174. Properties of Ion-exchange Resins in Relation to Their Structure. Part V.* Exchange of Organic Cations.

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Studies have been made of the absorption of quaternary ammonium ions by sulphonated polystyrene resins of different cross-linking. In column experiments using neutral solutions of the quaternary chlorides, the amount absorbed was found to decrease with increase in the degree of cross-linking of the resin and, in general, with increase in the size of the organic cation.

In equilibrium studies with a 15% divinylbenzene resin, the amount of tetraethylammonium ion taken up from alkaline solution was equal to the theoretical exchange-capacity of the resin, but at pH 5, the uptake was about half the full capacity. This marked dependence of the absorption on pH—which is not observed with simple inorganic cations—corresponds to a sharp decline in the affinity of the organic cation for the resin as the latter absorbs more of the quaternary ion. Thus the relative affinity coefficient K_H^Q decreases from about 10 to 10^{-5} as the equivalent fraction of quaternary ion on the resin $X_{\bar{Q}}$ increases from 0·1 to 0·9.

Changes in certain properties of the resin were observed after complete conversion into the tetraethylammonium form; in particular, the weight-swelling increases and the affinity for potassium ion decreases. It appears that the resin undergoes an irreversible change in structure, consistent with a decrease in the degree of cross-linking. Swelling data indicate that, at low values of $X_{\bar{Q}}$, absorption of tetraethylammonium ion by the 15% divinyl-benzene resin is accompanied by displacement of an equal volume of water, the volume of the resin phase being virtually unchanged. At high values of $X_{\bar{Q}}$, absorption of quaternary ions causes an irreversible distension of the resin structure.

THE influence of the degree of cross-linking of the resin on the ion-exchange behaviour of sulphonated polystyrenes in reactions with simple cations, *e.g.*, sodium and hydrogen, has been described in Part IV (*loc. cit.*). It seemed desirable to extend this study to large organic cations where the effects of polymer structure and ionic size would be expected to be even more pronounced.

With a phenolsulphonic acid resin, the affinities of quaternary ammonium ions have been shown to increase with increasing ionic size, the effect being attributed to increasing van der Waals forces (Kressman and Kitchener, *J.*, 1949, 1208). Similar results have been obtained with sulphonated polystyrenes of low cross-linking; but with resins of high cross-linking, the affinity decreases considerably with increase in ionic size and also with increase in cross-linking (Gregor and Bregman, *J. Colloid Sci.*, 1951, **6**, 323). Over a wide range of cross-linking, the rates of exchange of quaternary ammonium ions on sulphonated polystyrenes decrease with increase in both ionic size and degree of cross-linking (Gregor *et al.*, *ibid.*, p. 20). The exchange of large organic ions is so slow, indeed, that with commercial resins of this type, the amount absorbed in column experiments under practical conditions is normally much less than the theoretical exchange-capacity of the resin, a value readily obtained with univalent metallic cations (Gregor *et al.*, *loc. cit.*; Pepper, *J. Appl. Chem.*, 1951, **1**, 124). Evidence regarding the equilibrium absorption of quaternary ammonium ions is conflicting. Kressman (*J. Physical Chem.*, 1952, **56**, 118) concluded that the saturation capacity of a commercial sulphonated polystyrene resin for tetramethyl- and tetraethyl-ammonium ions was appreciably lower than that for ammonium ion. In these experiments, the hydrogen form of the resin was treated with solutions of the quaternary ammonium salts. Using the hydroxides, in otherwise similar experiments, Gregor *et al.* (*loc. cit.*) found that many quaternary ammonium cations (with the possible exception of tetra-*n*-butylammonium) gave saturation capacities identical with that of univalent metallic ions even with highly cross-linked resins.

* Part IV, *J.*, 1952, 3129.

These effects are of practical importance for the following reasons. (*a*) The effective capacity of a resin used for the removal or recovery of ions from solution should be as high as possible. It may be advantageous, therefore, to employ lightly cross-linked resins (possessing high swelling) for the absorption of large ions (Kunin and Myers, *Discuss. Faraday Soc.*, 1949, **7**, 114). (*b*) In difficult chromatographic separations, it is very desirable that the rates of exchange of ions between resin and solution should be high. Improved separations of amino-acid mixtures have been obtained by reducing the degree of cross-linking of the resin (Partridge, Brimley, and Pepper, *Biochem. J.*, 1950, **46**, 334). (*c*) Resins may be employed as " ionic sieves " in separations based upon differences in rates of exchange or saturation capacities of the different ions in a mixture (Kressman and Kitchener, *Discuss. Faraday Soc.*, 1949, **7**, 90; Partridge, *Nature*, 1952, **169**, 496).

In this investigation, a broad survey was first made of the behaviour of a number of organic cations toward sulphonated polystyrenes of different cross-linking. Since the equilibrium absorption of cations under alkaline conditions may be influenced by the dissociation constants of the corresponding bases, only quaternary ammonium cations and the cations of strongly basic dyes were examined. The absorption of tetraethylammonium ions on a resin of 15% nominal divinylbenzene content and the accompanying swelling changes were then studied in greater detail.

EXPERIMENTAL

Materials.—Sulphonated polystyrenes, containing nominally 2, 5, 10, and 15% of divinylbenzene (DVB) and possessing weight-swellings of 3·50, 1·47, 0·84, and 0·62 g. of water per g. of dry hydrogen-form resin, were prepared (Pepper, *loc. cit.*). After treatment with 2N-sodium hydroxide and 2N-hydrochloric acid, fractions of wet particle diameter within the range 230—270 μ were obtained by wet elutriation (Reichenberg, *J. Amer. Chem. Soc.*, in the press). These fractions were used in the column experiments; other fractions of the 15% divinylbenzene resin were obtained for the equilibrium experiments.

Recrystallised, laboratory-grade quaternary ammonium salts and dyes were used. Quaternary salts not commercially available were prepared by standard methods. For example, trimethyl-*n*-octylammonium iodide was prepared by reaction of *n*-octyl iodide with trimethylamine in nitromethane at 50° and recrystallisation of the product from alcohol–ether. Iodides and bromides were converted into the corresponding chlorides by passing a solution through a column of Amberlite IRA-400 (supplied by Messrs. British Drug Houses Ltd.) in the chloride form. Similarly, solutions of the quaternary ammonium hydroxides were obtained from the corresponding salts by using a column of Amberlite IRA-400 in the hydroxide form. The solutions of chlorides and hydroxides were standardized by titration with silver nitrate and hydrochloric acid respectively, and then diluted to the required concentration.

Column Experiments.—The bed of resin (4·0 × 0·4 cm. diameter), supported in a glass tube between two glass wool plugs (Djurfeldt and Samuelson, *Acta Chem. Scand.*, 1950, **4**, 165), was converted into the hydrogen form with 2N-hydrochloric acid and washed with deionized water. A 0·02N-solution of the quaternary ammonium chloride (pH 5·1) was then passed through the column at a constant rate of 0·5 ml. per minute, this rate being controlled by a dosage capillary and a constant-head device (*idem, ibid.*). The acid liberated in the exchange-reaction, QCl + HR $\rightleftharpoons$ QR + HCl, was determined by titrating the effluent with 0·02N-sodium hydroxide at appropriate intervals. The amount of quaternary ion absorbed was expressed as a percentage of the total exchange-capacity of the column for sodium ion, previously determined by using 0·02N-sodium chloride. In experiments with the salts of basic dyes, the titrations were carried out by means of a glass electrode and a direct-reading pH meter (Electronic Instruments Ltd.).

The absorption of quaternary ammonium ions from 0·02N-solutions of their hydroxides was determined by a procedure similar to the above except that the effluent was titrated at intervals with 0·02N-hydrochloric acid. The amount of quaternary ion taken up by the resin was then calculated from the volume of solution passed and this titre.

Equilibrium Experiments.—The uptake of tetraethylammonium ions on a 15% divinylbenzene resin (wet particle diameter 100—150 μ) from solutions of approx. constant total cationic concentration (0·02N) was determined as a function of the equilibrium pH. In one set of experiments, the resin samples were initially in the hydrogen form, and in a second set they started in the quaternary ammonium form. In the first set, different known amounts of 0·04N-tetraethylammonium hydroxide and 0·04N-tetraethylammonium chloride were added to flasks

containing weighed samples (approx. 0·2 g.) of air-dry hydrogen resin; in some cases 0·04N-hydrochloric acid was added instead of the hydroxide to give the more acidic systems. After dilution to 100 ml. with water, the flasks were shaken for 3 weeks at 25°; aliquots were then removed for determination of the pH of the solution (Doran " Alkacid " glass electrode) and for estimation of excess of acid or base by back-titration. In the second set of experiments, weighed samples of air-dry resin were converted into the quaternary form by a week's shaking with 0·04N-tetraethylammonium chloride and 0·04N-tetraethylammonium hydroxide, the amount of quaternary hydroxide added being equivalent to roughly twice the capacity of the resin samples. Different amounts of 0·04N-hydrochloric acid were then added, and the solutions made up to 100 ml. After 2 weeks' shaking, aliquots were removed for determination of pH and back-titration as before. The moisture content of duplicate samples of the air-dry resin was determined by drying (P_2O_5) *in vacuo* at 110°.

A comparison was also made of the absorption of tetraethylammonium ions by two different-sized fractions of the 15% divinylbenzene resin: (*a*) 50—100 μ and (*b*) 200—250 μ particle diameter. In principle, the hydrogen form of each fraction was titrated directly with the quaternary hydroxide, in presence of its chloride salt, to the pH given by an internal indicator of the anionic type. Samples of each size fraction (approx. 0·15 g.) were weighed into flasks and a mixture of 0·02N-tetraethylammonium hydroxide and 0·02N-tetraethylammonium chloride (total vol. 100 ml.) was added, the amount of quaternary hydroxide being less than the expected capacity of the resin at the pH under examination. After addition of a few drops of indicator solution, the flasks were shaken for 1—2 days, whereupon the solution became acid. This was due to absorption of organic cations, with consequent liberation of hydrogen ion in excess of the amount of quaternary hydroxide added. The excess of acid was titrated with tetraethylammonium hydroxide and the flasks again shaken. This procedure was repeated until there was no significant change in the colour of the indicator after a further 1—2 days' shaking. In all, the experiments required about 5 days. Equilibrium capacities at pH values of approx. 5, 7, and 9 were obtained by using bromocresol-green, phenol-red, and phenolphthalein as indicators.

RESULTS AND DISCUSSION

Column Experiments with Quaternary Ammonium Ions.—Curves of the form shown in Fig. 1 were obtained when the absorption of quaternary ammonium ions from *neutral* solution (expressed as a percentage of the capacity of the resin sample for sodium ion) was plotted against time or volume of effluent. The initial linear portion of the curve corresponds to complete removal of quaternary ion from solution; under the conditions used, the slope is determined by the capacity of the resin sample, which, since equal *volumes* of resin were taken, increases with increasing cross-linking.

With tetramethylammonium ion, the full capacity of the 2% divinylbenzene resin was attained; but with resins of higher cross-linking, the absorption of quaternary ion appeared to level off at much lower values. The amount of quaternary ion absorbed continued to increase slightly during 7 days; in general, however, the increase was small and the results obtained after 4 hours, as given in the following Table, may be taken as near-equilibrium values.

Absorption from neutral solution (pH 5·1).

	Nominal % of divinylbenzene			
	2	5	10	15
Tetramethylammonium (74)	100	90	69	63
Tetraethylammonium (130)	100	87	63	48
Benzyltrimethylammonium (150)	100	94	80	58
Trimethyl-*n*-octylammonium (172)	100	100	71	38
Dibenzyldimethylammonium (226)	100	94	43	15
Cetyltrimethylammonium (284)	74	48	10	—

The above values for the absorption of tetramethyl- and tetraethyl-ammonium ions on a 10% divinylbenzene resin (weight-swelling, 0·84) are in fair agreement with the results, 76% and 62%, obtained from neutral solutions by Kressman (*loc. cit.*) with a commercial resin of this type (weight-swelling, 0·80).

In all cases, the capacity for a given cation decreases with increasing cross-linking. The specific capacity of the resins for simple cations, when referred to unit bed-volume,

increases markedly with increase in divinylbenzene content, and hence on this basis the capacity for certain quaternary ions shows a maximum with resins of medium cross-linking. Thus the capacities of different resins for benzyltrimethylammonium ion expressed in mg.-equivs. per ml. of bed-volume are : 2%, 0·66; 5%, 1·15; 10%, 1·30; 15%, 1·19.

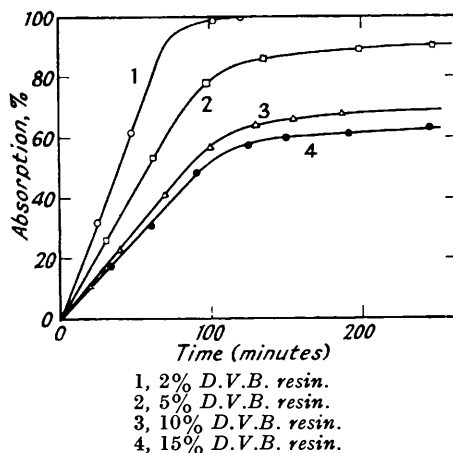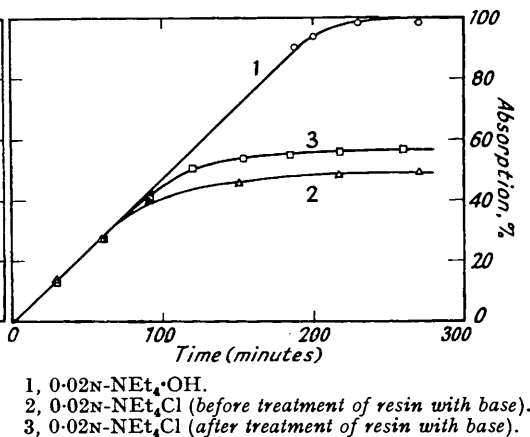FIG. 1. *Absorption of tetramethylammonium ion from neutral solution.*

FIG. 2. *Absorption of tetraethylammonium ion by 15% D.V.B. resin.*

1, 2% *D.V.B. resin.*
2, 5% *D.V.B. resin.*
3, 10% *D.V.B. resin.*
4, 15% *D.V.B. resin.*

1, 0·02N-NEt$_4$·OH.
2, 0·02N-NEt$_4$Cl *(before treatment of resin with base).*
3, 0·02N-NEt$_4$Cl *(after treatment of resin with base).*

The Table reveals a general tendency for the capacity to decrease with increase in the molecular weight of the organic cation (given in parentheses). There are, however, some anomalies; in particular, with the 5% and 10% divinylbenzene resins the capacity for tetramethyl- and tetraethyl-ammonium ion is lower than that for benzyltrimethyl- or trimethyl-*n*-octylammonium ion. This effect may be due to an increased contribution of

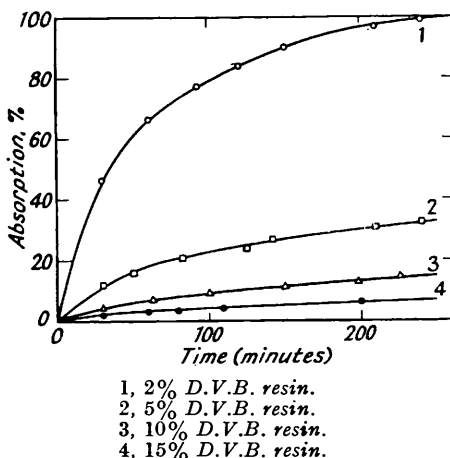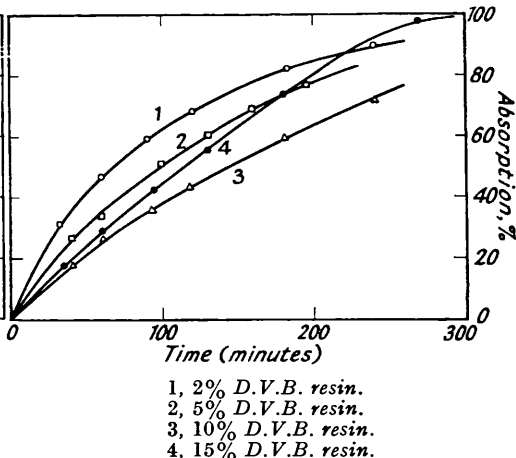FIG. 3. *Absorption of phenosafranine from neutral solution.*

FIG. 4. *Absorption of acridine-orange and zinc from neutral solution.*

1, 2% *D.V.B. resin.*
2, 5% *D.V.B. resin.*
3, 10% *D.V.B. resin.*
4, 15% *D.V.B. resin.*

1, 2% *D.V.B. resin.*
2, 5% *D.V.B. resin.*
3, 10% *D.V.B. resin.*
4, 15% *D.V.B. resin.*

van der Waals forces to the affinities of the larger organic cations, or possibly to hydration of the tetramethyl- and tetraethyl-ammonium ions.

The absorption of tetraethylammonium ions on a 15% divinylbenzene resin from a solution of the quaternary ammonium hydroxide is compared in Fig. 2 with the data obtained by using the quaternary ammonium chloride. From *alkaline* solution, the full capacity of the resin was readily achieved, but from *neutral* solution the curve of results

tended to level off at about 48% of the full capacity. With the same resin, dibenzyl-dimethylammonium ion showed a much higher capacity from alkaline solution (40%) than from neutral solution (15%). An effect of this magnitude was quite unexpected, since the capacity of monofunctional, strongly acidic resins for simple cations is substantially the same from neutral as from alkaline solution. The special behaviour of quaternary ammonium ions was therefore examined in greater detail.

Column Experiments with Basic Dyes.—The absorption of basic dyes from neutral solution was very slow, especially with the more highly cross-linked resins. The results obtained with phenosafranine chloride (Fig. 3) are typical; it will be seen that the linear portion of the curves is greatly reduced and that the " break-through " volume is small. Since absorption continued slowly over long periods, the 4-hour results given in the next Table do not represent equilibrium values but are of interest for comparative purposes. The rate of exchange of basic dyes and the final equilibrium may be expected to be influenced by the tendency to form aggregates in solution.

	Nominal % of divinylbenzene			
	2	5	10	15
Safranine (211)	43	13	—	—
Phenosafranine (287)	100	32	14	7
Methylene-blue (284)	56	25	12	7

In experiments with a 0·5% solution of the double salt of acridine-orange and zinc chloride (B.D.H. standard stain), it appeared that absorption (as measured by the amount of hydrogen ion liberated to solution) takes place more rapidly with the 15% than with the 10% divinylbenzene resin (Fig. 4). The curve for the 15% resin probably relates to the comparatively unhindered absorption of zinc cations, since the dye would be absorbed to a negligible extent. However, with the 10% resin, slow absorption of the organic cations apparently interferes with the absorption of zinc so that the uptake of zinc and dye cations proceeds more slowly. Clearly, a resin of comparatively high degree of cross-linking may be advantageous in applications involving the removal of inorganic ions from large organic electrolytes.

Equilibrium Experiments.—The amount of tetraethylammonium ion taken up by a 15% divinylbenzene resin is plotted in Fig. 5 against the pH of the ambient solution. The conclusions drawn from the column experiments are confirmed in that the full exchange-capacity of the resin is achieved in alkaline solution but at pH 5 the uptake is greatly reduced. In the lower pH range, the amount of quaternary ion absorbed by resin initially in the quaternary form is slightly greater than that absorbed by resin starting in the hydrogen form; *prima facie* this effect might be attributed to failure to achieve equilibrium, but this explanation is considered unlikely in view of other evidence. Of particular significance are the results given in the next table, which were obtained by using the internal indicator technique with fractions of the 15% resin of two sizes.

NEt_4^+ absorbed (mg.-equivs. per g. of dry hydrogen resin).

| Particle-diameter	Approx. pH of solution			Particle-diameter	Approx. pH of solution		
	5	7	9		5	7	9
50—100 μ	3·35	4·50	5·20	200—250 μ	3·30	4·65	5·05

The close agreement between the results obtained with the two sizes strongly suggests that in these experiments, where 5 days' shaking was required, true equilibrium was achieved. Hence it may be concluded that the 2—3 weeks' shaking allowed for the experiments with resin of intermediate size (Fig. 5) was entirely adequate. It is believed that both curves in Fig. 5 represent equilibrium conditions and that, on complete conversion into the tetraethylammonium form, the resin suffers an irreversible change in structure with consequent changes in behaviour. Additional evidence for this irreversible change is discussed in the next section.

In dilute solution, the relative affinity coefficient of the resin for tetraethylammonium ion is given by $K_{\bar{H}}^{\bar{Q}} = [\bar{Q}][H]/[\bar{H}][Q]$, where $[\bar{Q}]$ and $[\bar{H}]$ are the amounts of quaternary ion and hydrogen ion on the resin, $[Q]$ and $[H]$ being the concentrations in solution. Approx-

imate values of K_H^Q have been calculated from the results obtained in the equilibrium experiments at 0·02N total cation concentration; in Fig. 6, $\log_{10} K_H^Q$ is plotted against $X_{\bar{Q}}$, *i.e.*, the equivalent fraction of quaternary ion on the resin. At low values of $X_{\bar{Q}}$, the affinity is of the order of 10 but it decreases sharply as the resin becomes more nearly converted into the quaternary form. A similar trend is observed with simple cations (Reichenberg, Pepper, and McCauley, *J.*, 1951, 493), but the decrease with tetraethyl-ammonium ion which extends over several powers of ten is much more pronounced.

Since the affinity is very small at high values of $X_{\bar{Q}}$, the quaternary form of the resin can be partially regenerated readily with dilute acid. The remaining quaternary ion is, however, difficult to remove because the affinity is much greater than unity at low values of $X_{\bar{Q}}$. For example, a small column of the 15% divinylbenzene resin (capacity 5·11 mg.-equivs.) was converted into the tetraethylammonium form and then regenerated with approx. 0·1N-hydrochloric acid. The first 50 ml. of acid (5·12 mg.-equivs.) removed 4·14 mg.-equivs. of quaternary ion which corresponds to 81% regeneration; a second 50 ml., however, removed only a further 0·54 mg.-equiv. of quaternary ion. Similar behaviour has been observed during the regeneration of cation-exchange resins used for the absorption of nicotine and quinine (Sussman, Mindler, and Wood, *Chem. Industries*, 1945, **57**, 455, 549); the effect was previously attributed to a residual " storage " capacity.

FIG. 5. *Relationship between* NEt₄⁺ *taken up by* 15% *D.V.B. resin and* pH.
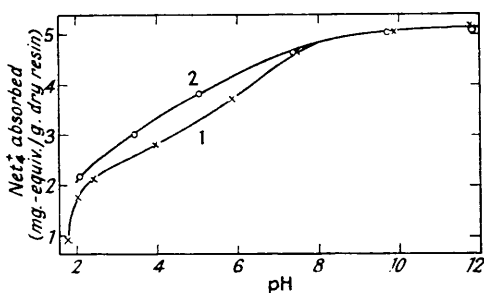
FIG. 6. K$_H^Q$ *for* 15% *D.V.B. resin at* 0·02N-*total cation concentration.*

1, *Resin initially in hydrogen form.*
2, *Resin initially in quaternary form.*
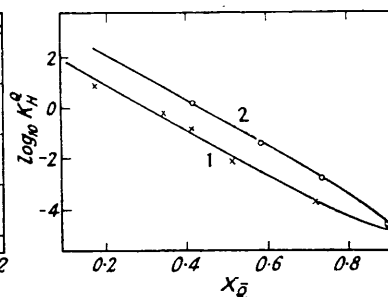
1, *Resin initially in hydrogen form.*
2, *Resin initially in quaternary form.*

Irreversible Behaviour.—Several observations support the view that the 15% divinyl-benzene resin undergoes irreversible structural changes on complete conversion into the tetraethylammonium form. In the column experiments (Fig. 2), it was observed that, after treatment with quaternary hydroxide, the resin had a higher capacity for quaternary ion from neutral solution than before, the absorption increasing from 48% to 57% of the full capacity. The capacity of the treated resin was a little lower than that of a 10% resin (63%). Significant changes in the apparent volume of the resin sample were also noted in similar experiments. The following table gives the settled bed-volumes (expressed as percentages of the initial value for the hydrogen form) after successive treatments of the hydrogen resin with 0·02N-solutions of (*a*) hydrochloric acid, (*b*) tetraethylammonium chloride, and (*c*) tetraethylammonium hydroxide. The measurements of settled bed-volumes were reproducible to ± 2%.

	1st Cycle	2nd Cycle	3rd Cycle
(*a*)	100	115	114
(*b*)	103	131	—
(*c*)	134	134	—

In the first cycle, the bed-volume was not significantly affected by the treatment with quaternary chloride, but when the quaternary hydroxide was used a marked expansion resulted. Some change in bed-volume persisted in subsequent cycles, but the effect does not appear to be progressive since, after the first cycle, the bed-volumes of the hydrogen and tetraethylammonium forms remained the same and there was no further increase in the capacity for quaternary ion from neutral solution. After each cycle, the capacity

3 K

of the resin for sodium ion was found to be equal to the initial value, thus proving that regeneration of the resin had been complete and that no gross degradation, involving loss of sulphonic acid groups, had taken place.

Additional evidence of structural change was provided by determinations of the weight-swelling of the 15% divinylbenzene resin in water. Samples in the hydrogen and in the tetraethylammonium form were examined and also the mixed hydrogen–quaternary forms as obtained from the equilibrium experiments at different pH. The centrifuge technique (Pepper, Reichenberg, and Hale, *J.*, 1952, 3129) was used, giving the results shown in Fig. 7, where $(W_M)_H$, *i.e.*, the weight of water absorbed by an amount of the M-form of the resin equivalent to 1 g. of dry hydrogen form, is plotted against $X_{\bar{Q}}$. After conversion into the quaternary form and subsequent regeneration, the resin had a weight-swelling of 0·78 g. of water per g. of dry resin, compared with the original value of 0·62. This new value corresponds to that of a resin containing 11% of divinylbenzene (Pepper *et al.*, *loc. cit.*).

All the changes described above in the behaviour of the 15% resin on conversion into the tetraethylammonium form are consistent with a small decrease in the degree of cross-linking of the polymer structure. Further confirmation of this view was afforded by determination of the relative affinity coefficient of the resin for potassium ion, K_H^K, at low $X_{\bar{K}}$—previous work having shown this property to be a sensitive criterion of cross-linking with resins of high divinylbenzene content (Reichenberg *et al.*, *loc. cit*). At $X_{\bar{K}} = 0\cdot2$,
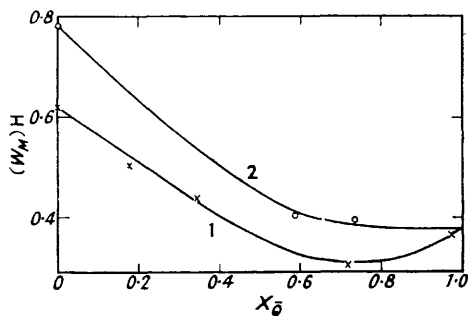

FIG. 7.   *Relationship between weight-swelling of 15% D.V.B. resin and* $X_{\bar{Q}}$.

1, *Resin initially in hydrogen form.*
2, *Resin initially in quaternary form.*

the relative affinity coefficient of the 15% resin was 6·7 $\pm$ 0·2, whilst that of the resin after conversion was 5·0 $\pm$ 0·2, corresponding to a 12% divinylbenzene resin. [The measurements of relative affinity coefficients were made by Mr. D. J. McCauley using the technique described in the paper cited above.]

It may be noted that, after complete conversion into the quaternary form, the resin beads showed surface cracks under the microscope, and it is possible that rupture of weak cross-links is responsible for the changes in behaviour observed.

Conclusions.—It will be seen from Fig. 7 that, starting with resin in the hydrogen form, the absorption of tetraethylammonium ion is accompanied by a decrease in the weight-swelling of the resin. At low values of $X_{\bar{Q}}$, the slope of the curve corresponds to a loss of about 7 mol. of water for each quaternary ion absorbed; this loss corresponds in turn to a volume of 210 Å³. The measurements of settled bed-volumes indicated, however, that the resin undergoes little change in volume at low values of $X_{\bar{Q}}$; hence it appears that the quaternary ion absorbed balances, in volume, the water lost. The mean diameter of the tetraethylammonium ion estimated from atomic models (Settatree, Thomas, and Yardley, *Nature*, 1950, **166**, 59) is of the order of 7·5 Å, giving a volume of 220 Å³ which is in reasonable agreement with the above value (210 Å³) for the volume of water lost. We conclude that *during the initial stages of the exchange-reaction*, where the resin volume is virtually unchanged, the absorption of a quaternary ion is accompanied by the displacement of a nearly equal volume of water—at least with a 15% divinylbenzene resin. From this result we infer that the uptake of quaternary ion may be determined in part by the volume of water available within the resin. The latter concept is in accord with the experimental observation that for a resin of given cross-linking, *i.e.*, possessing a fixed weight-swelling, the amount of quaternary ion absorbed from neutral solution tends to decrease as the

volume of the quaternary group increases. It is also consistent with the observation that the absorption of a given quaternary ion decreases with increasing cross-linking, *i.e.*, with decreasing weight-swelling.

At *high* values of $X_{\overline{Q}}$, the weight-swelling curve (Fig. 7) passes through a minimum, indicating that on absorption of further quaternary ion, the resin no longer loses the corresponding amount of water. This behaviour correlates well with other evidence that absorption of quaternary ion in this region causes an expansion of the resin, which is partly irreversible. The change in structure due to this irreversible distension corresponds with a decrease in the apparent degree of cross-linking of the copolymer from that of a 15% divinylbenzene resin to that of a resin containing 11—12% of divinylbenzene.

In view of these effects, it is clear that great caution is needed in the interpretation of data obtained in exchange-reactions involving large organic ions.