Members*

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The adsorption on carbon black of formic, acetic, and n-butyric acids from mixtures with benzene, cyclohexane, and carbon tetrachloride has been measured; the results are considered in conjunction with those published previously for the higher members of the homologous series. The same general effects (nature of second liquid component and polarity of solid surface) are important.

The qualitative extension of Traube's rule is discussed. Adsorption from the present systems is not in accordance with this extension: it is governed by the limited miscibility of the lowest member with the "solvent," the ready miscibility of the higher liquid members, and the limited solubility of the solid members of the series.

STUDIES of the adsorption of the fatty acids from solution by solids (especially charcoal) have usually been confined to a small number of adjacent members of the homologous series. The tendency to assume that conclusions about the behaviour of a few members can be applied to the whole series is particularly unsound, because the higher members have usually been adsorbed from organic solvents and the lower members from water. It is therefore desirable to compare results for a wide range of the homologous series and for a common solvent or set of solvents.

Adsorption by carbon blacks from solutions of the higher members in organic solvents has already been reported.[1] Several factors have been found to influence the extent of adsorption of a given acid, so that a simple pattern does not emerge for the series as a whole. The results for the lower members show that the same, and additional, factors are important. One of these, the chemisorption of acetic acid and of formic acid by Spheron 6, has been discussed in detail elsewhere.[2]

EXPERIMENTAL

The same adsorbents and solvents were used as previously.[1] Adsorption was carried out at 20°. Formic, acetic, and n-butyric acids were purified as described previously.[3,4]

The butyric acid and acetic acid systems and the formic acid–benzene mixtures were analysed interferometrically. Solutions of formic acid in carbon tetrachloride and in cyclohexane were analysed by titration with aqueous sodium hydroxide in the presence of cold neutral ethanol.

For experiments involving formic acid, Pyrex test-tubes were treated with a 3% solution of dimethyldichlorosilane, dried, washed with water, and re-dried before use; this prevents reaction of the formic acid with the glass.

Monolayer values for the acids were calculated from the isotherms for adsorption of the respective vapours.

RESULTS AND DISCUSSION

The Composite Isotherm.—The composite isotherms for the butyric acid systems are shown in Figures 1—3. Butyric acid competes more effectively with carbon tetrachloride for the surface of Spheron 6 than does octanoic acid.[1] This can be attributed to the greater importance of the carboxyl group in the butyric acid molecule, resulting in its being less readily retained in the liquid phase.

By contrast, benzene is adsorbed on Graphon preferentially to butyric acid over the whole range of concentration, whereas octanoic acid is adsorbed preferentially to benzene over a small range. This suggests that an aliphatic molecule must possess more than six carbon atoms in order to compete effectively with benzene for the Graphon surface. As

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[1] J. J. Kipling and E. H. M. Wright, *J.*, 1963, 3382.
[2] J. J. Kipling and E. H. M. Wright, *J. Phys. Chem.*, 1963, **67**, 1789.
[3] A. Blackburn and J. J. Kipling, *J.*, 1955, 1493.
[4] J. J. Kipling and D. A. Tester, *J.*, 1952, 4123.

the acids are thought to be adsorbed in dimeric form, the number of carbon atoms required per molecule for preferential adsorption may be considerably more than six. It is known [5] that benzene is adsorbed on Graphon preferentially to n-heptane.

The adsorption of butyric acid from cyclohexane on both Graphon and Spheron 6 (1000°), but not on Spheron 6, gives rise to a " stepped " isotherm. This may be due to a re-orientation of the butyric acid molecules within the adsorbed layer, as was found [1] in the adsorption of lauric acid from carbon tetrachloride by Spheron 6. It seems rather more likely, however, that it corresponds to a transition from an adsorbed layer one molecule thick (but containing both butyric acid and cyclohexane) to a thicker layer.[6] As the " step " occurs at a relatively high mole-fraction of butyric acid, the experimental

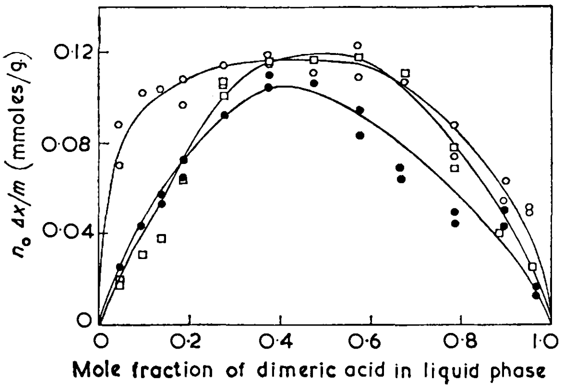

FIGURE 1. Adsorption (composite isotherms) from mixtures of butyric acid and carbon tetrachloride on: ○, Spheron 6; □, Spheron 6 (1000°); ●, Graphon

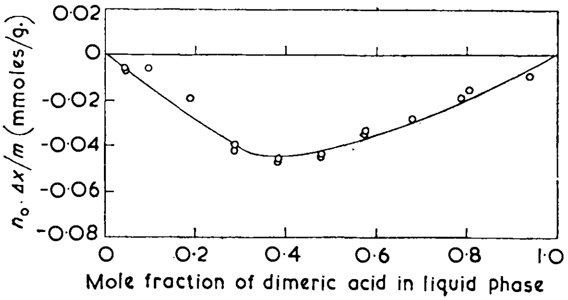

FIGURE 2. Adsorption (composite isotherm) from mixtures of butyric acid and benzene on Graphon

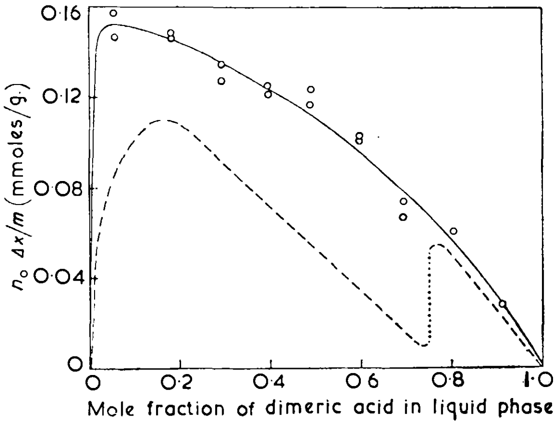

FIGURE 3. Adsorption (composite isotherm) from mixtures of butyric acid and cyclohexane on Spheron 6. The broken line shows the isotherm for adsorption on Graphon [6]

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[5] G. D. Parfitt and E. Willis, *J. Phys. Chem.*, 1964, **68**, 1780.

[6] P. V. Cornford, J. J. Kipling, and E. H. M. Wright, *Trans. Faraday Soc.*, 1962, **58**, 74.

error for the remainder of the isotherm is too great for it to be possible to calculate whether a complete second layer of butyric acid is formed. It is not clear why this behaviour should be shown only by butyric acid among the acids which we have examined, nor why the stepped isotherm is obtained with only one of the solvents. The isotherm for the adsorption of butyric acid vapour on Graphon is of the normal type II, showing no break corresponding to the completion of a second molecular layer.

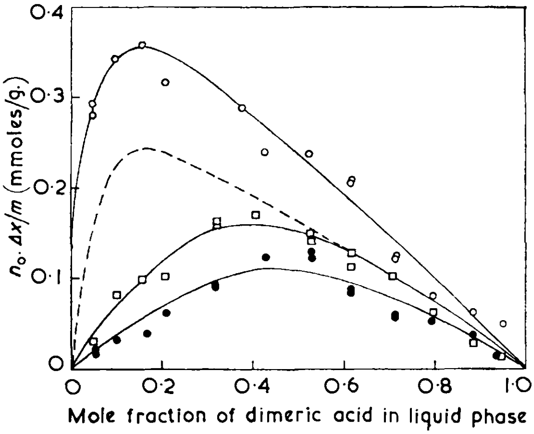


FIGURE 4. Adsorption (composite isotherms) from mixtures of acetic acid and carbon tetrachloride on: ○, Spheron 6;[2] □, Spheron 6 (1000°); ●, Graphon. The broken line is for physical adsorption on Spheron 6

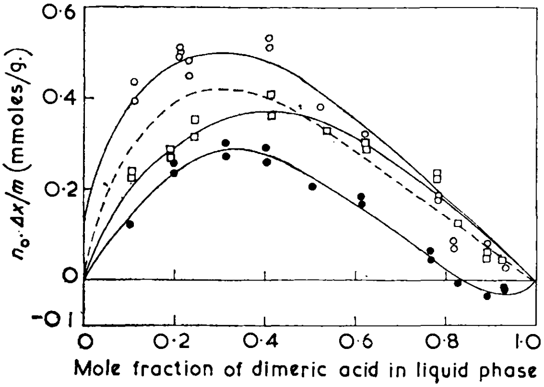


FIGURE 5. Adsorption (composite isotherms) from mixtures of acetic acid and cyclohexane on: ○, Spheron 6;[2] □, Spheron 6 (1000°); ●, Graphon. The broken line is for physical adsorption on Spheron 6

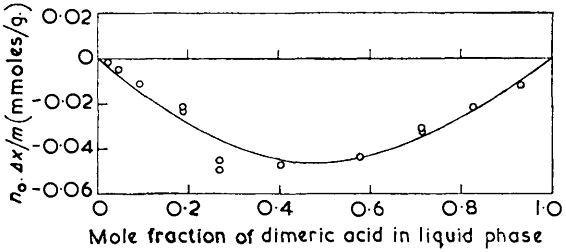


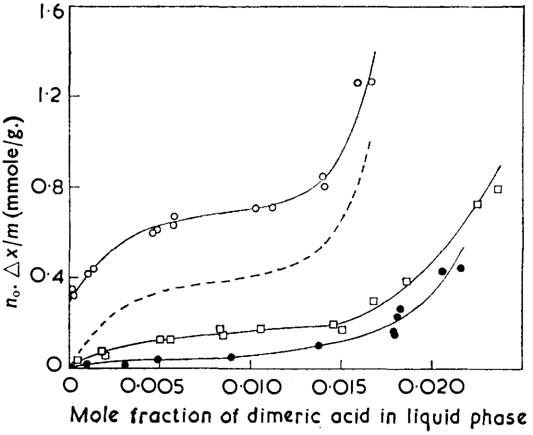
FIGURE 6. Adsorption (composite isotherm) from mixtures of acetic acid and benzene on Graphon

The results might also be interpreted in terms of a phase-change analogous to that observed in the adsorption of lauric acid by Spheron 6 from carbon tetrachloride.[1] The adsorbed phase would, however, still exceed a monolayer. It seems more likely that the behaviour of butyric acid is analogous to that of acetic acid.

The composite isotherms for adsorption of acetic acid are shown in Figures 4—6. Chemisorption of acetic acid is believed to occur on Spheron 6, to an extent discussed in an earlier Paper.[2] The dotted lines in Figures 4 and 5 have been drawn to show the effect of physical adsorption only. At low concentrations, these still show greater adsorption of acetic acid by Spheron 6 than by the carbons derived from it; this can be attributed to the polar character of Spheron 6, which remains even after some chemisorption has occurred.

The special character of benzene as a " solvent " is shown by its preferential adsorption on Graphon (Figure 6). It seems likely that there is interaction between the π-electrons of the benzene molecules and those of the graphitic platelets of the adsorbent.

FIGURE 7. Adsorption (composite isotherms) from mixtures of formic acid and carbon tetrachloride on: ○, Spheron 6;[2] □, Spheron 6 (1000°); ●, Graphon. The broken line is for physical adsorption on Spheron 6



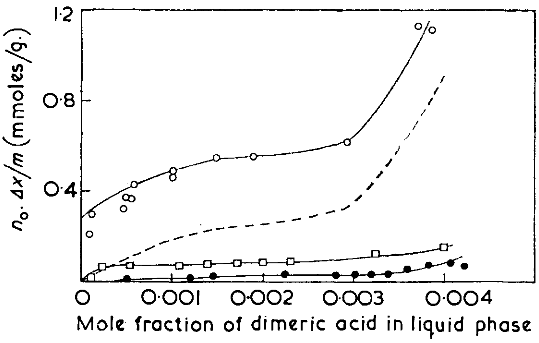
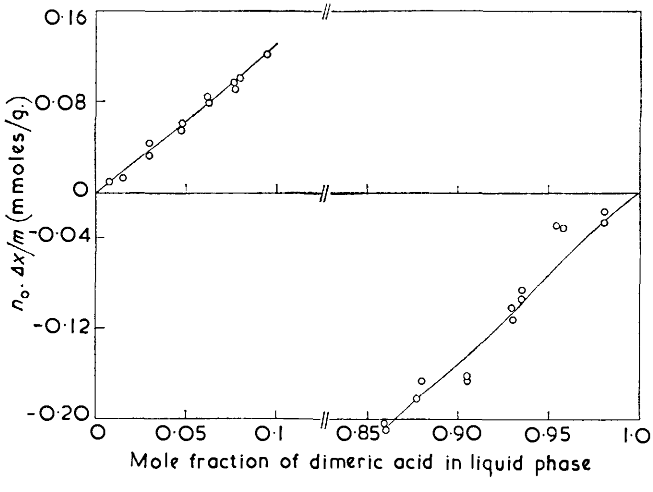


FIGURE 8. Adsorption (composite isotherms) from mixtures of formic acid and cyclohexane on: ○, Spheron 6;[2] □, Spheron 6 (1000°); ●, Graphon. The broken line is for physical adsorption on Spheron 6

FIGURE 9. Adsorption (composite isotherms) from mixtures of formic acid and benzene on Graphon



The composite isotherms for adsorption of formic acid are shown in Figures 7—9. The dotted lines again show the value of $n_0 . \Delta\, x/m$, which is attributed to physical adsorption only. A feature in which these systems differ from the acetic acid mixtures is that formic acid is only partly miscible with carbon tetrachloride, cyclohexane, and benzene. The composite isotherms, therefore, cover only a very small range of mole fractions. The sharp rise at high relative concentrations is typical of such systems, and has been attributed [7] to incipient phase-separation under the influence of the solid surface. It is clear from the individual isotherms [2] that the adsorption of formic acid from both carbon tetrachloride and cyclohexane becomes multimolecular in these regions.

For such partly miscible systems, the adsorption isotherm consists, in principle, of two parts, one for each region of miscibility. Only rarely have both parts of the isotherm been recorded. For the formic acid–benzene system, however, it has been possible to make the relevant measurements (Figure 9). For neither region do the measurements correspond to more than monolayer formation. Moreover, preferential adsorption is reversed between the two ends of the concentration range. This suggests that the adsorbent takes up preferentially the phase which is tending to separate as discrete droplets from the continuous medium, rather than being wetted preferentially by one of the two components. A similar result has been found by Hansen [8] in adsorption by Spheron 6 from mixtures of hexanoic acid and water.

The Individual Isotherms.—Comparisons between these systems, and with the higher members of the series, is most easily made with the individual isotherms, or curves derived from them. The calculation of the individual isotherms has been described previously,[1] and some of those for the present systems have been published.[2] A useful derivative is the curve of surface coverage with concentration. These are summarised in Figures 10—16 for all the members of the homologous series which have been investigated. The curves show the effects of the chemical nature of the surface of the three adsorbents; this is important mainly in the discrimination shown by the solid between the two components of the solution. The effects which have been discussed in relation to the higher members of the homologous series [1] are generally found to be significant for the lower members. The remaining features can be attributed to characteristics of the homologous series.

The Homologous Series.—The formulation of Traube's rule [9] to describe the regularity observed in the lowering of the surface tension of water by members of homologous series (including the fatty acids) has led to the expectation that a similar effect (to be observed as increasing extents of adsorption) would be found for the liquid–solid interface. Some progressive changes have been observed for the liquid–solid interface and have been claimed as examples of Traube's rule. This is a rather undesirable extension of the original rule, which dealt specifically with the ratio of the molar concentrations of solutions of adjacent homologues which gave the same lowering of surface tension, *i.e.*, it was a quantitative, not a qualitative rule. Further, it was regarded as true only in the limiting case of extreme dilution, whereas its qualitative application to the liquid–solid interface has sometimes been based on solutions of considerable concentration.

Some regularities have been found in the adsorption of fatty acids by solids, but insufficient notice has been taken of Nekrassow's results for adsorption on a series of charcoals.[10] These results were, unfortunately, limited to 0·01M-solutions. He found that, whereas Traube's rule, in the extended form, was obeyed for the adsorption of fatty acids from water, there was no general increase in adsorption from the less polar organic solvents (benzene, carbon tetrachloride, carbon disulphide) as the chain-length of the acid increased. Adsorption from the oxygen-containing solvents passed through a minimum in the region C_3—C_6.

Our results for the whole adsorption isotherm (Figures 10—16) show a rather more complex pattern. In some cases, one of the patterns found by Nekrassow is observed,

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[7] R. S. Hansen, Y. Fu, and F. E. Bartell, *J. Phys. Chem.*, 1949, **53**, 769.

[8] R. S. Hansen and R. P. Craig, private communication; in part, see R. S. Hansen and R. P. Craig, *J. Phys. Chem.*, 1954, **58**, 211.

[9] J. Traube, *Annalen*, 1891, **265**, 27.

[10] B. Nekrassow, *Z. phys. Chem.*, 1928, **136**, 18.

e.g., a minimum in adsorption from solutions in benzene by Graphon. The results can be classified in a simple way which leads to a consistent explanation. The acids can be classified into a group of solids, a group of liquids which are completely miscible with the " solvents," and the single member, formic acid, which is a liquid only partly miscible with the " solvents." These solubility characteristics are, of course, related to the position of the acid in the homologous series. In general, the number of methylene groups in the molecule is the most important factor but, for the lowest members, the ratio of polar to non-polar groups in the molecule becomes significant.

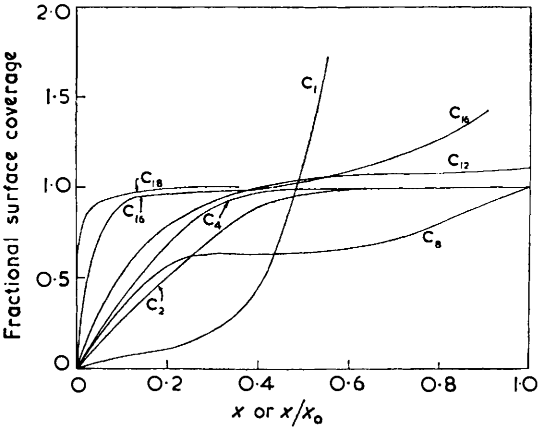

FIGURE 10. Surface coverage of Graphon in adsorption of fatty acids from carbon tetrachloride. (Abscissae to be read as x/x_0 for C_1, C_{12}, C_{16}, and C_{18}.)

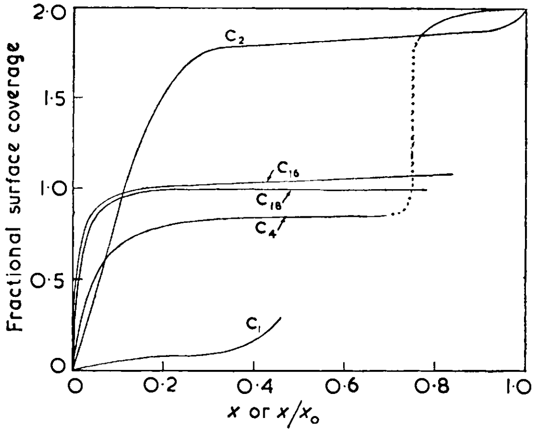

FIGURE 11. Surface coverage of Graphon in adsorption of fatty acids from cyclohexane. (Abscissae to be read as x/x_0 for C_1, C_{16}, and C_{18}.)

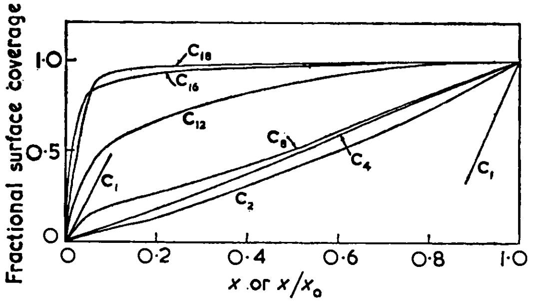

FIGURE 12. Surface coverage of Graphon in adsorption of fatty acids from benzene. (Abscissae to be read as x/x_0 for C_{12}, C_{16}, and C_{18}.)

The solids are readily adsorbed at low concentrations, forming a complete monolayer if the adsorbent does not attract the solvent strongly. The formation of the monolayer may be likened to incipient crystallisation of the acid, as the adsorbed layer appears to have a regular molecular arrangement similar to that of a single layer of a crystal. The higher the molecular weight of the acid, the more strongly it is adsorbed at low concentrations.

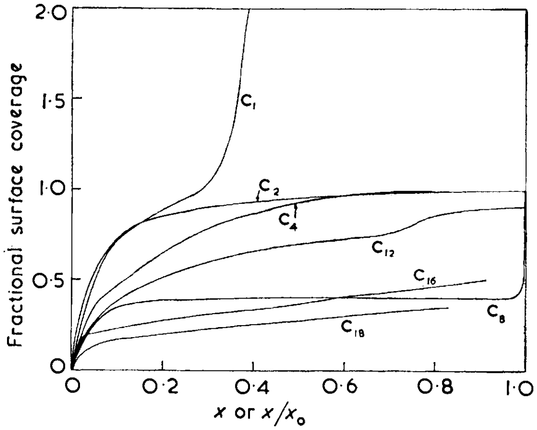

FIGURE 13. Surface coverage of Spheron 6 in adsorption of fatty acids from carbon tetrachloride. (Abscissae to be read as x/x_0 for C_1, C_{12}, C_{16}, and C_{18}.)

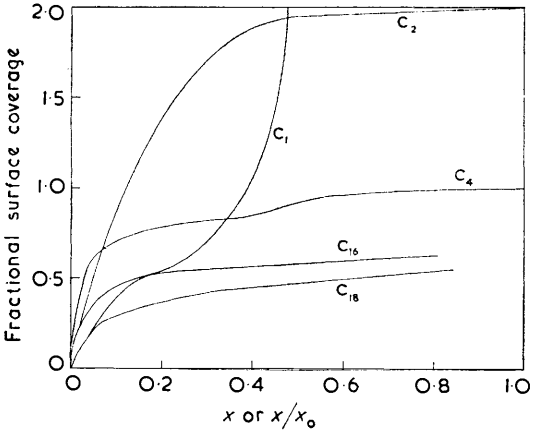

FIGURE 14. Surface coverage of Spheron 6 in adsorption of fatty acids from cyclohexane. (Abscissae to be read as x/x_0 for C_1, C_{16}, and C_{18}.)

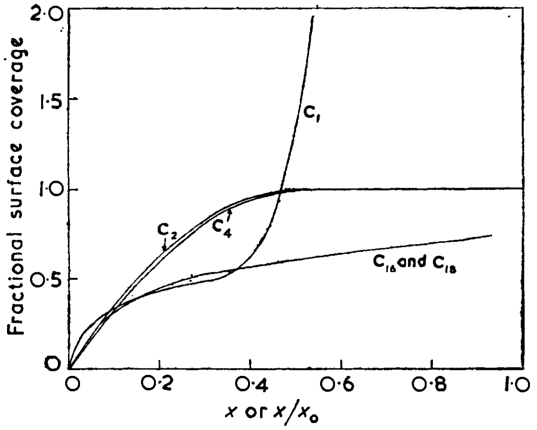

FIGURE 15. Surface coverage of Spheron 6 (1000°) in adsorption of fatty acids from carbon tetrachloride. (Abscissae to be read as x/x_0 for C_1, C_{16}, and C_{18}.)

Acids which are completely miscible with the second component form a complete monolayer only at a mole fraction of 1. The extent of adsorption at lower concentrations varies according to the nature of the second component. There is some evidence that the lower members in this group are more strongly adsorbed than the higher members, presumably because their increasing polar character renders the solution increasingly non-ideal. This is seen particularly in the adsorption of acetic acid by Spheron 6, the polar groups of which encourage strong adsorption. Adsorption from cyclohexane is more than can be accommodated in a single molecular layer. This system is shown, by the total and partial vapour-pressure curves, to be close to phase-separation at 20°, a situation that is believed to be conducive to multilayer adsorption.[11,12] The acetic acid–carbon tetrachloride system, although far from ideal, is not, by the same criterion, so close to phase-separation.

Formic acid shows a tendency to form multilayers at moderately high relative concentrations, though the " knee " in the composite isotherm corresponds to the formation of less than a complete monolayer. This phenomenon is known in other such systems, but no general explanation has yet been put forward.

The gradual rise in the individual isotherm for adsorption of formic acid from carbon tetrachloride by Graphon is analogous to the low adsorption of formic acid vapour on Graphon at low pressures. The isotherm for adsorption of the vapour is initially convex to the pressure axis. This may prove to be typical of the adsorption of highly polar substances by relatively non-polar solids; an extreme case is the adsorption of water vapour by Graphon.[13]

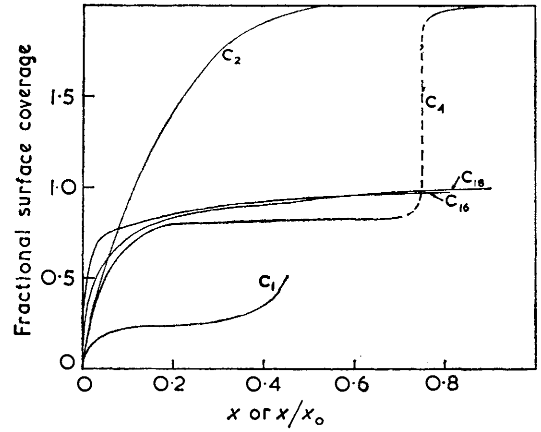

FIGURE 16. Surface coverage of Spheron 6 (1000°) in adsorption of fatty acids from cyclohexane. (Abscissae to be read as x/x_0 for C_1, C_{16}, and C_{18}.)

The more general explanation of the results arises from a consideration of the three factors [14] involved in adsorption from solution. In this case, they are the acid–surface interaction, the " solvent "–surface interaction, and the acid–" solvent " interaction. In adsorption on Spheron 6, the second of these is particularly important. In adsorption on Graphon, this is important only with benzene. In other cases, the balance of the other two factors tends to make for weaker adsorption of acids in the middle of the range investigated than at the two ends.

In the light of this analysis, conformity to the extension of Traube's rule is probably found only when there is a combination of favourable circumstances. Thus, in the adsorption of fatty acids from aqueous solution by charcoal observed by Nekrassow [10] and others,[3,15,16] the interaction between water and the charcoal is weak, the interaction between

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[11] C. G. Gasser and J. J. Kipling, Proceedings of the Fourth Conference on Carbon, Pergamon Press, London, 1960, p. 55.

[12] J. J. Kipling, Proceedings of the Third International Congress for Surface Activity, 1960, Verlag der Universitätsdruckerei, Mainz, vol. 2, p. 77.

[13] B. Millard, E. G. Caswell, E. E. Leger, and D. R. Mills, *J. Phys. Chem.*, 1955, **59**, 976.

[14] J. J. Kipling, *Chem. and Ind.*, 1964, 1007.

[15] E. Landt and W. Knop, *Z. phys. Chem.*, 1932, *A*, **162**, 331.

[16] R. U. Lemieux and J. L. Morrison, *Canad. J. Res.*, 1947, *B*25, 440.

the acid and the charcoal increases with increasing chain-length, whereas the interaction between the acid and the water becomes proportionately less as the ratio of polar to non-polar section of the molecules decreases. The combination of trends would lead to an increase in adsorption with increasing chain-lengths. Nekrassow observed decreasing adsorption with one charcoal; this had been prepared from sugar under strongly oxidising conditions, and thus had a high concentration of hydrophilic oxygen groups on the surface. The surface would therefore behave more like a silica gel than an average charcoal. The reversal of the normal trend is found in adsorption of fatty acids from aqueous solution by silica gel.[17]

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[17] F. S. Bartell and Y. Fu, *J. Phys. Chem.*, 1928, **32**, 676.