

15. Studies of a Cross-linked Poly(ethyleneimine) Ion-exchange Resin.

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A method of preparing transparent, colourless rods of an anion-exchange resin based on poly(ethyleneimine) (cross-linked by reaction with ethylene dibromide) has been developed, and the properties of the resin have been investigated. A large proportion of the ethylene dibromide reacted intramolecularly under the conditions used, and the titration curve indicated that each molecule of dibromide produced one extremely weakly basic nitrogen atom. Such atoms are probably at the centre of three $-\text{CH}_2\cdot\text{CH}_2\cdot\text{N}^+-$ groups which strongly repel protons from the central nitrogen atom.

Titration curves for different acids showed that the order of affinity of the resin for anions is acetate < chloride < nitrate < toluene-*p*-sulphonate < naphthalene-2-sulphonate < Orange II. This is also the order of decreasing swelling of the resin salts, indicating increasing ion-association due to van der Waals forces between the anions and the polymer chains. Even the chloride form is appreciably associated.

The resins took up copper (and, to a smaller extent, cobalt and nickel) by ammine formation.

OF the four principal types of ion-exchange resin, the weak-base anion-exchangers have received least attention. Potentiometric titrations and kinetic studies of commercial weak-base resins have been reported in a number of papers, particularly by Kunin and Myers,¹ and the swelling changes accompanying the sorption of hydrochloric acid have been studied by Davies and Jones.²

The older commercial weak-base resins were condensation products of phenols with amines, while most modern types are prepared by reaction of chloromethylated cross-linked polystyrene with amines. The present paper reports studies of a purely aliphatic

¹ Kunin and Myers, *J. Phys. Chem.*, 1947, **51**, 1111; *J. Amer. Chem. Soc.*, 1947, **69**, 2874.

² Davies and Jones, *J.*, 1951, 2615.

resin of high capacity, based on a network of poly(ethyleneimine), $-\text{[CH}_2\cdot\text{CH}_2\cdot\text{NH]}_n-$, which provides some features of special interest for fundamental studies. In particular, this structure contains an exceptionally high charge-density of ionic groups, even greater than that present in the weak-acid aliphatic material described in a previous paper.³

As in that work, it was desirable first to develop methods of preparing the resin in the laboratory in the form of colourless transparent rods of well-defined structure and purity. The rod form is particularly convenient when swelling changes are to be studied and only small quantities of material are available, as the resin can be readily freed from external solution.

EXPERIMENTAL

Preparation of Resin.—Ethyleneimine was first polymerised at room temperature in methanol solution, with 3 mols. % of acetic acid as catalyst.⁴ This was subsequently cross-linked with ethylene dibromide, rather than with formaldehyde or epichlorohydrin, which has sometimes been used, but with which some doubt exists as to the mechanism. Also, it seems likely that when ethylene dibromide reacts with a secondary amino-group the tertiary amine formed is present as the bromide and will not react with a second alkyl bromide molecule to produce a strongly basic quaternary ammonium group: this is not necessarily the case when epichlorohydrin is used to cross-link poly(ethyleneimine).⁵

The reaction mixture consisted of 0.06 g.-equiv. of poly(ethyleneimine) and 0.02 mole of ethylene dibromide, with 0.8—0.9 g. of methanol per g. of reactants. The mixture was introduced into glass tubes of 1—2 mm. bore which were then sealed and heated at 95° for 24 hr., the contents setting to a clear gel.

The resin rods were extracted from the tubes, washed with methanol, and converted into the free base form by treatment with carbonate-free potassium hydroxide. Finally the rods were washed with carbon dioxide-free water to remove electrolytes.

The cross-linkages produced by this method were found to be stable to 2N-acid or -alkali for 2—3 months. The reproducibility of water-content for different samples from the same batch and for samples from different batches made by the same method was satisfactory. The water-content of resin rods was independent of thickness and length of the rods.

Measurement of Swelling Changes.—The weights of the various salt forms of the resin, fully swollen, were determined by quickly and lightly mopping the rods with filter paper, and weighing them in a closed bottle. Dry weights were determined after drying to constant weight at 105°. (Resin so dried could not be used again as it would re-swell to only about 80% of its original swollen volume.)

Determination of Water-vapour Sorption Isotherms.—Small resin samples were allowed to equilibrate at $25^\circ \pm 0.1^\circ$ over saturated salt solutions, the water-activities of which have been given by Stokes and Robinson.⁶ The equilibrium weight of each piece of resin was recorded and the pieces were then dried at 105°. No significant hysteresis was found provided the resin was not completely dried. Similar isopiestic determinations were made on solutions of partly neutralised poly(ethyleneimine), the quantity of polymer present being determined by titration and checked by its weight after drying *in vacuo* at 90°.

Equilibrium Determination with Acids.—Portions of water-swollen free base resin of dry wts. 50—100 mg. were immersed in 10 ml. portions of acid of different concentrations, contained in stoppered test-tubes. The test-tubes were rocked until equilibrium was obtained. The time required for the resin to reach equilibrium was determined on separate samples of the resin by the measurement of the pH of the external solution, at intervals, until no further increase was found. For small inorganic ions the time varied from 10 days for hydrochloric acid to 14 days for sulphuric acid. For the larger organic ions, which considerably de-swelled the resin, up to 24 days were required.

The dye acids employed were prepared from the sodium salt by means of a strong-acid ion-exchange resin ("Zeo-Karb 225," The Permutit Co. Ltd.).

³ Howe and Kitchener, *J.*, 1955, 2143.

⁴ Cf. Shepherd and Kitchener, *J.*, 1956, 2448.

⁵ Manecke and Bonhoeffer, *Z. Elektrochem.*, 1951, 55, 475.

⁶ Stokes and Robinson, *Ind. Eng. Chem.*, 1945, 41, 2013.

The amount of acid sorbed was measured by the difference between that present initially and that present at equilibrium. The latter was determined, where possible, by back-titration of the acid or by recourse to the pH measurement. The pH value was calibrated against the

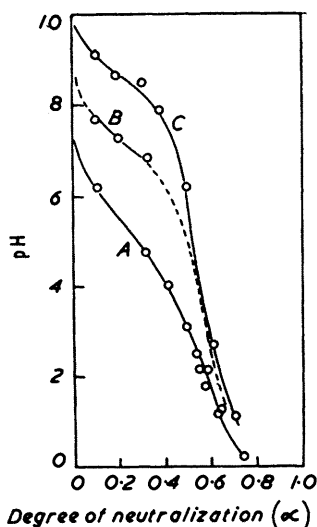


FIG. 1. Effect of neutral salts on the titration curve of resin with hydrochloric acid.

A, No salt. B, 0.01N-KCl. C, N-KCl.

FIG. 2. Titration curves of (A) hydrochloric, (B) nitric, and (C) sulphuric acid.

Acid sorbed (mequiv. per g. of dry base resin)

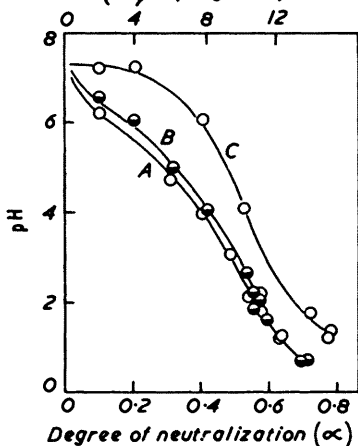
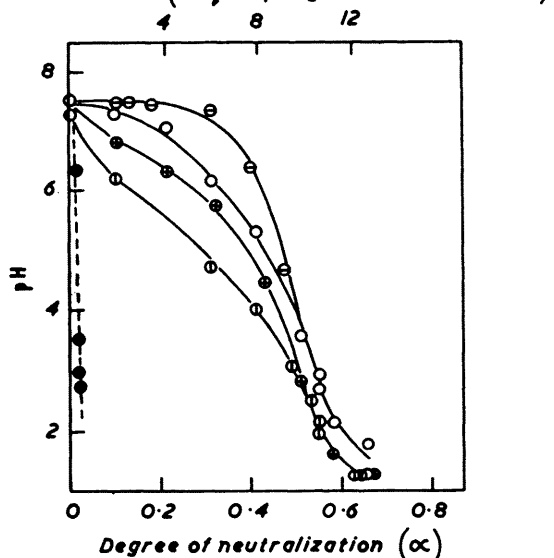


FIG. 3. Effect of increasing size of anion on the titration curve.

Acid sorbed (mequiv. per g. of free-base resin)



● Chlorazol Sky Blue acid. ⊕ Hydrochloric acid.
⊕ Toluene-p-sulphonic acid. ○ Naphthalene-2-sulphonic acid. ⊖ Orange II acid.

amount of acid present in solution for each acid used. The two dye acids were estimated colorimetrically. The pH of the solution was determined by means of a glass electrode. For measurement of pH in the 6–8 region the glass electrode after standardisation was conditioned in carbon dioxide-free water before measurement of the pH on a 2 ml. sample of the equilibrated acid solution.

The acids studied were acetic, nitric, hydrochloric, sulphuric, toluene-*p*-sulphonic, and naphthalene-2-sulphonic acid and the free acids of Orange II [4'-(2-hydroxy-1-naphthyl)azobenzene-4-sulphonic acid], and Chlorazol Sky Blue {3:3'-dimethoxydiphenyl-4:4'-ylenebis-[azo-7-(4-amino-8-hydroxynaphthalene-1:3-disulphonic acid)]}. For hydrochloric acid the effect of a neutral salt on the titration curve was investigated (Fig. 1).

The titration curves for the three inorganic acids studied are shown in Fig. 2, whilst Fig. 3 shows the effect of increasing the size of the anion on the titration curve. The results for the

FIG. 4. Sorption of (A) acetic and (B) hydrochloric acid.

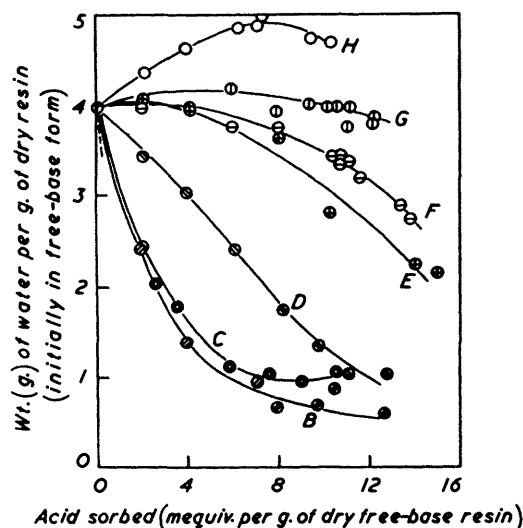
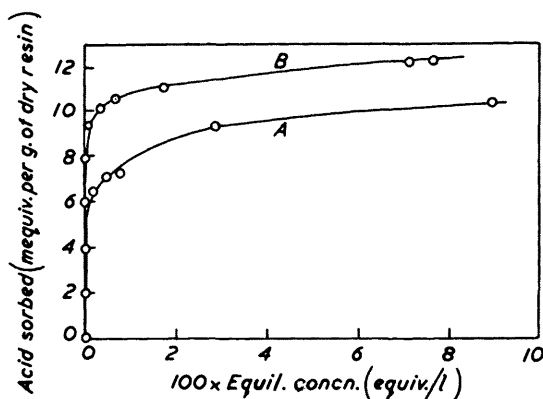


FIG. 5. Swelling of resin in acid.

A (broken line near vertical axis), Chlorazol Sky Blue acid; B, naphthalene-2-sulphonic acid; C, Orange II acid; D, toluene-*p*-sulphonic acid; E, sulphuric acid; F, nitric acid; G, hydrochloric acid; H, acetic acid.

sorption of acetic acid are given in Fig. 4 where they are compared with those for hydrochloric acid. The swelling data for all of the acids studied are recorded in Fig. 5.

Sorption of Copper by the Resin.—The polyamine resin sorbed certain ions of the transition elements such as mercury, cobalt, nickel, copper, etc., usually with a decrease in swollen volume. The coloured ions produced highly coloured resins: for example, the copper-resin was a deep blue similar to that of ammoniacal solutions of cupric salts. Samples of the free-base resin were allowed to equilibrate with 0.01N-cupric chloride solution containing different amounts of hydrochloric acid. The pH and the amount of copper sorbed by the resin at equilibrium were measured. The resin containing copper was digested with a mixture of sulphuric and nitric acid to remove organic matter, the solution evaporated to dryness, and the copper estimated colorimetrically by means of sodium diethyldithiocarbamate.

DISCUSSION

Structure of the Resin.—The minimum amount of ethylene dibromide required to produce a gel with poly(ethyleneimine) was 0.029 mole per g.-equiv. of poly(ethyleneimine). However, to produce a resin mechanically strong enough to undergo swelling changes without disintegrating, it was necessary to use much larger amounts of dibromide. With up to 0.16 mole per g.-equiv. all the dibromide reacted quantitatively; but with stoichiometric proportions or excess of dibromide, the maximum which reacted under the conditions chosen was about 0.28 mole per g.-equiv. of poly(ethyleneimine), and probably only a small proportion of this formed true cross-links between chains.

The evidence for this last conclusion is, first, that these materials did not behave like very highly cross-linked resins; they swelled considerably in water (taking up nearly 4 g. of water per g. of dry resin) and were noticeably elastic like gels with a few per cent of cross-links. Secondly, the nature of the titration curve did, nevertheless, suggest that about two-thirds of the nitrogen atoms were in situations such that they were surrounded by three $\text{CH}_2\cdot\text{CH}_2\cdot\text{N}$ groups (see below). Thirdly, few, if any, quaternary ammonium groups were produced. Fourthly, tests for *N*-2-bromoethyl groups in the resin, which might have been formed by "one-ended" reaction of ethylene dibromide, were made, on the assumption that the bromine of such groups would not be hydrolysed readily in dilute hydrobromic acid (by analogy with the stability of 2-chloroethyldiethylamine to hydrolysis); no evidence of such groups was found.

These observations lead to the conclusion that the poly(ethyleneimine) chains were linked by a relatively small proportion of true ethylene cross-linking, while the greater part of the ethylene dibromide reacted with single chains, producing small closed loops. However, the possibility that some piperazine rings or a small proportion of hydroxyethyl side-groups derived from one-ended reaction of the dibromide might be present cannot be entirely excluded.

Indeed, if the resin was subjected to drying at *ca.* 100°, its capacity remained unchanged, but it could not be reswollen completely to its original weight, although a new constant weight was reached after two days in water vapour. This indicates that some intermolecular cross-links were produced by this treatment.

Water-sorption Isotherms.—According to the current thermodynamic theory of ion-exchange resins,⁷ the "swelling pressure" (strictly, tension), Π , of the resin can be determined from water-sorption isotherms by means of the relation $\Pi = \frac{RT}{V_w} (\ln a_w^\circ - \ln a_w)$, where V_w is the partial molar volume of water (≈ 18 ml.), a_w is the activity of water in a resin of given water-content, and a_w° is the activity of water in a hypothetical resin of the same chemical composition but of negligible cross-linkage. In an attempt to use this theory, the terms a_w and a_w° were obtained for a resin and a linear poly(ethyleneimine), both partially neutralized with hydrochloric acid to $\alpha \approx 0.6$ (Fig. 6); however, in this system the method leads to anomalous results, Π going through a maximum of 130 atm. at 0.7 g. of water per g. of resin, and actually decreasing with further swelling. This simply indicates that the comparison between the resins and linear poly(ethyleneimine) is invalid which is not surprising in view of the large proportion of ethylene dibromide which was incorporated in the structure during the cross-linking.

The closeness of the isotherms and of the weights of swollen resin for the resin in the free-base and in the chloride form is particularly remarkable because normally a weak-base resin (or weak-acid resin³) swells on being converted into the salt form on account of the increase of ionic concentration in the resin. Equality of swelling implies equality of ionic strength (or, at least, osmotic coefficient) which, in turn indicates that either the free-base form is highly ionised or the chloride form is considerably associated. The

⁷ Glueckauf, *Proc. Roy. Soc.*, 1952, *A*, 214, 207.

former hypothesis is out of keeping with the titration curve and the fact that the specific electrical conductivity of the free-base form was found to be considerably lower than that of the chloride form, namely, 0.0078 compared with 0.0585 $\text{ohm}^{-1} \text{cm.}^{-1}$. The possibility of association in the chloride is supported by the fact that the acetate form is more highly swollen than the free base form; ion-association is explicable in terms of the exceptionally high charge-density on poly(ethyleneimine) chains.

Form of the Titration Curves.—The titration curve with hydrochloric acid is similar in general form to that of linear poly(ethyleneimine), which has been considered in a previous paper.³ The special characteristic of this compound is the proximity of the basic groups, and the consequent powerful electrostatic influence of neighbouring groups. But a new feature with the resin is the considerable proportion—about one-third—of the nitrogen

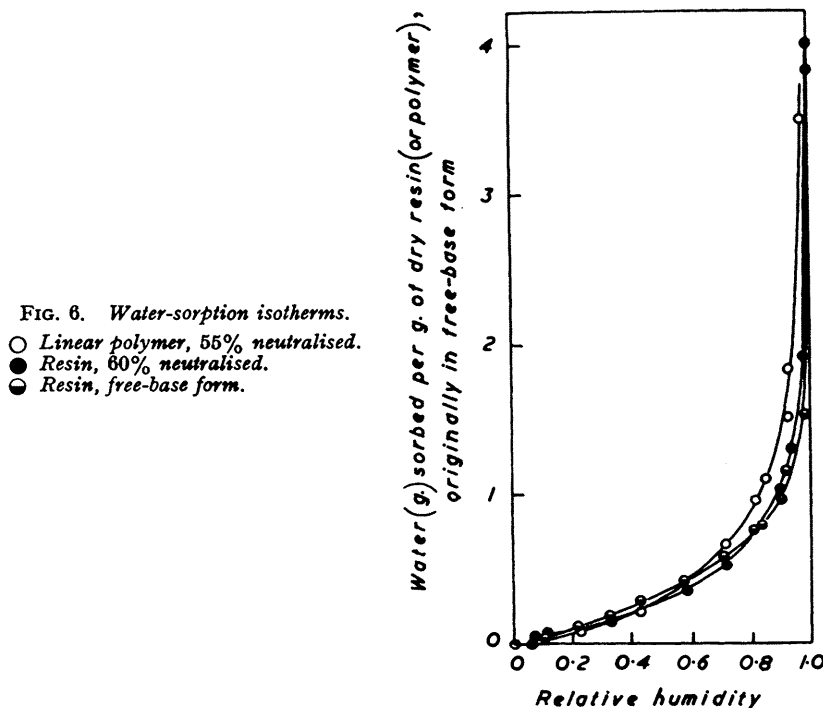


FIG. 6. Water-sorption isotherms.
 ○ Linear polymer, 55% neutralised.
 ● Resin, 60% neutralised.
 ● Resin, free-base form.

atoms which cannot be titrated even at pH 1—2, *i.e.*, they have become *extremely* weak bases. The number of "lost" groups corresponded closely with the number of ethylene dibromide molecules which reacted. The explanation is almost certainly that these are atoms which are joined to *three* $-\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_3^+$ groups, and the additive electrostatic influence of the three surrounding charges strongly repels protons from the central nitrogen atom. The electrostatic energy probably amounts to about 10 kcal./g.-ion, causing a weakening of pK value by about 8 units. Ackerman and Schwarzenbach,⁸ in fact, demonstrated such a strong reduction of basicity in simple alkylpolyamines containing nitrogen atoms surrounded by three 2-aminoethyl groups.

Affinity of the Resin for Anions.—The relative affinity of the resin for different anions is indicated by the position of the titration curves with the corresponding acids. The binding of strong acid, H^+A^- , involves uptake of both the ions and is therefore controlled by the product of their ion activities; consequently, if A^- is strongly bound by the resin,

⁸ Ackerman and Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 1543; 1953, **36**, 581.

the titration curve is displaced to higher pH values than for an acid with a weakly bound anion. The order of increasing anion affinity is seen to be (at least for small degrees of neutralisation) acetate < chloride < nitrate < toluene-*p*-sulphonate < naphthalene-2-sulphonate < Orange II. This is similar to the sequence found by Gregor and his co-workers with strong-base resins.⁹ The data for sulphuric acid are not strictly comparable because it is dibasic, and also because the second ionisation is partly repressed at the lower pH values; the strong uptake of the bivalent ion from very dilute solutions is, however, characteristic. With the present resin, no simple quantitative treatments leading to selectivity coefficients for the various pairs of ions can be employed because of the strong interaction between successively ionized groups, but the following qualitative deductions can be made: (a) Even the very strongly bound anions such as Orange II do not cause the ternary nitrogen groups (mentioned above) to combine at pH 2; the reason will appear from the next observation. (b) The greater affinity associated with large organic anions applies mainly at small degrees of neutralisation, where van der Waals forces between the non-ionic groups of the anion and the undissociated polymer chains are responsible for the binding. As more sites are neutralised, the opportunities for association of this kind are reduced, and the titration curves approach one another. Consequently, the intrinsic "affinity" of the resin decreases relatively much more with degree of neutralisation for large organic ions than it does for small ions such as chloride. A similar effect can be noted in the selectivity coefficients obtained by Gregor *et al.*⁹ with strong base resins. (c) The large anion of the dye Chlorazol Sky Blue, although strongly sorbed on the surface of the resin, is virtually unable to penetrate into the interior of the network. (d) There is a close correlation between anion binding and the equilibrium swelling of the resin, strongly bound anions causing marked de-swelling to various degrees, and only acetate causing an increase of volume. This is clear evidence that ion association is the reason for the binding, and it is noteworthy that the osmotic or activity coefficients of solutions of the corresponding salts of, say, potassium fall in the same order. (The correlation between resin affinity and electrolyte activity in solution is, of course, well known in the case of cation exchangers.)

Sorption of Copper.—The resin had a high affinity for copper, but a much lower one for cobalt and nickel, which is in agreement with the greater stability of the complex of copper with diethylenetriamine and triethylenetetramine.¹⁰ That the cupric ion is held by ammine formation is shown by the increased sorption of this ion with increasing pH of the external solution (as previously noted by Andelin and Davidson¹¹ for Amberlite IR-4B, a commercial weak-base resin).

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⁹ Gregor, Belle, and Marcus, *J. Amer. Chem. Soc.*, 1954, **76**, 1984.

¹⁰ Jonassen, Hurst, LeBlanc, and Meibohm, *J. Phys. Chem.*, 1952, **56**, 16.

¹¹ Andelin and Davidson, *J. Amer. Chem. Soc.*, 1953, **75**, 5413.