ION EXCHANGE
AND ITS APPLICATIONS

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9.30 *a.m., Monday, 5th April,* 1954

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INTRODUCTION

By

C. W. DAVIES

THE history of ion exchange has been told by several recent authors.[1–4] The papers of Thompson and Way, now a hundred years old, are classics in soil science, and in general chemistry the work of Gans and the widespread use of synthetic zeolites for water softening provide another familiar landmark. In some ways the zeolites are ideal for theoretical studies in ion exchange, and important work in this field is being done by Barrer.[5] Their practical use is beset by limitations, however, and the great developments of recent years in the use of ion exchange are due almost entirely to the organic exchangers now available.

These were first prepared and studied by B. A. Adams and E. Leighton Holmes at the Chemical Research Laboratory, and described by them in a paper read before the London Section of this Society in December 1934, and published in the Transactions for 1935. Ion-exchange resins have been greatly improved since then, but in this first paper most of their possible applications were given; for softening or completely deionizing water, for removing impurities, for recovering valuable material present in small concentrations, for the separation of ions and for preparing new materials by ion exchange. These potentialities captured the imagination at once, and here, in Germany and in the United States work was actively pursued. Owing to the war, little is to be found in European literature for a number of years, though a paper by Griessbach,[6] some valuable pioneering work by Samuelson,[7] and the development of kits for desalting sea-water are noteworthy. On the whole, however, the initiative seems to have passed largely to America, where the manufacture of resins was improved, data regarding their behaviour became available, and many technical applications were vigorously developed in a semi-empirical way.

With the end of the war it was obvious that here was a most promising field of study, and since then further development has been rapid, in part stimulated by the simultaneous growth of chromatography as a major chemical technique. The technical literature is still largely American, but in the basic studies of ion exchange which by this time were overdue it can fairly be claimed that British chemists have more than held their own—thanks, in great measure, to the active research schools represented in the three following contributions.

Exchangers are now available which behave as insoluble strong acids, strong bases, weak acids or weak bases. Those based on polystyrene are very stable and chemically inert, and can be prepared by suspension polymerization as beads of any desired size. A major difference in the behaviour of strong and weak exchangers is that whereas the former, in their commercial forms, are freely permeable to ions so that exchange is a quite rapid process, with weak exchangers this is only true of the ionized forms, i.e. of weak acids at high pH or weak bases at a low pH; an exchanger containing carboxylic groups will be almost un-ionized, and will swell little in dilute acid solution, and when the pH is raised, its complete penetration by cations from the solution will require hours rather than minutes.

The number of active groups in a resin, and the degree of cross-linking, can both be varied between very wide limits. Materials have been studied which range all the way from surface-sulphonated beads which are analogous to glass surfaces or inorganic precipitates in that ion exchange is a surface property, through tightly cross-linked resins which can be penetrated only by small ions and in which diffusion is relatively slow, to very lightly cross-linked resins which can take up many times their own volume of solution, and which then (apart from the non-diffusibility of the ionized groups anchored to the resin network) may themselves be treated for most purposes as an aqueous phase.

The commercial resins represent a compromise in which the cross-linking is not great enough to impede seriously the diffusion and exchange of ions, but is sufficient to prevent large swelling effects. Are we to regard such a material as an adsorbent with a very large internal surface at which ion exchange can occur, or as a homogeneous phase which can exchange its diffusible ions with the surrounding solution? The answer must depend on the problem being studied and the range of the intermolecular forces involved; and, although neither analogy can be perfect, each can be useful under given conditions. If the system contains only simple inorganic ions, the behaviour of these will be governed primarily by electrostatic forces, and the resultant of long-range Coulomb forces in the resin will be much the same as if the charges were homogeneously dispersed; in such systems, therefore, it is a good approximation to regard the ions in the resin as existing in a concentrated aqueous solution.[8,9] If, on the other hand, the added solution contains an organic non-electrolyte, interfacial effects can no longer be ignored, and preferential adsorption on the resin network may become important. The system now has analogies with a solid adsorbent in contact with solution, and the common adsorption equations can in fact be applied to the non-electrolyte taken up by the resin phase.[10] In equilibria involving non-ideal, and particularly organic, ions, the above effects are superimposed, and the affinity of the resin for the ion will depend both on the electrostatic factors (charge, effective size) and on van der Waals attractions.[11]

In many applications of exchange resins the differences in the affinity of the resin for different ions (usually small, for ions of the same valency) are not involved. A dissolved ion, in passing down a resin column, can encounter many millions of exchange sites in every centimetre, and exchange is therefore very efficient. Such a process is completely reversed when an excess of a regenerating solution is applied. In chromatographic procedures, on the other hand, these small differences in affinity are exploited in the separation of ions, and are often supplemented by using complexing agents (or, with weak electrolytes, by adjusting the pH) to reduce still further the retention of the ion by the resin for which it has the smaller affinity.[12] The use of ion exchangers in chromatography will be fully discussed in the course of the Conference. They combine a high capacity with the sensitivity and flexibility of other chromatographic media, and enable any element which forms an ion to be separated from any other in the periodic table.[4] Even so, the almost bewildering versatility of partition chromatography has not yet been much exploited in this field.

Much interest has been shown recently in the use of ion-exchange resins in the form of membranes. The behaviour of these (as, indeed, of resins in columns) will depend on the exact composition of the resin phase, and it may be useful to close this introduction with an example taken from experimental results.[9] If a sulphonated polystyrene resin containing 5·5% of divinylbenzene is brought into equilibrium with 0·5 molal HCl solution, it is found to absorb 1·38 times its dry weight of water. On the basis of this water content the concentration of hydrogen ions in the resin is 3·85 molal, and that of the chloride ions is 0·050 molal, the remainder of the hydrogen ions balancing the non-diffusible sulphonate groups. These figures can be understood by reference to the Donnan theory of membrane equilibria. A thermodynamic balance between the resin and solution phases includes a strain-energy term, but as a rough approximation this can be neglected and the condition for equilibrium is then $f_{\pm}^{2}[H^{\cdot}][Cl'] = \bar{f}_{\pm}^{2}[\bar{H}^{\cdot}][\overline{Cl}']$, where bars are superimposed on symbols referring to the resin phase. The concentration products in the present example are 0·25 and 0·19 respectively, the difference being primarily caused by differences in the activity coefficients. In a membrane made of this material, rather more than 1% of the diffusible ions would be chloride ions, and as a cationic membrane it would not be highly efficient owing to leakage of chloride. A more tightly cross-linked resin, of the same exchange capacity but containing 10% of divinylbenzene, absorbs 0·86 times its dry weight of water; the concentration of hydrogen ion is correspondingly higher, at 6·17M, and the chloride ion concentration drops to 0·012M. In a membrane of this material, a very high proportion of electrolytic transport would be in the direction of the cathode, and diffusion through the membrane of chloride ion would be greatly reduced. But every such improvement will be accompanied by a reduction in the rate of diffusion and an increase in electrical resistance, so again a compromise appears to be necessary.

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ION-EXCHANGE RESINS. STRUCTURE, SYNTHESIS AND GENERAL PROPERTIES

By

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1. Introduction

THE rapid progress which has taken place during the past ten or fifteen years in the development of new ion-exchange resins has largely been a result of the stimulus provided by the need for improved materials in industrial applications. In these developments much use has been made of existing knowledge of the chemistry of high polymers. The more recently developed ion-exchange resins, with their simple and well-defined structures, have been widely used for fundamental investigations that have not only added greatly to our knowledge of ion-exchange processes but have, in their turn, led to the introduction of new materials and new applications.

For many purposes ion-exchange resins may be regarded as insoluble acids or bases, the salts of which are also insoluble. The characteristic reactions of ion-exchange resins may be illustrated by the behaviour of an acidic resin (cation exchanger) in the hydrogen form (represented by HR). The resin may be neutralized with sodium hydroxide giving the sodium salt of the resin (NaR):

$$HR + NaOH \longrightarrow NaR + H_2O$$

The sodium salt of the resin can then be converted back to the hydrogen form by treatment with acid, e.g. $NaR + HCl \rightleftharpoons HR + NaCl$.

As this is a reversible process a cation-exchange resin in the hydrogen form can also be used for the liberation of acids from their salts; this latter reaction provides a convenient method for assessing the acid strength of a cation exchanger. A third reaction of acidic resins is that of base-exchange, e.g.

$$2NaR + CaSO_4 \rightleftharpoons CaR_2 + Na_2SO_4$$

This reaction is the basis of the use of cation-exchange resins for water softening.

Anion-exchange resins show analogous behaviour. The free base forms may be neutralized with acids and regenerated with alkali, and the salts used for the exchange of anions.

Fundamental studies of the behaviour of ion-exchange resins have established certain important features of the ion-exchange process. With a cation-exchange reaction such as $BR + A^+ \rightleftharpoons AR + B^+$, the following generalizations may be made:

(*a*) *Ion-exchange reactions are stoicheiometric*
That is for every g.equiv. of the exchanging-ion A^+ taken up by the resin, a g.equiv. of the ion B^+ is liberated to the solution. The equivalence of exchange is, however, sometimes obscured by other effects.

(*b*) *Ion-exchange reactions are, in general, reversible*
In the reaction shown above, the forward reaction will only approach completion if the resin absorbs A^+ much more strongly than B^+, or if there is a large excess of A^+ ions relative to the B^+ ions liberated to the solution. The forward reaction will also proceed more readily if B^+ ions are removed from the system through the formation of an incompletely dissociated compound, e.g. by complex formation.

(*c*) *Ion-exchange resins show no exchange hysteresis*
The ionic composition of a resin in equilibrium with a given solution is always the same, irrespective of the direction in which equilibrium is approached. Where hysteresis is apparently observed this may be due to failure to attain equilibrium or to changes in the structure of the resin.[1]

(*d*) *All the acidic (or basic) groups in an ion-exchange resin are accessible as exchange sites for small ions*
The total exchange capacity (expressed in g.equiv.) is therefore the same for all small ions and is quite independent of particle size; it is much greater than that of alumina or silica where absorption is restricted to the surface. The full capacity of the resin is determined simply by the number of ionized groups per unit mass or unit volume. In the laboratory the total exchange capacity is usually expressed as mg.equiv. per g. of dry resin (hydrogen or chloride form), or in column experiments as mg.equiv. per ml. of apparent volume.

2. Chemical structure and synthesis

Ion-exchange resins consist essentially of a cross-linked polymer network to which are attached ionized or ionizable groups. In the case of cation-exchange resins these groups are acidic groups (e.g. $-SO_3H$, $-PO_3H_2$, $-CO_2H$, phenolic $-OH$), while in anion-exchange resins the groups are basic in character (e.g. quaternary ammonium, aliphatic or aromatic amine groups). Although ion exchangers containing acidic or basic groups of intermediate strength have been prepared, nearly all the commercial resins may be classified into four main types, namely strongly acidic and weakly acidic cation-exchange resins, and strongly basic and weakly basic anion-exchange resins. It should be noted that most of the earlier ion-exchange resins contained two or more different types of active group, i.e. they were polyfunctional. Polyfunctional resins are classified according to the nature of the strongest group since this plays the dominant part in determining the ion-exchange behaviour.

In the synthesis of ion-exchange resins, the ionizable groups may be attached to the monomers or intermediates used in the preparation of the cross-linked polymer, or they may be introduced subsequently into a preformed polymer. For the preparation of the resin itself, either a polycondensation reaction or a vinyl-type polymerization may be employed. Methods which have been used for the preparation of the four main types of ion-exchange resins are described below:

(*a*) *Strongly acidic cation-exchange resins*

The earlier strongly-acidic resins were prepared by polycondensation reactions, for example by the condensation of phenol, phenolsulphonic acid and formaldehyde in the presence of sodium hydroxide as catalyst.[2, 3] The reaction mixture is evaporated until a gel is obtained which is dried and ground. The degree of cross-linking of the exchanger can be varied by varying the proportions of phenol and phenolsulphonic acid in the reaction mixture. Several procedures of this type were developed by I.G. Farben at Wolfen for the manufacture of different types of cation-exchange resins.[4] Wofatit K and Wofatit KS were prepared by the condensation of benzaldehyde-2 : 4-disulphonic acid, phenol, resorcinol and formaldehyde under alkaline and acid conditions respectively. Wofatit P was obtained by the condensation of cresol-ω-sulphonic acid (prepared from phenol, formaldehyde and sodium sulphite) with phenol and formaldehyde. The resin was subsequently treated with concentrated sulphuric acid to increase the number of sulphonic acid groups. It may be noted that resins containing methylenesulphonic acid groups are more stable than resins containing nuclear sulphonic acid groups. They can be prepared by methods similar to that just described or a phenol–formaldehyde resin may be treated with formaldehyde and sodium sulphite.[5, 6]

The most important of the cation-exchange resins are the strongly acidic resins prepared by the sulphonation of styrene–divinylbenzene copolymers. This synthesis, which was originally described by D'Alelio,[7] gives high capacity resins of exceptional stability and with a well-defined chemical structure as shown in Fig. 1.[8]

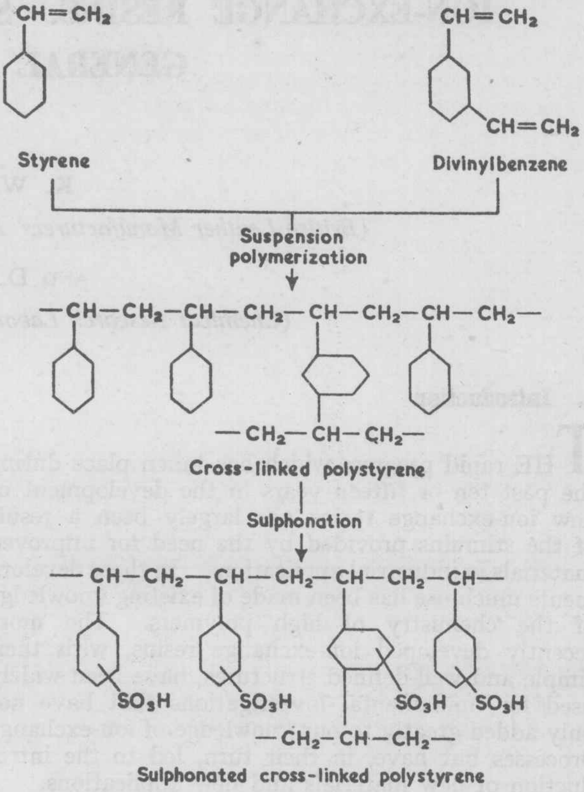


FIG. 1. *Preparation of a strongly acidic cation-exchange resin*

The copolymerization of styrene and divinylbenzene is normally carried out in suspension; the resulting beads are more easily sulphonated than the irregular particles obtained by the disintegration of bulk polymer, which break down further under the conditions necessary for complete sulphonation. Moreover, a product with a predetermined particle-size range can be obtained by suspension polymerization without the large losses of material associated with the use of grinding processes. Suspension polymerization is essentially similar to a bulk polymerization in which the monomers are dispersed into discrete globules, separated, and maintained at constant temperature by an aqueous solution.[9] To prevent aggregation of the monomer droplets during polymerization, a suspension stabilizer, such as polyvinyl alcohol, bentonite, starch, alginates, talc, etc., is employed. The particle size and particle size distribution of the product depend on the degree of mechanical agitation, the nature of the suspension stabilizer, the viscosity of the solution and other factors.[10] For ion-exchange resins, particle diameters of the order of 100–1000 μ are most useful but little difficulty is encountered in preparing beads with diameters from 1 μ to 2 mm.

The proportion of divinylbenzene may be varied over a wide range, but in commercial resins from 8 to 12% appears to be generally employed although a lower proportion (3–5%) may be used for special resins. A monomer-soluble catalyst, e.g. benzoyl peroxide, is used, formation of popcorn polymer being avoided by a suitable choice of catalyst concentration and polymerization conditions.

The styrene–divinylbenzene copolymer is insoluble but swells in many organic solvents. The degree of swelling in solvents such as benzene or toluene forms a criterion of the degree of cross-linking. As the proportion of divinylbenzene is decreased, the swelling rapidly increases until, with very small additions of cross-linking agent (of the order of 0·1%), a soluble polymer is obtained. The swelling of the styrene–divinylbenzene copolymers in toluene appears to agree closely with the Flory–Rehner equation (assuming complete copolymerization), and we may assume, to a first approximation, that the divinylbenzene is completely effective as a cross-linking agent. Support for this view is also afforded by the fact that monomer-free copolymers contain little or no residual unsaturation.

For the sulphonation of the cross-linked polystyrene various sulphonating agents, for example, chlorosulphonic acid, fuming sulphuric acid, or sulphur trioxide in nitrobenzene, can be used. Sulphonation with excess of concentrated sulphuric acid at 100° proceeds rapidly and, although the reaction is exothermic, quite smoothly. The rate of sulphonation decreases with increasing degree of cross-linking and with increasing particle size. Pretreatment of the copolymer beads with a swelling agent such as toluene, nitrobenzene, methylene chloride, trichloroethylene, etc. increases the rate of sulphonation and facilitates the preparation of beads of good shape and free from cracks.[8, 11] Preswelling has been shown, by observation with polarized light, to minimize the development of strains during sulphonation and also to minimize breakage of the resin particles during actual use.[12] After sulphonation, gradual dilution of the reaction mixture is necessary to avoid breakage of the particles.

Provided that sufficient time is allowed for the sulphonation, one and only one sulphonic acid group is introduced into each aromatic nucleus. The sulphur contents and exchange capacities of resins of this type are in good agreement with calculated values and the resins are essentially monofunctional. The sulphonated cross-linked polystyrenes are exceptionally stable and can be used at temperatures up to about 120°. They are resistant to concentrated acids and alkalis, and most oxidizing and reducing agents. The exchange capacities are normally about 5 mg.equiv. per g. of dry resin.

(*b*) *Weakly acidic cation-exchange resins*

The earlier weakly acidic cation-exchange resins were prepared by polycondensation. For example, the weakly acidic resin Wofatit C was prepared by condensing 1 : 3 : 5-resorcylic acid with formaldehyde. A monofunctional carboxylic resin can be prepared by the copolymerization of methacrylic acid with divinylbenzene (5–10%) in the presence of 1% benzoyl peroxide (Fig. 2). The product has a capacity independent of particle size and consistent with that calculated from the composition of the monomer mixture.[13, 14] Cross-linking agents other than divinylbenzene, e.g. ethylenedimethacrylate, may be employed.[15] Weakly acidic resins obtained by the copolymerization of styrene, maleic anhydride and divinylbenzene have also been described.[16, 17]

(*c*) *Strongly basic anion-exchange resins*

In view of their great industrial importance, attempts were made to prepare strongly basic anion-exchangers at an early stage in the development of ion-exchange resins. Satisfactory resins were not obtained however until a few years ago. A reaction route giving a product of well-defined structure is shown in Fig. 3. This method was discovered independently by the Rohm and Haas Co.,[18] by the Dow Chemical Co.[19] and, in this country, by Hawdon, Linstead & Thomas.[20] Cross-linked polystyrene is treated with chloromethyl methyl ether in the presence of a Friedel–Crafts catalyst. The chloromethylated product is then treated with a tertiary amine, e.g. trimethylamine, to give a resin containing strongly basic quaternary ammonium groups.

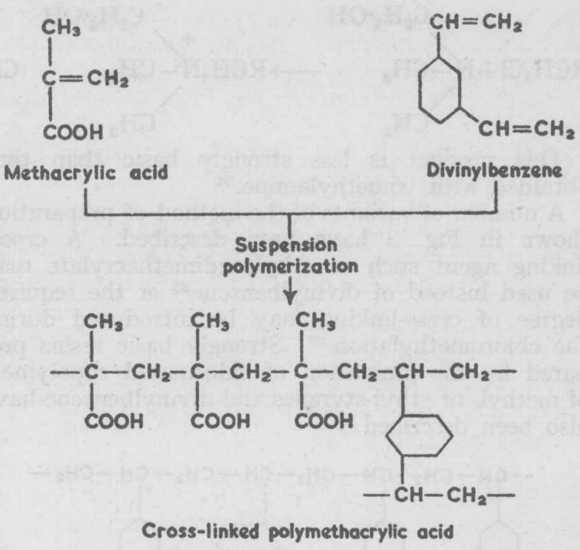


FIG. 2. *Preparation of a weakly acidic cation-exchange resin*

The cross-linked polystyrene in bead form is prepared by the method already described. In the case of the commercial resins, a copolymer containing about 6–8% of divinylbenzene appears to be employed.

For the chloromethylation reaction, various Friedel–Crafts catalysts such as aluminium chloride, zinc chloride or stannic chloride have been used.[21, 22] The chloromethylation reaction is more difficult to control than sulphonation; as monochloromethylation is approached, a side reaction occurs resulting in the formation of methylene bridges between neighbouring aromatic nuclei:

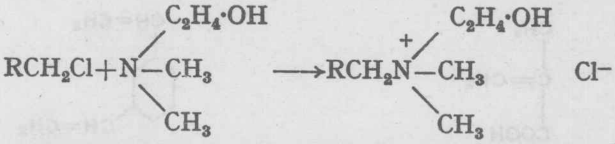
$$RCH_2Cl + RH \longrightarrow R\cdot CH_2\cdot R + HCl$$

As a result, there is an increase in the degree of cross-linking of the resin. However, since chloromethyl methyl ether is a good swelling agent for cross-linked polystyrene, the ether penetrates rapidly into the beads of copolymer and consequently the rate of chloromethylation is largely independent of both particle size and degree of cross-linking.[23]

For the preparation of strongly basic resins, the chloromethylated copolymer is treated with a tertiary amine, either anhydrous or in aqueous solution. This reaction proceeds quantitatively and quite rapidly provided that a swelling agent for the chloromethylated intermediate, e.g. benzene, dioxan or tetrahydrofuran, is present. The nitrogen contents and capacities of the products are in very good agreement with values calculated from the chlorine contents of the intermediates, if quantitative quaternation is assumed.

$$RCH_2Cl + NMe_3 \longrightarrow RCH_2N^+Me_3Cl^-$$

The effective basic strength of the quaternary group depends to some extent on the nature of the substituents attached to the nitrogen atom. In some of the commercial resins the chloromethylated copolymer is treated with dimethylethanolamine:



$$RCH_2Cl + N(C_2H_4{\cdot}OH)(CH_3)_2 \longrightarrow RCH_2\overset{+}{N}(C_2H_4{\cdot}OH)(CH_3)_2 \quad Cl^-$$

This product is less strongly basic than that obtained with trimethylamine.[24]

A number of variants of the method of preparation shown in Fig. 3 have been described. A cross-linking agent such as ethylenedimethacrylate may be used instead of divinylbenzene[25] or the required degree of cross-linking may be introduced during the chloromethylation.[26] Strongly basic resins prepared by the amination of chlorinated copolymers of methyl- or ethyl-styrenes and divinylbenzene have also been described.[27]

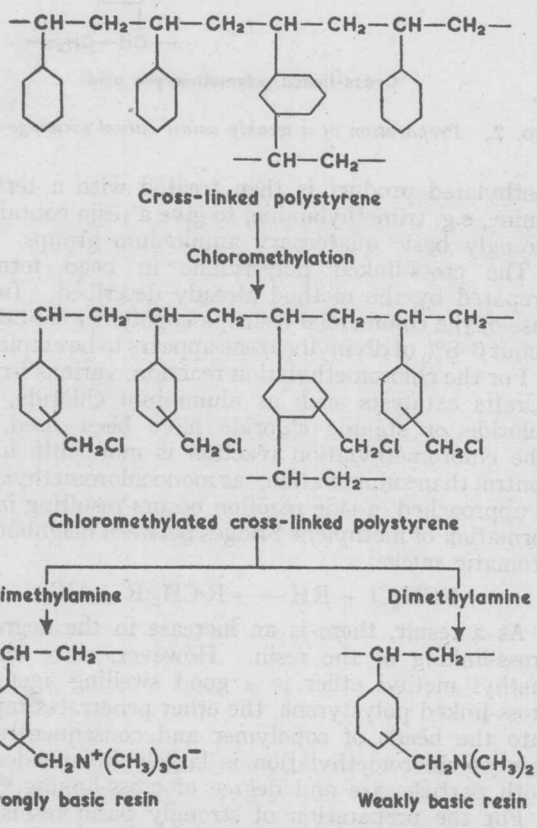


FIG. 3. *Preparation of anion-exchange resins*

The exchange capacity of commercial strongly basic resins derived from cross-linked polystyrene is usually 2·5 to 3·5 mg.equiv. per g. of dry resin. The resins are stable in the salt form up to 50° and the free bases possess good stability at room temperature.

(*d*) *Weakly basic anion-exchange resins*

The earlier types of weakly basic resins were prepared by methods similar to those used for the first cation-exchange resins. For example, *m*-phenylenediamine may be condensed with formaldehyde to give a weakly basic anion-exchange resin.[28] Resins of higher capacity and improved stability were obtained by the condensation of *m*-phenylenediamine and a polyethylenepolyamine with formaldehyde, e.g. Wofatit M,[4] or by the condensation of phenol, a polyethylenepolyamine and formaldehyde.[29]

Although weakly basic resins prepared by polycondensation reactions are still widely used, they are now being replaced by materials of greater stability derived from cross-linked polystyrene.[18, 30] As shown in Fig. 3, weakly basic resins can be obtained by treating chloromethylated cross-linked polystyrene with ammonia or primary or secondary amines. With dimethylamine or diethylamine, a monofunctional resin containing weakly basic tertiary amine groups is obtained.

$$RCH_2Cl + NHMe_2 \longrightarrow RCH_2{\cdot}NMe_2 + HCl$$

With ammonia or primary amines, however, the anion-exchangers are polyfunctional and additional cross-linking may be introduced during the amination.[23]

3. General characteristics

As a consequence of the high proportion of polar groups in their structure, ion-exchange resins are strongly hydrophilic, complete solubility in water being prevented by the cross-linked network. They behave as hygroscopic gels, swelling and shrinking reversibly with absorption and desorption of moisture. When saturated, commercial resins absorb 0·5–1·0 g. of water per g. of dry resin, but specially prepared 'porous' resins may absorb from 1·0 to 3·0 g. of water per g. of dry resin.

As already mentioned, the full capacity of an ion-exchange resin is determined by the number of ionized or ionizable groups per unit mass or unit volume; for most of the recently developed resins, the observed capacity for small ions is in excellent agreement with the theoretical value. It should, however, be mentioned that, with very large molecules such as proteins, the full capacity will not be obtained, and large organic ions such as alkaloids or dyes may be absorbed so slowly that for all practical purposes the exchange capacities are less than the theoretical value.[1, 31]

While the number of ionizable groups determines the total exchange capacity of the resin, the ion-exchange behaviour depends very largely on the nature of the groups. The characteristic properties of ion-exchange resins containing the four main types of ionizable group are summarized in Table I.

Information on the types of group present in an ion-exchange resin can be obtained by titrating the resin with standard acid or alkali. As the reaction is not always rapid, the best method is to shake samples of the resin with different amounts of acid or alkali and, when equilibrium is attained, measure the pH of the solution and the uptake of acid or alkali by the resin.[32, 33] Determinations of the 'titration curves' of ion-exchange resins of known structure have shown that the characteristic behaviour of the ionizable groups in simple compounds is reproduced very closely in the resins (Table I). A cation-exchange resin containing sulphonic acid groups, as would be expected of a strong acid, appears to be more or less completely ionized under all

Table I

Characteristics of typical ion-exchange resins

	Cation exchangers		Anion exchangers	
	Strongly acidic	Weakly acidic	Strongly basic	Weakly basic
Functional group	Sulphonic	Carboxylic	Quaternary ammonium	Amino
Effect of increasing pH value on capacity	Independent	Increases	Independent	Decreases
Salts	Stable	Hydrolyse on washing	Stable	Hydrolyse on washing
Regeneration	Excess of strong acid required	Readily regenerated	Excess of strong base required	Readily regenerated with sodium carbonate or ammonia
Rates of exchange	Rapid	Slow unless ionized	Rapid	Slow unless ionized

conditions. The theoretical capacity can be obtained over a wide range of pH values provided that an excess of the exchanging ion is present. A carboxylic resin, on the other hand, behaves as a weak acid; the theoretical capacity can be achieved in alkaline solution, but in acid solution the capacity is negligible. Similarly, the strongly basic anion-exchange resins are more or less completely ionized under all conditions and show the theoretical exchange capacity over a wide range of pH values. The weakly basic resins, however, are effective only in acid solutions. Weakly basic resins cannot therefore be used for the absorption of weak acids since the latter are appreciably ionized only in alkaline solution. Strongly basic resins will however absorb weak acids such as carbon dioxide and silica, and are used for this purpose in water treatment. After regeneration, strongly basic resins should be washed with water containing as little carbon dioxide as possible otherwise there will be a loss of capacity.

Other properties of strongly acidic and strongly basic resins are consistent with the view that they are more or less fully ionized under all conditions. The salts are stable and do not hydrolyse on washing; only small volume changes occur on conversion of the free acid or free base form of the resin to the salt, and high rates of exchange are observed both with the free acids or free bases and the salts.

The salts of the weakly acidic and weakly basic resins, on the other hand, are not stable and are slowly hydrolysed when washed with water. On conversion to the salt form, a large increase in volume is observed with weakly acidic and weakly basic resins as a result of the increase in hydration on ionization. High rates of exchange are observed with weakly acidic or weakly basic resins when they are in the salt form, i.e. when they are fully ionized. The free acids or bases, however, react very slowly.

For the regeneration of a weakly acidic resin, a slight excess of acid suffices since the carboxylic group is only very slightly dissociated under acid conditions. The reaction

$$R{\cdot}COO^-Na^+ + H^+ \longrightarrow R{\cdot}COOH + Na^+$$

proceeds very readily, whereas the reverse reaction (under acid conditions) is negligible.

A large excess of acid is needed, however, for the regeneration of a strongly acidic resin.

$$RSO_3^-Na^+ + H^+ \rightleftharpoons RSO_3^-H^+ + Na^+$$

In this case, both the forward and reverse reactions proceed readily.

Similarly, a large excess of sodium hydroxide is required for the regeneration of strongly basic resins, but weakly basic resins are much more easily regenerated and ammonia or sodium carbonate may be used.

4. Ion-exchange equilibria

A short account will now be given of the quantitative relationships that determine the equilibrium distribution of ions between a resin and solution. It should be emphasized that the distribution of ions is not determined solely by the ion-exchange reaction. For example if a dry cation-exchange resin in the hydrogen form is added to an aqueous solution of an acid, the resin absorbs water and, also, acid diffuses into the resin. Since the resin anions are fixed, the conditions are similar to those in a Donnan equilibrium and the equilibrium concentration of acid within the resin is very much less than that in the external solution. The preferential absorption of water results in an increase in the acid concentration of the surrounding solution.[34–36] This effect can cause serious errors in investigations of ion-exchange equilibria if changes in concentration of the external solution are assumed to arise solely as a result of an ion-exchange process. It should be mentioned that non-electrolytes or undissociated electrolytes may be appreciably absorbed by the swollen resin.[37] This phenomenon is the basis of the process known as 'ion-exclusion'.[38]

The best available evidence confirms that the exchange process itself is strictly stoicheiometric. The exchange of cations between an acidic resin and a solution can therefore be represented by the reversible reaction

$$AR + B^+ \rightleftharpoons BR + A^+$$

One of the most important properties of ion-exchange resins is that, in general, they show some selective absorption, i.e. they possess different