Adsorption from Binary Liquid Mixtures; the Effect of Hydrogen Bonding between the Components.

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Further studies of adsorption, by charcoal, from binary mixtures of completely miscible liquids confirm the view that the adsorbed phase is normally confined almost entirely to a monolayer. Weak hydrogen bonding between the components does not affect this result, but stronger interaction may lead to secondary adsorption on to the layer held by the solid surface. Pyridine, which is preferentially adsorbed from aqueous solutions, holds large amounts of water in a second layer by hydrogen bonding, but all material beyond this second layer is regarded as part of the bulk liquid phase.

Recent theories of adsorption from binary mixtures of completely miscible liquids have been based almost exclusively on experiments with organic compounds (Innes and Rowley, *J. Phys. Colloid Chem.*, 1947, **51**, 1172; Elton, *J.*, 1951, 2958; Kipling and Tester, *J.*, 1952, 4123; see also Kipling, *Quart. Reviews*, 1951, **5**, 60). The systems used in such work have shown relatively small molecular interaction between the two components. In many systems of practical importance, however, molecular interaction is considerable, and especially so in aqueous solutions. Water not only interacts, by hydrogen bonding, with almost all non-electrolytes with which it is completely miscible, but furthermore is itself associated to a degree which is still uncertain. It is not immediately evident to what extent these various types of association are likely to affect adsorption; indeed, the possibility of such an effect seems generally to have been overlooked until recently (cf. Fu, Hansen, and Bartell, *J. Phys. Colloid Chem.*, 1948, **52**, 374; Hansen and Fackler, *ibid.*, 1953, **57**, 634). Even these last workers have confined their investigations mainly to systems of limited miscibility.

As an approach to the problem, a study has been made of adsorption on charcoal from four systems in which the molecular interaction in the liquid phase is carefully graded from a small effect in saturated hydrocarbons to strong hydrogen bonding in an aqueous system. The four systems, in order of increasing interaction, are:

Benzene–*cyclo*hexane: this system is a convenient mixture of hydrocarbons of approximately the same molecular size.

Chloroform–acetone: this system shows a pronounced negative deviation from Raoult's law (Zawidski, *Z. physikal. Chem.*, 1900, **35**, 129), and weak hydrogen bonding between the components has been postulated (Glasstone, *Trans. Faraday Soc.*, 1937, **33**, 200; Zellhoefer, Copley, and Marvel, *J. Amer. Chem. Soc.*, 1938, **60**, 1337; Gordy, *J. Chem. Phys.*, 1939, **7**, 163).

Pyridine–ethyl alcohol: evidence for a moderate degree of hydrogen bonding in this system has been summarised elsewhere in a report on the unexpected observation that the system obeys Raoult's law at room temperature (Blackburn and Kipling, *Nature*, 1953, **171**, 174).

Pyridine–water: analogy with tertiary aliphatic amines, for which Moore and Winmill's results are available (*J.*, 1907, **91**, 1373, 1379; 1912, **101**, 1635), suggests that very considerable hydrogen bonding between the components must occur in this system. This would also explain the large difference in miscibility with water between benzene and pyridine, the molecules of which are in many ways very much alike.

Discussion

The isotherms of concentration change are presented in Figs. 1—4. For the first three systems, concentrations are expressed in mole fractions; for aqueous systems it is doubtful whether this is the appropriate unit and we have therefore used weight fractions for the fourth system.

A survey of the literature shows that, for adsorption on charcoal, such curves normally either cross the concentration axis to give two branches, or, if there is only one branch, remain at all points concave to this axis (cf. Elton, *loc. cit.*). Figs. 1 and 2 are normal in this sense, but Figs. 3 and 4 differ in showing a point of inflexion in a one-branch curve. (The convexity of Fig. 4 would be more pronounced if it were plotted in terms of nominal mole fractions.) This type of curve has often been presented without comment for other adsorbents (*e.g.*, for alumina and other gels by Rao and Rao, *Proc. Indian Acad. Sci.*, 1936, 4, *A*, 562), but rarely for charcoal. The only recent examples are for adsorption from aqueous solutions of the lower fatty acids (Nestler and Cassidy, *J. Amer. Chem. Soc.*, 1950, 72, 680).

The curves of Figs. 3 and 4 suggest that there is, in the adsorbed phase, either an excess of alcohol or water, respectively, or in each case, a deficiency of pyridine, compared with the amounts expected for a normal system. Analysis of the four curves to give adsorption isotherms for the individual components was carried out by Kipling and Tester's method (*loc. cit.*), by assuming that adsorption is confined to a monolayer and using known molecular areas. The results for the first three systems are of the expected type (Figs. 5—7). The analysis for the last system, however, gives curves showing both a maximum and a minimum (broken curves, Fig. 8). Adsorption from the vapour phase confirms these individual isotherms for the first three systems, but gives quite different results for the fourth.

Isotherms of concentration change for adsorption from :

FIG. 1. *Benzene*–cyclo*hexane.*

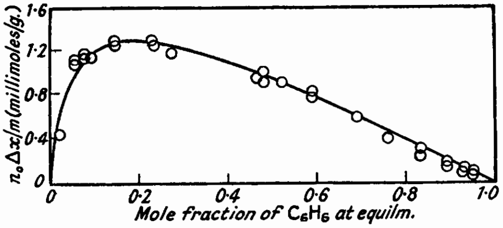


FIG. 2. *Chloroform–acetone.*

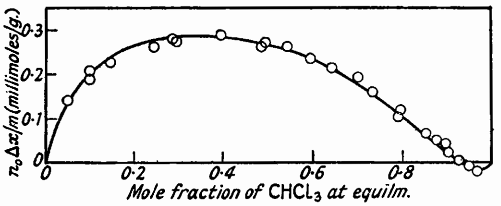


FIG. 3. *Pyridine–ethyl alcohol.*

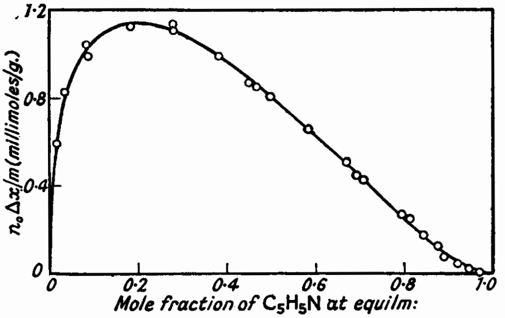
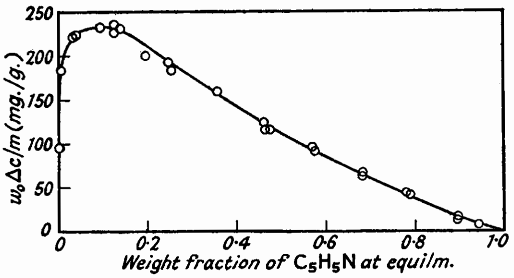


FIG. 4. *Pyridine–water.*



(Fig. 4. w_0 = wt. of original mixture; Δc = change in wt. fraction.)

For aqueous systems, the possibility of hydrogen bonding within the adsorbed phase makes it reasonable to depart from the concept of the monolayer which is advanced for normal systems. We suggest that the initial layer is able to hold further molecules, by hydrogen bonding, to form a partial or complete second layer. It is clear that pyridine is strongly adsorbed in preference to water and may be expected to cover a large fraction of the surface at nearly all concentrations. Reference to molecular models shows that there is room for each pyridine molecule to hold two water molecules in a second layer. The extent to which this occurs must be expected to vary with the composition of the liquid phase. We have therefore used the equation $z = KX(1 - c)^2$ as a crude approximation to a law of mass action expression in which z, the number of millimoles of adsorbed pyridine which have taken up water, is expressed as a function of X, the number of millimoles of unhydrated pyridine, and $(1 - c)$, the weight fraction of water in the liquid phase, K being a constant. We have also assumed that the water adsorbed directly on to the charcoal surface is in the form of dimeric molecules. The full curves shown in Fig. 8 are then obtained for $K = 5{\cdot}55$, the value, chosen empirically, which gives the best agreement with the vapour-phase results.

Adsorption (individual isotherms) from :

FIG. 5. *Benzene*–cyclo*hexane.*

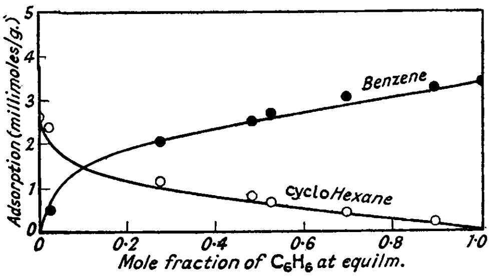


FIG. 6. *Chloroform–acetone.*

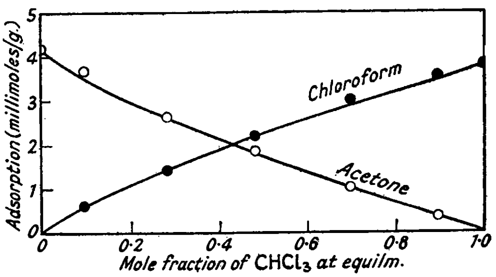


FIG. 7. *Pyridine–ethyl alcohol.*

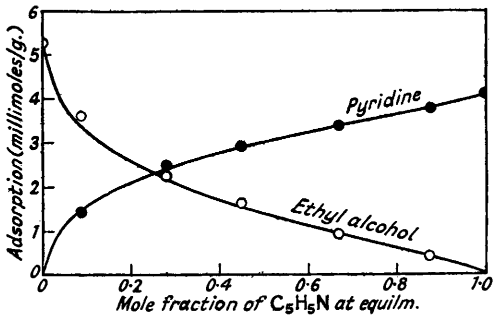
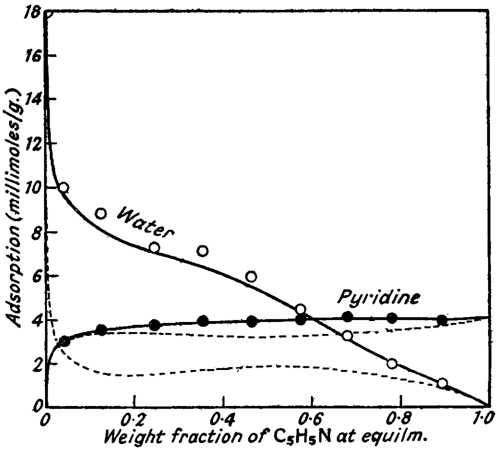


FIG. 8. *Pyridine–water.*



Figs. 5—8. Points = vapour-phase results. Curves = calc. from liquid-phase results.

Fig. 8. Broken curves = calc. from liquid-phase results, on the assumptions that water is adsorbed as monomer and that there is no interaction between components.

Full curves = calc. from liquid-phase results, on the assumptions that water is adsorbed as dimer and that there is interaction between components.

These simple assumptions could be refined; one might, for example, take account of the possibility that small amounts of pyridine may be held in the second layer by the water adsorbed in the first layer. In fact, however, such an assumption would make very little difference to the analysis.

A similar phenomenon occurring at high mole fractions of pyridine in the pyridine–alcohol system, *viz.*, the attachment of alcohol molecules to adsorbed pyridine, would explain the inflexion in Fig. 3. The effect on Fig. 7 would be to alter very slightly the shape of the individual isotherms, but the effect is too small to be confirmed with certainty. The space available in the pores of this type of charcoal limits very considerably the amount of alcohol which can be adsorbed in a second layer, whereas the much smaller water molecule can be admitted much more freely.

There is no reason for supposing that an appreciable second layer is built up in the adsorbed phase of the chloroform–acetone system, but we would not preclude the possibility that there may be considerable interaction between the components in the adsorbed phase. The benzene–*cyclo*hexane system we regard as fitting in entirely with previous concepts for normal organic systems.

An alternative explanation of the results obtained from the pyridine–water system might be that the small water molecules penetrate to parts of the charcoal surface which are inaccessible to the larger pyridine molecules. This may well happen to some extent, as steam-activated charcoal almost certainly contains pores of about the dimensions of the water molecule. The remainder of the adsorption process could then be confined to a monolayer covering the surface available to both substances. Our calculations have shown that no value can be assigned to the area available to water only which leads to satisfactory isotherms for the components of the monolayer. We conclude, therefore, that this effect cannot alone explain the observed results and can be only a minor contributory factor.

It has recently been suggested (Hansen and Hansen, *J. Colloid Sci.*, 1954, **9**, 1*) that the monolayer theory of adsorption from solution is inadequate, and that a more consistent interpretation of experimental results is, in general, obtained in terms of a pore-filling mechanism. The equations based on this approach may find use with a wider range of systems than can be dealt with by Kipling and Tester's equations; possibly, for example, with binary mixtures of incompletely miscible liquids, and with oxide gel adsorbents. They may also be easier to use in dealing with adsorption from mixed vapours. On the other hand, a pore-filling mechanism does not account specifically for the change in concentration of a binary liquid mixture caused by adsorption. In some cases this may be due to multilayer adsorption, such as has been found by Hansen in work on partially miscible systems (in which there is clearly scope for multilayer adsorption as the region of immiscibility is approached) and with totally miscible systems in which extensive hydrogen bonding is possible. Thus in the present case, the pore-filling mechanism might be expected to apply most adequately to the pyridine–water system. Reference to Fig. 8, however, shows that, between 0·25 and 1 weight fraction of pyridine, the adsorption of pyridine rises by about 0·3 millimole/g. In pores of constant volume, this would replace about 1·3 millimoles of water per g., whereas the observed decrease is about 7 millimoles per g. We suggest that attention must be paid more specifically to the forces responsible for adsorption, and conclude that, for this system, there is an appreciable change from the composition of the bulk liquid only in the first two layers from the solid surface.

For liquids such as benzene and *cyclo*hexane it is difficult to see how the effect of the surface forces can extend significantly beyond the monolayer. Indeed the work of Cines and Ruehler (*J. Phys. Chem.*, 1953, **57**, 710) on vapour-phase adsorption of mixed hydrocarbons by silica gel leads them to the conclusion that "although some selectivity persists in the multilayers, it seems evident that selectivity is rested primarily in the monolayer. . . ." Certainly the existence of multilayer adsorption in strongly interacting systems is insufficient ground for postulating multilayer adsorption in relatively non-polar systems.

Finally, the isotherms for adsorption and desorption of benzene vapour on the type of charcoal which we have used (Davies, *Chem. and Ind.*, 1952, 160) show a very small region of hysteresis, suggesting that adsorption is essentially unimolecular, with only a very small volume of pore space available for capillary condensation or multilayer adsorption. Such a view is consistent with recent estimates of pore sizes in active charcoals made by Davies and by others.

EXPERIMENTAL

The adsorbent was the steam-activated coconutshell charcoal used previously (Kipling and Tester, *loc. cit.*). It was found, however, that acetone extracted ash from the charcoal, and this interfered with refractometric analysis. The charcoal was therefore freed from soluble ash by extraction with water in a Soxhlet apparatus. As far as we are aware, this method has not previously been advocated, though a similar method has been used for the purification

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* We are grateful to the authors for allowing us to see the MS. of this paper before its publication.

of the shell before carbonisation (Reyerson, *Ind. Eng. Chem.*, 1925, **17**, 1114). Although our method does not remove all the ash from the charcoal, it is more convenient than the traditional acid extraction, provided (as in this case) that it is not disadvantageous to leave the water-insoluble ash in the charcoal.

Benzene and ethyl alcohol were purified as described previously. *cyclo*Hexane was fractionally distilled. The fraction used had n_D^{20} 1·4262, in agreement with the values given by Timmermans (" Physico-Chemical Constants of Pure Organic Compounds," Elsevier, London, 1950). Chloroform was purified by a modification of Gillo's method (*Ann. Chim.*, 1939, **12**, 281) and had n_D^{20} 1·4458 and d_4^{20} 1·4889, in close agreement with the values given by Timmermans.

" AnalaR " Acetone was further purified by Conant and Kirner's method (*J. Amer. Chem. Soc.*, 1924, **46**, 235) and gave n_D^{20} 1·3588. This acetone is of high purity, but is probably not as completely free from water as that of Thirion and Craven (*J. Appl. Chem.*, 1952, **2**, 210).

Pyridine (analytical reagent grade) was allowed to stand over pellets of potassium hydroxide and was then fractionated. The fraction used had n_D^{20} 1·5098 and d_4^{20} 0·9823.

The determinations were carried out at 20° by the methods previously described. For the benzene-*cyclo*hexane system, concentrations were determined interferometrically as well as refractometrically. For this purpose a Hilger–Rayleigh interferometer was used in the manner described by Bartell and Sloan (*J. Amer. Chem. Soc.*, 1929, **51**, 1657); their important observation that a well-fitting cover must be used with the cell was confirmed. A 12-v, 24-w bulb was found to be a convenient source of light.

Values of the molecular areas were based on vapour adsorption, except for water, for which a calculated value of 10 sq. Å per molecule was used, assuming a surface area for the charcoal of 540 sq. m./g., based on the observed monolayer value of 2·93 millimoles/g. for adsorption of carbon tetrachloride vapour.

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The University, Hull.

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