

STUDIES IN BINARY SYSTEMS.

PART IV. ADSORPTION FROM MIXTURES OF TOLUENE AND ACETIC ACID BY DE-ASHED ANIMAL CHARCOAL.

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INTRODUCTION.

It was shown in Part I (*This Journal*, 21A, 331-44) that the S-type of adsorption isotherm of the system animal charcoal, toluene and acetic acid, might be due to two components of opposite nature present in animal charcoal, *viz.*, ash and carbon. According to Miller (*Jour. Phys. Chem.*, 1926, 30, 1162) the difference in the adsorption capacity and specificity of various charcoals is due to their ash content and the amount of acids and alkalis adsorbed on the surface, and all adsorbent charcoals after thorough purification have the same properties of selective adsorption, which are identical with those of pure ash-free activated sugar charcoal. Results given in literature are discordant because charcoals are ill-defined substances and it is very difficult to remove ash even by digestion with *aqua regia*. Miller recommended the use of hydrofluoric acid to remove silica.

It followed that if the animal charcoal is freed from ash by digestion with acids, it might yield a complete *negative* adsorption isotherm similar to that given by sugar charcoal.

The treatment with hydrochloric acid would remove the alkali contained in the ash, while the hydrofluoric acid would remove silica, both of which might have modified the apparent adsorption of acetic acid from toluene.

EXPERIMENTAL.

The apparatus used and the experimental procedure followed was the same as described in Part I.

The animal charcoal after treatment with nitric and hydrochloric acids was wetted with hydrofluoric acid in a platinum dish and warmed over a flame. After the removal of acid, the charcoal was boiled with concentrated hydrochloric acid. This treatment was repeated until the ash content was brought down to 1% after activation. Activity of this charcoal was 25%. A new lot of sugar carbon was prepared and it was also activated to 25%.

For comparison of adsorption, 0.25 gram lots of the two charcoals were separately weighed in glass-stoppered flasks, 5 c.c. of the solution added and shaken for half an hour. The changes in concentration were measured, as before, refractometrically. Results are given in the following table and shown in Fig. 1.

Acetic acid in Toluene %	% Change in minutes		Change in strength $C_0 - C$	
	Animal Charcoal	Sugar Charcoal	Animal Charcoal	Sugar Charcoal
9.6	6.4	-0.2	0.51	-0.02
19.9	6.25	-1.2	0.50	-0.096
27.9	6.0	-1.75	0.48	-0.14
49.0	2.9	-3.70	0.23	-0.30
67.3	1.25	-5.05	0.10	-0.40
89.0	0.35	-4.70	0.028	-0.38

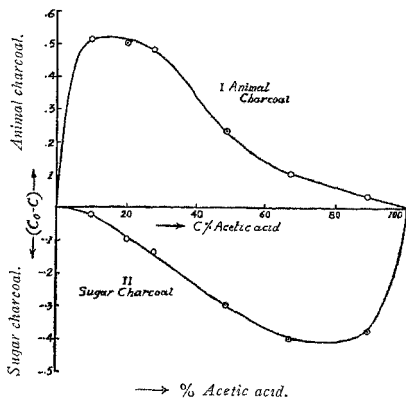


FIG. 1.

System: Toluene-Acetic acid—
 I Animal charcoal
 II Sugar charcoal

Contrary to expectation, the de-ashed animal charcoal shows *positive* adsorption and sugar charcoal *negative* adsorption for the same system.

Although the sugar charcoal showed only an activity of 25% as determined by the adsorption of benzoic acid, a very flat minima is shown in the selective adsorption curves in the range 70 to 84% of the acid, in which region the complexes formed are $C_6H_5CH_3(CH_3COOH)_2$, $C_6H_5CH_3 \cdot 2(CH_3COOH)_2$, $C_6H_5CH_3 \cdot 3(CH_3COOH)_2$, and $C_6H_5CH_3 \cdot 4(CH_3COOH)_2$, as in the case of experiments described in Part I. The de-ashed charcoal shows a positive adsorption which is flat in the region 15–25% acid.

It may be pointed out that the activities of both the charcoals used in this investigation were measured by the adsorption of benzoic acid from aqueous solution. Both these samples of charcoal were activated in a limited supply of air at 1000°. It would appear from the results given in the present paper, that there are two types of carbon particles on the surface of the adsorbent which have got different specific adsorptive properties, one adsorbing the polar and the other non-polar compounds, the actual adsorption by any particular charcoal being the sum of the individual specific adsorption of each type of active centre, which may vary according to the conditions of activation and which may be modified by impurities such as alkali, silica, etc., which form the ash in the charcoal.

Most of the charcoals studied for adsorption from binary liquid mixtures, have been activated by heating in oxidising atmospheres, which is not likely to leave the highly active carbon centres to remain unaffected at the high temperature of activation. We have, therefore, undertaken a systematic research on the adsorptive properties of different carbons activated by steam and also by treatment with salts such zinc chloride, etc.

The results presented in this paper were reported by one of the authors (J. G. K.) to the proceedings of the Indian Science Congress as early as September 1930. Since then B. Il'in and Simananov (*Z. Physik*, 1930, **66**, 613–8) have published experimental data on the *inversion* of adsorption from aqueous fatty acid solutions by two modifications of active carbon prepared from sugars. The Debye figures for these carbons were identical. No satisfactory explanation for this inversion of adsorption has been given, although numerous similar instances are known, in which Traube's rule is reversed.

Very recently Bartell and Lloyd have published a paper on "Alteration of Adsorption Properties of Charcoal" (*Jour. Amer. Chem. Soc.*, 1938, **60**, 2120) in which they report that sugar charcoal could be changed from extremely organophilic charcoal, to charcoal approaching the hydrophilic adsorbent, silica, in adsorption properties.

by controlling the temperature and nature of the oxidising atmosphere. These authors do not mention the extensive work of B. Il'in on a similar subject (*cf. Z. Physik. Chem.*, 1931, **A 155**, 403). The binary systems benzene-ethanol was used for the study of preferential adsorption, all the curves obtained being of the S-type, which indicated zero adsorption for the various charcoals at 0.1, 0.2, 0.25, 0.3, 0.6 and 0.7 mol. fraction of ethyl alcohol, and showed a flat negative maxima at 0.8 mol. fraction of ethyl alcohol in all cases. This would indicate that the complexes formed in the system benzene-ethyl alcohol, will have molar proportions of 1:4, 1:3, 1:2, 1:1 and 4:1, as the zero selective adsorption by the adsorbent has been previously shown by us to be due to the preferential adsorption of the complex of the composition of the liquid mixtures giving zero selectivity. We have carried out the adsorption of the system benzene-ethyl alcohol by silica gel prepared from nickel silicate and by Norite charcoal, which seem to confirm the above conclusion. The results of these investigations will be reported in the near future.

Further work is in progress.

SUMMARY.

Animal charcoal treated with hydrofluoric acid to remove ash, and activated in the usual way, has been found to give, when brought into contact with mixtures of toluene and acetic acid in different proportions, an adsorption isotherm the reverse of that obtained with sugar charcoal, indicating that the latter preferentially adsorbs toluene and the former acetic acid.

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