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## ADSORPTION OF ORGANIC ACIDS FROM AQUEOUS SOLUTION ON CHARCOAL

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**Abstract.** Adsorption of various organic acids (monobasic and dibasic) from aqueous solution on charcoal has been studied by the usual titration method. The Freundlich and Langmuir plots have been drawn and the constants involved in the Freundlich and Langmuir isotherms were evaluated. The values of the constants were used to throw light on the mechanisms and the nature of forces involved in adsorbate-adsorbent interactions.

Adsorption of organic acids on charcoal and other adsorbents has been studied by many authors.<sup>1,2</sup> In general, it has been shown that the adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series. However, Holmes and McKelvey<sup>3</sup> have noted that the adsorption processes in a homologous series may be reversed if a polar adsorbent and a nonpolar solvent were used. It has been further observed that the less soluble the material in a solvent, the more strongly it is adsorbed onto the solid surface.

The adsorption from solution, therefore, is a relatively complex phenomenon depending upon the adsorbent-solute, and adsorbent-solvent interactions. It also depends largely on the nature of interfacial region.

The adsorption of mono and dibasic organic acids from aqueous solutions has been studied. The values of constants namely,  $1/K$  and  $1/K_1K$  for Langmuir isotherms and  $1/n$  and  $\log K$  for Freundlich isotherms have been computed. An attempt here has been made to correlate the adsorption behaviour of acids with their mode of packing and orientations on the solid surface.

### Experimental

#### *Purification of Substances*

(i) *Purification of Charcoal.* The active charcoal (industrial coconut) contains small amount of acid. It was, therefore, purified before using. The charcoal sample was shaken with water, allowed to stand for sometime and decanted off. The process was repeated a number of times and the supernatant was checked for any acid content. The charcoal was washed until there was no significant amount of acid left. It was then dried by heating at 200°C in an oven for 24 hr.

(ii) *Purification of Acetic Acid.* The acid was purified by freezing at -22°. This procedure was repeated thrice in order to get pure acid. Other acids used were

purified by freezing, distillation or crystallization methods.

### Procedure

At first, a test experiment was performed by taking 50 ml acid, 50 ml distilled water and 1 g charcoal in a stoppered bottle. The bottle was shaken for 15 min. The sample (10 ml) was pipetted out and titrated against standard NaOH solution. The bottle was again shaken for 15 min and the titration was repeated till a constant concentration of acid was obtained. In the main set of experiment the bottles were shaken 50% longer than the minimum time indicated by the test experiment.

Nine stoppered reagent bottles were cleaned and dried. Into each bottle 1 g finely ground charcoal was weighed accurately. Then, 90, 80, 70, 60, 50, 40, 30, 20 and 10 ml 0.5N acid was pipetted out into each bottle and 10, 20, 30, 40, 50, 60, 70, 80 and 90 ml distilled water was added respectively. The bottles were shaken for 1 hr and then the contents were filtered. The first 1-2 ml portion of the filtrate from each bottle was rejected. Filtrate from each bottle was titrated against standard NaOH solution.

### Calculation and Results

From the adsorption isotherms (Figs. 1-3), Langmuir and Freundlich plots have been obtained (not given here) and values of constants namely  $1/K$  and  $1/K_1K$  for Langmuir plots and  $1/n$  and  $\log K$  for Freundlich plots were computed. These values are tabulated in Table 1. The values of constants correspond to the following two well-known equations:

$$\frac{C}{(x/m)} = \frac{1}{K_1K} + \frac{C}{K} \quad (\text{Langmuir}) \text{ and}$$

$$\frac{x}{m} = KC^{\frac{1}{n}} \quad (\text{Freundlich}).$$

The symbols have their usual meaning.

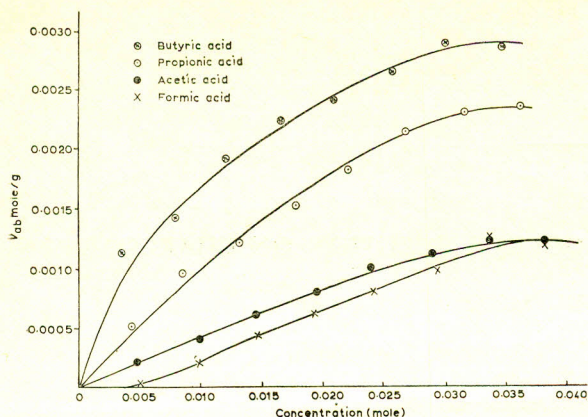


Fig. 1. Adsorption of organic acids on charcoal.

### Discussion

The adsorption behaviour of certain organic monobasic and dibasic acids on charcoal has been studied. The results shown in Figs. 1-3 can be divided into two broad categories. The first category consists of those acids which contain only one carboxylic group and a side-chain. The second category is of those acids which contains two carboxylic groups and show a markedly different set of isotherms as compared to the first category. There is a significant difference in the shape of the curves. The monobasic acids do not yield conventional Langmuir type of isotherms when the side-chain is small although their behaviour tends to obey the Freundlich as well as Langmuir isotherms as the side-chain is increased.

The shape of the curves is explainable if one assumes that the partially polar ends of the acid molecules have a tendency to attach themselves at the active sites of the solid surface. If side-chain is small as is the case with formic and acetic acids, the polarity of the carboxyl group may effect the side-chain as well. Therefore, the probability of attachment at the polar or less polar end is significant. In other words the molecules either tend to stand erect or lie flat on the surface. Statistically, some molecules will orient one way and some in the other, this destroys the unimolecular packing and leave gaps in between. It would, therefore, be difficult to compute accurately the specific surface area of the solid with the help of adsorption of formic acid or acetic acid on carbon.

However, if the side-chain is long the curve resembles that of a Langmuir plot and obeys both Freundlich and Langmuir isotherms. With a long side-chain, the polar effect of the carboxylic group is not transmitted through to the side-chain and the overall effect is that the molecules will stand erect with their polar groups attached to the surface. This enables them to pack together so as to make a monolayer on the surface. Therefore, acids like valeric and caproic can be used for determining surface areas of the activated charcoal. This has been successfully done by Lemieux and Morrison.<sup>4</sup>

The lengthening of the side-chain has another significant effect on Freundlich isotherm. It is seen from the data of  $1/n$  and  $\log K$  given in Table 1 that as the length of the side-chain increases, the value of

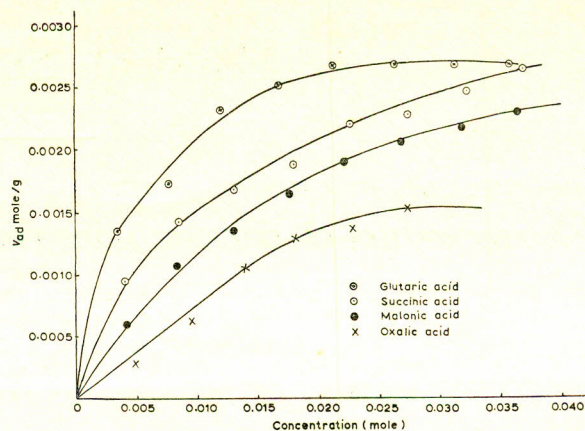


Fig. 2. Adsorption of organic acids on charcoal.

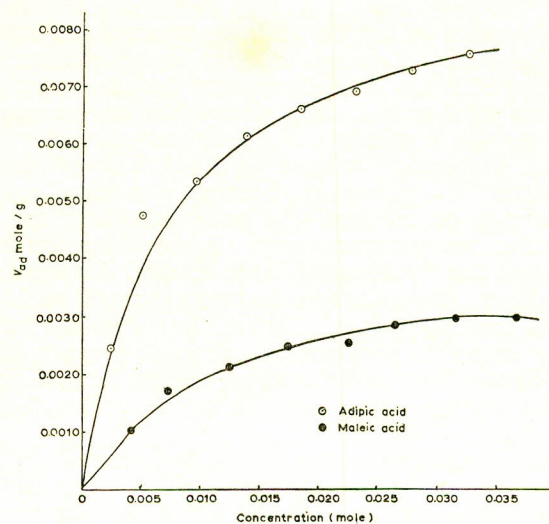


Fig. 3. Adsorption of organic acids on charcoal.

TABLE 1.

Acid	Langmuir plots		Freundlich plots	
	$\frac{1}{K}$	$\frac{1}{K_1 K}$	$\frac{1}{n}$	$\log K$
Formic	—	—	1.33	-2.26
Acetic	—	—	0.96	-1.37
Propionic	1.09	7.95	0.75	-0.64
Butyric	0.128	3.5	0.44	-0.052
Oxalic	—	—	1	-1.34
Malonic	0.128	6.12	0.518	-0.33
Succinic	0.133	3.5	0.45	-0.124
Glutaric	0.166	1.44	—	—
Adipic	0.06	0.09	—	—
Maleic	0.133	2.30	0.366	0.115

$1/n$  decreases from 1.33 for formic acid to 0.44 for butyric acid. The values for  $\log K$  tend to become less negative as the length of the side-chain is increased. The  $\log K$  value for formic acid is  $-2.26$  while for butyric acid it equals  $-0.052$ .

The values of parameter  $1/n$  may be interpreted in a more useful way. In most of the cases,  $1/n < 1$ , so that the amount of adsorbed material increases less rapidly than the concentration. If it were unity, the adsorption equation would be equivalent to the distribution law.<sup>5</sup> On the other hand if  $1/n$  approaches zero then  $x/m$  equals  $K$  which amounts to the formation of a monolayer with no further adsorption.

The above explanation has been based on the assumption that the adsorption of acids from solutions on charcoal is essentially unimolecular. This is a reasonable assumption if the length of the side-chain in acids is restricted to four carbon atoms. Hansen *et al.*<sup>6</sup> found that, for acids and alcohols containing more than four carbon atoms the adsorption on carbon from aqueous solutions showed no saturation effect. There was an indication of multilayer adsorption in such cases. In the present work no acid

with more than four carbon atoms in the side-chain has been used. Keeping this in view, the possibility of multilayer adsorption has not been given much attention. The adsorption isotherms for dibasic acids are of type I. In this case, it appears that the dibasic acids tend to give conventional Langmuir type plots.

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