583. *Molecular Adsorption on Ion-exchange Resins.*

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Weak acids and weak bases are taken up by ion-exchange resins by a process of molecular adsorption. Data for a number of systems are reported and discussed.

Brief references to this work have already been made (Davies, *Chem. and Ind.*, 1948, 51; 1949, 25), and the importance of adsorptive forces in ion-exchange chromatography has been emphasised (*idem, Biochem. J.*, 1949, **45**, 38). A short record of our measurements will therefore be sufficient.

Experimental.

Materials.—The resins used were four cation exchangers in the hydrogen form : Wofatit C, which contains only carboxylic acids groups; and Zeo-Karb 215, Amberlite 1R-100, and Zeo-Karb H1, which are strong acid exchangers, but contain phenolic and carboxylic as well as sulphonic acid groups. The Zeo-Karb 215 was dry sieved to three sizes, 20/40 mesh, 60/90 mesh, and a fine sample passing 100 mesh. The Wofatit and Amberlite were sieved to 20/40 mesh, and the Zeo-Karb H1 was used as received. The resins were conditioned in the usual way, and were air-dried after prolonged washing with distilled water. At the time each series of adsorption measurements was begun, the moisture content of the resin was determined by heating separate samples to constant weight.

Adsorption of Organic Acids.—Some measurements to study the effect of particle size were carried out with the Zeo-Karb 215, but Wofatit C and Amberlite 1R-100 were used for the bulk of the work. The organic acids were the purest laboratory reagents available, and were used without further purification. 2-G. samples of resin were weighed into bottles with tightly fitting ground stoppers. 50 Ml. of a standard acid solution were added to each from a calibrated pipette, and the bottles were kept at room temperature with daily agitation for 28 or 56 days; in the rate experiments the time of contact was varied. Two 20-ml. aliquots were then withdrawn and titrated against standard baryta with phenolphthalein as indicator. Each series was accompanied by blank experiments (2 g. of resin; 50 ml. of water) and in the adsorption calculations it was assumed that the resin lost acid to the solutions studied at the same rate as to water.

There are two main sources of error in the results. First, no allowance has been made for swelling. Water is simultaneously adsorbed, with the result that our calculated apparent adsorption of acid will be too low. From the available information on commercial resins we estimate that approximately $N/2$ milliequivs. per g. should be added to our adsorption figures, where N is the equilibrium acid normality. This is supported by some measurements with 0·1N-hydrochloric and sulphuric acids, which showed an apparent *negative* adsorption of acid of approximately 0·05 milliequiv. per g. The second uncertainty is in the blank correction. Many investigators have found that these resins in the hydrogen form are not entirely stable, and our blank corrections were often quite considerable. If, now, acid diffuses less readily from the resin into the acid solutions than into water, our calculated adsorptions, especially in the more concentrated solutions of low pH, will be too high. It is unknown how important this effect is, but it will act in opposition to the other source of error, and by neglecting both we think that our results will only exceptionally be in error by more than 1 or 2 units %.

Adsorption of Bases.—The adsorption of ammonia and pyridine was studied on Zeo-Karb H1 and Amberlite 1R-100. Bromocresol-purple and bromophenol-blue, respectively, were used as indicators in the final titration against standard acid. 1-G. samples of resin and 100 ml. of solution were used in this work, so swelling errors were less important. Blank experiments were carried out as before.

RESULTS AND DISCUSSION.

The adsorption of organic acids on Wofatit C can be adequately represented by the Freundlich equation, as Fig. 1 shows, and the same is true of Amberlite 1R-100. This provides a convenient basis for tabulation, and our results for these two resins are as follows :

	Wofatit C.			Amberlite 1R-100.		
Acid.	A	n	$(x/m)_{0·01}$	A	n	$(x/m)_{0·01}$
Phenylacetic	8·3	1·43	0·331	9·0	1·55	0·466
Benzoic	15·2	1·38	(0·536)	35	1·2	(0·73)
Phthalic	6·9	1·28	0·192	—	—	—
Octanoic	—	—	—	18·1	1·39	(0·63)
Butyric	3·06	1·18	0·063	2·96	1·35	0·098
Acetic	1·48	0·97	0·013	1·31	1·09	0·019
Adipic	7·6	1·09	(0·11)	—	—	—
Glutaric	3·2	1·10	0·051	—	—	—

Cols. 2 and 3 show the values of A and n in the equation $x/m = AC^{1/n}$, where x/m is the adsorption in milliequivs. per g. of dry resin, and C is the concentration of acid at equilibrium. Col. 4 shows the adsorption in milliequivs. from a 0·01N-solution, the figures in parentheses being extrapolated values.

If the effect is one of molecular adsorption on the resin framework, the nature of the ionising groups of the resin would not be expected to be of overriding importance, and actually it will be seen that the adsorption of acids is considerably *greater* on the strong sulphonic acid Amberlite resin than on the carboxylic acid Wofatit resin.

Some measurements on both resins in the presence of added hydrochloric acid are compatible with the view that it is the undissociated acid molecule that is adsorbed. The effect of the hydrochloric acid in every case was to increase the adsorption by an amount commensurate with the slight increase in the concentration of undissociated acid at equilibrium.

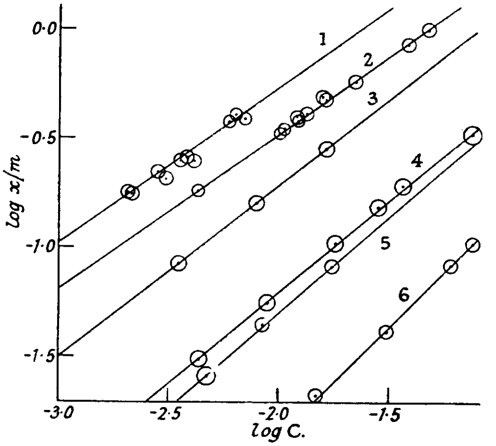
The measurements on Zeo-Karb 215 were not over a wide enough concentration range to provide values of A and n, but at the concentrations studied the adsorptions of phenylacetic, phthalic, butyric, and acetic acids were almost the same as on Wofatit C. That for mandelic acid came between the figures for butyric and phthalic, and, as would be expected, formic acid was less adsorbed than acetic, and succinic less than glutaric acid.

The value of n is close to 1 for acetic and the other weakly adsorbed acids. The equilibrium in these cases might be described as a simple distribution of solute between the resin phase and the outer solution. It has been shown before, however (preceding paper), that the amount of water taken up by a typical commercial resin from aqueous solution is only sufficient to provide an approximately unimolecular film of water on the internal surface of the resin, so the analogy with typical cases of surface adsorption seems more likely to be useful. For the more highly adsorbed acids n is greater than 1, but at the concentrations studied there is no evidence of curvature in the Freundlich plots. The highest adsorption measured was 1·19 milliequivs. per g. of Amberlite resin for phenylacetic acid at an equilibrium concentration of 0·0426N. If the extended resin framework is assumed to present its whole surface to the intermicellar liquid, this would correspond to 6 or 7% of the surface being covered by acid molecules. This, and the fact that the Freundlich plot shows no sign of a saturation limit, suggests that at higher concentrations the adsorption of an aromatic acid might reach values as great as or even greater than the maximum ion-exchange capacity of the resin.

The order of adsorbability of the various acids studied is the same on all three resins as on an active carbon. The aromatic acids are strongly adsorbed. Traube's rule is obeyed by both the monocarboxylic and the dicarboxylic series of aliphatic acids, and the effect of polar substituents, as in phthalic and mandelic acids, is to reduce adsorption from aqueous solutions. Other examples of this, not previously mentioned, are citric and tartaric acids, which we found to be only very weakly adsorbed on Zeo-Karb 215.

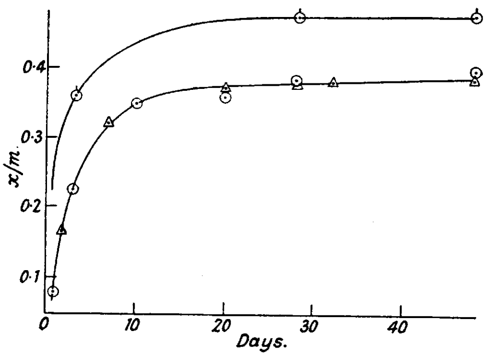
Effect of Particle Size.—Measurements with most of the acids so far mentioned were carried out on the three graded samples of Zeo-Karb 215, and the amount adsorbed was found to be independent of particle size. There did appear to be an effect, however, with benzene-, naphthalene-2- and anthraquinone-sulphonic acids. These three strong acids showed negligible adsorption on the larger resin granules but appreciable adsorption on the sample passing 100-mesh. The size of this effect is rendered a little uncertain by the large " blank " correction given by the fine resin, but it seems worthy of further study. It seems to suggest that these anions are unable to diffuse into the resin interior, but are heavily adsorbed at the external surface.

FIG. 1.



Adsorption on Wofatit C : 1, Benzoic acid ; 2, phenylacetic acid ; 3, phthalic acid ; 4, butyric acid ; 5, glutaric acid ; 6, acetic acid.

FIG. 2.



○ *Phenylacetic acid on Wofatit C ;*

⦽ *phenylacetic acid on Amberlite* IR-100 ;

△ *benzoic acid on Wofatit C.*

Adsorption of Bases.—When aqueous pyridine solutions were equilibrated with Zeo-Karb H1 there was a loss of pyridine from the solution of 2·1 milliequivs. per g. at low residual concentrations of pyridine, corresponding to salt formation at the sulphonic acid groups. At higher concentrations the amount of pyridine removed from the solution increased progressively to 5·9 milliequivs. at 0·57N. This increase is far greater than can be explained by the ionisation of the carboxylic groups contained in Zeo-Karb H1 (cf. Davies, *Chem. and Ind.*, 1948, 52), and salt formation between the phenolic groups and so weak a base as pyridine will be scarcely appreciable. Almost the whole of the additional 3·8 milliequivs. of pyridine removed by the resin must therefore be regarded as held by molecular adsorption.

In similar experiments with aqueous ammonia solutions, the amount of ammonia held by Amberlite IR-100 increased to 4·31 milliequivs. at an equilibrium concentration of 0·270N. This is considerably greater than the amount of sodium hydroxide neutralised at the same pH, so here too there is some evidence for the adsorption of ammonia molecules, though, as would be expected, the effect in this case is much less marked.

Rate of Adsorption.—Fig. 2 shows some measured rates of adsorption for benzoic and phenylacetic acids. The slowness of the reverse process, also, was shown in some experiments in which resin was added to 0·06N-phenylacetic acid, and left in contact for 18 days, an equal quantity of water then being added. After a further 32 days the adsorption, on both Wofatit C and Amberlite IR-100, was significantly greater than in experiments where the additional water had been present from the beginning of the 50-day period. The tenacity with which pyridine is held by Zeo-Karb H1, Amberlite 1R-100, and Wofatit C was shown in a series of experiments in which samples of the resin, after being treated overnight with 0·5N-pyridine solutions, were washed with water and successive portions of hydrochloric acid (1 g.-mole per g. of resin in all), over a period of months. After this treatment the resins gave the characteristic odour of pyridine when treated with sodium hydroxide.

With simpler and less heavily adsorbed molecules the rates of adsorption and desorption are probably much greater than in the above cases. No further adsorption of butyric acid could be detected after 6 days' contact.

We thank the Department of Scientific and Industrial Research for the award of a maintenance allowance, during the tenure of which (by G. G. T.) this work was carried out.

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[*Received, April* 30*th*, 1951.]