582. *Adsorption and Swelling Experiments with an Amine-type Ion Exchanger.*

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The behaviour of the resin Amberlite IR-4B has been studied in aqueous solutions of hydrochloric acid, with and without the addition of added chlorides. The measurements enable the uptake of water by the ionised resin to be calculated, and it is shown that it corresponds to little more than a monolayer. This knowledge of the water adsorption enables the adsorption of acid to be correctly calculated, and the results are compared with the equations of Bishop and Bauman. A new equation is proposed which better represents the ionisation equilibrium.

It is found that a regenerated basic resin normally contains significant amounts of carbonate. This exchanges with the anions of added neutral salts, and also complicates the determination of the moisture content of the resin.

The uptake of acid by amine-type ion-exchange resins has been studied by a number of authors. It is convenient to describe the process as one of adsorption, but it is generally agreed that the mechanism is given by one or other of the following equations :

$$(a)\ \mathrm{R{\cdot}N} + \mathrm{H}^{\bullet} + \mathrm{A}' \rightleftharpoons \mathrm{R{\cdot}NH}^{\bullet} + \mathrm{A}', \text{ or}$$

$$(b)\ \mathrm{R{\cdot}NH{\cdot}OH} + \mathrm{H}^{\bullet} + \mathrm{A}' \rightleftharpoons \mathrm{R{\cdot}NH}^{\bullet} + \mathrm{A}' + \mathrm{H_2O}$$

where A′ is an acid anion, N is the nitrogen of a primary, secondary, or tertiary amino-group, and R represents the remainder of one chemical equivalent of the resin. Although there has been some discussion as to which of these is the more appropriate, they are for most purposes equivalent, as are the corresponding formulations for a simple monomeric base.

The data so far available, mostly presented graphically, give a general picture of the behaviour of the amine resins, but do not provide a basis for a quantitative study of the dissociation equilibrium. Our object was to obtain results which could be utilised for this purpose, and we have therefore studied the system Amberlite IR-4B–hydrochloric acid–water as accurately as possible, paying special attention to reproducibility, moisture content, and the correct formulation of acid adsorption by a swollen resin.

Experimental.

Materials.—The resin used for this work was a sample of " Amberlite IR-4B A.G.," made by the Rohm & Haas Co. of Philadelphia. It contained considerable quantities of carbonate and sulphate. When the latter was removed by alternate treatments with 0·1N-hydrochloric acid and 0·1N-sodium hydroxide the measured acid adsorption in successive cycles was found to be 6·43, 7·20, 6·94 milliequivs. per g. The increase after one alkali treatment was due to the removal of sulphate, but the subsequent decrease was real. Heating of the solid resin, *e.g.*, for moisture determination, also led to a decrease of adsorptive capacity. Sodium carbonate and sodium hydrogen carbonate, when used as regenerants, caused similar but smaller decreases in capacity. The resin imparted a yellow colour to sodium hydroxide solutions, and to neutral and acid solutions when hot, and all solutions after contact with resin gave a greenish-yellow colour with Nessler's solution. Contact with acid for some hours at 60° appears to cause considerable breakdown of the cross-linked resin structure. Swelling becomes excessive and the mechanical strength of the resin particles is permanently lost. These results show that a resin intended for quantitative work must be thoroughly aged, and even then results may not be exactly reproducible unless a single batch of resin is used throughout.

Treatment of the resin with 0·1N-sodium hydroxide caused a loss of 2—3 milliequivs. of alkali per g. of resin, presumably through salt formation at phenolic groups. Very prolonged washing was required to remove the alkali gradually liberated when these groups hydrolyse.

For the experiments reported later, a large batch of resin was prepared by thorough treatment with 2% sodium carbonate, followed by washing with distilled water until the specific conductivity had fallen to 2×10^{-6} ohm^{-1} cm.$^{-1}$. For particle-size experiments, part of this air-dried material was ground, and, after being kept for a few days in water, was wet sieved, and fractions of 20/40, 40/60, 60/80, and 80/90 mesh size were collected and thoroughly washed.

Determination of Moisture.—The air-dried resin contains 25—30% of water and, as this figure was required accurately, the following methods of moisture determination were tried : (*a*) prolonged evacuation over phosphoric oxide at room temperature; (*b*) heating at atmospheric pressure to 130°; (*c*) heating to intermediate temperatures in a vacuum-oven; and (*d*) entrainment in AnalaR light petroleum, b. p. 100—120°, in a standard Dean and Stark apparatus (Tate and Warren, *Analyst*, 1936, **61**, 367). In the first method, the greater part of the water is lost fairly rapidly, especially by the resins of smallest particle size, but a slow loss continues for a very long time; in an experiment with 20/40 mesh resins, the loss after 1 day was 88·5%, after 1 week 94·2%, after 1 month 97·5%, and after 2 months 99·2% of the total loss recorded after 4 months' treatment. Method (*b*) gives a considerably greater loss of weight than method (*a*), and, as will be shown later, the additional volatile matter consists of carbon dioxide. In method (*c*) an initially rapid loss of weight is succeeded by a further slow loss during several days. When the % loss in weight is plotted against time, the steep curve obtained over the first few hours passes rather abruptly into a linear portion, the slope of which is steeper the higher the temperature. It is believed that this linear portion represents loss of carbon dioxide, for when it is continued back to zero time the extrapolated loss agrees with that obtained by method (*a*). Method (*d*) also gives values agreeing with method (*a*) within the accuracy, of about 3%, obtainable by the distillation method. The concordance between the results of methods (*a*) and (*d*) and the extrapolated values from (*c*) satisfied us that they led to a correct value for the moisture content of the resin, in spite of the higher value obtained by the other procedure, and a further examination of method (*b*) is described in the next section.

Determination of Carbonate.—The moisture content of six samples of a uniform batch of resin was determined by evacuation at room temperature. The variation was very small, and the mean loss after 124 days was 24·94%. For a further six samples heated at 130° for 3 days the mean loss was 30·47%. If the difference is ascribed to carbonic acid, it implies the presence of 2·4 milliequivs. of carbonate per g. of dried resin. The dried samples were then given prolonged contact with 0·1N-carbon dioxide-free sodium hydroxide, and the solutions subsequently examined; the unheated samples clearly showed the presence of carbonate. Indicators cannot be used with heated samples owing to the pronounced colour of the solutions, but potentiometric titrations against hydrochloric acid showed carbonate to be present in the unheated, and absent from the heated, samples. The amount of carbonate found by analysis for the unheated samples was 2·2 milliequivs. per g., which agrees reasonably well with the calculated figure. Further experiments gave 1·88 milliequivs. of carbonate present after 13 days in a vacuum-oven at 70°, and a definite trace after further prolonged treatment at 110°, so it is clear that a temperature of at least 120—130° is necessary for the complete removal of carbonate in a reasonable time.

A further check on the carbonate of the resin is provided by the loss in weight occurring when the resin is equilibriated with hydrochloric acid solutions. This figure, obtained repeatedly in the course of later work, agreed well with the calculated figure of 2·4 milliequivs. per g. The most convenient method of moisture determination, which we finally adopted, was therefore to determine the total loss in weight at 130° and to calculate the moisture content by subtracting the known figure for the carbonate content of the resin.

Experiments with Neutral Salt Solutions.—Preliminary experiments showed that reaction occurred when neutral salt solutions were added to the prepared resin. With silver nitrate there was some reduction; with sodium chloride the solution became alkaline and lost chloride; and with barium chloride there was copious precipitation.

Quantitative experiments were carried out with sodium chloride. 100 Ml. of the solution were left in contact, in flasks with closely fitting ground-glass stoppers, with a weight of resin corresponding to 1 g. of the dry material. After 7 days, with intermittent shaking, 50 ml. of the solution were withdrawn through a sintered-glass filter and analysed for total alkalinity. The results are in Table I.

TABLE I.

NaCl, g.-equiv./l.	0	0·02	0·10	0·20	1·00
Milliequiv. of alkali released/g. of dry resin	0·02	0·21	0·41	0·63	1·15

The only anions, other than chloride, found in the solution after contact were carbonate and bicarbonate. The concentrations of each were determined for the 0·20N-solution as follows. More than sufficient sodium hydroxide (e_1 milliequivs.) to convert the bicarbonate into carbonate was added to 50 ml. of the solution, and after being heated to boiling and addition of 2 ml. of 10% barium chloride, the solution was rendered colourless to phenolphthalein with hydrochloric acid (e_2 milliequivs.). An excess of acid (e_3 milliequivs.) was added to dissolve the barium carbonate, and after the carbon dioxide had been boiled off the solution was titrated with sodium hydroxide and use of bromocresol-purple (e_4 milliequivs.). The bicarbonate, $2(e_1 - e_2)$, was found to be 0·50 milliequiv./g. of dry resin, and the carbonate, $2(e_3 - e_4) - 2(e_1 - e_2)$, was 0·13 milliequiv. 1·57 Milliequivs. of carbonate were extracted from the wet resin after the experiment.

Experiments with Hydrochloric Acid Solutions.—A large quantity of resin (batch A, 20/40 mesh) was weighed out at one time into 1-g. samples, some of which were used during the course of the work for periodic moisture determinations. In making a measurement of the apparent adsorption of hydrochloric acid by the resin, 100 ml. of acid of suitable concentration were added from a calibrated pipette to a numbered bottle with closely fitting stopper. The weighed portion of resin was added, and the contents of the bottle mixed by careful swirling two or three times a day. After 14 days the solution was transferred to another dry bottle, and aliquots were titrated against carbonate-free sodium hydroxide with bromocresol-purple as indicator. Just before the end-point the solution was boiled for 2—3 minutes, and cooled while protected from carbon dioxide. The alkali was standardised by potassium hydrogen phthalate dissolved in boiled-out water, and also, *via* hydrochloric acid, by recrystallised borax.

Considerable carbon dioxide was lost during the adsorption experiments, and the loss in weight of the bottles agreed with that calculated from the carbonate determinations. Control bottles treated in the same way, but containing no resin, showed no loss of weight and no change in concentration. Experiments on the rate of adsorption showed that equilibrium was attained within 7 days for 20/40-

mesh resin and in considerably shorter periods with the finer fractions. However, a constant time of 14 days was allowed. The results are in Table II, where the first line gives the concentration of acid at equilibrium in g.-equivs./l. The four values for the adsorption of hydrochloric acid, in milliequivs., are discussed later. It may be noticed that all show a maximum.

TABLE II.

Adsorption of HCl *by resin* (*Batch A*).

$C \times 10^3$	3·72	20·01	64·5	112·8	411·4	914	1938
X_1, Eqn. 1 *	5·63	6·42	6·83	7·04	7·46	7·52	7·45
X_2, Eqn. 2 *	7·63	8·71	9·26	9·55	10·11	10·20	10·10
X_3, Eqn. 3 *	7·63	8·70	9·24	9·50	9·95	9·87	9·41
Γ^1_{HC}, Eqn. 6 *	7·63	8·70	9·25	9·52	10·03	9·99	9·71

* See p. 2619.

The above results do not give full information about the state of the system, as will be shown later, and further series of measurements were carried out with hydrochloric acid and added chlorides, in which all analyses referred to known weights of solution, and in which the chloride was determined gravimetrically in addition to loss of acidity. Preliminary measurements showed that the resin was chloride-free, and that in the absence of added chlorides the determination of free acid and of chloride gave identical results (cf. Table IV, line 1). The determination of chloride followed the details given by Keenan, McLeod, and Gordon (*J. Chem. Physics*, 1945, **13**, 466). All analyses were in duplicate (at least), and agred to 1 part in 3000 parts. Resin from a different batch, though conditioned in the same way, had to be used for these series. Periodical moisture checks were made as before. The results are in Tables III and IV, which give the mean of concordant duplicates, all concentrations being in g.-equivs./kg. of solution. The added salt was sodium chloride in every case except the one marked with an asterisk in Table IV.

TABLE III.

Original HCl *concn. approx.* 0·134N. *Batch B resin. Dry weight of resin samples,* 1·012 *g.*

Nos.	Wt. of soltn. (g.).	Moisture in resin (g.).	Original concns.: acid.	chloride.	Equilibrium concns.: acid.	chloride.
1, 2	99·85	0·217	0·12940	—	0·04440	—
3, 4	100·05	0·216	0·12905	0·17934	0·04255	0·09360
5, 6	100·72	0·218	0·12818	0·32660	0·04037	0·24165
7, 8	103·90	0·230	0·12553	1·0858	0·03714	1·0064
9, 10	107·74	0·230	0·12219	1·9730	0·03439	1·8985
11, 12	114·88	0·223	0·11563	3·5658	0·03023	3·4985

TABLE IV.

Original HCl *concn. approx.* 0·20N. *Batch B resin. Dry weight of resin samples,* 1·012 *g.*

Nos.	Wt. of soltn. (g.).	Moisture in resin (g.).	Original concns.: acid.	chloride.	Equilibrium concns.: acid.	chloride.
13, 14	100·04	0·215	0·2061	0·2061	0·1175	0·1175
15, 16	100·85	0·215	0·2036	0·4010	0·1135	0·3136
17, 18	107·75	0·215	0·1909	2·0232	0·1009	1·9464
19, 20	114·88	0·215	0·1784	3·6140	0·09116	3·5450
21, 22 *	111·87	0·214	0·1837	1·3708	0·09846	1·2968

* Added salt $BaCl_2$. These solutions were also analysed for barium (as $BaSO_4$) before and after contact with the resin. Original and equilibrium concentrations of barium were 1·1822 and 1·1952, respectively.

TABLE V.

No.	Wt. of soltn. (g.).	Moisture in resin (g.).	Acid concns.: original.	equilibrium.	NaCl concn.
23	100·73	0·231	0·6144	0·5243	0
24	101·14	0·231	0·6131	0·5224	0·0989
25	102·69	0·231	0·6023	0·5118	0·487
26	104·68	0·231	0·5971	0·5059	0·955
27	108·42	0·231	0·5748	0·4844	0·1847
28	101·43	0·230	1·0101	0·9211	0
29	102·23	0·230	0·9968	0·9070	0·1957
30	105·10	0·230	0·9319	0·8421	0·9515
31	103·01	0·219	1·8778	1·7938	0
32	103·73	0·220	1·8607	1·7761	1·1925
33	106·73	0·219	1·8091	1·7252	0·9372

Some further measurements with the same batch of resin were made at higher concentrations of acid, and the results are in Table V. These solutions were not analysed for chloride.

Discussion.

Our preliminary results need not be discussed in detail, since they agree in most respects with much that has been published since this work began (Kunin and Myers, *J. Phys. Colloid Chem.*, 1947, **51**, 1111; *J. Amer. Chem. Soc.*, 1947, **69**, 2874; "Ion Exchange," Ed. F. C. Nachod, Academic Press, N.Y., 1949, pp. 23, 62). Thus, it is widely agreed that the adsorption of acid by a weak base resin (or, in general, the ionisation of a resin containing weak acid or basic groups) is a much slower process than that of ion exchange. Reduction of particle size greatly accelerates the process without affecting the capacity of the resin. The reduction in capacity that we observed on heating the air-dried resin deserves emphasis, since it means that moisture determinations involving heating must be carried out on separate samples of resin not used for other purposes. Our results indicated that the heating affected in some way the linking of some of the basic groups, since no material (other than water and carbon dioxide) appeared to be lost, either during the heating or on subsequent extraction with water.

The high carbonate content of a basic resin that has been regenerated with sodium carbonate has not been reported before. It is usually assumed that the carbonate radical is lost by hydrolysis during washing (Duncan and Lister, *Quart. Reviews*, 1948, II, 327). Apart from the fact that the carbonate must be allowed for in any accurate study of acid adsorption, it has a very important bearing on both moisture determination and the question of "salt splitting" by a basic resin. To remove all water from a resin by evacuation over phosphoric oxide requires several months; whereas heating the resin leads to a slow loss of carbon dioxide which is not completed in a reasonable time at temperatures under about 130°. Heating to constant weight at 110°, which Duncan and Lister (*loc. cit.*) quote as the customary procedure, would have required several weeks with our resin samples.

Salt Splitting.—The possibility of anion exchange between a free base resin and a neutral salt has been discussed by several writers (cf. earlier refs.). Kunin and Myers, who regenerated their Amberlite IR-4 with sodium hydroxide, found a very slight degree of exchange, some of the added ion being taken up by the resin, and the pH of the solution becoming greater than 7. This result is usually taken as evidence that the resin contains free hydroxyl groups which are available for exchange, but the nature of the material, and the results themselves, suggest that the degree of ionisation of the resin is only very small.

With a carbonate-treated resin, anion exchange can be very considerable, as is shown by the results in Table I. A quantitative treatment of these data is rendered difficult by the simultaneous presence of bicarbonate and carbonate radicals, as well as chloride; but they strongly suggest an exchange between chloride and bivalent carbonate ions, preferential adsorption being shown by the resin, as would be expected, for the bivalent radical. For instance, when 0·20N-sodium chloride was equilibriated with 1 g. of the resin, the ultimate distribution of the chloride radical was 0·63 milliequiv. in the resin phase and 19·37 milliequivs. in the solution, whereas the corresponding figures for the carbonate radical were 1·57 in the resin and 0·63 in the solution. Even in 1N-sodium chloride only one-half of the carbonate is exchanged, and not the 90% or more that would be expected for a normal uni-univalent exchange. This is strong evidence that the carbonate is present on the resin as bivalent ions, and a theoretical argument pointing in the same direction is that at the surface of the positively charged resin the electrical field will greatly favour the right-hand side of the equilibrium $HCO'_3 \rightleftharpoons H^{\cdot} + CO_3''$, as compared with conditions in the solution.

From our results with different batches of resin it would appear that Amberlite IR-4B, after regeneration with sodium carbonate and prolonged washing, will always contain 2·2—2·4 milliequivs. of carbonate per g., and for this reason will show extensive exchange with neutral salts. Even a resin regenerated with sodium hydroxide would tend to acquire an appreciable carbonate content through preferential adsorption, unless rigorous precautions against carbon dioxide were taken during regeneration, washing, and air-drying. Kunin and Myers (*loc. cit.*) determined the amount of anion exchange by titrating the alkali released from the resin with phenolphthalein as indicator. As this would not detect bicarbonate resulting from anion exchange followed by hydrolysis, it is possible that appreciably more anions were taken up by their resin than their results would indicate.

Adsorption of Acid.—Previous authors who have reported on the adsorption of acids by basic resins (Bhatnagar *et al.*, *J. Indian Chem. Soc.*, 1939, **16**, 249, 261; 1940, **17**, 361; Akeroyd and Broughton, *J. Physical Chem.*, 1938, **42**, 343; Schwartz, Edwards, and Boudreaux, *Ind. Eng. Chem.*, 1940, **32**, 1462; Kunin and Myers, *loc. cit.*; Bishop, *J. Phys. Colloid Chem.*, 1946, **50** 6; 1950, **54**, 697) appear to have all used volumetric procedures. For instance, v ml. of

nM-hydrochloric acid are put in contact with a known weight of air-dried resin composed of r g. of dry resin and w g. of water. If at equilibrium the solution is found to be m molar, the hydrochloric acid adsorbed per g. of (air-dried) resin may be given as

$$X_1 = (n - m)v/(r + w) \text{ milliequivs.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It is not always clear in the literature whether the water content of the resin has been allowed for. If the moisture content is known, the adsorption of acid may be reported as

$$X_2 = (n - m)v/r \text{ milliequivs.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (2), however, does not allow for the diluting effect of the water introduced with the resin. If this is assumed to form part of the solution at equilibrium, then $(v + w)$ ml. of this solution contain $(v + w)m$ milliequivs. of hydrochloric acid and the amount adsorbed per g. of dry resin is given by

$$X_3 = [nv - (v + w)m]/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Equations (2) and (3) involve tacit assumptions as to the distribution of the water in the system, and differ for this reason. Moreover, neither makes allowance for the changing density of the solution. A correct expression for the adsorption of acid (and of water, to be discussed later) is derived as follows. $(r + w)$ G. of moist resin are treated with vd g. of nM-hydrochloric acid, of density d. This solution contains $nvM/1000$ g. of hydrogen chloride (M = molecular weight) and $v(d-nM/1000)$ g. of water. The equilibrium solution is found to be m-molar, and its density is d'. If its volume is v', it contains $mv'M/1000$ g. of hydrogen chloride and $v'(d'-mM/1000)$ g. of water. Writing the composition of the resin phase as (r g. of resin + $r\Gamma^{g.}_{H_2O}$ g. of water + $r\Gamma^{g.}_{HCl}$ g. of hydrogen chloride) we therefore have :

$$\Gamma^{g.}_{H_2O} = \frac{v(d - nM/1000) + w - v'(d' - mM/1000)}{r}$$

and

$$\Gamma^{g.}_{HCl} = (nv - mv')M/1000r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If the adsorption of hydrogen chloride is expressed in milliequivs. per g. of dry resin

$$\Gamma_{HCl} = (nv - mv')/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The volume v' in these expressions is not accessible to direct measurement, and any evaluation of Γ_{H_2O} and Γ_{HCl} must depend on some assumption regarding the position of the boundary between the two phases. If we assume, as in equation (3), that the adsorption of water is zero, then on this arbitrary convention we have :

$$v'(d' - mM/1000) = v(d - nM/1000) + w$$

and substituting for v' in the expression for the adsorption of hydrogen chloride

$$\Gamma^{1}_{HCl} = \frac{1}{r}\left[nv - \frac{m\{v(d - nM/1000) + w\}}{(d' - mM/1000)}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This differs from equation (3) in containing, as correction factors, the weights of water in 1 ml. of the initial and final solutions, respectively.

The four equations (1), (2), (3), and (6) are applied to one series of measurements in Table II. At any concentration of acid over 0·1N., they lead to appreciably different results, and these differences would be particularly important in any attempt to study the dissociation equilibrium of the resin quantitatively. For such a purpose it would be necessary to know the small number of basic groups, per g. of resin, still un-ionised at high concentrations of acid; but with no criterion to guide us as to the correct equation to use, any calculated figure would be totally unreliable. It will be noticed also that all four equations used in Table II show a feature that is almost certainly artificial, a maximum in the acid adsorption curve. This, and much independent evidence on the swelling of resins, leads us to conclude that equilibrium studies of acid adsorption are quite unreliable unless accompanied by simultaneous measurements of the adsorption of water by the resin. Similar criticisms and conclusions apply to dissociation studies of weak acid resins at high pH values and high salt concentrations.

Before leaving equations (5) and (6), we derive the relation between Γ_{HCl} and $\Gamma^{1}_{\mathrm{HCl}}$, as this will be useful later. We have

$$\begin{aligned}\Gamma_{\mathrm{HCl}} - \Gamma^{1}_{\mathrm{HCl}} &= \frac{1}{r}\left[\frac{mv(d - nM/1000) + mw}{(d' - mM/1000)} - mv'\right] \\ &= \frac{m}{r}\left[\frac{v(d - nM/1000) + w - v'(d' - mM/1000)}{(d' - mM/10000)}\right] \\ &= m\Gamma^{\mathrm{g.}}_{\mathrm{H_2O}}/(d' - mM/1000) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)\end{aligned}$$

That is, the correction to be added to $\Gamma^{1}_{\mathrm{HCl}}$ to obtain the true adsorption of HCl is :

$$\Gamma^{\mathrm{g.}}_{\mathrm{H_2O}} \frac{\text{milliequivs. of HCl in 1 g. of equilibrium solution}}{\text{g. of } H_2O \text{ in 1 g. of equilibrium solution}}$$

Water-adsorption Measurements.—To determine both water and acid adsorption at least two analyses are necessary, and in addition some assumption must be made as to the distribution in the system of a third reference substance. The experiments reported in Tables III and IV were designed to this end. Weighed samples of resin were equilibrated with hydrochloric acid solutions containing added chlorides. All analyses were based on weights, and the solutions before and after contact were analysed for both acid and total chloride. It was assumed, in the first place, that the added salt was not adsorbed by the resin. This enabled the system to be arbitrarily divided into two phases :

(*A*.)	(*B*.)
Solution, containing H_2O, HCl, and XCl.	Resin + adsorbed H_2O + adsorbed HCl.

This provides self-consistent values for the adsorbed water and acid, but does not preclude the subsequent adjustment of the model to include part of phase *A* (*i.e.*, the three constituents in their known proportions) in the resin phase if independent evidence for the presence of salt in the resin can be adduced. The adsorptions were calculated as follows : Let the initial system consist of r g. of dry resin + w g. of water ; s g. of XCl, h g. of HCl, and W g. of H_2O. After contact, the weight, a g. of the solution containing s g. of XCl is calculated ; the weight, b g. of HCl in a g. of solution is then found, hence the composition of the solution is s g. of XCl, b g. of HCl, and $(a - s - b)$ g. of H_2O ; and therefore :

$$\Gamma^{\mathrm{g.}}_{\mathrm{H_2O}} = [W + w - (a - s - b)]/r \text{ g. per g. of dry resin}$$

and

$$\Gamma_{\mathrm{HCl}} = \frac{.1000}{36{\cdot}47}\,\frac{(h - b)}{r} \text{ milliequivs. per g. of dry resin} \quad . \; . \; . \; . \quad (8)$$

The data are tabulated in this way in Tables VI and VII.

TABLE VI.

Equilibrium acid concn. approx. 0·04N. r = 1·012 grams.

Nos.	s.	h.	$W + w$.	a.	b.	$a - s - b$.	Γ_{HCl}.	$\Gamma^{\mathrm{g.}}_{\mathrm{H_2O}}$.
3, 4	0·29411	0·47083	99·50	98·56	0·15294	98·11	8·615	1·37
5, 6	1·1682	0·47078	99·30	99·29	0·14617	97·98	8·796	1·31
7, 8	5·8327	0·47561	97·82	102·95	0·13942	96·98	9·111	0·83
9, 10	11·656	0·48006	95·83	106·97	0·13415	95·18	9·374	0·64
11, 12	23·168	0·48438	91·45	114·28	0·12598	90·99	9·713	0·45

In Curve 1 of Fig. 1 the water adsorptions at both acid concentrations are plotted against the total chloride concentration of the solution (given in Tables III and IV). Except for the determination in barium chloride the points for both series lie very close to a common curve.

TABLE VII.

Equilibrium acid concn. approx. 0·1N. r = 1·012 grams.

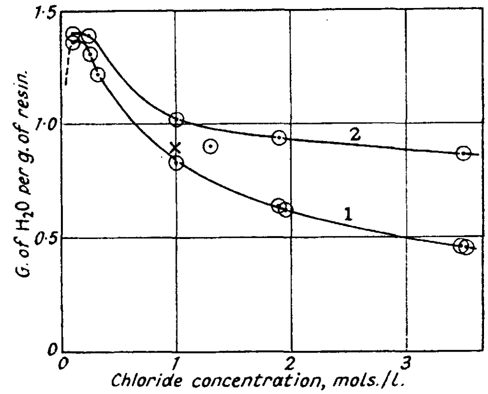
Nos.	s.	h.	$W + w$.	a.	b.	$a - s - b$.	Γ_{HCl}.	$\Gamma^{\mathrm{g.}}_{\mathrm{H_2O}}$.
15, 16	1·1637	0·74876	99·15	99·49	0·41177	97·91	9·133	1·22
17, 18	11·541	0·75008	95·67	106·98	0·39361	95·05	9·661	0·62
19, 20	23·070	0·74733	91·28	114·27	0·37985	90·82	9·959	0·45
21, 22 *	13·830	0·74938	97·51	110·82	0·39789	96·59	9·526	0·90

* Added salt : barium chloride.

At first sight this appears surprising, since the acid adsorption, and therefore the ionisation of the resin, is appreciably greater in the second series, and it might be thought that this would lead to greater swelling and higher Γ_{H_2O} values. The whole picture, however, closely resembles the Donnan effects for weak electrolyte colloids, such as gelatin (Loeb, *J. Gen. Physiol.*, 1918, **1**, 363). At very low acid concentrations the ionisation of the resin, and therefore the swelling pressure, will be increasing very rapidly with increasing concentration; but, as Table II shows, the resin is already highly ionised in 0·02N-acid, and thereafter the increasing ionic concentrations in the outer solution become the dominant factor, and the counter-osmotic pressure leads to a maximum followed by the curve of Fig. 1. Some evidence for this view is provided by the point for the barium chloride solution. If we correct for the bivalent cation (assuming ideal-solution laws) by plotting number of ions in outer solution instead of chloride concentration, we obtain the point marked by a cross, which agrees as closely as would be expected with the curve for sodium chloride additions.

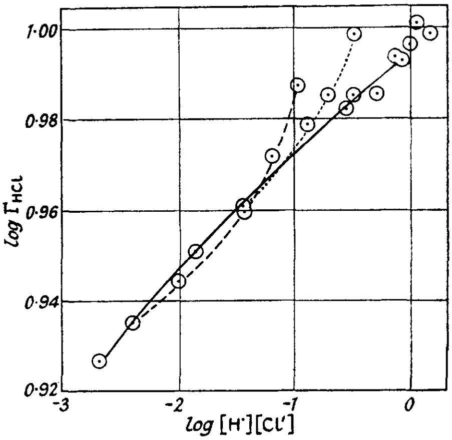
If this explanation of the curve in Fig. 1 is qualitatively correct, then at all acid concentrations above 0·04N. the water adsorption will be determined almost entirely by the total concentration of the ambient solution, and will be insensitive to the actual acid concentration. For evaluating the small correction term given in equation (7) we have therefore read Γ_{H_2O} values from Fig. 1, Curve 1. Application of this procedure to the salt-free points of Tables III and IV and to the experiments of Table V provides the further Γ_{HCl} figures reported in Col. 5 of Table VIII.

FIG. 1.



Curve 1 : Γ_{H_2O} ; *Curve* 2 : *total* H_2O *per g. of resin.*

FIG. 2.



Plot of Bishop's equation. Data from Table VI — — —; *from Table VII* . . . .

TABLE VIII.

	Equilibrium concns. :					Equilibrium concns. :			
No.	acid.	chloride.	$\Gamma^{g.}_{H_2O}$.	Γ_{HCl}.	No.	acid.	chloride.	$\Gamma^{g.}_{H_2O}$.	Γ_{HCl}.
1, 2	0·04442	0·04444	1·40	8·45	28	0·9211	0·9211	0·86	9·83
13, 14	0·1175	0·1175	1·37	8·93	29	0·9070	1·103	0·80	9·91
23	0·5243	0·5243	1·08	9·60	30	0·8421	1·794	0·64	9·97
24	0·5224	0·621	1·02	9·66					
25	0·5118	0·999	0·83	9·67	31	1·794	1·794	0·64	9·94
26	0·5059	1·461	0·70	9·85	32	1·776	1·969	0·62	10·03
27	0·4844	2·331	0·57	10·02	33	1·725	2·662	0·53	10·00

The adsorption figures so far presented are based on the convention that the adsorption of salt is zero. There is no reason to suppose that salt is entirely excluded from the resin phase, and there is some evidence to the contrary (cf. Bauman and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2831).

The Donnan theory may again be invoked here to provide a rather more accurate picture of actual conditions in the resin. For instance, in Expts. 3 and 4 of Table VI, the system has so far been arbitrarily divided into homogeneous solution consisting of 98·11 g. of water, 0·2941 g. of NaCl (0·05105 weight normal) and 0·1529 g. of HCl (0·04255 weight normal); and a resin phase containing the surface excess of acid and water, the proportions being: 1 g. of resin, 1·37 g. of water, and 8·615 milliequivs. of acid. The arbitrary boundary between the phases may now be moved, as it were, further from the resin surface, so that part of the solution constituents are included in the resin phase; and the true position is fixed by the Donnan equation of products:

$$[a_{\mathrm{Na}^{\cdot}}a_{\mathrm{Cl}'}]_{\mathrm{Resin}} = [a_{\mathrm{Na}^{\cdot}}a_{\mathrm{Cl}'}]_{\mathrm{Solution}}$$

Here we encounter the well-known difficulties that the ion activities in the resin phase are not known, and that the resin hydrochloride may not be completely dissociated. However, an approximate solution is enlightening, and if we replace activities by weight-concentrations, and assume complete dissociation, we have:

$$\frac{0{\cdot}051x(8{\cdot}615 + 0{\cdot}0936x)}{(x + 1{\cdot}37 + 0{\cdot}3142)^2} = 0{\cdot}05105 \times 0{\cdot}0936$$

where x is the number of g. of solution included per g. of dry resin. The equation gives $x = 0{\cdot}0327$ g., and although the percentage error in this figure may be high, its order of magnitude will be correct. It leads to the following composition of the resin phase: 1 g. of resin (8·617 milliequivs. protonated), 1·40 g. of $\mathrm{H_2O}$, 8·617 milliequivs. of Cl', 0·0014 milliequiv. of $\mathrm{H}^{\cdot}$, and 0·00167 milliequiv. of $\mathrm{Na}^{\cdot}$. The weight-normal concentrations in the resin phase are: $\mathrm{Cl}' = 5{\cdot}01$, $\mathrm{H}^{\cdot} = 8{\cdot}07 \times 10^{-4}$, and the approximate potential difference between resin and outer solution is: $58 \log [0{\cdot}04255/(8{\cdot}07 \times 10^{-4})] = 100$ millivolts, which agrees with another estimate made by an entirely different method (Davies, *Biochem. J.*, 1949, **45**, 38). The other points have been treated in the same way, and Curve 2 of Fig. 1 gives the total water content of the resin per g., obtained by adding the water just introduced as part of the solution to the corresponding $\Gamma_{\mathrm{H_2O}}$ value. These calculated values may carry a very considerable error at high concentrations, as has already been pointed out, and the most important result of the calculations is, perhaps, to show that at acid concentrations around 0·1N. or less, the $\Gamma_{\mathrm{H_2O}}$ values must give the correct water content of the swollen resin to within a few units %; *i.e.*, 100 g. of the ionised resin comprising approximately six or seven carbon atoms and a nitrogen atom, are accompanied by 140 g., or about eight molecules, of water. The extended resin, therefore, seems to accommodate approximately a monolayer of water containing the chloride gegen-ion, a very different picture from the diffuse double layer supposed to exist at a plane charged surface. Even if the hydrochloride is assumed to be largely undissociated the value of x does not increase very greatly and the picture remains sensibly unchanged.

The Ionisation Equilibrium.—If our object were to estimate the total acid present in the resin, treating this as a homogeneous phase, then the values for hydrogen chloride in Tables VI, VII, and VIII, like those for the water adsorption, would be subject to a small correction for the free hydrogen and chloride ions necessary to satisfy the Donnan equation of products. The uncorrected figures are of more interest, however, as these clearly measure the amount of hydrogen ion bound by the resin, that is, the extent of ionisation.

Bishop (*loc. cit.*) has studied the adsorption of a number of acids by basic resins, and has reported an approximately linear relationship between the logarithms of the amount of acid adsorbed and of the concentration product of hydrogen ion and anion in the equilibrium solution. This is not obeyed by our data, as will be seen from Fig. 2, where the values of Tables VI—VIII are plotted in this way. The points lie reasonably close to a common line so long as the concentration of neutral chloride is not high, but there are regular deviations at the higher concentrations.

Bauman ("Ion Exchange," ed. F. C. Nachod, Academic Press, N.Y., 1949, p. 68) has outlined an approximate treatment of the ionisation equilibrium of a weak basic resin which can be applied to our results as follows. For the process $\mathrm{R{\cdot}NH_3{\cdot}OH} + \mathrm{H}^{\cdot} + \mathrm{Cl}' \rightleftharpoons \mathrm{R{\cdot}NH_3}^{\cdot} + \mathrm{Cl_R}' + \mathrm{H_2O}$ the (concentration) equilibrium constant is written:

$$K = [\mathrm{R{\cdot}NH_3}^{\cdot}][\mathrm{Cl}']_{\mathrm{R}}/[\mathrm{R{\cdot}NH_3{\cdot}OH}][\mathrm{H}^{\cdot}]_{\mathrm{S}}[\mathrm{Cl}']_{\mathrm{S}}$$

where the suffixes R and S refer to resin phase and solution phase, respectively. If we eliminate $[\mathrm{Cl}']_{\mathrm{R}}$ from this equation by means of the Donnan relation $[\mathrm{Cl}']_{\mathrm{R}}/[\mathrm{OH}']_{\mathrm{R}} = [\mathrm{Cl}']_{\mathrm{S}}/[\mathrm{OH}']_{\mathrm{S}}$, and multiply by $K_w = [\mathrm{H}^{\cdot}][\mathrm{OH}']$, we obtain

$$KK_w = [\mathrm{R{\cdot}NH_3}^{\cdot}][\mathrm{OH}']_{\mathrm{R}}/[\mathrm{R{\cdot}NH_3{\cdot}OH}] = K_{\mathrm{B}}$$

where K_{B} is the basic dissociation constant of the resin. K can be evaluated from the experimental data if we put $[\mathrm{Cl}']_{\mathrm{R}} = \Gamma_{\mathrm{HCl}}$, and

$$[\mathrm{R{\cdot}NH_3}^{\cdot}]/[\mathrm{R{\cdot}NH_3{\cdot}OH}] = \Gamma_{\mathrm{HCl}}/(C - \Gamma_{\mathrm{HCl}})$$

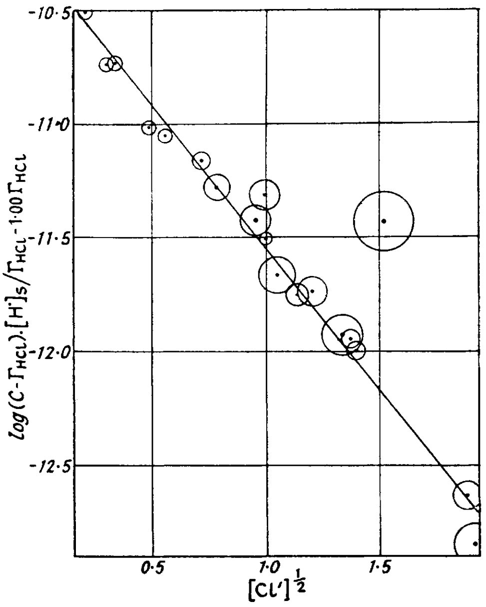
where C is the total combining capacity, in milliequivs. per g. of the resin. Values of K_R derived in this way for the salt-free solutions are given in Table IX. The value of C is fixed within fairly close limits, on the one hand by the adsorption of slightly over 10 milliequivs. per g. at the highest concentrations, and on the other by the nitrogen content of the resin, which corresponded for Batch B with a theoretical capacity of approximately 10·3 milliequivs. We used the value $C = 10{\cdot}10$, but the conclusions reached would not be invalidated by any reasonable change in the value taken.

TABLE IX.

Nos.	$[H^{\cdot}] = [Cl']$.	Γ_{HCl}.	log K_R.	Nos.	$[H^{\cdot}] = [Cl']$.	Γ_{HCl}.	log K_R.
1, 2	0·04440	8·45	$\overline{10}{\cdot}342$	28	0·9211	9·83	$\overline{12}{\cdot}625$
13, 14	0·1175	8·93	$\overline{11}{\cdot}673$	31	1·794	9·94	$\overline{12}{\cdot}283$
23	0·5243	9·60	$\overline{12}{\cdot}827$				

This treatment involves several approximations. Concentrations, and not activities, have been used throughout; it is assumed that all the basic groups of the resin are equivalent in position and inherent strength; the resin hydrochloride is assumed to be completely dissociated, and changes in swelling and swelling pressure are ignored (the concentration unit of K_R is moles/kg. of dry resin). Clearly, one or more of these assumptions must be completely at variance with the facts. Not only does K_R vary by more than 100-fold for a comparatively narrow range of Γ_{HCl} values, but the magnitude of K is many powers of ten smaller than would be expected for the basic constant of aliphatic amino-groups.

FIG. 3.



An approach to the problem involving fewer explicit assumptions can be made in the way proposed by Hartley and Roe (*Trans. Faraday Soc.*, 1940, **36**, 101) for a somewhat similar problem.

If all the ionising groups in the resin are equivalent, the primary ionisation process should conform to the equilibrium condition

$$K = [R{\cdot}NH_2][H^{\cdot}]^*/[R{\cdot}NH_3^{\cdot}] = (C - \Gamma_{HCl})[H^{\cdot}]^*/\Gamma_{HCl}$$

where the term $[H^{\cdot}]^*$ is the concentration of hydrogen ion at the resin surface, and represents the probability of a hydrogen ion arriving at the critical distance from a $R{\cdot}NH_2$ site for ionisation to occur. $[H^{\cdot}]^*$ will be related to the concentration of hydrogen ion in the equilibrium solution by the equation

$$[H^{\cdot}]^* = [H^{\cdot}]_S e^{-W/RT}$$

where W is the work done in transporting a hydrogen ion from the solution to the resin surface, partly against electrical forces and partly against the forces opposing swelling. In our experiments the concentrations of acid and added salt were both varied, and as the two independent variables in analysing the data we take Γ_{HCl} and [Cl′]. The former is primarily responsible for the density of the positive charge carried by the resin, and for the degree of swelling; the latter, the total ionic concentration, influences both the potential difference between the resin and the solution phase, and the counter-osmotic pressure. By interpolating from our data, the effects of the two terms were considered separately, and in this way we were led to the equation

$$\log K = \overline{11}\cdot71 = \log (C - \Gamma_{\text{HCl}})[\text{H}^{\cdot}]_{\text{S}}/\Gamma_{\text{HCl}} - 1\cdot00\Gamma_{\text{HCl}} + 1\cdot24[\text{Cl}']^{\frac{1}{2}} \quad . \quad . \quad (9)$$

That the data should depend on the square-root of the total concentration was unexpected, and this dependence is probably not exact, but it will be seen from Fig. 3 that the equation expresses the results within the experimental uncertainty.

The size of the circles drawn round the points indicates the effect of a 0·2% error in the adsorption measurements. The three measurements numbered 31—33 are omitted from Figs. 2 and 3 as this series shows irregularity; we think that the resin structure is not stable at such high acid concentrations and that swelling in these cases was greater than was assumed in the calculations. No quantitative significance is attached to equation (9), as the constants (representing the opposing effects of resin charge and ionic concentration) could be simultaneously modified by 5% or more without affecting the extent of agreement with the data. The wide variations in acid and salt concentrations covered by an equation of this form suggest, however, that the approach is probably along correct lines. Moreover, the mean value of log K, *viz.*, $\overline{11}\cdot71$, corresponds to a basic dissociation constant, under ideal conditions of zero ionic strength and zero charge, of

$$K_{\text{B}} = [\text{R}\cdot\text{NH}_3^{\cdot}][\text{OH}']/[\text{R}\cdot\text{NH}_2] = K_w/K = 2\cdot0 \times 10^{-4}$$

which agrees well with the value to be expected of a monomeric aliphatic amine.

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