CCCLVIII.—*Adsorption and Constitution: The Adsorption of Organic Acids on Animal Charcoal.*

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IT has been shown that the expression C_2/C_1 gives a comparable measure of the adsorption of substances from solution (Richardson and Robertson, J., 1925, **127**, 553), *i.e.*, the order of the values of C_2/C_1 found for a number of compounds agreed with the relative position of their adsorption isotherms, the effect of initial concentration being limited to that due to differences in the slope of the isotherms. Further, the magnitude of C_2/C_1 varied over a wide range with changes in the structure of the substances compared.

The equilibrium of an adsorbed substance in contact with its solution—the adsorption isotherm—is generally expressed by the exponential formula of Freundlich, $a = \alpha c^{1/n}$, or $C_2 = KC_1{}^{1/n}$, which gives satisfactory results at least for dilute solutions. An examination of the values of $1/n$ for a number of widely diverse substances (Freundlich, " Kapillarchemie," 1923, 236) showed very little dependence on the nature of the molecule adsorbed : n lay between 1·8 and 4·2. Richardson and Robertson (*loc. cit.*) made a similar observation with a variety of organic compounds. Apart from the ambiguity of its actual significance, therefore, and the experimental difficulties of its determination in solvents where adsorption is slight, n does not seem to be a suitable function for the examination of constitutive influences.

The relative extent to which substances are adsorbed varies much more considerably than does n : some comparative studies on this basis, of the adsorption of organic acids from aqueous solution, have been reported (Freundlich, *op. cit.*, p. 267; Bartell and Miller, *J. Amer. Chem. Soc.*, 1923, **45**, 1109). However, for a more general examination of organic compounds, owing to their slight solubility in water, organic solvents would be necessary. In the present paper, the adsorption by animal charcoal from ethyl-alcoholic solution of a number of carboxylic acids has been determined. The concentration chosen as a basis of comparison was $N/20$; C_2/C_1 was calculated from this after titration of the equilibrium filtrate, and then the "relative adsorption" with reference to a standard acid (acetic for the aliphatic series, benzoic for the aromatic) was taken for comparison. This "relative adsorption" was found to be almost independent of the activity of the charcoal.

EXPERIMENTAL.

The method of experiment was as described in the literature : 5 g. of charcoal were shaken mechanically for 4 hours with 50 c.c. of an $N/20$-alcoholic solution of the acid, the liquid was rapidly filtered, and 10 c.c. portions of the filtrate were titrated with $N/20$-alcoholic potash with phenolphthalein as indicator. The original solution was titrated at the same time as the filtrate from the charcoal, to allow for error due to esterification. Only those titration values that differed by less than 0·1 c.c. were accepted; agreement was generally within 0·05 c.c.

The reagents used were carefully purified. The animal charcoal was supplied by the British Drug Houses as "Animal Charcoal, Acid-free," and since it had at first a slightly alkaline reaction, it was repeatedly extracted with hot water until neutral to phenolphthalein. Before use, it was activated by heating to redness for some hours in a Vitreosil tube, a steady stream of dry nitrogen being passed through towards the end of the operation and continued until the tube was cold. After being sieved, the charcoal was kept in a large, stoppered bottle for several days before use, for its activity fell off somewhat immediately after activation. Since the amount of charcoal used in a series of experiments was considerable, it became necessary to recover it after use and reactivate it : this was effected in the same manner as the preliminary activation. After reactivation, the activity of the charcoal as measured by a standard substance such as acetic acid was found to have changed slightly: in one series of reactivations, C_2/C_1 for acetic acid was successively 1·35, 1·19, 0·98, 1·10, 0·75; another charcoal gave 0·36, 0·46, 0·43, 0·33, 0·39. To enable comparable results to be obtained with charcoals of different activity, the values of C_2/C_1 found for a series of compounds with any one charcoal were divided by the previously determined value of C_2/C_1 for a standard acid with that charcoal. As noted above, these "relative adsorptions" obtained for any compound with different charcoals were in satisfactory agreement, but in certain instances the deviations were greater than the experimental error. It would appear that when the structure of the compounds differed considerably, the relative adsorption might be influenced to some extent by the nature of the charcoal. This is shown by observations on acetic and benzoic acids:

Charcoal.	C_2/C_1, acetic acid.	C_2/C_1, benzoic acid.	Relative adsorption (acetic acid = 1).
I	0·362	1·67	4·61
II	0·463	2·24	4·84
III	0·433	2·48	5·73
IV	0·330	2·08	6·32
V	0·387	2·59	6·69
VI	0·067	0·339	5·1

Charcoals II, III, IV, and V were obtained by successive reactivations of charcoal I; reactivation caused a slight but steady increase in the relative adsorption of benzoic acid as compared with acetic acid. Charcoal VI was a sample of different origin, and considerably less active; the value it gave for the relative adsorption of benzoic acid fell amongst those of the previous charcoals. The other aromatic acids resembled benzoic acid in showing appreciable deviations among their relative adsorptions with different charcoals, when the value for acetic acid was taken as unity. For this reason, the values for their relative adsorptions that appear in Table II were calculated on the basis of benzoic acid; the results so obtained showed satisfactory agreement for different samples of charcoal.

In Tables I and II are given the mean values found for the relative adsorptions from alcoholic solution of aliphatic and aromatic acids, respectively. For the former, acetic acid was taken as standard; for the latter, benzoic.

The effect of constitution is on the whole definite. In the normal fatty acids, the adsorption falls to a minimum and then rises with increasing molecular weight; further, the property is an alternating one, the odd-numbered members being less adsorbed than the even.

TABLE I.

Acid.	Relative adsorption.	Acid.	Relative adsorption.
Acetic	1·00	Lactic	0·58
Propionic	0·65	Phenylacetic	3·26
Butyric	0·87	Phenylpropionic	4·04
*iso*Butyric	0·27	Cinnamic	6·25
*iso*Valeric	0·21	Mandelic	2·29
Hexoic	1·13	Succinic	1·44
Heptoic	0·92	Adipic	1·05
Octoic	1·50	Sebacic	2·30
Nonoic	1·32	Monobromosuccinic	1·77
Lauric	2·15	Ethylsuccinic	0·85
Stearic	2·32	Malic	1·22
Monochloroacetic	2·31	Tartaric	1·60
Trichloroacetic	0·27	Fumaric	4·15
Monobromoacetic	2·70	Citraconic	5·54
α-Bromopropionic	1·92	Mesaconic	3·41
α-Bromo*iso*butyric	1·38		

With regard to the effect of substituents, small alkyl groups and the hydroxyl group reduce the adsorption, and halogen (except in trichloroacetic acid) and the phenyl group increase it. Dibasic acids are adsorbed more strongly than the corresponding monobasic acids. Unsaturation (the ethylenic link) causes an especially marked increase in relative adsorption.

TABLE II.

Acid.	Relative adsorption.	Acid.	Relative adsorption.
Benzoic	1·00	*p*-Nitrobenzoic	3·64
o-Toluic	0·97	*o*-Chlorobenzoic	0·86
m-Toluic	1·19	Salicylic	1·64
p-Toluic	1·36	*o*-Acetoxybenzoic	0·75
o-Bromobenzoic	1·01	*p*-Methoxybenzoic	2·30
m-Bromobenzoic	2·10	Phthalic	2·30
p-Bromobenzoic	2·42	*o*-Aminobenzoic	2·91
o-Nitrobenzoic	1·34	*o*-Acetamidobenzoic	2·30
m-Nitrobenzoic	3·32	*s*-Tribromobenzoic	2·51

Generally the relative adsorption of the aromatic acids is 5 to 20 times that of the aliphatic acids (compare table, p. 2707). Substituents in the para-position increase the relative adsorption, the effect of the groups being in the order alkyl, halogen, nitro-; in the meta-position there is a corresponding but smaller enhancement; and ortho-substitution has usually a smaller or even a depressing effect. The enhancement attributable to *o*-hydroxy- and *o*-amino-groups was reduced by acetylation. As in the aliphatic series, the additional carboxyl group of a dibasic acid increased adsorption.

Summary.

1. The relative adsorption of organic acids from alcoholic solution, on animal charcoal, varies within wide limits; *e.g.*, *iso*valeric acid

has the value 0·21, and *p*-nitrobenzoic acid 17, if acetic acid is taken as unity.

2. In general, the relative adsorption tends to increase with molecular weight, but this increase is subject to marked constitutive effects.

3. Aromatic acids are much more strongly adsorbed than aliphatic acids; substitution, especially in the para-position, increases the adsorption.

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[*Received, August* 23*rd*, 1928.]