

Fundamental Properties of Cross-linked Poly(methacrylic Acid) Ion-exchange Resins.

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A method has been developed for preparing homogeneous, transparent gels of polymethacrylic acid cross-linked with ethylene bismethacrylate. The swelling, water-sorption, and titration curves of gels of different degrees of cross-linking have been studied in conjunction with varying degrees of neutralization with potassium hydroxide, tetraethylammonium hydroxide, barium hydroxide, and triethylenediaminecobalt(III) hydroxide. The valency of the cation used has a particularly marked influence on the swelling, indicating a high degree of ion-association in the multivalent salts of poly(methacrylic acid).

The properties of the gels are interpreted qualitatively in terms of current theories of ion-exchange resins and chain polyelectrolytes.

THE properties of ion-exchange resins depend on the nature of the functional groups, on the polymer framework, and on the degree of cross-linking. Much work has been devoted to the aromatic sulphonic acid type of resin, but comparatively little has yet been published on the aliphatic carboxylic acid type, although resins based on poly(methacrylic acid) have been commercially available for some years, and their general properties, titration curves, and kinetic behaviour have been reported in a number of papers (see, *e.g.*, Kunin and Barry, *Ind. Eng. Chem.*, 1949, **41**, 1269; Hale and Reichenberg, *Discuss. Faraday Soc.*, 1949, **7**, 79; Conway, Green, and Reichenberg, *Trans. Faraday Soc.*, 1954, **50**, 511). Marked differences are observed between the behaviour of the two classes of resin. In addition to their chemical applications, carboxylic acid resins are of particular interest for their relation to naturally occurring materials such as cellulose, alginic acid, and the proteins.

Commercial granular poly(methacrylate) resin is an unsuitable medium for careful study, first because the true degree of cross-linking is unknown (since impure divinylbenzene is used as cross-linking agent); secondly, because such resins are found to release into solution small amounts of colloidal poly(methacrylic acid) which is adsorbed on the surface of glass electrodes, giving erroneous pH values; and thirdly, because the swelling of the resins, which is of particular importance with weak-acid resins, cannot be readily determined with granular resins.

The present paper reports investigations of carefully characterised poly(methacrylic acid) resins of various degrees of cross-linking, prepared in the laboratory in the form of smooth, transparent rods.

EXPERIMENTAL

Preparation of Resins.—The methacrylic acid was purified by fractional distillation of the commercial product *in vacuo*.

As cross-linking agent ethylene bismethacrylate was selected as being (a) structurally similar to methacrylic acid, (b) likely to copolymerize more or less statistically with methacrylic acid ("block" co-polymers being undesirable), and (c) preparable in a state of purity. The stability of the ester link in the resins so prepared was remarkable: no hydrolysis could be detected after 6 months in 5*M*-potassium hydroxide. Ethylene bismethacrylate was prepared from methyl methacrylate (750 g.) and ethylene glycol (100 g.) by the ester-exchange method (White, *J.*, 1943, 238), 5 g. of concentrated sulphuric acid being used as catalyst and 50 g. of quinol as stabilizer. The methyl alcohol-methyl methacrylate azeotrope was distilled off through a Widmer column as formed. After removal of acid, washing, and drying, the ethylene bismethacrylate was fractionated through a Widmer column at reduced pressure, the main product being collected at 111°/8 mm. in 51% yield (Found: C, 60.3—60.4; H, 7.2—7.3. Calc. for C₁₆H₁₄O₄: C, 60.6; H, 7.1%).

The following procedure was developed for carrying out the polymerization so as to produce clear, homogeneous gels. Approximately equal volumes of methacrylic acid and a 0.2% aqueous solution of ammonium persulphate (as catalyst) were weighed into a small flask, together with

the requisite weighed amount of ethylene bismethacrylate (which was varied in different preparations from 0.1% to 20% of the methacrylic acid). With more than 2% of ethylene bismethacrylate, the mixture was immiscible at room temperature, but became homogeneous as the temperature was raised. The flask was therefore held in a bath of water slightly above the clearing temperature.

For the production of thin rods of resin (which proved the most convenient for handling small quantities of experimental resins) the polymerization was carried out in clean, U-shaped, thin-walled capillary tubes of 1 or 2 mm. bore, which were heated in a beaker of water, initially at 50°. The capillary tubes were charged with the previously warmed monomer mixture, and the temperature of the water-bath was then raised very slowly. The solution set to a gel at temperatures below 80°. As polymerization proceeded, the thin rod of gel was seen to contract from the sides of the tube. To complete the reaction, the water was boiled for 15 min. and then allowed to cool. The glass tubes were cut, and the resin rods gently drawn out. The rods were then boiled in water for 1 hr. to ensure that no unchanged monomer remained. Transparent rods have been obtained with as little as 0.01% and as much as 20% of cross-linking agent. The rods can be stored indefinitely in methanol, but are liable to crack when dried too rapidly, or to be attacked by moulds if left in water for a long time.

Absorption of Water by the H-Form of Poly(methacrylic Acid) Gels.—Resin rods of low cross-linking swell considerably in water, ethanol, and particularly methanol, and are flexible and

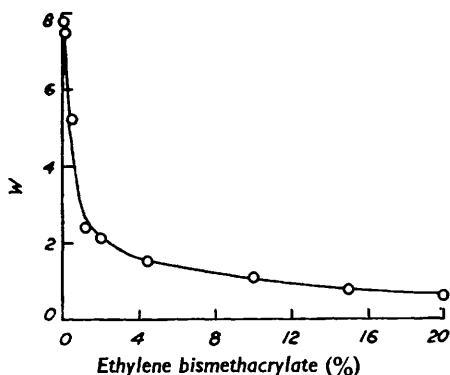


FIG. 1. Water content (W) of hydrogen form of resin of different degrees of cross-linking (% of ethylene bismethacrylate).

rubber-like, though weak; those with 10% of bismethacrylate are stronger and tough. No swelling is observed with acetone or ether. Individual pieces of rod can be handled with tweezers, provided special care is taken to avoid damaging those having 1% or less of cross-linking agent.

The swollen weight of the small rods was readily obtained by mopping the specimen quickly with filter-paper and weighing it in a closed bottle within 30 sec. The water content was obtained by the loss of weight when dried to constant weight in an oven at 125°. Most of the water is readily removed, but the last part is held very strongly and is not evolved at 115°. No decomposition occurs at temperatures below 140°. The reproducibility of water-content between different samples from the same batch was satisfactory and independent of the thickness and length of the rods. Results for the swelling in water of H-rods of different cross-linking are shown in Fig. 1.

If rods were dried very slowly, they could be re-swollen reversibly in water. Those of 5% or 10% cross-linking regained their original swollen weight within a few hours, and the rate of water absorption was increased by rise of temperature, but those of lower cross-linking needed several days and the process was not accelerated by heating. In fact, rise of temperature causes a contraction of the swollen gels, as with other rubber-like macromolecular materials. Maximum swelling of the weakly cross-linked gels evidently involves untangling of the chain molecules.

In studying properties such as the titration curves of the resins, the rods were not dried until after the experiment; specimens were weighed in the water-swollen condition and one sample was dried to obtain the water-content of the batch.

The sorption of water vapour by the resins from air at different relative humidities was determined approximately by suspending small pieces of rod (5–40 mg. when dry) in tubes inside bottles of controlled humidity, and weighing them until they attained constant weight.

The controlled humidities were obtained with solutions of glycerol (Johnson, *Ann. Appl. Biol.*, 1940, 27, 295) or sodium hydroxide at $20^\circ \pm 2^\circ$ (I.C.T., Vol. V). No significant hysteresis was observed. Surprisingly, the water-absorption graphs for resins of 0.15, 1, 5, and 10% cross-linking were superimposable (at least within the rather large limits of experimental error) from 0 to 90% relative humidity (Fig. 2), indicating that the considerable differences in swelling behaviour of the different resins are confined to the region 90–100% humidity. Some water-absorption data for $25^\circ \pm 0.1^\circ$, obtained by Miss N. Fraser [by using controlled humidities of the saturated salt solutions recommended by Stokes and Robinson (*Ind. Eng. Chem.*, 1949, 41, 2013)], are shown in Fig. 3. However, no attempt has been made to examine the isotherms for different resins and different temperatures in detail, as has been done by Waxman, Sundheim, and Gregor (*J. Phys. Chem.*, 1953, 57, 969, 974) for sulphonated polystyrene resins.

The form of the isotherms shows immediately that about 0.1 g. of water per g. of dry H-resin is very strongly absorbed; in fact, it is retained in a desiccator over solid sodium hydroxide and is removable only above 120° . This water-content corresponds to $\frac{1}{2}$ mole per mole of methacrylic acid ($C_5H_8CO_2H$). The sorption of water is obviously by hydrogen bonding on to the carboxyl groups. Application of the Brunauer, Emmett, and Teller isotherm theory (cf. Brunauer, "The Adsorption of Gases and Vapours," O.U.P., London, 1944) leads to an estimate

FIG. 2. Water sorption isotherm for hydrogen forms of resin at 20° (mean curve for resins of 0.1–10% of ethylene bismethacrylate).

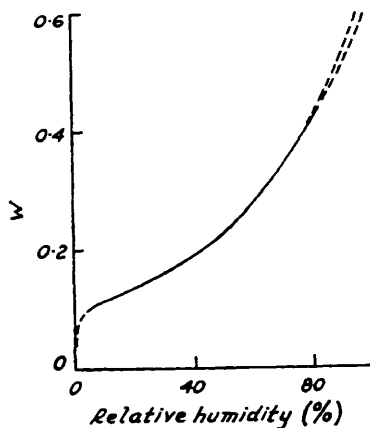
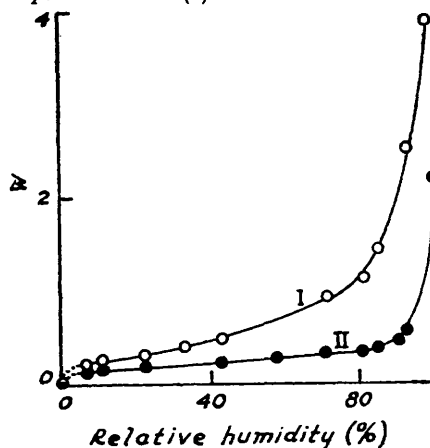


FIG. 3. Water sorption isotherms for 1% cross-linking resin at 25° in the hydrogen form (II) and neutralized to $\alpha = 0.8$ with potassium ions (I).



of the heat of adsorption of the "first layer" of water, *viz.*, *ca.* 12 kcal. per mole of water. This indicates the formation of *two* hydrogen bonds per water molecule; thus the first water molecule is apparently bonded to two adjacent carboxyl groups.

Above 5% relative humidity the isotherm rises only slowly, and is convex to the pressure axis. Clearly, sorption is now on to low-energy sites; the hydrophilic groups have been satisfied, and the polymer chains are hydrophobic. Only at high relative humidities can the interior of the resin be rendered appreciably hydrophilic by introduction of several molecules of water around each site. It is beyond this region that swelling and stretching of the gel framework sets in.

Titration of Resin Rods with Bases.—The uptake of four typical alkalis by resins of 1, 5, and 10% cross-linking was investigated, both in the absence of neutral salt and in the presence of 0.01N- and 0.1N-solutions of the chloride of the base. On account of the slowness of the reaction and the small quantities of resin available, the titration curves were determined by equilibrating single pieces of rods, weighing 5–8 mg. when dry, with 50-ml. portions of solution in stoppered flasks, carbon dioxide being excluded by nitrogen, and the flasks being rocked gently on a tray until equilibrium was reached. The pH of the solutions was then determined on a 5-ml. sample by means of a glass electrode (with exclusion of carbon dioxide). The pH was measured again after a further 2 days' shaking to ensure that equilibrium was reached. The weights of the swollen rods, and also their diameters and lengths, were determined to obtain the degree of swelling and the approximate densities of the resin salts.

The alkalis used were potassium, tetraethylammonium, and barium hydroxides and, as an example of a soluble, strong base of a trivalent cation, trisethylenediaminecobalt(III) hydroxide,

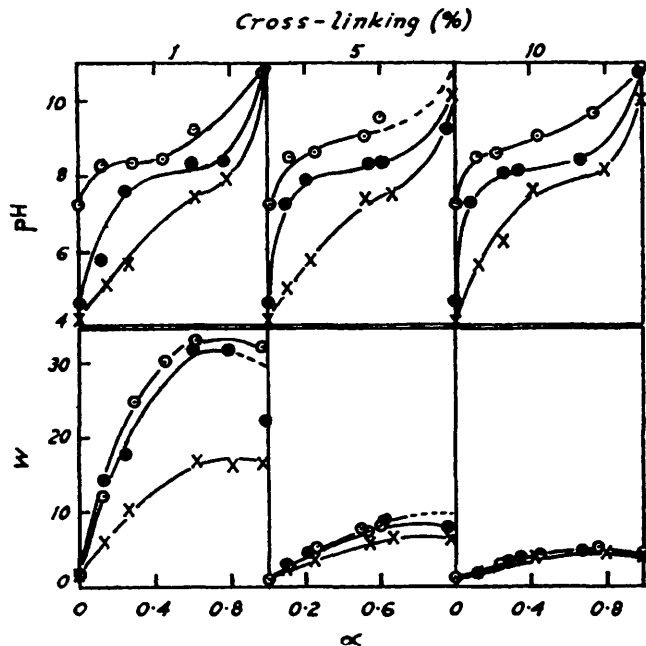


FIG. 4. Titration curves and swelling isotherms for resins of 1, 5, and 10% cross-linking treated with potassium hydroxide, with and without added potassium chloride.

KCl: ○, Nil; ●, 0.01N; X, 0.1N.

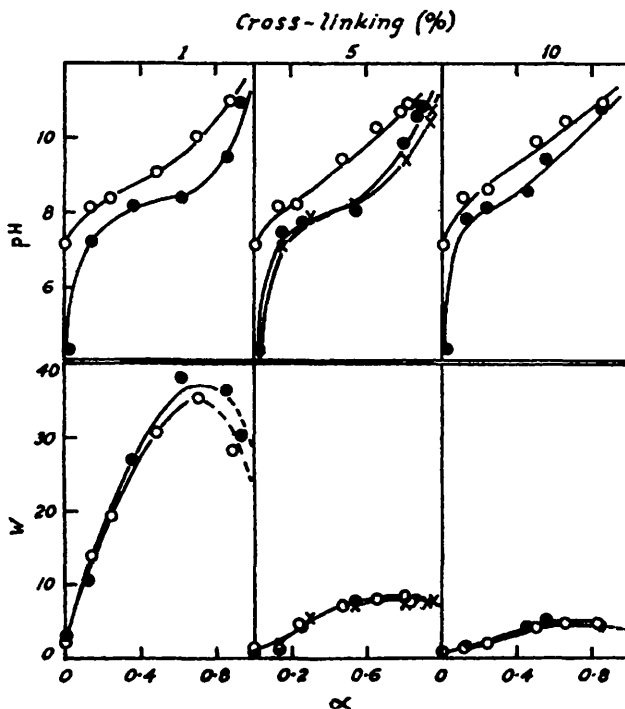


FIG. 5. Titration curves and swelling isotherms for resins of 1, 5, and 10% cross-linking treated with tetraethylammonium hydroxide, with and without added tetraethylammonium chloride.

$(C_2H_5)_4NCl$: ○, Nil; ●, 0.01N; X, 0.05N.

$Co(en)_3(OH)_3$, prepared from the chloride (*Inorg. Synth.*, 1946, 2, 221) by means of a strong-base ion-exchange resin ("Deacidite FF," Permutit Co. Ltd.). The potassium and tetraethylammonium hydroxides required about 1 week to come to equilibrium with resins of 5% cross-linking, barium hydroxide needed 2 weeks, and $Co(en)_3(OH)_3$ 3 weeks. The time was shorter

with 1% cross-linked resins and longer with 10% cross-linking, the cobalt complex taking over a month for full neutralization of the latter resin.

The amount of base remaining in solution (C_{OH^-}) at equilibrium was calculated from the final pH reading by the expression, $\log(C_{OH^-}) = \text{pH} - 14 - \log f_{OH^-}$, and f_{OH^-} was estimated

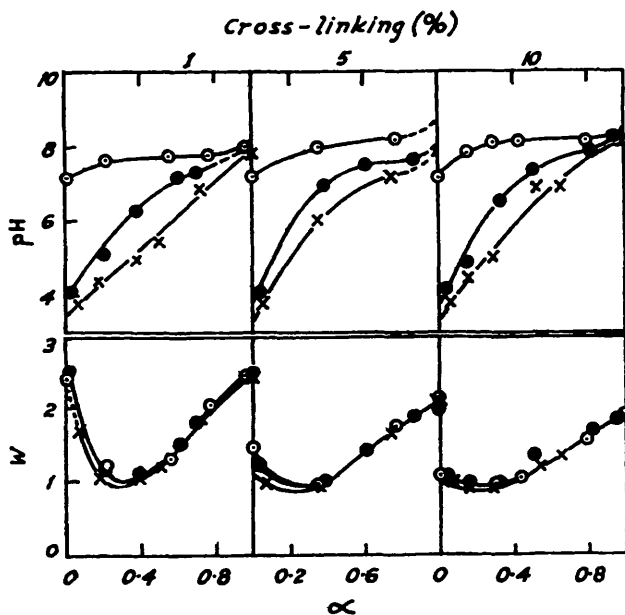


FIG. 6. Titration curves and swelling isotherms for resins of 1, 5, and 10% cross-linking treated with barium hydroxide, with and without added barium chloride.

BaCl₂: ○, Nil; ●, 0.01N; X, 0.1N.

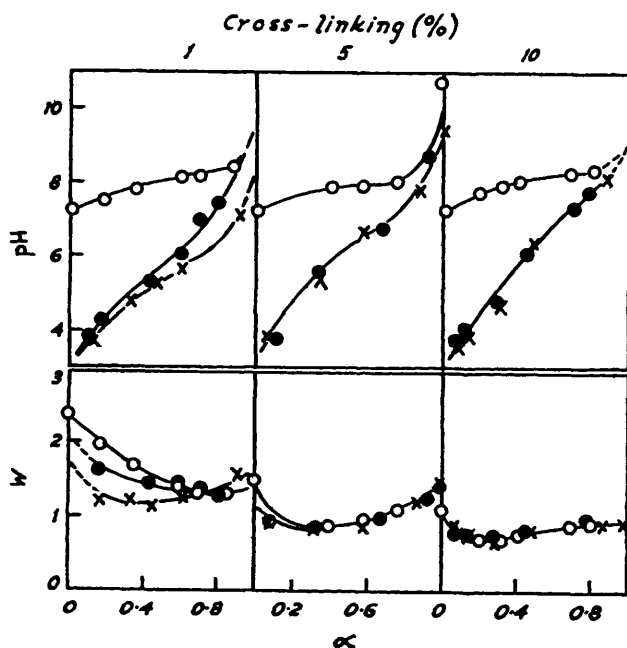


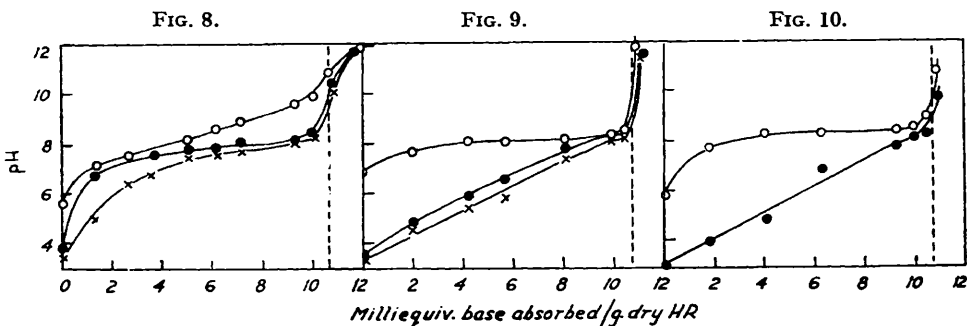
FIG. 7. Titration curves and swelling isotherms for resins of 1, 5, and 10% cross-linking treated with triethylenediaminecobalt(III) hydroxide, with and without added triethylenediaminecobalt chloride.

Triethylenediaminecobalt chloride: ○, ●, 0.01N; X, 0.1N.

by use of the limiting Debye-Hückel equation. The majority of pH readings with the multivalent bases were below 8, where the difference between the added and adsorbed base was very small. The accuracy of the calculated degree of neutralization (α) is therefore not greatly affected by errors in f_{OH^-} .

Particular care was needed to obtain reliable pH values for the unbuffered solutions in the

pH region 5.5—8.5; the glass electrode, after standardization, was "conditioned" for several min. in distilled water stirred by a stream of nitrogen, and then normally gave a reading of 7.2. The water was then run off and replaced by the solution under test, and nitrogen was passed in until a steady reading was obtained. This procedure gave reproducible readings on different samples of the same solution.



The results of the titration experiments with small pieces of rod are summarised in Figs. 4—7, and serve to show the main features of the processes. The accuracy obtainable by this technique was, of course, not high. It is useful to compare these results with those obtained by using larger samples (0.3 g.) of a laboratory batch of a commercial, granular poly(methacrylic acid) resin ("P.11") (kindly provided by the Permutit Co. Ltd.). Before use, this resin was "cycled" with sodium hydroxide and hydrochloric acid solutions and then washed to pH 5—6. Titration curves obtained by the batch shaking method with potassium, barium, and trisethylene-

FIG. 11. Settled volumes of granular resin "P.11" in potassium hydroxide solutions of different pH.

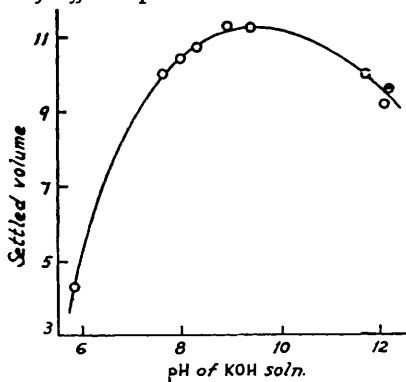
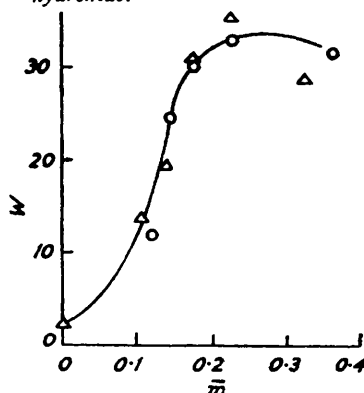


FIG. 12. Relation between swelling and internal molality of cation, for 1% cross-linked resin in potassium hydroxide and tetraethylammonium hydroxide.



diaminecobalt(III) hydroxides are shown in Figs. 8, 9, and 10; these results provide more detailed information than was available from the rod experiments concerning the form of the titration curves in the neighbourhood of the equivalence point.

The titration curves are consistent with the assumption that all the carboxylic acid groups present in the resins (as calculated from their known content of methacrylic acid) are available for salt-formation.

The swelling behaviour of the resin rods used in the titrations is also shown in Figs. 4—7; W is the weight of water taken up by 1 g. of dry H-resin.

Fig. 11 shows the settled volumes of the granular resin in potassium hydroxide solutions of different pH; the resin showed negligible volume changes in $\text{Ba}(\text{OH})_2$ and $\text{Co(en)}_3(\text{OH})_3$.

DISCUSSION

Structure of the Resins.—The reversible swelling, the rubber-like elasticity of the swollen H-resins, and the fact that coherent gels are obtained with as little as 0.01% of cross-linking agent indicate that the resins consist of partially coiled chain macromolecules of a high degree of polymerization. A molecular model of the poly(methacrylic acid) chains shows clearly that the carboxyl groups are only about 4.5 Å apart. Consequently, the electrostatic field in the neighbourhood of an ionized polymethacrylate chain is very intense. Approximate calculations show that the attraction for even univalent cations is great enough to hold the counter-ions in the vicinity of a chain. Inside a three-dimensional network of chains the situation is more complicated, and an internal diffuse double layer probably exists, the extension of the layer depending on the prevailing local ionic strength, and hence being sensitive to the amount of internal diffusible salt.

Swelling.—The hydrogen-form of poly(methacrylic acid) in solution probably approximates in structure to the well-known statistical-coil model (Kuhn, *Kolloid Z.*, 1934, 68, 2), although the solvation energy of the polar groups and the possible intramolecular hydrogen-bonding of adjacent carboxyl groups introduce complicating factors not allowed for in the theory of chain molecules.

The great expansion of the cross-linked gels which occurs when the acid is converted into its salt form is a well-known effect; with the soluble polyelectrolytes it is manifested by a great increase of intrinsic viscosity (Katchalsky, Kunzle, and Kuhn, *J. Polymer Sci.*, 1950, 5, 283; Katchalsky, *ibid.*, 1951, 7, 393), which arises from an extension of the chain as a result of electrostatic repulsion between the parts of the poly-ion. In this case, the counter-ions form a diffuse atmosphere in the neighbourhood of the chains, and their presence tends to screen the charges on the chains and hence reduce the extension. The screening is greatly enhanced by increase of ionic strength of the solution. Consequently, addition of salts causes a great reduction of intrinsic viscosity.

In the case of polyelectrolyte gels, where the counter-ion cloud is confined to the inter-chain interstices, swelling is determined by the balance between the osmotic effect tending to dilute the internal solution, and the elastic contractility of the network. The osmotic contribution of the polymer chains is normally negligible compared with that of the counter-ions, since each chain is a single "solute particle," but it may contribute a large number of counter ions.

The validity of the statistical theory of polyelectrolyte gels has been demonstrated for polymethacrylate gels of very low degree of cross-linking by Katchalsky, Lipson, and Eisenberg (*J. Polymer Sci.*, 1951, 7, 571). However, the current theory is not quantitatively applicable to concentrated gels; in particular, no allowance is made for specific properties of different ions—an aspect of vital importance in ion-exchange resins.

An alternative approach is the formal thermodynamic treatment on the model of the Donnan membrane equilibrium, as has been used for the sulphonic acid resins by Glueckauf (*Proc. Roy. Soc.*, 1952, A, 214, 207) and others. Water-sorption data can then be used to calculate formal osmotic coefficients for the resin materials, and the magnitude of the swelling pressure can be deduced from a comparison of the isotherms for resins of high and low degrees of cross-linking. In this way it has been clearly established (Glueckauf, *loc. cit.*; Gregor and Frederick, *Ann. N.Y. Acad. Sci.*, 1953, 57, 87; Boyd and Soldano, *Z. Elektrochem.*, 1953, 57, 162) for poly(styrenesulphonate) resins and for strong-base resins (Boyd and Soldano, *loc. cit.*) that the swelling pressure, Π , is a linear function of the swelling volume and substantially independent of the nature of the counter-ion. The same relation probably holds for polymethacrylate resins. At osmotic equilibrium between a resin material of internal molality \bar{m} and an external, dilute solution of a 1 : 1 electrolyte of molality m , it can be shown that $\Pi V_w / RT \approx 0.018 (\bar{\phi}\bar{m} - 2\phi m)$, where V_w is the molar volume of water, and $\bar{\phi}$ and ϕ the osmotic coefficients in the resin and in the external solution. Application of this to resins, with K^+ or NEt_4^+ cations, in the absence of salts, gives $2\phi m \ll \bar{\phi}\bar{m}$, and $\bar{m} \propto \alpha/W$. By analogy with the findings by Boyd and others, it can be assumed that $\Pi = aW + b$, where a and b are constants for a given resin. Hence, $(aW + b) \approx 0.018RT\bar{\phi}\bar{m}/V_w$, and W should be a linear function of $(\bar{\phi}\bar{m})$. Further, by analogy with

potassium acetate solutions, $\bar{\phi}$ might be expected to be about 0.9 and not very sensitive to concentration in the region of 1M. Such elementary considerations would therefore lead one to expect that W would be roughly linear with \bar{m} .

Examination of the data shows that these expectations are not even approximately realised. The W - \bar{m} graph is strongly sigmoid (Fig. 12). The swelling in the region $\alpha = 0-0.5$ is more nearly proportional to \bar{m}^2 , suggesting that increasing electrostatic repulsion between the polymer chains contributes as much to the extension as does the osmotic effect of the counter-ions. Alternatively, neutralization of the carboxyl groups may be eliminating intramolecular hydrogen bonding and thus weakening the mechanical strength of the gel. An analogous effect has been noticed in the viscosity of solutions of partially neutralized polymeric acids (Katchalsky *et al.*, *loc. cit.*). Beyond $\alpha = 0.5$ this effect would be complete, and the declining effect of increase of \bar{m} can be ascribed to the pronounced fall of $\bar{\phi}$ with α , found for poly-acid salts in solution (Kern, *Z. phys. Chem.*, 1938, A, 181, 249, 283; 1939, A, 184, 197, 302; Katchalsky *et al.*, *loc. cit.*). This is an electrostatic effect due to the high charge density on the polymer chains (Lipson and Katchalsky, *J. Polymer Sci.*, 1954, 13, 43).

The marked effect of salts in de-swelling the resins of lower cross-linking is, of course, due primarily to the counter-osmotic pressure of the external solution. The swelling of the fully neutralized 1% cross-linked potassium resin is approximately halved by addition of 0.1M-potassium chloride in the external solution. This suggests that for this case (by applying the swelling energy theory and neglecting internal potassium chloride),

$$[\bar{\phi}\bar{m}]_{\text{no salt}} \approx 2[\bar{\phi}\bar{m} - 2\phi m]_{0.1\text{M-salt}}$$

which leads to the conclusion that $\bar{\phi} \approx 0.35$. This can be compared with the value of 0.17 found by Kern (*loc. cit.*) for a solution of sodium polyacrylate. Thus, even potassium ions have a low osmotic activity in the neighbourhood of the poly-ion chains.

The swelling curves for Ba^{++} and $\text{Co}(\text{en})_3^{+++}$ (with $W < 2.5$) are in striking contrast to those for K^+ and NET_4^+ (with W up to 37). The actual de-swelling of 1% cross-linked resin in the hydrogen-form, when partly neutralised by Ba^{++} , must be due to contraction of the polymer chains on replacement of two carboxyl groups by $\cdot\text{CO}\cdot\text{O}\cdot\text{Ba}^{++}\cdot\text{O}\cdot\text{OC}\cdot$, the Ba^{++} ion being strongly associated with the carboxylate ions. At higher values of α , a small positive swelling is present, showing that the Ba^{++} ions are not entirely associated. The fully neutralized Ba-resin (1% cross-linked) has a "normality" of 4.6, whereas that of the corresponding K-resin is only 0.35. The osmotic coefficient of the barium resin material is roughly about 0.004.

The trivalent $\text{Co}(\text{en})_3^{+++}$ ion produces no significant swelling. This ion must therefore be almost entirely associated with the polymethacrylate chains.

Titration Curves.—As with the swelling curves, the titration curves do not agree with those expected from the elementary theory for the neutralization of a monomeric weak acid. They are also markedly different from those obtained with materials such as wool, where the ionizing groups act as isolated sites (Gilbert and Rideal, *Proc. Roy. Soc.*, 1943, A, 182, 335; Alexander and Kitchener, *Text. Res. J.*, 1950, 20, 203). The abnormal forms are due to (a) electrostatic activity coefficient effects for the polymer ions and counter-ions arising from the high charge density along the polymer chains, and (b) changes of the swelling energy with α and with external salt concentration. The first factor has been discussed by Katchalsky, Shavit, and Eisenberg (*J. Polymer Sci.*, 1954, 13, 69) but the overall problem is too complicated to be analysed quantitatively in the absence of information about (b). The following qualitative observations must therefore suffice at present.

(1) The half-neutralization point is about pH 9, largely owing to the necessity of introducing K^+ and OH^- from the solution into the gel. The ordinary pK value of the individual carboxyl groups is known to be about 4.9 (*idem, ibid.*), and the electrostatic effect causes a displacement of about 2 pH units only.

(2) The displacement of the titration curves to lower pH values by addition of salts is, of course, a form of common-ion effect, since a cation must be introduced into the resin as well as H^+ being abstracted.

(3) Increase of cross-linking has little effect on the titration curve for K^+ , showing that the swelling energy is small in this case, but with NEt_4^+ there is a displacement to higher pH values with higher cross-linking, and the shape of the curve at large values of α also shows that with this large ion the steric resistance is important. These conclusions are similar to those reached with sulphonated polystyrene resins (cf. Kitchener, in "Ion Exchange and Its Applications," Soc. Chem. Ind., London, 1955).

(4) With Ba^{++} and $Co(en)_3^{+++}$ the half-neutralization point is at about pH 8; the displacement by 1 pH unit is due to strong adsorption of these cations on the polymer framework—an effect already detected from the swelling measurements.

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