Adsorption on Charcoal from Aqueous Solutions of Fatty Acids: a Further Interpretation of Traube's Rule.

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The adsorption by charcoal from aqueous solutions of formic, acetic, propionic, and *n*-butyric acids severally has been studied over the complete concentration range. The adsorption isotherms for the individual components have been obtained. It is suggested that the same type of hydrogen-bonding occurs in the adsorbed phase as in the bulk liquid phase for these systems, and molecular orientations are proposed which explain the application of Traube's rule to these systems. The formic acid system is slightly anomalous, owing to the absence of an alkyl group in the acid molecule.

IN early investigations of adsorption from liquids, aqueous solutions of various fatty acids were frequently used (Freundlich, " Colloid and Capillary Chemistry," Methuen, London, 1926), though the experiments were usually confined to very low concentrations. Results recently reported (Blackburn and Kipling, *J.*, 1954, 3819) suggest that these systems, in which extensive hydrogen-bonding can take place between acid and acid, water and water, and acid and water molecules, might be among the most complicated of binary systems to investigate, and were quite unsuited to early studies in the subject.

We have shown that adsorption from non-interacting systems on charcoal is essentially unimolecular and that for the interacting system pyridine–water, the effect of hydrogen-bonding is to add one further layer to the adsorbate (Kipling and Tester, *J.*, 1952, 4123; Blackburn and Kipling, *loc. cit.*). It was therefore of interest to discover whether any relatively simple interpretation would be possible of the adsorption from aqueous solutions of acids over the entire concentration range.

Discussion.—Fig. 1 shows the isotherm of concentration change for adsorption on charcoal from aqueous solutions of formic, acetic, propionic, and *n*-butyric acids. As we are concerned with completely miscible systems, we are limited to these four members of the homologous series. The results are closely similar to those of Nestler and Cassidy (*J. Amer. Chem. Soc.*, 1950, **72**, 680).

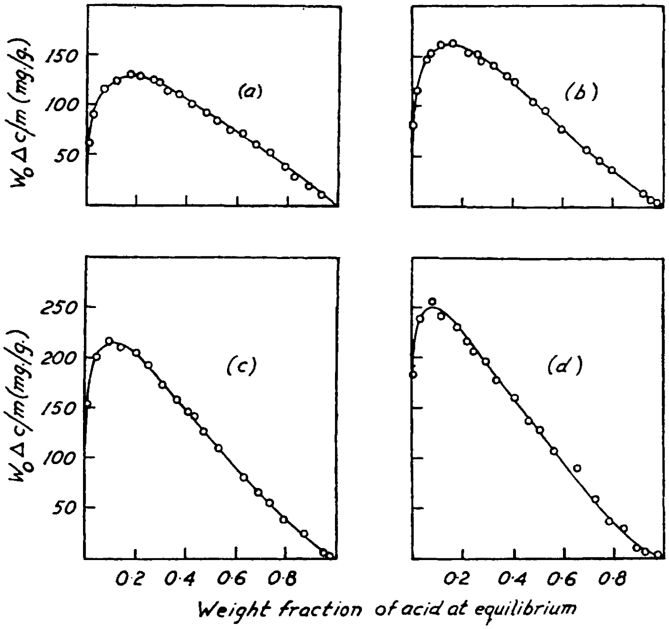
Figs. 2—4 show the adsorption isotherms for the individual components, obtained from vapour-phase experiments. This procedure was originally suggested by Williams (*Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 27), who attempted to apply it to the acetic acid–water system. He found that a long period was required to establish equilibrium and failed to produce complete isotherms because his solutions were attacked by fungus. We have succeeded in applying his method to aqueous solutions of the first three acids, for which increasing times are required to reach equilibrium, but found that the time available was inadequate to reach equilibrium for the fourth.

An analysis of the isotherms of concentration change in terms of Kipling and Tester's monolayer theory for non-interacting systems failed (see Figs. 2—4), as did the simple analysis for the pyridine–water system. Comparison of the three vapour-phase results suggests a possible elaboration. The number of millimoles of water adsorbed per g. of charcoal *decreases* (at corresponding concentrations) as the number of millimoles of acid adsorbed decreases (from formic to propionic acid). The only simple way in which this can occur is for the acid molecules to be adsorbed with their major axes along the solid surface, and not perpendicular to it as has sometimes been assumed for aliphatic substances (*e.g.*, by Lemieux and Morrison, *Canad. J. Res.*, 1947, **25**, *B*, 440) by analogy with close-packed (insoluble) films on aqueous substrates.

The molecules then have the orientations shown in Fig. 6 with respect to the solid surface represented as horizontal. The significance of these is best appreciated by reference to models (cf. Kipling and Norris, *J. Colloid Sci.*, 1953, **8**, 547).

This suggestion is supported by a comparison of the ratios of the molar volumes for the

FIG. 1. *Isotherms of concentration change for adsorption from mixtures of*: (a) *formic acid and water*, (b) *acetic acid and water*, (c) *propionic acid and water*, (d) *butyric acid and water*.



FIGS. 2—5. *Adsorption (individual isotherms) from* :

Fig. 2. *Formic acid–water.* Fig. 3. *Acetic acid–water.*

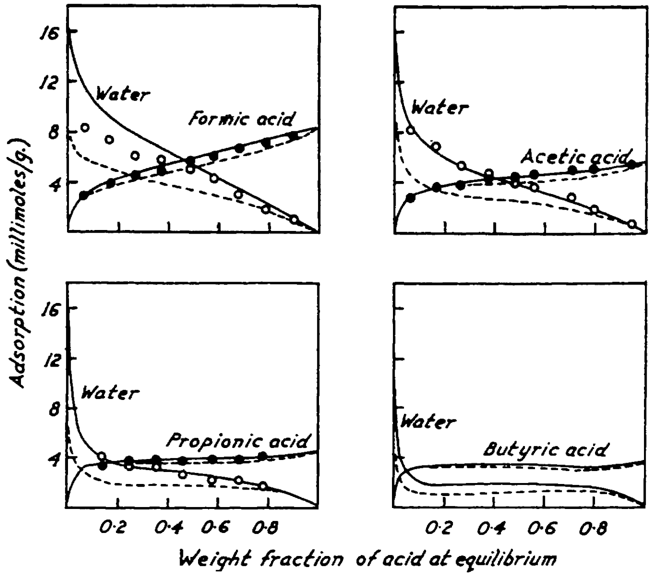
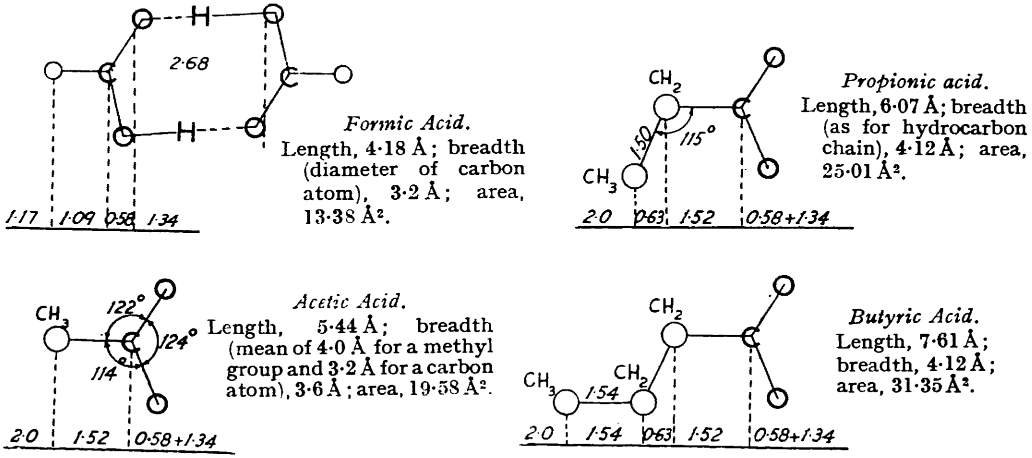


Fig. 4. *Propionic acid–water.* Fig. 5. *Butyric acid–water.*

● Vapour-phase results (acids). ○ Vapour-phase results (water). - - - Calc. from liquid-phase results on the assumption that water is adsorbed as monomer. —— Calc. from liquid phase results on the assumption that water is adsorbed as dimer.

acids in the bulk liquid phase and the molecular areas in the adsorbed monolayers (obtained from experiments with the single vapours). These are shown in the annexed Table. In this, a further comparison is also made with the ratios of the calculated molecular areas of the acids, assumed to be adsorbed with the orientations shown in Fig. 6; the alkyl chains lie along the surface, the planes of carboxyl groups are perpendicular to the surface, and the molecules are assumed to be associated, with consequent shortening of the length of the monomeric unit.

FIG. 6. *Configurations of adsorbed fatty acids.*



Formic Acid. Length, 4·18 Å; breadth (diameter of carbon atom), 3·2 Å; area, 13·38 Å^2.

Propionic acid. Length, 6·07 Å; breadth (as for hydrocarbon chain), 4·12 Å; area, 25·01 Å^2.

Acetic Acid. Length, 5·44 Å; breadth (mean of 4·0 Å for a methyl group and 3·2 Å for a carbon atom), 3·6 Å; area, 19·58 Å^2.

Butyric Acid. Length, 7·61 Å; breadth, 4·12 Å; area, 31·35 Å^2.

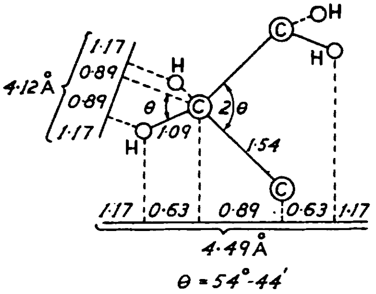


FIG. 7. *Dimensions of hydrocarbon chain.*

Acid	Millimoles/g. adsorbed	Ratio of molecular areas (exptl.)	Calc. molecular areas (sq. Å)	Ratio of molecular areas (calc.)	Ratio of molar volumes
Formic	8·42	1	13·38	1	1
Acetic	5·65	1·49	19·58	1·46	1·53
Propionic	4·50	1·87	25·01	1·87	1·96
n-Butyric	3·60	2·34	31·35	2·35	2·44

[The dimensions of the molecules are shown in Fig. 6, and are based on the means of values given by Morrison and Robertson (*J.*, 1949, 980, 987, 993, 1001) together with the van der Waals radii of 2·0 and 1·17 Å for the methyl group and hydrogen atom, respectively. With this value for the hydrogen atom, the cross-section of the hydrocarbon chain can be represented as a rectangle of sides 4·12 and 4·49 Å (Fig. 7), giving an area of 18·5 sq. Å, which is close to the observed value (Müller, *Proc. Roy. Soc.*, 1927, *A*, **114**, 542; 1928, *A*, **120**, 437).]

The close correspondence between the three sets of ratios implies that the increase, from formic to butyric acid, of both molecular area and molar volume is due to increase in one dimension only.

With the orientation shown in Fig. 6, there is little to choose, in analysing the isotherms of concentration change, between assuming that the acids are monomeric and assuming some degree of polymerisation. On the other hand, we have previously assumed, with success, that the water is adsorbed in the dimeric form. Figs. 3 and 4 show that this assumption allows a satisfactory analysis to be made for the systems acetic acid–water and propionic acid–water. Although we have no direct experimental confirmation of the analysis for the butyric acid–water system, the analysis shown in Fig. 5 seems satisfactory when compared with those of Figs. 3 and 4.

From Fig. 2 it will be seen that for the formic acid–water system the experimental points lie between the curves for the two theoretical analyses. We suggest that this is due to the anomalous behaviour of formic acid, as the first member of the homologous series, owing to the absence of a hydrocarbon chain. A further consideration of the nature of the adsorbed phase may elucidate this.

For the present four aqueous systems, the analysis gives less direct indication about the nature of hydrogen-bonding in the adsorbed phase than for the pyridine–water system discussed previously. There is, however, abundant evidence that in the liquid phase the fatty acids are dimerised and that water is associated to an indefinite degree. In aqueous solutions of acetic acid (which we take to be typical) there is evidence of the formation of di- and mono-hydrated acetic acid (Fénéant-Eymard, *Mém. Serv. Chim.*, 1952, **37**, 297; Kipling, *J.*, 1952, 2858). Extensive hydrogen-bonding may therefore be expected to take place in the adsorbed phase. On the surface, the dimeric water molecule has a height of between 5 and 6 Å, and the carboxyl group a height of about 5 Å. The " dimeric " adsorbed water may therefore be present either in the form of dihydrated acid, or as the dimeric molecule adsorbed alongside organic molecules of comparable height. The adsorbed phase will thus contain dimeric water molecules, dimeric acid molecules, and dihydrated (and possibly monohydrated) acid molecules. This picture is compatible with the analyses given in Figs. 3—5.

In formic acid, however, the carboxyl group has no hydrocarbon chain to support it and may therefore have some tendency to lie flat on the surface instead of perpendicular to it. It then has the height of one carbon atom (about 3·2 Å) which is comparable with the height of a monomeric instead of a dimeric water molecule. Thus in the *second* layer from the charcoal surface, there should be more opportunity for direct competition between the two components. (This contrasts with the position of a monomeric water molecule alongside an upright carboxyl group, where, in general, space is only available for adsorption of a second monomeric water molecule.) Moreover, the carboxyl group occupies a greater surface area when flat than when vertical, and this again reduces the extent to which water can be adsorbed. The two effects combine to give adsorption of water intermediate between that calculated for monomeric water only and that for dimeric water only. Only a fraction of the acid molecules would have to lie flat to account for the observed results for the aqueous mixtures, and there is no need to suppose that this orientation is adopted at all in a monolayer of the acid alone.

This picture of the adsorbed phase provides an interpretation of Traube's rule as applied to these systems (Freundlich, *op. cit.*). The " horizontal " orientation of the acid molecules means that, when equal numbers of molecules of formic, acetic, propionic, and butyric acids are adsorbed, the number of water molecules which can be adsorbed on the remainder of the surface decreases in this order. Further, the increasing heat of adsorption per molecule to be expected as the number of methylene groups in the hydrocarbon chain increases would lead one to expect that the higher acids would compete with water for the hydrophobic surface more effectively than the lower acids. These two effects, operating in the same direction, combine to give the result expressed in Fig. 1. The explanation is similar to that given by Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1848) for the adsorption of the lower fatty acids at the air–water interface of dilute aqueous solutions, though this has been criticised by Ward (*Trans. Faraday Soc.*, 1946, **42**, 399) on the grounds that the acid molecules are more likely to be spheroidal than cylindrical. It is difficult to see how molecules as small as those of formic and acetic acids can be regarded as spheroidal, and the concept can be applied only qualitatively to butyric acid, however well it may apply to higher acids. On the other hand, the concept of a linear orientation does allow an approximate calculation to be made of the molecular areas, the results being shown in the Table above. Jones and Saunders (*J.*, 1951, 2944) concluded that, at the nitromethane–air interface, fatty acid molecules arrange themselves intermediately between a horizontal and a random orientation. They point out that in this sytem the surface forces are inadequate to produce a completely ordered surface layer. Stronger forces might be expected to operate at a charcoal surface. It may be added that, in a different approach to this manifestation of Traube's rule, Hansen and Craig (*J. Phys. Chem.*, 1954, **58**, 211) found a regularity in behaviour for acetic, propionic, and butyric acids, but unfortunately they did not study formic acid.

EXPERIMENTAL

The absorbent was the steam-activated coconut-shell charcoal described previously (Kipling and Tester, *loc. cit.*). Acetic acid reacts with the ash in the charcoal, even that which is left after Soxhlet extraction with water (Blackburn and Kipling, *loc. cit.*). It was therefore extracted in a Soxhlet apparatus with glacial acetic acid and subsequently washed with distilled water until all traces of acetic acid had been removed. The resulting charcoal caused only negligible alterations to the refractive indexes of the four acids, when shaken with them in the ratios used for the adsorption runs.

The experimental procedures have been described previously, as has the purification of acetic acid.

"AnalaR" formic acid (98—100%), twice distilled from phosphoric oxide under reduced pressure, had m. p. 8·3° and n_D^{20} 1·3713, in agreement with the values of Dreisbach and Martin (*Ind. Eng. Chem.*, 1949, **41**, 2875).

A commercial sample of propionic acid was fractionally distilled, refractionated from dried alumina gel, and again fractionally distilled. The product had n_D^{20} 1·3858, as compared with Dreisbach and Martin's value of 1·3865.

A commercial sample of butyric acid was fractionally distilled; it had n_D^{20} 1·3980, in good agreement with Dreisbach and Martin's value (cf. Jones and Saunders, *loc. cit.*).

Laboratory distilled water was redistilled in an all-glass apparatus and the fraction used had n_D^{20} 1·3330.

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