297. *The Adsorption of Acetic Acid and* n-*Butylamine from Aqueous Solutions by Activated Charcoals.*

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Adsorption by charcoal of acetic acid and *n*-butylamine from aqueous solutions has been investigated over a range of pH and other conditions. Adsorption takes place only through the undissociated molecules. It is concluded that the variation of degree of adsorption with pH is a function of the electrochemical properties of the solution only and does not depend on changes in the nature of the charcoal surface. On this basis, equilibrium adsorption under any stated conditions of pH and concentration can be calculated from the adsorption isotherm.

It is also shown that (within the practical limits of the activation process) the adsorption capacity of the charcoal for these substances increases with decreasing activation yield, but is not affected by the temperature of activation.

ADSORPTION by charcoal from solutions may be of different types according to the nature of both solute and solvent. The present study is restricted to one type only, *viz.*, that of weak organic electrolytes in aqueous solution. It is concerned with ascertaining, first, whether both ions and undissociated molecules are adsorbed, and secondly, whether the adsorbate is held by " physical " or " chemical " forces (using Brunauer's definitions, " The Adsorption of Gases and Vapours ", Oxford, 1944) or by electrochemical forces. Adsorbates of small molecular size were chosen for this work, so that complications due to steric effects might be avoided.

Fromageot and Wurmser (*Compt. rend.*, 1924, **179**, 972) investigated the adsorption of oxalic acid on charcoal, but offered no adequate explanation of their results, which, however, are readily interpreted in the light of the present work.

Phelps and Peters (*Proc. Roy. Soc.*, 1929, **124**, *A*, 554) found that the adsorption of the lower fatty acids and of simple aliphatic amines depends on the pH of the solution and closely follows the ionic dissociation curves of the acids and bases respectively. They concluded, therefore, that adsorption takes place through the undissociated molecule only. If this conclusion is correct, it should be possible to deduce the extent of adsorption at any pH from the adsorption isotherm of the free acid or base. In referring to the fall in adsorption of the acids with increasing pH, Phelps and Peters observe that " the fall in adsorption may be correlated almost quantitatively with the percentage of un-ionised molecules present." This seems to involve a tacit assumption that the extent of adsorption is proportional to the number of undissociated molecules present, whatever their concentration in the solution may be, which is equivalent to assuming that the adsorption isotherms of the acids are linear. We shall consider whether their main conclusion remains applicable if the observed isotherm is used as a basis for calculation.

The work of Phelps and Peters implies that the adsorption from these solutions is probably similar to that of gases like carbon tetrachloride. Such gases are held by " physical " forces and their adsorption does not depend on the precise chemical nature of the charcoal surface; the most important factor has been shown to be the activation yield (paper in preparation). On the other hand, King (*J.*, 1937, 1489) finds that adsorption of acetic acid on charcoal activated by oxygen depends on the temperature of activation, and that increase in adsorption of acetic acid is accompanied by decrease in adsorption of ammonia. He concludes that the chemical or electrochemical nature of the charcoal surface may influence adsorption.

To investigate these two problems, experiments have been designed to show the effect of the following variables on the adsorption of a simple acid and a simple amine : (*a*) pH of solution, (*b*) activation conditions, (*c*) activation yield, (*d*) nature of raw material from which the charcoal was made, and (*e*) concentration of solution.

EXPERIMENTAL.

Reagents.—The adsorbates were acetic acid and *n*-butylamine, which were chosen as having approximately equal electrolytic strength and molecular size. The solutions were buffered with sodium acetate and hydrochloric acid respectively.

The charcoals were used in granular form, graded 8—18 B.S.S. They were prepared from carbonised nutshell and briquetted coal by steam activation at 890° in the laboratory, as described elsewhere. Special charcoals were activated at 700° and 1000°. To extend this range, a further charcoal which had been activated at 890° was heated with steam at 600° for 3 hours to allow it to assume the surface structure appropriate to that temperature; activation is too slow at 600° for the whole of the activation to be carried out at that temperature. A few results were also obtained with commercially activated charcoals.

Methods.—In general, the charcoal and the buffered solution were shaken together for 12 hours. The (equilibrium) pH of the solution was then measured. For acetic acid, the adsorption was determined from the difference in total acetate concentration before and after adsorption. The method described by

Phelps and Peters (*loc. cit.*) was followed, except that the titrations were carried out electrometrically. A similar method was used for determining " total butylamine " (*i.e.*, free base + butylamine hydrochloride). This required a determination of the dissociation constant of *n*-butylamine; an approximate value of $4 \cdot 2 \times 10^{-4}$ was obtained.

Results.—The results below have been calculated to test the assumption that only undissociated acid or base is adsorbed by the charcoal. Unless otherwise stated, concentrations refer to " total acetate " or " total butylamine ".

Effect of pH. For acetic acid, adsorption is at a maximum in acid solutions, but falls rapidly between pH 5 and 6, and is negligible in alkaline solutions. This is shown in Fig. 1 and Table I. For butylamine, there is a continuous fall in adsorption from pH 12 to zero at about pH 6 (Fig. 2, Table II).

<p align="center">FIG. 1.</p>

<p align="center">*Effect of* pH *on adsorption of acetic acid.*</p>
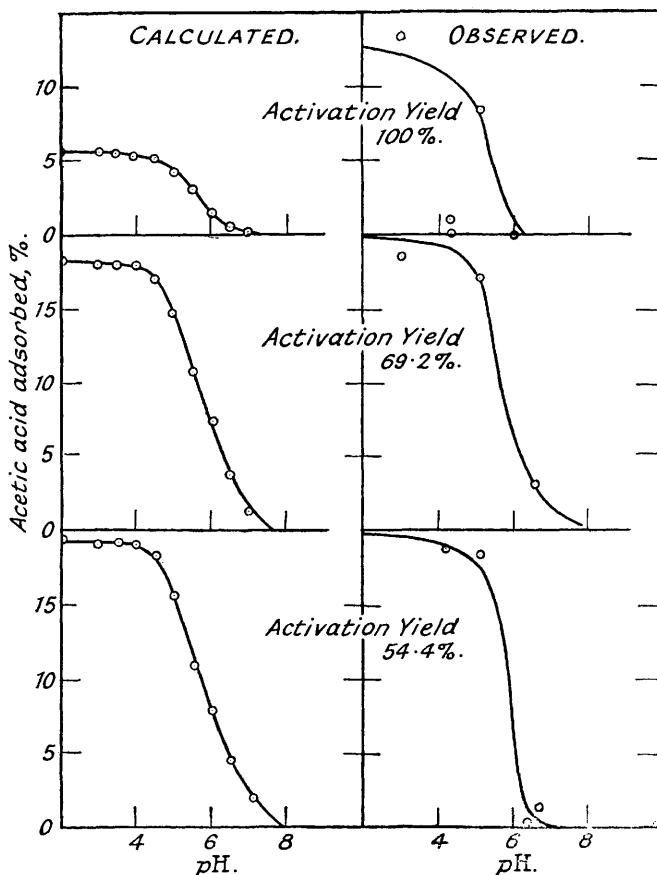
The curves of adsorption against pH will be described in terms of two quantities : (*a*) the value of the maximum adsorption; (*b*) the pH of the "point of inflexion " of the curve, taken arbitrarily as the point at which adsorption is one-half of the maximum value.

Effect of activation yield. The point of inflexion is independent of the activation yield. The maximum adsorption increases with continued activation. These results apply to both acetic acid and butylamine (Fig. 3, Tables I and II).

Effect of concentration of solution. Most of the work was done with N-solutions. For acetic acid, however, the work on nutshell charcoals was repeated with N/10-solutions. The same results were obtained, except that the maximum adsorption was found to be less in this case. This depends on the isotherm for adsorption of unbuffered acetic acid. Representative isotherms are shown in Fig. 4. Similar isotherms were obtained for *n*-butylamine.

Effect of temperature of activation. There is no appreciable change in point of inflexion or total adsorption which can be attributed to the temperature of activation within the range practicable for steam activation, *viz.*, 600—1000° (Table III).

Nature of the activation process. The curve for adsorption of acetic acid against pH for a " chemically activated " charcoal (" Sorbonorit ") is precisely similar in form to those for the other charcoals investigated, having a maximum adsorption of 15·7% and a point of inflexion at pH 6·0.

FIG. 2.

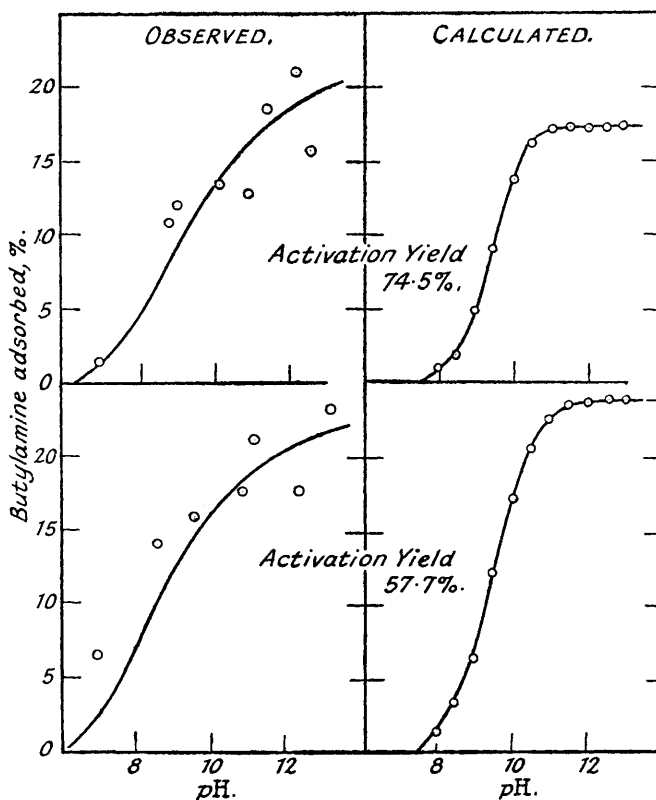*Effect of* pH *on adsorption of* n-*butylamine.*

TABLE I.

Adsorption of acetic acid on charcoals.

Activation yield (%).	Maximum adsorption (%).	pH at point of infln. Obs.	Calc.	Activation yield (%).	Maximum adsorption (%).	pH at point of infln. Obs.	Calc.
			On nut charcoals from N-solution.				
100	12·5	5·3	5·6	54·4	19·5	6·0	5·8
81·9	18·7	5·9	—	43·2	21·2	5·8	—
69·2	19·5	5·9	5·8	24·4	25·0	6·0	—
			On nut charcoals from N/10-solution.				
100	2·6	5·5	4·9	54·4	8·7	5·4	5·4
81·9	7·0	5·8	—	38·8	8·0	6·1	—
69·2	9·2	5·7	5·3	22·0	8·8	5·8	—
			On coal charcoals from N-solution.				
100	7·0	5·6	5·6	47·2	20·0	5·6	5·7
75·2	13·5	5·6	6·1	37·6	19·2	5·6	—
57·2	14·8	6·0	—	26·8	17·5	5·9	—

TABLE II.

Adsorption of n-*butylamine on nut charcoals from* N-*solution.*

Activation yield (%).	Maximum adsorption (%).	pH at point of infln. Obs.	Calc.	Activation yield (%).	Maximum adsorption (%).	pH at point of infln. Obs.	Calc.
100	4·3	10·5	10·0	57·7	24·8	8·8	9·5
74·5	20·6	9·3	9·4	37·9	28·5	8·5	—
65·6	22·5	8·7	—	23·4	31·5	8·8	—

TABLE III.

Effect of temperature of activation on adsorption of acetic acid on nut charcoals from N-*solution.*

Temp. of activation.	Activation yield (%).	Maximum adsorption (%).	pH of point of infln.	Temp. of activation.	Activation yield (%).	Maximum adsorption (%).	pH of point of infln.
1000°	48·9	17·7	5·9	700°	55·2	17·0	5·9
890	43·2	19·5	5·9	600	59·0	18·5	5·8

FIG. 3.

Effect of activation yield on adsorption of acetic acid and n-*butylamine.*
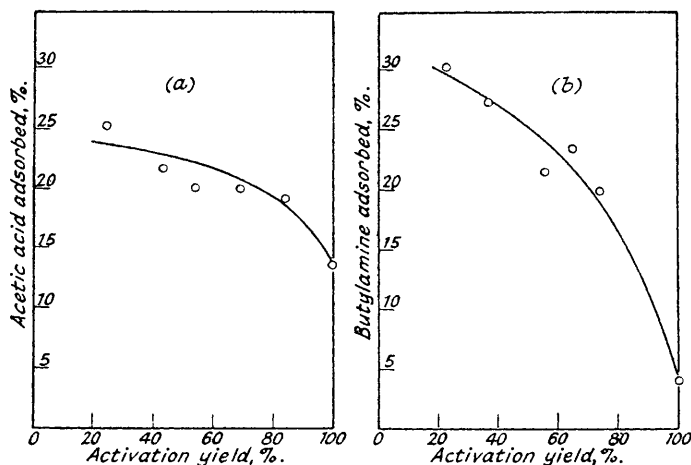
DISCUSSION.

In Figure 1 the observed variation of adsorption of acetic acid with pH is compared with the calculated results. The calculations are based on the experimentally determined isotherm of unbuffered acetic acid. The two curves agree very closely. The calculated adsorption does in fact also follow the dissociation curve of the acid very closely. This is due partly to the small pH range through which the fall in free acetic acid concentration takes place and partly to the shape of the isotherm, most of which is nearly linear over a wide range of concentration. Thus the approximation of Phelps and Peters does hold very closely for this particular case, but it is important to realise that it might not hold for substances with isotherms of a very different shape or with shallower dissociation curves.

The corresponding curves for butylamine are shown in Fig. 2. The observed curves follow the calculated curves qualitatively, but drop less sharply than expected from maximum to zero adsorption. Thus the general conclusion reached for acetic acid, that adsorption takes place through the undissociated molecule, is confirmed. The slight quantitative discrepancy is probably due to the basic character of the mineral content of the charcoals. This will raise the pH of the solution which first reaches the charcoal surface and so give an abnormally high adsorption. When an equilibrium pH is established, some desorption of butylamine should take place. It is shown in the following paper, however, that such desorption is slow and hence a false equilibrium is maintained.

The experimental data considered up to this point are thus in complete accord with the theory that only the undissociated acid or base is adsorbed and that the extent of adsorption follows an isotherm of the Langmuir type. This theory will account for the observation of " hydrolytic adsorption " in the case of salts of a weak acid or base. This phenomenon is essentially the adsorption of some component from the solution of a salt which results in a change in the pH of the solution (see, *e.g.*, Bartell and Miller, *J. Amer. Chem. Soc.*, 1922, **44**, 1866). It has been connected with specific chemical structures of the charcoal surface (*idem, J. Physical Chem.*, 1924, **28**, 992). Although such an explanation may be required for some types of adsorption (*e.g.*, of strong acids and bases), it is clearly unnecessary for salts of weak acids and bases.

There is quantitative evidence that the charcoal surface exhibits no specific acidic or basic

behaviour. Fig. 5 shows that equal numbers of molecules of acetic acid and butylamine are adsorbed on unit weight of a given charcoal. It is probable (from the shape of the isotherms) that these substances form only a unimolecular layer on the charcoal surface, and it is likely that they then occupy the same area per molecule as in the corresponding layers on liquid surfaces. This is 20·5 sq. A./molecule for both substances (Adam, " The Physics and Chemistry of Surfaces ", Oxford, 1941). Hence they can separately occupy equal areas of charcoal surface. We conclude, therefore, that the adsorption of acetic acid and butylamine on charcoal is independent of the chemical and electrochemical nature of the surface and that possibly the surfaces of these charcoals are all, in this respect, essentially similar.

FIG. 4.

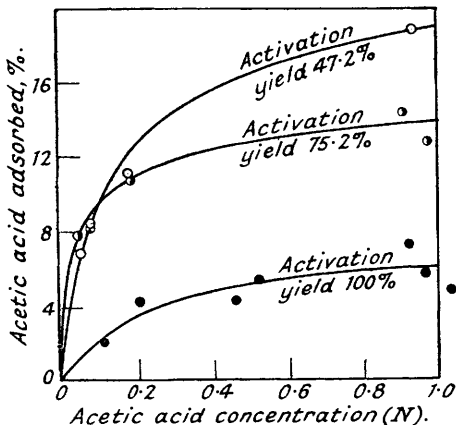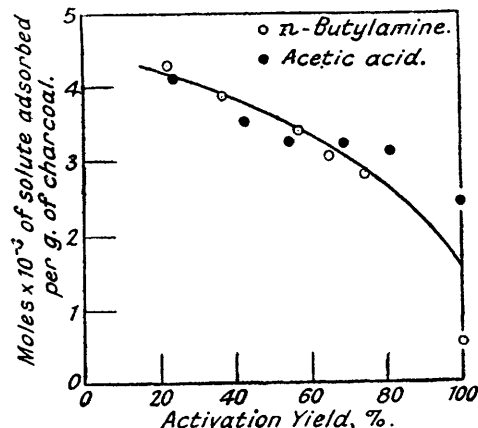Adsorption isotherms of acetic acid on charcoal.

FIG. 5.

Molar adsorption of acetic acid and n-butylamine on charcoal.

This conclusion is supported by two further results. (i) The same phenomena are observed when the charcoal is made from different raw materials or by different methods of activation. (ii) The easy reversibility of adsorption referred to in the following paper confirms that this adsorption is of a physical and not a chemical nature.

Our conclusions do not accord with those of King. We would tentatively suggest that his varying adsorption according to the temperature of activation may be due to the different degrees of activation obtained as a result of variation in the rates of oxidation as the temperature varied.

Finally, it should be emphasised that this discussion applies to the adsorption of acetic acid and butylamine and does not necessarily apply to the adsorption of all solutes.

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