688. *Ion-exchange Studies. Part I. The Sodium–Hydrogen System.*

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The mass-action constants governing the exchange of sodium ions and hydrogen ions between solution and two ion-exchange materials have been determined (*a*) by a batch equilibrium process, (*b*) by the saturation of a column of exchanger with solutions of different sodium : hydrogen ion ratio, and (*c*) by calculation from the elution rear boundary obtained when sodium ions are removed from the column with acid. It has been shown that the mass product is approximately constant over the greater part of the exchange isotherm, but rises significantly for low values of the molar fraction of sodium ions.

INVESTIGATIONS have been made from time to time of the exchange properties of materials such as greensand, clay, and bentonite (naturally occurring) and sulphonated lignite and tannins (synthetic). Although many attempts have been made to fit the experimental results to a mass-action law, very few of the exchangers were found to obey such a law.

With the advent of synthetic ion-exchange materials based upon a phenol–formaldehyde condensation (*e.g.*, the Amberlites) and upon polymerisation of divinylbenzene (*e.g.*, Dowex 50), materials are now available which obey a mass-action law to a first approximation at least. The work of Bauman and Eichhorn (*J. Amer. Chem. Soc.*, 1947, **69**, 2830) and Boyd, Schubert, and Adamson (*ibid.*, p. 2818) has shown that both Dowex 50 and Amberlite I.R.-1 obey a mass-action law. The present paper assesses the extent to which a mass-action law may be applied, and provides a test of the validity of the assumptions made by these workers. The conclusions reached are valid only for exchange between two closely similar univalent ions.

The exchange reaction between a resinous exchanger in the hydrogen form and sodium ions in solution may be written :

$$\mathrm{Na^+_S} + \mathrm{H_R} = \mathrm{Na_R} + \mathrm{H^+_S} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where the subscripts S and R refer to the ions in solution and in the resinous exchanger respectively. The mass-action constant K_a is defined as :

$$K_a = a_{\mathrm{Na_R}}a_{\mathrm{H_S}}/a_{\mathrm{Na_S}}a_{\mathrm{H_R}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where the a values represent the thermodynamic activities of the respective ions. The activities of the ions in solution are, in general, known, but the difficulty in the application of the mass-action law to ion exchange is always that the activities of the ions in the resin phase cannot be directly evaluated.

Boyd, Schubert, and Adamson (*loc. cit.*) have assumed that the activities of the ions in the resin phase are proportional to the molar fractions of the ions ($X_{\mathrm{Na_R}}$, $X_{\mathrm{H_R}}$) and have obtained results to show that the mass-action law is obeyed over a range of $0{\cdot}3 < X_{\mathrm{Na_S}} < 0{\cdot}9$. In their treatment the mass-action law is written :

$$K = X_{\mathrm{Na_R}} a_{\mathrm{H_S}} / X_{\mathrm{H_R}} a_{\mathrm{Na_S}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

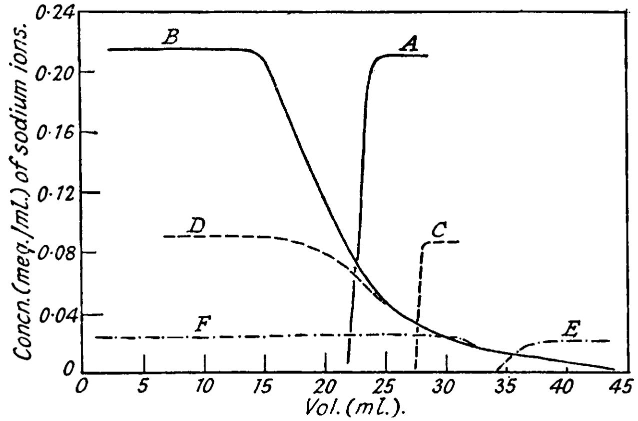
On the other hand, Bauman and Eichhorn (*loc. cit.*) have written the mass-action law :

$$K = \frac{c_{\mathrm{Na_R}}\, c_{\mathrm{H_S}}\, f_{\mathrm{H_S}}}{c_{\mathrm{H_R}}\, c_{\mathrm{Na_S}}\, f_{\mathrm{Na_S}}} = \frac{c_{\mathrm{Na_R}}\, a_{\mathrm{H_S}}}{c_{\mathrm{H_R}}\, a_{\mathrm{Na_S}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where the c terms are molar concentrations, and the f terms activity coefficients. In general, equations (3) and (4) are equivalent, but care must be taken in the case of exchange between ions of different valency to ensure that similar units are used in the two equations. It should also be noted that for heterovalent exchange the value of the mass-action constant depends on the units in which $c_{\mathrm{Na_R}}$ and $c_{\mathrm{H_R}}$ are expressed. For exchange between ions of the same valency K_a is independent of the units.

FIG. 1.

Front and rear boundaries for different mixtures of sodium and hydrogen ions in solution, using Dowex 50.



Curves A and B, $X_{\mathrm{Na_S}} = 1{\cdot}00$; *C and D,* $X_{\mathrm{Na_S}} = 0{\cdot}42$; *E and F,* $X_{\mathrm{Na_S}} = 0{\cdot}087$.

In the present paper the mass-action constant K_a has been calculated from the molar fraction of the sodium ions in the resin phase and in solution by the equation :

$$\frac{X_{\mathrm{Na_R}}}{1 - X_{\mathrm{Na_R}}} = \frac{K_a X_{\mathrm{Na_S}} f_{\mathrm{Na_S}}}{(1 - X_{\mathrm{Na_S}}) f_{\mathrm{H_S}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Allowance has been made for the activity coefficients, $f_{\mathrm{Na_S}}$, $f_{\mathrm{H_S}}$, of the ions in solution by investigating the exchange of sodium and hydrogen ions, with chloride as the only anion, in which solutions the activity data are accurately known over a considerable range of concentration.

Three different methods of obtaining the mass action constant (K_a) have been used.

(1) *From batch equilibrium methods.* A given weight of exchanger was allowed to come to equilibrium with solutions containing sodium chloride and hydrochloric acid in different proportions, and the amount of sodium taken up from solution was determined.

(2) *From the volume of solution necessary to saturate a chromatographic column.* If the column of exchanger is converted into the hydrogen form by saturation with hydrochloric acid and a solution of sodium chloride is then passed through, the volume of eluate which passes before sodium ions appear at the bottom is a direct measure of the amount of sodium taken up by the column. If pure sodium chloride solution is passed through the column, this volume (the so-called " breakthrough volume ") measures the total exchange capacity of the resin. If mixtures of sodium chloride and hydrochloric acid are used, the amount of sodium taken up by the exchanger in equilibrium with a given mixture of sodium and hydrogen ions is obtained, from which the mass-action constant K_a can be determined.

(3) *By calculation from the rear boundary of a chromatogram.* If a solution of sodium chloride is passed through the hydrogen-saturated exchanger, the concentration history of sodium in the eluate is given by a curve such as *A* in Fig. 1. It will be noticed that the concentration changes

sharply as soon as sodium ions appear in the eluate. When hydrochloric acid is passed through the sodium-saturated exchanger the shape of the elution curve is as shown in the curve *B*, Fig. 1. This rear boundary for the removal of sodium ions from the column is not sharp, the concentration in the eluate falling only gradually to zero. The shapes of these curves show that the sodium ions are held on the column more strongly than the hydrogen ions, and that the mass-action constant of the exchange reaction (1) must be greater than unity.

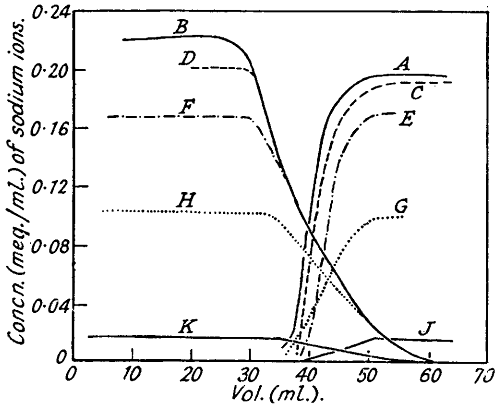
The chromatographic studies of de Vault (*J. Amer. Chem. Soc.*, 1943, **65**, 532) and Glueckauf (*Proc. Roy. Soc.*, 1946, *A*, **186**, 35; *Nature*, 1945, **156**, 748; *J.*, 1947, 1302, 1315, 1321) have shown that the shape of the adsorption isotherm of a solute on an adsorbent may be derived by calculation from the rear boundary obtained when the solute is removed from the chromatographic column by development wtih a suitable solvent. If a diffuse rear boundary is not produced under these conditions, the calculations may be made on the diffuse front boundary. The method of calculation in the present paper is that given by Glueckauf (preceding paper) using the equation :

$$\bar{x}f^*(c) = \mu_c + (v - a\bar{x})c + \varepsilon(k/\bar{x})v^2(\partial c/\partial v)_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the symbols have the same meaning as given by Glueckauf. By application of this equation to the rear boundaries obtained in the present work, the amount of sodium ions adsorbed by the resin [$f^*(c)$] may be related to the concentration in solution. For small values of the elution volume, the value of $f^*(c)$ is a constant, this value being a measure of the total capacity of the column of exchanger and equal to the capacity measured by means of the breakthrough volume. As soon as hydrogen ions appear in the eluate $f^*(c)$ progressively decreases from this constant value to zero. Dividing the values of $f^*(c)$ obtained for different points on the rear boundary by the total capacity, we obtain $X_{\mathrm{Na_R}}$, the molar fraction of sodium ions in the exchanger. X_{NaS} is obtained by dividing the concentration in solution by the total equivalent concentration (equal to the equivalent concentration of hydrogen and sodium together), correction being applied if necessary to obtain the activities of the ions in solution. K_a is calculated by using equation (5) above.

FIG. 2.

Front and rear boundaries for different mixtures of sodium and hydrogen ions in solution, using Amberlite I.R.-100H.



Curves A and B, $X_{\mathrm{Na_S}} = 1{\cdot}00$, pH = 7; *C and D*, $X_{\mathrm{Na_S}} = 1{\cdot}00$, pH = 4; *E and F*, $X_{\mathrm{Na_S}} = 0{\cdot}802$; *G and H*, $X_{\mathrm{Na_S}} = 0{\cdot}483$; *J and K*, $X_{\mathrm{Na_S}} = 0{\cdot}088$.

EXPERIMENTAL.

Chromatographic Technique.—The apparatus used is shown in Fig. 3. A small column, 6 mm. in diameter and 8 cm. long, was filled with the exchanger (mesh size 180—250) by allowing the wet resin to settle in the column filled with water. In this way uniform packing was obtained. The concentration of sodium ions in solution was measured by using the 14·8-hour half-life ^{24}Na activity as a radiochemical tracer. The solution, seeded with tracer, and kept at a constant head in the reservoir *A*, was allowed to flow down the column and through (or past) a Geiger–Müller counter immediately at the bottom of the column. The hard radiation emitted by ^{24}Na (β-energy 1·4 Mev., γ-energy 1·4 and 2·8 Mev.) was easily detected in the counter even though the solution was contained in a tube 1 mm. in diameter made of glass 35 mg./cm.^{2} thick.

Two types of counter have been used. In the first (see Fig. 3*a*) the liquid flows past a thin mica window, in the second (see Fig. 3*b*) it flows through a spiral tube of 1 mm. diameter and total capacity of about 0·3 ml., in the internal sensitive space of the Geiger–Müller counter. This latter arrangement leads to much more efficient counting than in the first case and was preferred.

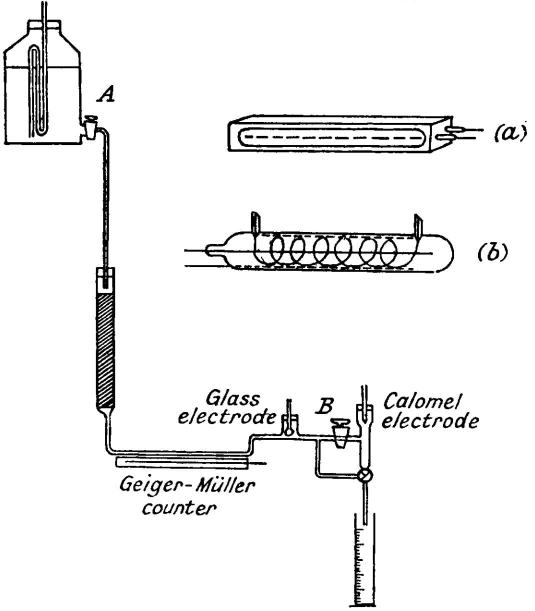
From the counter, the active solution flowed through the pH cell (*B*) and was collected in a graduated cylinder where the volume flow was measured. The counts obtained from the Geiger–Müller counter were recorded by feeding into a counting-rate meter (the time constant of which was 1 min.) and after amplification into a recording milliameter. In this way a complete record was obtained of the radioactivity (and hence the concentration) of the radio-sodium in solution. Occasional readings of the volume and the pH enabled a complete record of the experiment to be obtained.

In later experiments at an elevated temperature the column was surrounded by a jacket of trichloroethylene vapour. The formation of bubbles in the column is very likely under these conditions unless care is taken to ensure that solutions are prepared with distilled water previously boiled for at least 10 minutes. It is also desirable to keep the solution in a reservoir surrounded by a boiling water-bath, so that it does not readily dissolve air and quickly reaches temperature equilibrium when entering the column.

Maintenance of a constant and sufficiently slow flow rate is important. It is shown by Glueckauf (*loc. cit.*) that flow rates of the order of 10^{-2} cm./sec. are necessary (for particle sizes less than 0·01 cm.) before the shape of the elution curve can be relied upon to give accurate experimental data for the calculation of the adsorption isotherm. Several factors must be considered in this respect: the grain size, the rate of diffusion of the ions in solution, and the rate of diffusion of the ions into and out of the resin phase are all liable to distort the acid elution boundary. The magnitude of the errors due to non-equilibrium phenomena has been investigated by Glueckauf (*Chem. and Ind.*, 1949, 12), who has estimated that the mass-action constant K_a for Dowex 50, calculated from the present experimental data, may be of the order of 5% too high for the range $0{\cdot}2 < X_{\mathrm{Na_S}} < 0{\cdot}7$, and has given a method for correcting for this deviation (preceding paper).

FIG. 3.

Diagrammatic representation of the apparatus.



The particle size of the exchanger must be sufficiently small to allow complete equilibrium to be maintained, and it is desirable that it should be below 0·1 mm. In the present experiments material in the range 180—250 British Standard Mesh size (particle size between 0·01 and 0·05 mm. diameter) was used. The rate of diffusion of ions into the solid phase is also important in the maintenance of solid–liquid equilibrium, and the flow rate was in general reduced to less than 20 ml. per hour ($17{\cdot}5 \times 10^{-3}$ cm./sec.). It was shown that the elution curve obtained was independent of the flow rate in a range of $1{\cdot}75 \times 10^{-3}$—$10^{-2}$ cm. per second, and equilibrium was assumed to have been established under these conditions.

Batch Equilibrium Methods.—Solutions of sodium chloride (containing radioactive ^{24}Na) and hydrochloric acid in different proportions were added to a sample of the exchanger which had been weighed in the dry state. The solution and resin were stirred well for a period of 1 hour, the exchanger was allowed to settle, and an aliquot was withdrawn, evaporated to dryness on a small aluminium tray, and counted under a bell-type Geiger–Müller counter. The count obtained was compared with that obtained from a control sample.

Analysis of Chromatographic Data.—In all the experiments performed, corrections had to be applied to the counts obtained for (*a*) dead time of the counting assembly, (*b*) natural background count, and (*c*) decay caused by radioactive disintegration. These corrections having been applied, the activity–volume curve was constructed. The constant activity obtained when the column had been saturated with sodium ions (*i.e.*, after the initial breakthrough at the sharp front boundary) was shown to be that of the solution entering the column. The concentrations of solutions at different parts of the elution curve were assumed to be proportional to the corrected radioactivities, and in this way a concentration–volume curve was obtained.

Several different tests were applied before the curves obtained were considered to be reliable for the calculation of the mass-action constant. First, since the mass-action constant of the sodium–hydrogen exchange is greater than unity (the sodium ions are held more strongly than hydrogen ions) a sharp boundary should be obtained when the sodium ions displace the hydrogen ions from the exchanger. A front boundary which extended over a volume more than 5% of the initial elution volume (up to the breakthrough point) was regarded as doubtful and (together with its corresponding rear boundary) was not used for calculation. A column with bad channelling is likely to give poor boundaries, and the column was immediately repacked after such boundaries were obtained. At least two curves were obtained under each given set of conditions and the results were regarded as of a value only if these were in agreement within the experimental error over the whole range of the elution boundary.

Another difficulty was the determination of the last portion of the diffuse rear boundary where the concentration in solution is becoming very small, and observation of complete removal of the sodium ions from the column is difficult. An accurate determination of the latter part of the rear boundary was made in a number of cases by the use of high tracer activities.

When an accurate elution curve had been obtained, the adsorption isotherm was calculated by Glueckauf's method using equation (6) above, corrections being made for disturbing phenomena as described elsewhere (this vol., p. 3280). If the value of $f^*(c)$ obtained from this calculation on the initial flat portion of the rear boundary is not equal to the total capacity (expressed in meq./g. of the exchanger), this is a clear indication that error is involved either in the calculation or in the experimental results. The $f^*(c)$ values obtained over this range for a given exchanger were the same within experimental error, and this was used as a method of determining the total capacity of the exchanger. The value of $f^*(c)$ in equilibrium with a given concentration in solution ($c_{\mathrm{Na_S}}$) divided by the total capacity is $X_{\mathrm{Na_R}}$, the molar fraction of sodium in the exchanger, from which the isotherm of $X_{\mathrm{Na_S}}$ against $X_{\mathrm{Na_R}}$ may be constructed, and the value of the mass-action constant K_c determined. By such a method accurate values of K_c could be obtained over the whole range of the isotherm. The value of K_a is equal to K_c multiplied by the ratio of the activity coefficients of the hydrogen ions and the sodium ions in solution. Allowance for these activity coefficients may be made by use of the two equations :

$$\log f_{\mathrm{HCl}} = \log f^0{}_{\mathrm{HCl}} - \alpha_{12}c_{\mathrm{NaCl}} \quad \text{and} \quad \log f_{\mathrm{NaCl}} = \log f^0{}_{\mathrm{NaCl}} - \alpha_{21}c_{\mathrm{HCl}}$$

familiar in solution theory. In these equations f_{HCl} and f_{NaCl} are the activity coefficients of hydrochloric acid and sodium chloride in mixtures of the two electrolytes, c_{NaCl} and c_{HO} are the molar concentrations of the sodium chloride and hydrochloric acid, $f^0{}_{\mathrm{HCl}}$ and $f^0{}_{\mathrm{NaCl}}$ are the activity coefficients of hydrochloric acid and sodium chloride in pure solutions of the single electrolytes at the same total ionic strength, and α_{12} and α_{21} are constants for a given ionic strength. The values of $f^0{}_{\mathrm{HCl}}$ and $f^0{}_{\mathrm{NaCl}}$ being known, the values of the activity coefficients were calculated for different mixtures of the two electrolytes, α_{12} being assumed to be 0·04, and α_{21} to be 0·057 at the concentration used (0·2M.) (see Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, N.Y., 1943).

RESULTS AND DISCUSSION.

Two exchangers were used in these experiments—Dowex 50, a simple sulphonic acid type of exchanger, and Amberlite I.R.-100H, in which phenolic groups (and possibly carboxylic groups) were active in the exchanger as well as sulphonic acid groups. The following are the main results obtained.

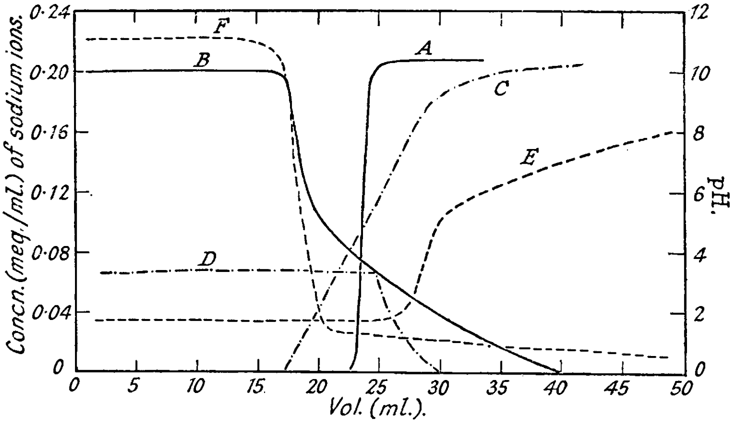
(1) *Column Behaviour with Solutions of Different Composition.*—The columns were first saturated with sodium ions using *ca.* 0·2M-sodium chloride solution, and the initial front boundaries obtained. These are shown as curve *A* in Figs. 1 and 2 for the two exchangers. When the exchangers had been saturated, they were regenerated by passing through the column a solution of hydrochloric acid of the same molar concentration as that of the sodium chloride used. If the exchange of ions between the solution and the exchanger is equivalent, one would expect that the same concentration of sodium ions would be initially obtained in solution on regeneration as was present after saturation. This was so in the case of Dowex 50, but for Amberlite I.R.-100H the concentration of sodium initially obtained in solution on regeneration was a little higher than 0·2M. (curves *B*). It was considered that this might have something to do with the presence of phenolic groups in the Amberlite exchanger, although this by itself could not account for the observations if the exchange was truly equivalent. It is known that the hydrogen or part-hydrogen forms of both Amberlite I.R.-100H and Dowex 50 liberate in water enough acid to maintain an equilibrium pH of about 3 or 4. At this pH the stability of the sodium salts of the phenolic hydroxyl groups is very small. It was thought that possibly the replacement of some of the sodium groups by hydrogen on regeneration gave enough acid (either by hydrolysis or by degradation) to decrease the pH to 3 and liberate a little sodium by a non-equivalent process. If this were so one might expect that equivalent exchange would be obtained in the case of Amberlite I.R.-100H if the pH in solution were never allowed to rise to more than 3 or 4. Solutions containing different ratios of sodium chloride and hydrochloric acid (at a total concentration of 0·2M.) were therefore used to saturate the exchanger and the family of curves (shown in Fig. 2) was obtained (*C, E, G,* etc.). After saturation the sodium was eluted with 0·2M-hydrochloric acid, and the concentration of sodium ion in solution obtained during the initial part of the regeneration was exactly equivalent to the concentration used during saturation. Not until solutions of pH 4 or greater were used was there any sign of non-equivalent exchange.

A similar series of curves was obtained for Dowex 50 and these are shown in Fig. 1. From these it will be seen that (subject to the flow rate being small enough) the elution of sodium ions from the column with hydrogen ions always produces an eluate concentration which is constant until an envelope curve is reached, down which the concentration of sodium ions in solution falls to zero. It is this envelope which represents the true rear boundary of the system and which can be used for the calculation of K_c values. The same is true for Amberlite I.R.-100H, provided that saturation of the exchanger has been stopped as soon as the initial breakthrough has been reached (see later).

(2) *Effect of Flow Rate.*—Since the flow rate has a pronounced effect on the shape of the elution curves, it is essential to ensure that it is sufficiently small for equilibrium to be maintained. In the present experiments flow rates of 0·8—80 × 10^{-3} cm./sec. were used (1—100 ml./hr.). Above 16 × 10^{-3} cm./sec. the sharp front boundary assumed a more diffuse character, becoming more or less linear with a constant gradient. The volumes required to wash out the sodium ion completely were also considerably increased, some runs (in the case of Dowex 50) continuing for 50—60 ml. compared with the 40 ml. which was normally necessary. There was some evidence that Dowex 50 required a slower flow rate than Amberlite (see Ketelle and Boyd, *J. Amer. Chem. Soc.*, 1947, **69**, 2800) and, in all the accurate runs from which mass-action data were calculated, the flow rate was maintained at less than 4 × 10^{-3} cm./sec.

FIG. 4.

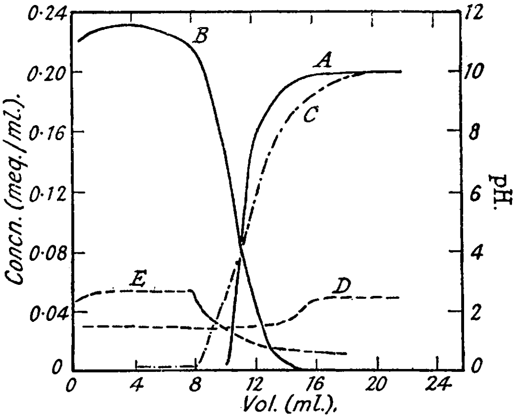
Variation of pH *in experiments with Dowex* 50.



Curves A and B, Na^+ *ion concentration ; D and C,* H^+ *ion concentration ; E and F,* pH *values.*

FIG. 5.

Variation of pH *in experiments with Amberlite I.R.*-100*H*.



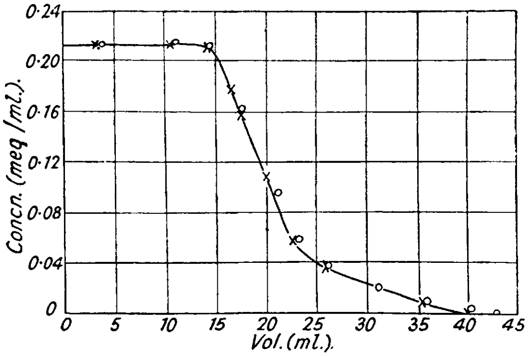
Curves A and B, Na^+ *ion concentration ; C,* H^+ *ion concentration ; D and E,* pH *values.*

(3) pH *History.*—If the exchange of sodium ions and hydrogen ions is exactly equivalent, one would expect the pH of the eluate to become equal to that of the in-going solution as soon as the column has become saturated ; pH measurement should therefore be an effective means of ascertaining when the column is completely saturated.

Typical pH curves for the saturation and regeneration of the two exchangers are shown in Figs. 4 and 5. It will be seen that, as would be expected, there is a sharp change in pH close to the breakthrough point of the front boundary. In the case of Dowex 50, for instance, the pH rises from 1·5 to 5·0 over a range of 3 ml. The pH boundary is not nearly so sharp as the sodium-ion breakthrough boundary, but it should be remembered that a pH plot is logarithmic. The actual hydrogen-ion concentration calculated from these pH values is also given. The hydrogen-ion concentration varies as one would expect for a system in which the ionic strength in solution is constant. It was noticed, however, that even though the pH of the ingoing solution might be 7 or more, the pH of the eluate did not attain this value until some 100 ml. of solution had been passed, *i.e.*, at a volume more than four-fold greater than the initial breakthrough volume. Experiments were performed in which the pH of the original solution was varied up to values of 12, by addition of sodium phosphate or sodium hydroxide. In no case did the pH of the eluate become equal to that of the original solution in a volume of less than 100 ml., and with Amberlite I.R.-100H, for which a similar situation obtains, volumes up to 20 times the breakthrough volume were sometimes needed.

FIG. 6.

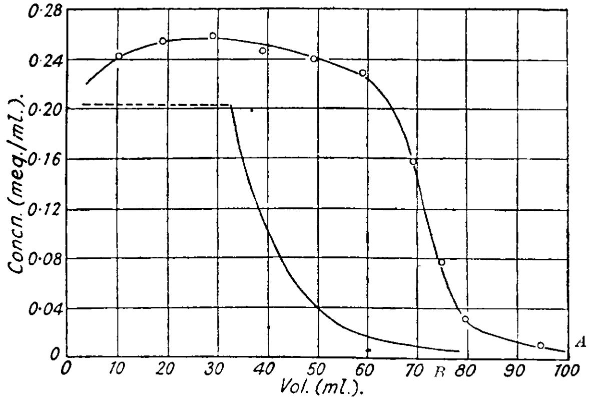
Effect of pH *of original solution on acid elution rear boundaries with Dowex* 50.



×, *Original solution pH* 12 ; ○, *original solution pH* 7.

FIG. 7.

Effect of pH *of original solution on acid elution rear boundaries with Amberlite I.R.*-100*H.*



Curve A, pH *of original solution* 12 ; *B, rear boundary for* –SO$_3$H *group only.*

Nevertheless, in spite of the long time necessary for the rise in pH of the eluate to that of the initial solution, no detectable removal of sodium ions was obtained in the case of Dowex 50, no matter how long the flow of sodium chloride was continued. Not only did the sodium concentration in the eluate remain constant, but on regeneration of the Dowex 50 with acid, an elution rear boundary of exactly the same shape and breakthrough point was obtained as when the flow of sodium chloride through the column had been stopped immediately after the sharp front boundary had been completed. This is demonstrated by the curves of Fig. 6. Although no substantial exchange takes place after the initial breakthrough point, the slow rise in pH may be evidence that exchange is not complete. Since hydroxyl groups are removed in this region, either they react with free hydrogen ions on the exchanger, or possibly they may exchange with anions (presumably chloride) held on the exchanger by Donnan equilibrium. Remembering that pH plots are logarithmic, it will be seen that the total sodium or hydroxyl ions exchanging after the initial breakthrough cannot be more than 0·005 meq./g. If exchange of sodium and hydrogen accounts for this, there must be a very considerable fall in the value of the mass-action constant for very high values of $X_{\mathrm{Na_S}}$, the molar fraction of the sodium ions in solution. It is considered more probable that impurities (*e.g.*, phenolic groups, degradation products, etc.) introduced during manufacture account for these effects which are of very small magnitude.

In the case of Amberlite I.R.-100H, there was certainly some exchange occurring between the sodium ions in solution and hydrogen ions remaining on the exchanger in the region where the pH slowly rises after the initial sharp boundary. This was shown by the fact that the shape of the rear boundary obtained on regeneration with acid, and the breakthrough point, depended on the volume of sodium chloride solution which previously had been passed through the exchanger. Two such curves are shown in Fig. 7, curve *A* being that obtained after the pH of the eluate had reached a value of 12, equal to that of the inflowing solution during the original saturation of the exchanger with sodium ions.

It is known that the capacity of exchangers having both phenolic and sulphonic acid groups as active constituents greatly increases as the pH is raised; Topp (private communication) has determined the capacity of I.R.-100H at different values of pH and has shown that it behaves in this way. It was therefore considered that the slow removal of sodium ions from solution, which occurred simultaneously with the slow rise in pH after the initial breakthrough, was most probably due to exchange of the sodium ions with the hydrogen ions of groups other than sulphonic acid.

If this interpretation is correct, the capacities which may be estimated from the areas contained by these concentration–volume regeneration curves should agree with those found by the titration method of estimating the total capacity. In the following table the calculated capacities have been compared with those obtained from a titration curve furnished by Topp.

Comparison between capacity data obtained from regeneration curves and values obtained from titration curves.

Exchanger.	pH.	Capacity due to SO_3H groups (meq./g.).	Capacity due to other active groups (meq./g.).	Total capacity (meq./g.).	Total capacity from titration curves (meq./g.).
Amberlite I.R.-100H	3	1·50	—	1·50	1·38 *
	7	1·50	0·13	1·63	1·48
	11·5	1·50	1·02	2·52	2·32
Dowex 50	all pH's	4·30	—	4·30	—

* Extrapolated.

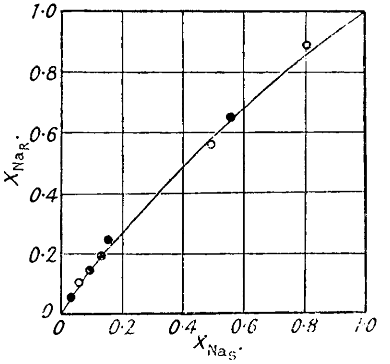
It is also possible (from the curves of Fig. 7) to estimate the exchange capacity (in I.R.-100H) of the sulphonic acid groups only. This is done by assuming that the true elution curve for the sulphonic acid group only is given by the envelope curve of Fig. 2, with the initial concentration set equal to that of the original sodium chloride solution, as curve *B* shown in Fig. 7. This assumption, of course, neglects any disturbing factors which account for the non-equivalence of the sodium chloride and the acid in certain cases, but since at pH values below 4 (where the sulphonic acid groups might still be expected to show their maximum capacity) these do not appear, it is considered that no serious error is caused. The above table gives values of the capacity due to sulphonic acid groups, and due to other groups at different pH values, the latter being estimated by difference between the total capacity and that due to sulphonic acid groups only. There are no exchanging groups other than sulphonic acid in Dowex 50, the capacity of which is also given.

An objection which may be raised is that if as much as 1·02 meq./g. of sodium chloride is taken up after the breakthrough point (see table), compared with 1·50 meq./g. before, there should be some observable effect on the shape of the concentration–volume plot after the breakthrough point. This extra uptake of 1·02 meq./g. was observed in the case when 850 ml. of 0·2M.-solution, pH 12, were passed through the column. If it were uniformly removed from solution throughout the total volume passed after the breakthrough, a drop in concentration of less than 0·006 meq./ml. would account for the observations. A drop of this order did not occur in the first day (pH 3·0, 250 ml. passed), and owing to the decay of the radio-sodium it is difficult to be certain of the concentration changes which might have occurred during the second and the third day, when the pH rose from 3 to 12, the range in which the phenolic groups might be expected to be operative.

(4) *Calculation of Exchange Isotherm.*—For Amberlite I.R.-100H, the value of the sodium-ion concentration in the initial part of the rear boundary was taken as that which would have been obtained if only sulphonic acid groups had been present; *i.e.*, the concentration was equated to that of the original solution with which the exchanger had been saturated. The conclusions obtained from these data refer therefore only to the sulphonic acid groups in the exchanger. In the case of Dowex 50, the actual elution curve was used in these calculations.

FIG. 8.

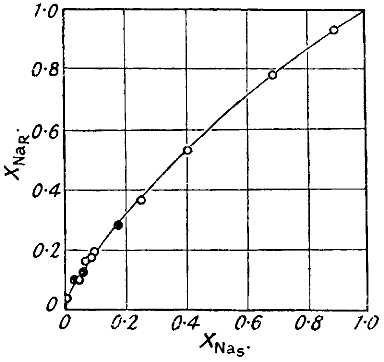
Sodium–hydrogen exchange isotherm on Amberlite I.R.-100H.



○ *Breakthrough determinations.*
● *Batch determinations.*
—— *Chromatographic rear boundary measurements.*

FIG. 9.

Sodium–hydrogen exchange isotherm on Dowex 50.



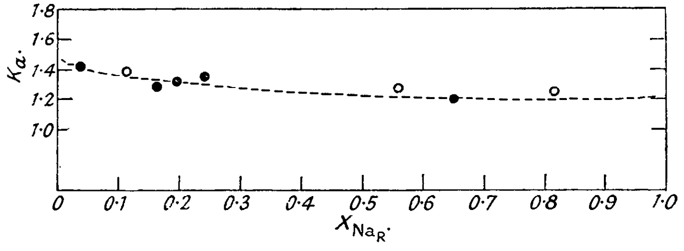
○ *Breakthrough determinations.*
● *Batch determinations.*
—— *Chromatographic rear boundary measurements.*

From the values of $f^*(c)$ obtained, $X_{\mathrm{Na_R}}$ was calculated, and the values plotted against $X_{\mathrm{Na_S}}$. The two exchange isotherms obtained are shown in Figs. 8 and 9.

Values of $X_{\mathrm{Na_R}}$ and $X_{\mathrm{Na_S}}$ were also obtained from batch equilibrium data, and from the breakthrough volumes determined with different sodium chloride–hydrochloric acid mixtures (Figs 1. and 2). These points are also shown in Figs. 8 and 9.

FIG. 10.

Mass product for Amberlite I.R.-100H at 20°.



○ *Breakthrough determination.* ● *Batch determination.* ---- *Chromatographic determination.*

(5) *Mass-action Constant.*—By use of the experimental data (rather than any points interpolated from the exchange isotherm), the values of the mass-action constant K_a were calculated from $X_{\mathrm{Na_S}}$ and $X_{\mathrm{Na_R}}$, according to equation (5). Corrections were applied for the variation in activity coefficients of the ions in the aqueous phase. The values of K_a calculated from the data provided by each of the three experimental methods are plotted against $X_{\mathrm{Na_R}}$ in Figs. 10 and 11, from which it will be seen that good agreement is obtained.

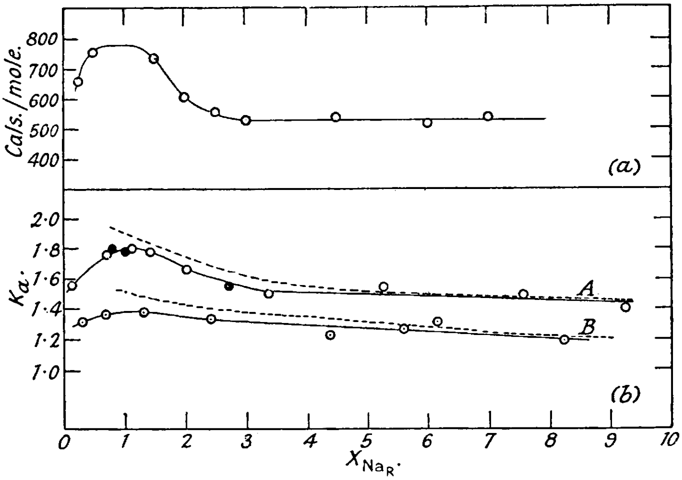
The broken line gives the K_a values calculated from the elution rear boundary. It will be seen that the value of K_a is almost constant over a large part of the exchange isotherm. At high values of $X_{\mathrm{Na_R}}$ ($>0{\cdot}7$) the chromatographic method gives results which are likely to be subject to error, because of the difficulty of deciding the exact shape of the elution boundary immediately after the concentration falls from its initial value. In the case of Amberlite I.R.-100H there is also the difficulty of being quite sure of the sulphonic acid rear boundary over the range where the disturbing influences become operative.

If care is taken to obtain the breakthrough point accurately, the method of determining the mass-action constants by saturation of the column of exchanger with given mixtures of hydrochloric acid and sodium chloride furnishes the most accurate data. The rise in K_a obtained with both exchangers is believed to be real since it is confirmed by this method. The variation of K_a is important from the point of view of attempts which might be made to estimate the behaviour of an exchanger under conditions where micro- or radio-tracer quantities of ions are present, from conditions obtaining with macro-quantities. It is clearly necessary to determine separately the constants governing exchange under such conditions.

The values obtained for the mass-action constant K_a at room temperature are $1{\cdot}24 \pm 0{\cdot}015$ for Amberlite I.R.-100H and $1{\cdot}52 \pm 0{\cdot}05$ for Dowex 50 for a range of $0{\cdot}3 < X_{Na_S} < 0{\cdot}8$. It will be noticed that, although the exchange isotherms for the two materials at room temperature are very close together, the K_a values are considerably different. The similarity in the isotherms is deceptive, for an X_{Na_R}–X_{Na_S} plot is a very insensitive method of expressing changes in K_a. The value of K_a given for Amberlite agrees well with the value of 1·25 given by Cannan (*Ann. N.Y. Acad. Sci.*, 1946, **47**, 135) and the value of $1{\cdot}25 \pm 0{\cdot}15$ given by Juda and Carron (*J. Amer. Chem. Soc.*, 1947, **70**, 3295). The Dowex 50 value, however, is to be compared with a value of 1·20 given by Bauman and Eichhorn (*loc. cit.*). Their value was determined by titration of the acid liberated in batch experiments. The shapes of the elution boundaries for the two exchangers show, however, that the value of K_a for Dowex 50 must be greater than that of the Amberlite.

FIG. 11.

Curves for Dowex 50.



(*a*) *Heat of exchange* (20—87°); (*b*) *mass product at* 20° (*Curve A*) *and* 87° (*Curve B*).

○ *Breakthrough determinations* (20°). ● *Batch determinations* (20°).

⊙ ,, ,, (87°). – – – – *Chromatographic determinations.*

The shape of the rear boundary confirms that the mass product is not constant over the whole range of the isotherm. By using the following derivation and assuming a constant value of K_a, it is possible to estimate the volume required to elute sodium at a given concentration, and hence to construct the rear boundary which would obtain for a constant mass product. The mass-action constant K_c may be expressed as

$$c_{Na_R}c_{H_S}/c_{H_R}c_{Na_S} \qquad (7)$$

and if c_R is the total capacity of the exchanger (meq./g.) and c_S is the total equivalent concentration in solution (meq./ml.) we have

$$c_R = c_{Na_R} + c_{H_R}$$

and

$$c_S = c_{Na_S} + c_{H_S}$$

Hence by substitution of c_{H_R} and c_{H_S} in equation (7) and transformation,

$$c_{Na_R} = \frac{K_c c_{Na_S} c_R}{c_S + c_{Na_S}(K_c - 1)} \qquad (8)$$

Now it has been shown by de Vault (*loc. cit.*) and Weiss (*J.*, **1943**, 297) that the volume v required to elute (at concentration c) an absorbed solute from a chromatographic column, containing x grams of absorbent is given by

$$v = xf'(c)$$

where $f'(c)$ is the differential with respect to c of the function describing the shape of the adsorption isotherm. In the present case of uni-uni-valent exchange

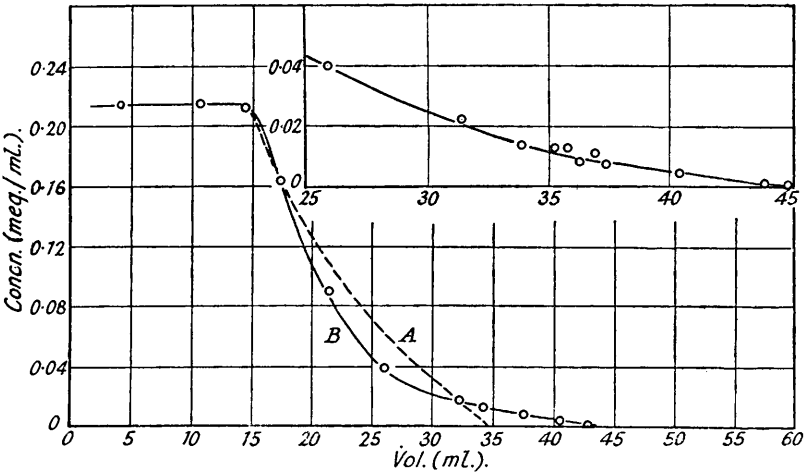
$$f'(c) = \frac{dc_{\mathrm{Na_R}}}{dc_{\mathrm{Na_S}}} = \frac{K_c c_{\mathrm{R}} c_{\mathrm{S}}}{[c_{\mathrm{S}} + c_{\mathrm{Na_S}}(K_c - 1)]^2}$$

Hence

$$v = \frac{xK_c c_{\mathrm{R}} c_{\mathrm{S}}}{[c_{\mathrm{S}} + c_{\mathrm{Na_S}}(K_c - 1)]^2} = \frac{xK_c c_{\mathrm{R}}/c_{\mathrm{S}}}{[1 + (K_c - 1)c_{\mathrm{Na}}/c_{\mathrm{S_S}}]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

FIG. 12.

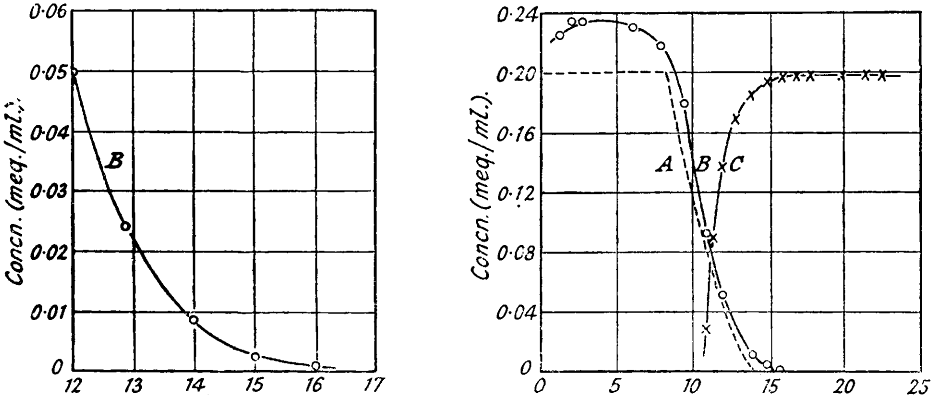
Comparison between calculated and experimental rear boundaries with Dowex 50.



Curve A, calculated elution curve ; B, accurately determined elution curve.

FIG. 13.

Comparison between calculated and experimental rear boundaries with Amberlite I.R.-100*H*.



Curve A, calculated elution curve ; B, accurately determined elution curve ; C, front boundary.

By use of this expression, the value of v has been calculated for both Dowex 50 and Amberlite I.R.-100H at different values of $c_{\mathrm{Na_S}}$ for elution at room temperature. For this purpose an estimate was made of the values of K_c which would obtain when $K_a = 1{\cdot}24$ for I.R.-100H, and 1·52 for Dowex 50 for the different values of $c_{\mathrm{Na_S}}$ used. The elution rear boundaries obtained are shown in Figs. 12 and 13, from which it will be seen that good agreement is obtained over the greater portion of the boundary. At the tail end, however, the deviation is quite large, owing to the large rise in the apparent K_a which obtains over this region. Nevertheless, using such a method, it is possible to calculate the essential chromatographic characteristics (breakthrough volume, concentration, etc.) of the system and to predict that point at which elution of the rear boundary would have been complete, if the mass product had been constant. If the apparent value of K_a increases for low values of $X_{\mathrm{Na_R}}$ complete elution will require a greater volume of eluate.

(6) *Effect of Temperature.*—A number of determinations of the mass-action constant of Dowex 50 were made at a temperature of 87° by heating the column in a jacket of trichloroethylene vapour. The mass-action constant was estimated both by the breakthrough-volume method and by calculation from an elution rear boundary. The values of K_c obtained are plotted against $X_{\mathrm{Na_R}}$ in Fig. 11, from which it will be seen that a similar curve to that at room temperature is obtained, and K_c is equal to $1{\cdot}25 \pm 0{\cdot}05$ for $0{\cdot}3 < X_{\mathrm{Na_R}} < 0{\cdot}8$. From these data an estimate may be made of the value of the heat of exchange, which is also plotted in Fig. 11. The heat of exchange for the sodium–hydrogen system is constant over the greater part of the isotherm. The rise of the heat of exchange from 525 cals. to 720 cals./mole for low values of $X_{\mathrm{Na_R}}$ suggests that some secondary process is becoming operative, possibly adsorption.

In this connection it is interesting to compare the value of 525 cals./mole, given above, with values of the same order obtained by other workers; *e.g.*, Kressman and Kitchener (this vol., p. 1201) give 1·95 kcals./mole for the heat of reaction of potassium and hydrogen ions on Zeokarb 215, and Boyd, Schubert, and Adamson (*loc. cit.*) obtained 2 ± 2 kcals./mole for the heat exchange of potassium ions and sodium ions on Amberlite I.R.-100H. It will be seen that the heat of exchange is small compared with heats of reaction obtained for most chemical reactions.

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