515. *Solvent-modified Polymer Networks. Part II.*[1] *Effect of Structure on Cation-exchange Kinetics in Sulphonated Styrene–Divinylbenzene Copolymers.*

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The kinetics of exchange of hydrogen ions for sodium and tetra-methyl-, -ethyl-, -n-propyl-, and -n-butyl-ammonium ions on expanded-structure and macroporous resins have been investigated and compared with those on a conventional ion-exchange resin, a pseudo-infinite bath technique being used at a total cation concentration of 0·02N. The values of the conventional interdiffusion coefficients and activation energies for the exchange of the larger ions in the solvent-modified copolymer confirm the view that solvent-modification increases the effective porosity of the network by reducing entanglement rather than by affecting the overall covalent cross-linking.

AN earlier paper[1] described the preparation and characterisation of styrene–divinylbenzene copolymers made by polymerisation in the presence of toluene, as well as of cation-exchange materials derived from them. The latter have internal structures very different from those of conventional cation-exchange resins, and the effect of this difference on their ion-exchange kinetic behaviour was studied. At the concentration used (0·02N), the initial rates of Na^+–H^+ exchange were governed by interdiffusion of the two ions through the bounding Nernst film[2] (F-kinetics), while for the organic cations the interdiffusion of the ions through the resin structure[2] was rate-controlling (P-kinetics). The rates of exchange of hydrogen ion with organic ions were compared for five resins, of different divinylbenzene contents. Two of the resins, one of expanded structure and one slightly macroporous, were made in the presence of different proportions of toluene to have the same specific water regain as the conventional resin Zeo-Karb 225 made in absence of solvent, since it is the specific water regain which normally defines the degree of cross-linking.[3] The remaining two resins were highly macroporous.

From the structure previously postulated[1] for this type of resin, faster P-kinetics might be expected for the larger ions as the divinylbenzene content increased, even though the apparent cross-linking was unaltered. For the highly macroporous resins, high exchange rates for large ions would be expected, with correspondingly low activation energies for diffusion inside the resin particle, at least in the initial stages of the exchange.

EXPERIMENTAL AND RESULTS

Materials.—The solvent-modified resins were prepared in the presence of toluene as already described; the conventional resin was Zeo-Karb 225 identical with that used previously.[4] Their properties are given in Table 1. Quaternary ammonium salts were of standard laboratory grade, and other reagents were " AnalaR " materials.

TABLE 1.

Divinylbenzene content (v/v of monomer mixture)	7	15	27	34	55
Volume fraction of monomers (F_M)	1·00	0·62	0·51	0·33	0·33
Toluene regain (ml./g.) of hydrocarbon matrix	0·79	0·87	1·14	1·95	2·21
Sulphonated copolymer:					
Wt. cap. (mequiv./g.)	4·98	4·90	4·36	4·40	3·83
Specific water regain (ml./mequiv.)	0·20	0·20	0·22	0·40	0·54
Wt.-average particle diameter in water (microns)	549	516	527	516	511

These resins will be referred to as 7%, 15% tol, 27% tol, 34% tol, and 55% tol, respectively.

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[1] Part I, Millar, Smith, Marr, and Kressman, *J.*, 1963, 218.

[2] Boyd, Adamson, and Myers, *J. Amer. Chem. Soc.*, 1947, **69**, 2836.

[3] Kressman and Millar, *Chem. and Ind.*, 1961, 1833.

[4] Millar, Smith, and Marr, *J.*, 1962, 1789.

Kinetics.—Reichenberg's "pseudo-infinite" bath method[5] was used, with the modifications previously described.[4] A weight of wet centrifuged resin containing 1·00 mequiv. of replaceable hydrogen ion was used for each determination, together with 300 ml. of solution containing a quantity of cation hydroxide equivalent to the desired extent of exchange, cation halide to give a cation concentration of 0·02N at the end-point, and 25 drops of 0·1% Bromocresol Purple solution. The halides used were sodium chloride, tetramethyl- and tetraethyl-ammonium bromide, and tetra-n-propyl- and tetra-n-butyl-ammonium iodide. It is, however, known that P-kinetics are not affected by the nature of the co-ion.[6]

The equation for F-kinetics in the pseudo-infinite bath,[5] valid only for low values of the extent of exchange Q_t/Q_∞, is:

$$\mathrm{d}Q_t/\mathrm{d}t = 4\pi r^2 D_B C_B/\Delta r = \text{Constant}. \qquad (1)$$

If Q_t, the amount of exchange in time t, is plotted against t, a straight line is obtained (whose slope gives a value for the thickness Δr of the Nernst film surrounding the resin particle of weight-average radius r, if the concentration C_B and diffusion coefficient D_B of the entering ion are known).

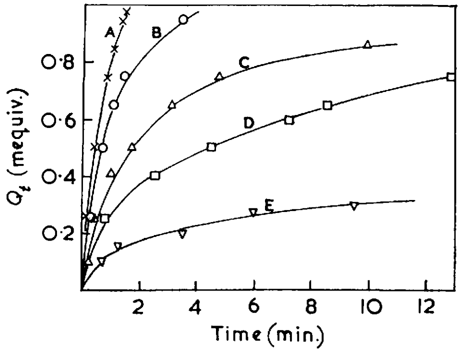

FIG. 1. Exchange kinetics on Zeo-Karb 225 at 25° and 0·02N.

(A) Na^+–H^+; (B) NMe_4^+–H^+; (C) NEt_4–H^+; (D) $NPr^n{}_4^+$–H^+; (E) $NBu^n{}_4^+$–H^+.

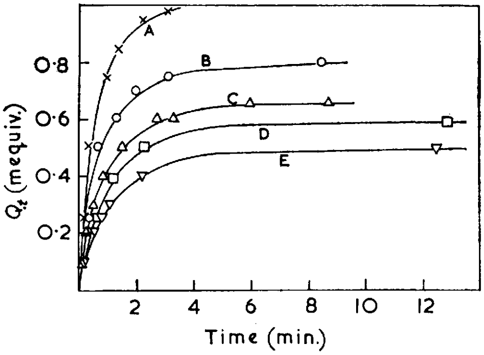

FIG. 2. Exchange kinetics on 55% tol resin at 25° and 0·02N.

(A) Na^+–H^+; (B) NMe_4^+–H^+; (C) NEt_4^+–H^+; (D) $NPr^n{}_4^+$–H^+; (E) $NBu^n{}_4^+$–H^+.

The corresponding equation used to describe P-kinetics is:

$$F = Q_t/Q_\infty = 1 - (6/\pi^2).\textstyle\sum_{n=1}^{\infty}(1/n^2)\exp(-n^2Bt). \qquad (2)$$

From this equation the interdiffusion coefficient of the two ions in the resin phase (D_i), can be obtained from the extent of exchange, since the function Bt has been tabulated[5] for appropriate values of Q_t/Q_∞, and the Bt–t plot gives the slope $B = D_i\pi^2/r^2$.

Helfferich and his co-workers[7] have since shown this equation to be strictly valid only when both ions have the same mobility in the resin phase, a condition which cannot be assumed to apply here. Although the mobility ratios of the ions in the exchange-resins are unknown, self-diffusion coefficients of the quaternary ions, calculated from the appropriate mobility ratios in solution, show essentially the same variation as do the conventional interdiffusion coefficients obtained from equation (2). The latter have therefore been used throughout this work to provide a single parameter comparable with results already in the literature,[2, 4–6, 8]

Figs. 1 and 2 present experimental results for the amount of exchange Q_t as a function of time t for all the ions on the conventional 7% and the highly macroporous 55% tol resin, respectively. The results for NEt_4^+–H^+ and $NBu^n{}_4^+$–H^+ exchange are plotted according to

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[5] Reichenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 589.

[6] Kressman and Kitchener, *Discuss. Faraday Soc.*, 1949, **7**, 90.

[7] Helfferich and Plesset, *J. Chem. Phys.*, 1958, **28**, 418; Plesset, Helfferich, and Franklin, *ibid.*, 1958, **29**, 1064; Helfferich, *J. Phys. Chem.*, 1962, **66**, 39.

[8] Gregor, Bregman, Gutoff, Broadley, Baldwin, and Overberger, *J. Colloid Sci.*, 1951, **6**, 20.

TABLE 2.

Resin	10^6D_i (cm.$^{-2}$ sec.$^{-1}$ at 25°) for NMe_4^+	NEt_4^+	$NPr^n_4{}^+$	$NBu^n_4{}^+$
7%	1·08	0·26	0·10	0·015
15% tol	—	0·29	—	0·032
27% tol	—	0·23	—	0·088
34% tol	0·49	0·32	0·31	0·24
55% tol	0·62	0·42	0·48	0·32

equation (2) in Figs. 3 and 4, and the straight lines show that these kinetics are indeed controlled by particle diffusion. This was confirmed by the lack of conformity to equation (1). Substantially similar results were obtained in NMe_4^+–H^+ and $NPr^n_4{}^+$–H^+ exchange. Values of D obtained from the slopes of the straight lines are shown in Table 2.

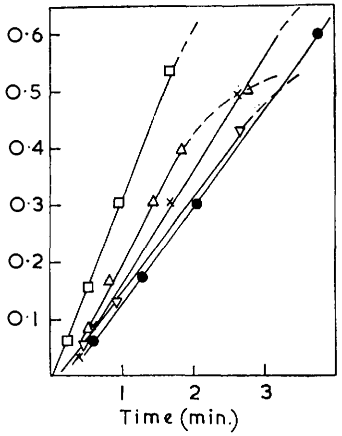

FIG. 3. Test of mechanism: tetraethylammonium exchange at 25° and 0·02N.

●, 7% (Zeo-Karb 225); ×, 15% tol; ▽, 27% tol; △, 34% tol; □, 55% tol resin.

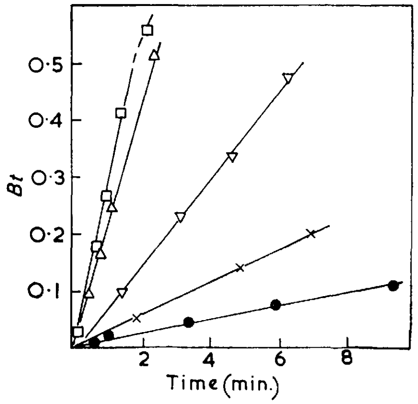

FIG. 4. Test of mechanism: tetra-n-butylammonium exchange at 25° and 0·02N.

(Symbols as for Fig. 3.)

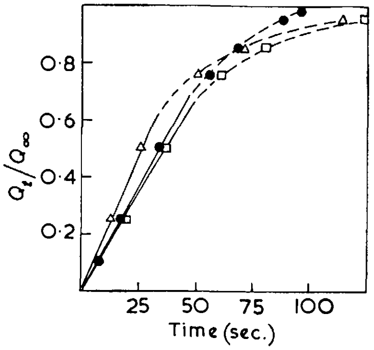

FIG. 5. Test of mechanism: sodium exchange at 25° and 0·02N (as F-kinetics).

(Symbols as for Fig. 3.)

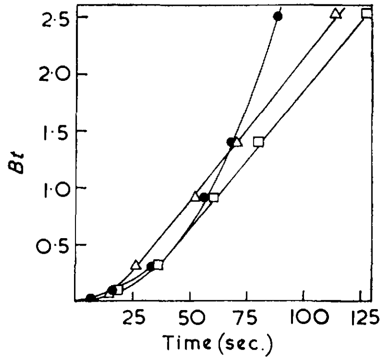

FIG. 6. Test of mechanism: sodium exchange at 25° and 0·02N (as P-kinetics).

(Symbols as for Fig. 3.)

Figs. 5 and 6 show the corresponding tests of mechanism for Na^+ exchange on the 7%, 34% tol, and 55% tol resins.

Measurement of Q_∞.—With simple inorganic ions the value of Q_∞ in equation (2) approximates to the total exchange capacity of the amount of resin used in the experiment, measured, for example, by the exchange of hydrogen for sodium ion.[4] With some of the larger ions used in the present work this capacity was not achieved, even after several months, and the exact value of Q_∞ was measured for each ion on each resin under the conditions of the kinetic experiments.

Several flasks were arranged to contain resin and solution exactly as for a kinetic run, quantities of the cation hydroxide being used corresponding to the estimated value of Q_∞ and to values just less and just greater than this. The flasks were then kept at 25° for 4—6 months, with occasional shaking, and then examined. If the indicator in one of the flasks showed its neutral point exactly, the amount of cation hydroxide giving this condition is the required value of Q_∞. Generally, however, two of the flasks were found of which one showed an acid and the other an alkaline reaction. The latter was then titrated with 0·01N-hydrochloric acid and, provided that not more than 0·05 mequiv. of alkali was present, the titre was used to calculate the extent of exchange on the resin. If more alkali was present, three more mixtures were made so as to reach neutrality more nearly. The limiting Q_∞ values were thus estimated within $\pm 0{\cdot}02$ for all the systems, except the $NBu^n{}_4{}^+$ exchanges where the uncertainty was $\pm 0{\cdot}03$. The values of Q_∞ at 40° and 55° were found to differ insignificantly from those at 25°.

The results are shown in Table 3 where they are expressed as a fraction Ω of the total exchange capacity achieved with an excess of sodium ion. Thus Q_∞ for any kinetic system is ΩC, where C is the total exchange capacity of the quantity of resin in the system. The values were confirmed by treating the resin samples with an excess of sodium chloride solution, the acid liberated by exchange of the remaining hydrogen ion in the resin being found to correspond to $1 - \Omega$.

TABLE 3.

Fractional extent of exchange at t_∞.

Resin	$NMe_4{}^+$	$NEt_4{}^+$	$NPr^n{}_4{}^+$	$NBu^n{}_4{}^+$
7%	1·0	1·0	0·95	0·92
15% tol	—	1·0	—	0·82
27% tol	—	0·87	—	0·67
34% tol	0·95	0·90	0·72	0·65
55% tol	0·90	0·80	0·67	0·63

No evidence was obtained in these experiments of an irreversible structural change similar to that observed by Hale *et al.*[9] for the exchange of tetraethylammonium ion on a conventional 15% divinylbenzene resin in the presence of an excess of the tetraethylammonium hydroxide.

Activation Energies.—The apparent activation energies for the exchange of tetraethyl- and tetra-n-butyl-ammonium ion on all the resins were determined by measuring exchange velocities at 40° and 55° as well as at 25°. The results were plotted as the reciprocals of the absolute temperature against log B, and the activation energies obtained from the slopes of these lines are given in Table 4.

TABLE 4.

Arrhenius activation energies (kcal./g.-ion) for exchange interdiffusion of ions with hydrogen ion.

Resin	7%	15% tol	27% tol	34% tol	55% tol
$NEt_4{}^+$	5·0	3·4	3·9	4·9	3·9
$NBu^n{}_4{}^+$	12·9	10·2	6·0	4·1	4·6

DISCUSSION

Structures for the solvent-modified polymers have been discussed in Part 1.[1] It was there suggested that the sulphonated copolymers consist of nuclei characteristic of the divinylbenzene content of the monomer mixture, and of comparatively high covalent cross-linking but with little entanglement, interspersed with regions where the cross-linking is lower and entanglement virtually absent. In extreme cases, *i.e.*, at high divinylbenzene content and dilution, regions of true macroporosity exist between the nuclei.

The heterogeneity of structure can be increased in two independent ways, by a decrease in the volume fraction of monomers (F_M) or by an increase in the divinylbenzene content of the monomer solution. Although the F_M values of the 15% tol and the 27% tol resin

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[9] Hale, Packham, and Pepper, *J.*, 1953, 844.

were chosen to give the same specific water regain as the 7% resin, the increasing divinylbenzene content and decreasing F_M result in an increase in heterogeneity in the order 7%, 15% tol, and 27% tol. The 15% tol material has an expanded structure, 27% tol is intermediate between an expanded and a macroporous structure, and both the 34% tol and the 55% tol resin contain an appreciable proportion of their porosity in the form of macropores.[1]

The effect of this increasing heterogeneity of pore-size distribution on the value of D_i is clearly seen from Fig. 7, where this is plotted against the unhydrated ionic diameter for the several organic cations (which are known to be unhydrated in solution). In both the 7% and the 15% tol resin, D_i decreases rapidly with increasing ionic diameter, the figures for the two resins being very similar. This is consistent with the purely expanded structure postulated for the 15% tol resin. The 34% tol and the 55% tol resin are fully macroporous and the ease with which the ions can move through these macropores is reflected in the small change in D_i with increasing ionic diameter for these two materials. The 27% tol resin, in spite of its having a specific water regain virtually identical with that of the 7% and the 15% tol material, has a porosity intermediate between those of an expanded structure and a fully macroporous material. As expected, the D_i values lie between the two extremes.

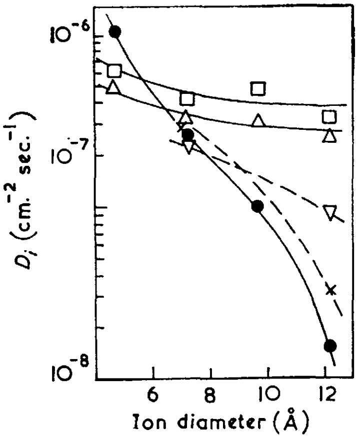

FIG. 7. Variation of D_i with ionic diameter.
(Symbols as for Fig. 3.)

The structures proposed for these materials are confirmed by the activation energies. The values for exchange of tetraethylammonium ion (7·2 Å diam.) are very nearly the same for all the resins and scarcely differ from the value of 3—5 kcal. per mole found for the diffusion of most ions in water. This implies the virtual absence of steric interaction of the ion with the resin structure.[6] Evidently, in the solvent-modified materials diffusion occurs through the areas occupied by the internuclear chains and through the macropores, little or no exchange occurring within the most highly cross-linked portions of the nuclei over the range represented by the linear portions of the *Bt–t* plots. It follows that the exchange sites on the internuclear chains are directly accessible to the ions, which do not, in consequence, have to pass through the regions occupied by the nuclei to reach those sites.

The high value for tetrabutylammonium ion (12·2 Å diam.) on the 7% resin indicates, as would be expected for such a large ion, considerable interaction with the resin structure and this is also shown, though to a slightly smaller extent, with the 15% tol resin which has an expanded structure. With the onset of macroporosity which occurs in the 27% tol resin the interaction even with this large ion has been virtually eliminated and on the more macroporous materials—34% tol and 55% tol—the activation energies are again virtually identical with that in aqueous solution, indicating passage of the ions through water-filled spaces with no steric interaction with the resin structure.

This conclusion again only refers to those portions of the structure into which the tetrabutylammonium ion can enter. The most highly cross-linked portions within the nuclei are inaccessible under the conditions of the experiments, and, as Table 3 shows, these portions represent up to about 35% of the total ion-exchange capacity.

A consequence of the heterogeneity of the 34% tol and the 55% tol resin is the existence of P-kinetics in the exchange with the sodium ion at 0·02N where film diffusion is normally the rate-controlling step. The 7% resin, as expected, shows F-kinetics, at least up to $Q_t/Q_\infty = 0{\cdot}65$ (Fig. 5), with no evidence of P-kinetics (Fig. 6). The two macroporous resins, however, initially show F-kinetics up to $Q_t/Q_\infty \approx 0{\cdot}5$, the kinetics thereafter being controlled by particle diffusion at least up to $Q_t/Q_\infty = 0{\cdot}9$ ($Bt = 1{\cdot}80$). The earlier part of the exchange is clearly occurring within the larger pores (including the macropores), while the later part represents diffusion into the areas of higher cross-linking in the nuclei. That P-kinetics can occur at all at this comparatively low concentration is a consequence of D_{i} values for the sodium ion in the two resins which are lower than that in the 7% resin. In the more highly cross-linked regions of the two resins the values of D_{i} obtained from Fig. 6 are both about $1{\cdot}48 \times 10^{-6}$. This is to be compared with the figure of $5{\cdot}9 \times 10^{-6}$ for the 7% resin previously reported.[4]

This is an interesting example of an intermediate (I) type of kinetics [2,6] where evidence of both F- and P-kinetics is shown. At concentrations below 0·02N the kinetics may be expected to become wholly of F and at concentrations above 0·02N to become wholly of P type. The precise form of the I-kinetics with pure F giving way to pure P is, however, an attribute of the markedly heterogeneous structure of the resins. In contrast, I-kinetics in a conventional resin are characterised [2] by a rate of exchange which is slower than either pure P or pure F but involves no abrupt change of mechanism.

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