690. *Properties of Ion-exchange Resins in Relation to their Structure. Part I. Titration Curves.*

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The titration curves have been determined for a series of synthetic ion-exchange resins containing known ionisable groups. Sulphonated cross-linked polystyrene is shown to behave as a monofunctional, strong acid; the amount of sodium ion absorbed is independent of pH, provided there is a sufficient excess of sodium ion in solution. Cation exchangers containing carboxyl groups alone or hydroxyl groups alone behave as weak acids, the uptake of sodium ion being markedly dependent on pH.

These results provide a basis for the interpretation of the titration curves of polyfunctional exchangers. Thus resins containing both hydroxyl and sulphonic or carboxylic groups give titration curves which consist of segments characteristic of each ionisable group present.

Ion-exchange resins consist of a cross-linked, high-polymer structure to which are attached ionisable groups; they may be regarded as insoluble acids or bases. Their complete characterisation requires knowledge both of the nature of the polymer structure and of the nature and number of ionisable groups. In this paper, the exchange behaviour characteristic of certain acidic and basic groups has been demonstrated by determining the titration curves of resins of known preparation. Reference may be made to similar studies on commercial ion-exchange resins (Griessbach, *Angew. Chem.*, 1939, **52**, 215; Davies, *Chem. and Ind.*, 1948, 51; Gregor and Bregman, *J. Amer. Chem. Soc.*, 1948, **70**, 2370).

Cation-exchange properties arise from the presence of one or more of the following groups: the strongly acidic SO_3H, the weakly acidic CO_2H, or the very weak phenolic OH. Until recently, the resins available contained more than one type of group; *e.g.*, the condensation products of phenolsulphonic acid and formaldehyde contain both SO_3H and phenolic OH. In this work, the behaviour of each of the above groups *per se* has been characterised by examination of monofunctional resins, *i.e.*, exchangers containing only one type of ionisable group. The results obtained provide a basis for the interpretation of the behaviour of polyfunctional exchangers.

The functional groups responsible for anion-exchange properties are normally weakly basic amino-groups. The titration curves of two anion-exchange resins have also been determined.

The method used for the determination of titration curves is described fully below. Briefly, with cation exchangers, different amounts of base were added to weighed samples of the hydrogen form of the resin in separate flasks. After 48 hours' shaking, the pH of the solution was determined and aliquot samples were withdrawn for analysis. A parallel series of experiments was made in presence of neutral electrolyte. The above method was adopted in preference to a straightforward titration, where successive additions of base are made to a single sample of acid, on the grounds of convenience and reliability.

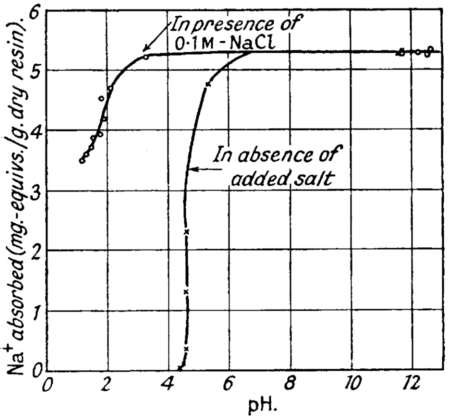
The hydrogen–sodium exchange reaction may be represented by $HR + Na^+ \rightleftharpoons NaR + H^+$, where HR represents the resin in the acid form. In the method described, the amount of sodium ion taken up by the resin is assumed to be equivalent to the amount of hydrogen ion liberated, which is determined either directly or by back-titration of excess of base. The uptake of sodium ions under given conditions (the "capacity") will be limited by the amount of ionised hydrogen on the resin. This will depend on the strength of the acidic groups and on the pH of their environment. Hence, determinations of the amount of sodium ion taken up as a function of pH may be expected to provide information on the strength of the acidic groups present. If a group behaves as a strong acid and is fully ionised under all conditions, the exchange reaction may be regarded as a simple distribution of sodium and hydrogen ions between resin and solution. In this case, the uptake of sodium ions is a function of the ratio $[Na^+]/[H^+]$ in solution.

Results.

Monofunctional Cation Exchangers.—When sodium hydroxide in absence of neutral salt is added to sulphonated cross-linked polystyrene, little change in pH is observed until the amount of alkali added exceeds the total acidic hydrogen on the resin (the "full capacity"). In the presence of 0·1M-sodium chloride, however, the system is at first acid, and the full capacity is

FIG. 1.

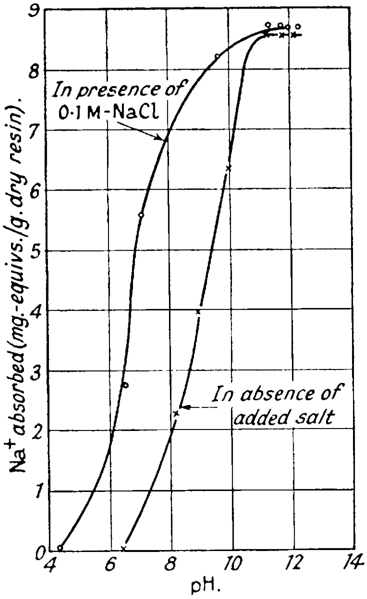
Sulphonated cross-linked polystyrene.



Ionisable group : SO_3H.

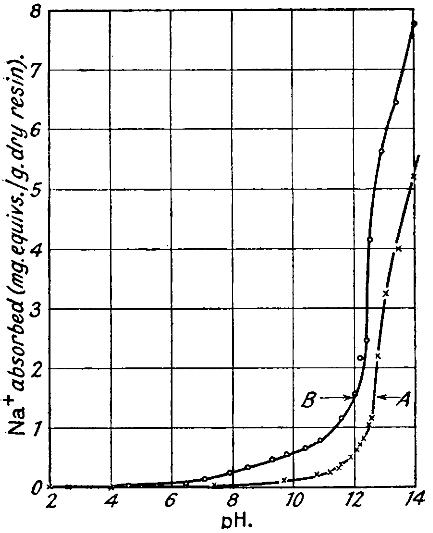
FIG. 2.

Cross-linked poly(methacrylic acid).



Ionisable group : CO_2H.

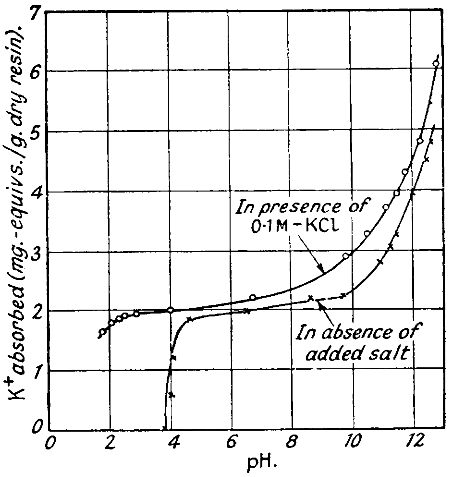
FIG. 3.



A. Phenol–formaldehyde.
Ionisable group : phenolic OH.
B. Resorcinol-formaldehyde.
Ionisable group : resorcinol OH.
(*In absence of added salt.*)

FIG. 4.

Sulphonated phenol–formaldehyde.



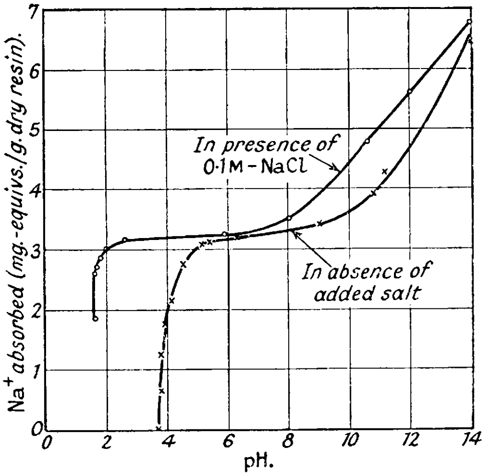
Ionisable groups : nuclear SO_3H *and phenolic* OH.

realised even at low pH owing to increase in the ratio [Na$^+$]/[H$^+$] in solution (see Fig. 1). Indeed, the full capacity has been obtained at pH $\simeq$ 1·5 in presence of 5M-sodium chloride. The capacity of sulphonated cross-linked polystyrene is therefore independent of pH, at least over the range 1·5—13, provided there is a large excess of sodium ions in solution. Its behaviour is consistent with that of a monofunctional, strong acid.

The amount of sodium ion taken up by cross-linked poly(methacrylic acid) is markedly dependent on pH (see Fig. 2). In the absence of added salt, exchange is negligible at pH's below 6, but increases progressively up to a pH of 11. In the presence of 0·1M-sodium chloride, the uptake of sodium ion is greatly increased at intermediate values of pH. It has been shown that the amount of sodium ion absorbed is a function only of the ratio [Na$^+$]/[H$^+$] in solution and that this ratio must be greater than 10^8 for complete exchange of carboxylic hydrogen for sodium to occur (Hale and Reichenberg, Faraday Soc. Discussion, in the press). These results are consistent with the view that cross-linked poly(methacrylic acid) is a monofunctional weak acid and that only a small fraction of the carboxylic hydrogen is ionised.

FIG. 5.

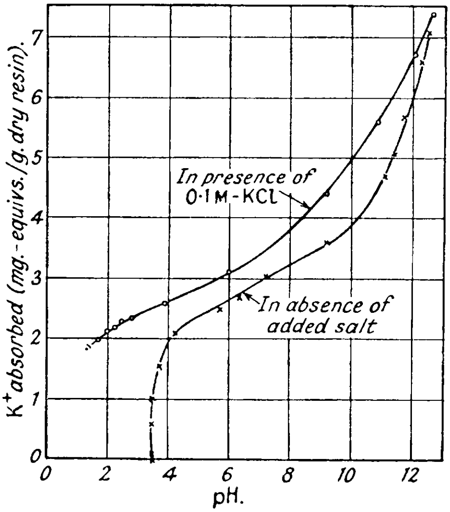
Sulphited phenol–formaldehyde.



Ionisable groups : methylene SO$_3$H *and phenolic* OH.

FIG. 6.

Resorcinol–benzaldehydedisulphonic acid–formaldehyde.



Ionisable groups : nuclear SO$_3$H, CO$_2$H, *and resorcylic* OH.

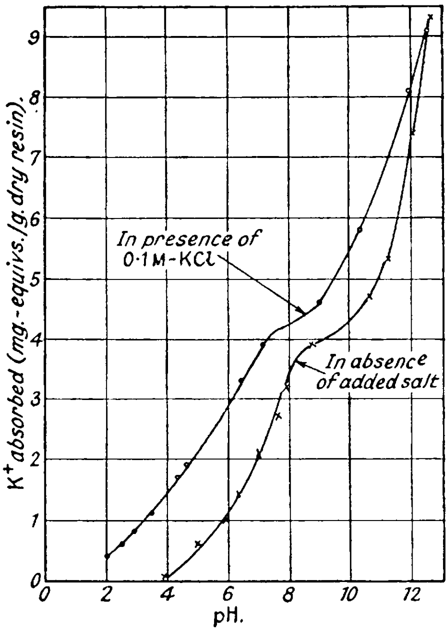
The capacity of phenol–formaldehyde resins for sodium ion is small at pH's below 11 (Fig. 3, *A*). This result suggests that the resin contains no ionisable group other than the weakly acidic phenolic hydroxyl (pK $\simeq$ 11). Resorcinol–formaldehyde resins at comparable pH possess about twice the capacity of the phenolic resin (Fig. 3, *B*). At pH greater than 12, both materials swell and the uptake of sodium ion increases markedly. It is not possible to obtain a limiting value, since the resins disperse in strong alkali.

Polyfunctional Cation Exchangers.—The curves for phenolic resins containing nuclear sulphonic acid groups (Fig. 4) and methylenesulphonic acid groups (Fig. 5) are of the same form. They consist of two portions : that at pH 2—7, where in the presence of added salt the amount of cation taken up is independent of pH, and that at pH >10, where the capacity increases with pH. The former is characteristic of the sulphonic acid group and the latter indicates the presence of a phenolic hydroxyl group. The higher capacity at low pH of the material containing methylenesulphonic acid groups corresponds with its higher sulphur content (10·4% compared with 5·4%). A resin derived from resorcinol and benzaldehydedisulphonic acid reveals the same two groups and in addition shows the presence of a group active in the pH range 4—10 (Fig. 6). This is characteristic of a carboxyl group which may be formed by oxidation of the aldehydic group. The amount of cation taken up by a resorcylic acid–formaldehyde resin increases with pH over the whole range (Fig. 7). It is, however, possible to distinguish portions characteristic of carboxyl and phenolic hydroxyl groups.

Anion Exchangers.—The structure of *m*-phenylenediamine–formaldehyde resins is illdefined. They probably contain a variety of weakly basic groups including primary aromatic amino- and mixed aliphatic–aromatic secondary and tertiary amino-groupings. The resin behaves as a weak base, the acid capacity increasing as pH is decreased (Fig. 8). Even at very low pH, the amount of acid taken up is much less than that calculated from the nitrogen content. A small capacity for bases is observed at high pH; this may be due to aromatic imino-groups or impurity of a phenolic nature in the *m*-phenylenediamine. The addition of neutral electrolyte increases the uptake of acid.

FIG. 7.

Resorcylic acid–formaldehyde.



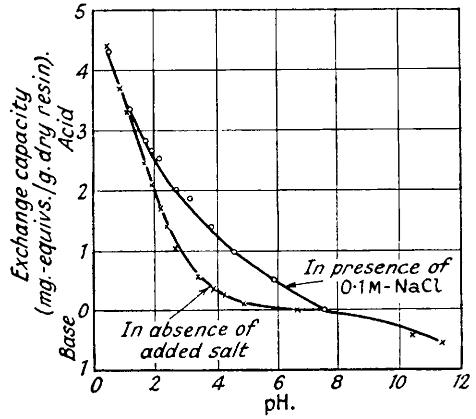
Ionisable groups: CO_2H *and resorcylic* OH.

An anion exchanger containing primary and secondary aliphatic amino-groups has been prepared by reaction of poly(vinyl chloride) with ammonia. The material behaves as a stronger base than the *m*-phenylenediamine resin, reflecting the greater basicity of the aliphatic amino-groups (Fig. 9). Again, a capacity for bases is revealed at high pH, and it will be observed that addition of neutral electrolyte increases both the acid- and the base-binding capacities. The product is known from chemical analysis to contain some 10% of oxygen and it is believed that oxidation (leading to the formation of weakly acidic groups) occurs at double bonds formed by elimination of hydrogen chloride.

Discussion.—Titration curves provide a convenient initial survey of ion exchange resins in that information is obtained on the following: (*a*) Number of types of ionisable group present, provided that the groups possess appreciable differences in acidic or basic strength. (*b*) Full exchange capacity due to each group. (*c*) Acidic or basic strength of each group.

FIG. 8.

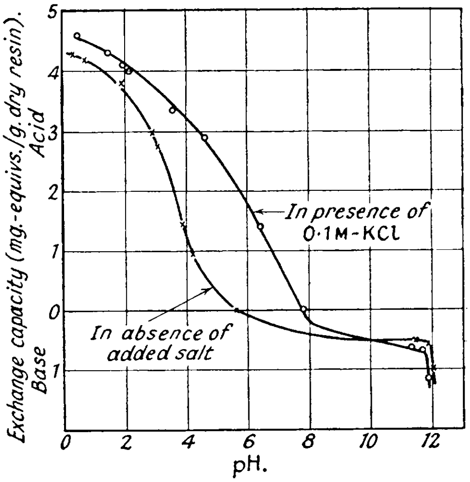
m-*Phenylenediamine–formaldehyde.*



Ionisable groups: aromatic NH_2, NHR, *and* NR_1R_2.

FIG. 9.

Poly(vinyl chloride)–ammonia compound.



Ionisable groups: aliphatic NH_2 *and* NHR.

The curves obtained on resins of known preparation show that, with monofunctional exchangers, the characteristic behaviour of the ionisable group in simple compounds is reproduced in the resin. Polyfunctional exchangers behave as mixtures; where there are appreciable differences in strength between different groups, the titration curve consists of portions characteristic of each group.

In applications where the pH varies only slightly, a poly-functional material may be quite satisfactory, but where large variations in pH are encountered, *e.g.*, in some chromatographic separations, monofunctional resins are superior in that only one set of fundamental data regarding distribution constants, rates of exchange, and swelling is required.

EXPERIMENTAL.

Preparation of Resins.—*Sulphonated cross-linked polystyrene.* Styrene was copolymerised with *ca.* 10% of divinylbenzene in bead form by heating an aqueous suspension of the monomers, with 1% benzoyl peroxide as polymerisation catalyst, at 80° for 18 hours. The copolymer was sulphonated with concentrated sulphuric acid at 100° for 8 hours, 1% of silver sulphate being used as catalyst (U.S.P. 2,366,007). The product after being washed, dried, and sieved consisted of regular, sandy-yellow spheres.

Cross-linked poly(methacrylic acid). Freshly distilled methacrylic acid was copolymerised with *ca.* 10% of divinylbenzene in presence of 1% of benzoyl peroxide. Polymerisation was carried out in a sealed tube at 60° for 24 hours (U.S.P. 2,340,111). The product was ground, leached with 2N-sodium hydroxide to remove soluble matter, washed with water, dried, and sieved.

Phenol-formaldehyde. Phenol (1 mol.), sodium hydroxide (0·25 mol.), and formaldehyde (1·5 mols., as formalin) were heated under reflux to gelation (4—5 hours). The gel was heated for 3 hours, disintegrated, and the 40—60-mesh fraction sieved out.

Resorcinol-formaldehyde. Resorcinol (1 mol.), sodium hydroxide (0·1 mol.), and formaldehyde (0·6 mol.) were heated at 60° for 2 hours. A further 0·6 mol. of formaldehyde was then added, yielding a gel in 10 minutes. The gel was broken up, dried, and sieved.

Sulphonated phenol-formaldehyde. Phenol-*p*-sulphonic acid (1 mol.), prepared by heating phenol (1 mol.) with concentrated sulphuric acid (1·2 mols.) at 100° for 2 hours, was treated with formaldehyde (2 mols.) (B.P. 489,437). The resulting gel was cooled, broken up, and washed thoroughly with sodium carbonate solution before being dried, ground and sieved.

Sulphited phenol-formaldehyde. The product obtained by heating phenol (1 mol.), formaldehyde (1·3 mols.), and a 1 : 1 mixture of sodium sulphite and sodium metabisulphite (1·25 mols.) was heated to gelation with more phenol (0·5 mol.) and formaldehyde (2·2 mols.) (B.P. 498,251). The product was dried, ground, and sieved.

Resorcinol-benzaldehydedisulphonic acid-formaldehyde. This material of German origin (B.I.O.S. Report No. 621) is prepared by condensing resorcinol with benzaldehyde-2 : 4-disulphonic acid to give 3 : 5 : 3′ : 5′-tetrahydroxytriphenylmethane-2″ : 4″-disulphonic acid, which is condensed with formaldehyde in presence of sodium hydroxide.

Resorcylic acid-formaldehyde. This material, also of German origin, is prepared by condensing 1 : 3 : 5-resorcylic acid with formaldehyde (B.I.O.S. Report No. 621).

m-*Phenylenediamine-formaldehyde.* *m*-Phenylenediamine hydrochloride (1 mol.), dissolved in water, was cooled in ice and mixed with formaldehyde (4 mols.), also cooled. Within 5 minutes, a gel was formed which was dried, ground, and sieved.

Poly(vinyl chloride)-ammonia derivative. Poly(vinyl chloride) with liquid ammonia in excess was heated in an autoclave at 125° for 12 hours in the presence of zinc dust (B.P. Appl. No. 24101/48). The insoluble product was filtered off, well washed with water and alcohol, and exhaustively dried.

Determination of Titration Curves.—After preliminary cycling in a column between 2M-sodium chloride and 2N-hydrochloric acid, cation exchangers were regenerated with 2N-hydrochloric acid and well washed. Washing was continued until the effluent was free from chloride ion and had a pH of about 4. The resin in acid form was filtered off and air-dried at room temperature. After several days had been allowed for the moisture content to become uniform throughout, samples were taken for determination of moisture content. Determination of moisture content was effected by drying over phosphoric oxide at room temperature, except for those materials which had been shown to be stable at higher temperatures. Different amounts of sodium or potassium hydroxide were added to each of several 0·5-g. samples in 100-ml. flasks, the solid/liquid ratio being kept approximately constant (75 ml. of solution to 0·5 g. of solid). The flasks were kept in a 25° air-thermostat for 48 hours with intermittent shaking. The pH of the equilibrium solution was determined with a glass electrode, a Cambridge ALKI electrode being used for solutions of pH greater than 9. Finally, 25-ml. samples of solution were withdrawn and titrated for acid liberated or excess of base. A parallel series of experiments was made in which the solution was maintained at 0·1M. with respect to sodium or potassium chloride.

For anion exchangers, preliminary cycling with 2N-hydrochloric acid and 2N-sodium hydroxide was employed and prolonged washing with carbon dioxide-free water was necessary after regeneration. The 0·5-g. samples were equilibrated with different amounts of hydrochloric acid and excess of acid titrated after 48 hours.

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