340. Interpenetrating Polymer Networks. Part II.[1] Kinetics and Equilibria in a Sulphonated Secondary Intermeshed Copolymer.

By J. R. Millar, D. G. Smith, and W. E. Marr.

For an ion-exchange resin prepared by sulphonation of a styrene–divinylbenzene coplymer with deliberately enhanced network entanglement (see Part I [1]), the equilibria and kinetics of exchange of H^+ for Na^+ and NEt_4^+ have been measured; they are compared with those for the conventional ion-exchange resin, Zeo-Karb 225, of the same capacity and water regain. Compared with the conventional exchanger, the secondary intermeshed product was markedly more selective, but both ions had higher diffusion coefficients inside the latter resin. The implications of these findings are discussed.

The exchange behaviour of a conventional sulphonated polystyrene resin is determined by its water-swelling characteristics, *i.e.*, by its water regain which in turn is a measure of its degree of cross-linking.[2] If two such resins have the same total exchange capacity and the same water regain (expressed as g. of water per g. of dry resin in a standard ionic form, usually the H^+ form), they are essentially identical and behave in the same way in their ion-exchange kinetics and equilibria. If their total exchange capacities are not identical but do not differ greatly, the parameter determining their behaviour is the water regain per unit of capacity (specific water regain).

It is of interest to compare the behaviour of a conventional sulphonated polystyrene resin, Zeo-Karb 225 (The Permutit Co. Ltd., London), with that of a sulphonated resin containing two interpenetrating networks, yet with the same swelling characteristics, *i.e.*, the same apparent degree of cross-linking. The preparation and properties of a number of these copolymers were described in a previous paper [1] where it was shown that almost any swelling characteristics could be achieved by an appropriate choice of divinylbenzene (DVB) content in the two networks. In particular, intermeshed copolymers could be produced in which the overall average divinylbenzene content was identical with that of

---

[1] The paper by Millar, *J.*, 1960, **1311**, is considered to be Part I.

[2] Pepper, *J. Appl. Chem.*, 1951, **1**, 124.

the individual networks. In the present work, a sulphonated secondary intermeshed copolymer of the latter kind containing 4·5% of divinylbenzene in each of the networks (called 4½ × 4½ resin in the sequel) has been used, since its specific water regain is identical with that of the sample of Zeo-Karb 225 under investigation.

Exchange rates and relative affinity coefficients[3] at 25° have been compared for the exchange of H^+ with Na^+, a typical small hydrated univalent ion, and for that with tetraethylammonium (NEt_4^+), a typical large unhydrated univalent ion. The rate measurements have been made under conditions where the exchange is controlled by particle diffusion and the results are expressed in terms of the average interdiffusion coefficients of the two ions with H^+ in the resin phase. The variation of the Na^+–H^+ interdiffusion coefficient with cross-linking has been investigated by making similar measurements on two other conventional resins of different divinylbenzene contents.

EXPERIMENTAL

Materials.—Styrene, toluene, azoisobutyronitrile, and polyvinyl alcohol (as stabiliser) were the same as before,[1] as was the divinylbenzene, except that the solution which was used this time contained 55% by weight of divinylbenzene isomers. Sodium chloride and hydroxide, and hydrochloric acid, were " AnalaR " reagents; other materials were of standard laboratory grades. The Zeo-Karb 225 was the standard commercial SRC-13 material. The secondary intermeshed copolymer containing two networks, each of 4·5% divinylbenzene content, was prepared and sulphonated as previously described,[1] as also were two primary copolymers of 4% and 12% nominal divinylbenzene content.

Kinetics.—To ensure that the samples of the several resins used were of the same particle-size range they were wet-screened to −25 + 36 B.S.S. mesh after an initial fractionation by means of a multi-tube elutriator similar to that of Reichenberg.[4] This size separation was carried out with the resin in the sodium form; the resin was then converted fully into the hydrogen form with 2N-hydrochloric acid and washed free from acid and chloride with demineralised water. The washed resin was placed in sintered-glass tubes of the type used for water-regain determinations,[1] centrifuged at 2000 r.p.m. for 30 min., and transferred to a closed weighing bottle, which was stored at 100% relative humidity.

Particle diameters were measured microscopically on 100—150 beads from each sample, both in demineralised water and in 2N-sodium chloride. The weight-average particle diameters were calculated from the expression $\bar{d}_w = (\sum d^3/n)^{1/3}$ and are given in Table 1. The appropriate figures were used to afford the coefficients of interdiffusion from the slopes of the relevant (*Bt–t*) graphs.

TABLE 1.

Weight average particle diameter (microns).

	4% DVB	Zeo-Karb 225	12% DVB	4½ × 4½
In H_2O	565	549	517	563
In 2N-HCl	518	535	519	537

Reichenberg's " pseudo-infinite " bath method[4] was used, modified by the use of a centrifugal stirrer made of rigid polyvinyl chloride but otherwise identical with that of Kressman and Kitchener.[5] A weight of wet centrifuged resin containing 1·00 mequiv. of replaceable H^+ ion was used for each determination, together with 300 ml. of a solution containing a quantity of cation hydroxide equivalent to the desired extent of exchange, cation halide (chloride or bromide) to give the required normality at the end-point (2·0N with the Na^+–H^+ and 0·02N with the NEt_4^+–H^+ exchange), and 25 drops of 0·1% Bromocresol Purple. The solution was contained in a 400-ml. straight-sided beaker.

Care was taken that both the solution and the stirrer assembly were initially at 25° ± 0·1°, the temperature at which all measurements were made. The stirrer speed was exactly 1000 r.p.m., as used by Kressman and Kitchener,[5] and the time of exchange was measured from the instant the already rotating stirrer was lowered into the solution until the indicator changed colour.

---

[3] Reichenberg, Pepper, and McCauley, *J.*, 1951, 493.
[4] Reichenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 589.
[5] Kressman and Kitchener, *Discuss. Faraday Soc.*, 1949, **7**, 90.

Equilibria.—The resin in the H^+-form and the appropriate salt solution were mixed in a glass-stoppered flask and kept in an air-thermostat at 25° ± 0·2°. The weight of resin and the volume and concentration of the solution were adjusted to give various extents of exchange, $\bar{X}$. Since the exchange was between univalent ions, the position of equilibrium was independent of concentration, and 0·01N- or 0·05N-solutions were used as convenient to give various extents of exchange. That equilibrium had been established was confirmed when two or more identical experiments gave the same results when left for different times. Generally, the Na^+–H^+ equilibria were established within seven and the NEt_4^+–H^+ equilibria within fourteen days. In all cases the resin–solution mixtures were left for at least twice these times. The solution was then decanted from the resin, and aliquot portions were analysed to determine the amount of H^+ ion liberated. A knowledge of this quantity, together with the total exchange capacity of the resin and the quantity and concentration of the salt solution, enables the extent of exchange $\bar{X}$ and the equilibrium quotient K to be calculated. Since the external solution is dilute, the equilibrium quotient K, defined for the exchange reaction $\bar{R^-A^+} + B^+X^-$ aq. $\rightleftharpoons$ $\bar{R^-B^+} + A^+X^-$ aq. as $[\bar{B}][A]/[\bar{A}][B]$, is equivalent to the relative affinity coefficient [3] K_A^B for the resin. (Barred symbols denote quantities within the resin phase.) The accuracy of measurements at $\bar{X}$ values less than 0·2 and greater than 0·85 is somewhat less than that in the intermediate range where it is estimated to be ±3%. In consequence, the equilibria have mostly been investigated in this middle range only.

RESULTS AND DISCUSSION

The 4½ × 4½ resin had a water regain of 1·08 g./g. and a total capacity of 5·13 mequiv./g. (specific water regain 0·21 g./mequiv.), figures which compare with 1·04 g./g., and 4·98 mequiv./g. (specific water regain 0·21 g./mequiv.) for the Zeo-Karb 225. The known relation between specific water regain and divinylbenzene content [6] shows the apparent divinylbenzene content of both these resins to be 7·0% v/v. On the same basis the other two primary copolymers contained 3·9 and 12·0% of divinylbenzene, respectively.

The results of kinetic and equilibrium experiments involving large ions need to be interpreted with care, in view of the irreversible change observed by Hale *et al.*[7] in a 15% divinylbenzene cross-linked resin during the exchange of NEt_4^+ for H^+. This effect was found to be completely absent with Zeo-Karb 225 and to occur only at values of $\bar{X}$ above about 0·9 with the 4½ × 4½ resin. Since no measurements were made with NEt_4^+ at $\bar{X}$ greater than about 0·7, the results are free from this complication.

Figs. 1 and 2 show the curves of fractional exchange against time for Na^+–H^+ exchange at 2N- and NEt_4^+–H^+ at 0·02N-concentration. The corresponding (*Bt–t*) plots, shown in Figs. 3 and 4, are rectilinear and demonstrate that the kinetics are controlled by particle diffusion under these conditions. The non-conformity of the kinetic results to the film-diffusion equation [2,5] confirms this. The interdiffusion coefficients in the resin phase at 25° have been calculated [4] from the values of B obtained from Figs. 3 and 4, and are given in Table 2.

TABLE 2.

Resin	Apparent DVB content from specific water regain (% v/v)	Interdiffusion coefficients ($10^6 D_i$)	
		Na^+–H^+	NEt_4^+–H^+
4% DVB	3·9	8·2	—
Zeo-Karb 225	7·0	5·9	0·27
12% DVB	12·0	2·5	—
4½ × 4½ Resin	7·0	7·3	0·43

The value for Na^+–H^+ diffusion in Zeo-Karb 225 is in line with values for the same pair of ions in similar resins of different divinylbenzene contents (see Fig. 5). In this graph D_i values from the literature have been plotted against the divinylbenzene contents

---

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

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

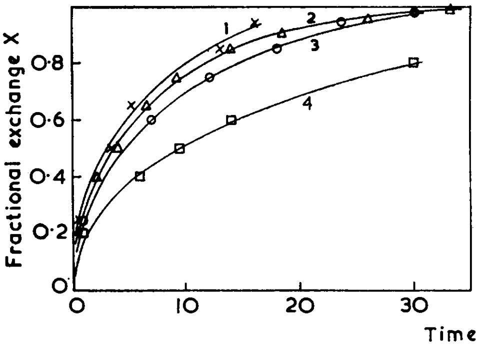

FIG. 1.

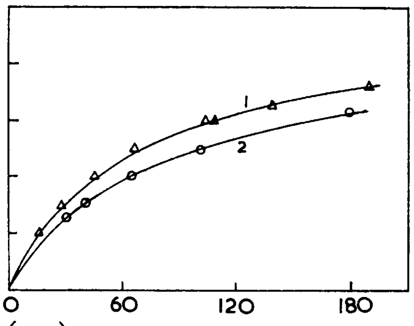

FIG. 2.

FIG. 1. Sodium exchange kinetics (25°; 2N).
(1) 4% DVB resin, (2) 4½ × 4½ resin, (3) Zeo-Karb 225, (4) 12% DVB resin.

FIG. 2. Tetraethylammonium exchange kinetics (25°; 0·02N).
(1) 4½ × 4½ resin, (2) Zeo-Karb 225.

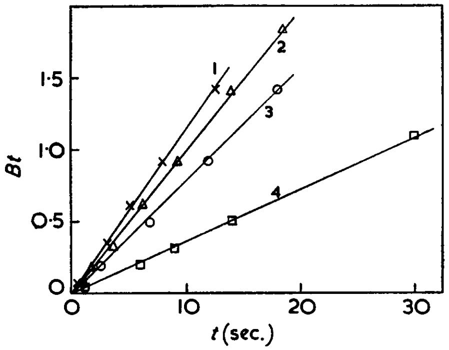

FIG. 3. Test of mechanism: sodium exchange.
(1) 4% DVB resin, (2) 4½ × 4½ resin, (3) Zeo-Karb 225, (4) 12% DVB resin.

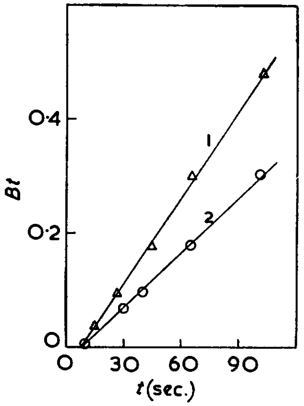

FIG. 4. Test of mechanism: tetraethylammonium exchange.
(1) 4½ × 4½ resin, (2) Zeo-Karb 225.

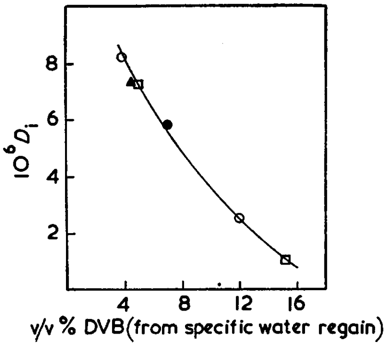

FIG. 5. Variation of Na^+–H^+ interdiffusion coefficient (D_i) with cross-linker content.
● Zeo-Karb 225. ▲ 4½ × 4½ Resin (plotted as actual DVB content). ○ Sulphonated cross-linked polystyrene resins (☐ are as ○ but from ref. 4).

deduced from their water regain and capacity figures,[6] rather than those quoted by the author,[4] in order to maintain consistency with the present work.

The D_i value for the 4½ × 4½ resin implies an effective cross-linking corresponding to the overall 4·5% v/v divinylbenzene content rather than to the apparent content of 7% indicated by its specific water regain. The value of $0·27 \times 10^{-6}$ for the NEt_4^+ ion in Zeo-Karb 225 is in excellent agreement with that of $0·29 \times 10^{-6}$ found by Gregor *et al.*[8] for a 6% divinylbenzene resin. Again, the higher value for the 4½ × 4½ resin is clearly not determined by its apparent divinylbenzene content of 7·0% but by its lower overall content.

From this it might be supposed that the relative affinity coefficients in the 4½ × 4½ resin would be either similar to or lower than those for Zeo-Karb 225. The equilibrium curves in Figs. 6 and 7 show, however, that the network entanglement in the 4½ × 4½ resin has resulted in an increase in selectivity for both Na^+ and NEt^+. Indeed its selectivity in the Na^+–H^+ exchange is similar, over the range $\bar{X} = 0·27$—0·7, to that of a conventional resin containing 15% of divinylbenzene, but the curve is convex to the $\bar{X}$ axis and shows a very large K value at low $\bar{X}$ (Fig. 6). The curve for Zeo-Karb 225 is consistent with that of a resin of the degree of cross-linking (7·0%) indicated by its water regain.

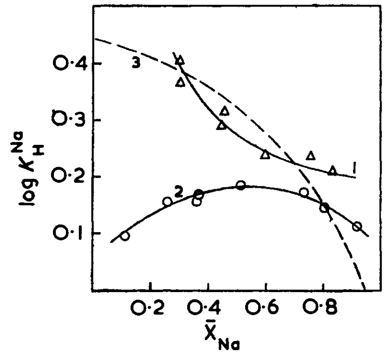

FIG. 6. Sodium–hydrogen exchange equilibria (25°).

(1) 4½ × 4½ Resin, (2) Zeo-Karb 225, (3) 15% DVB resin (ref. 9).

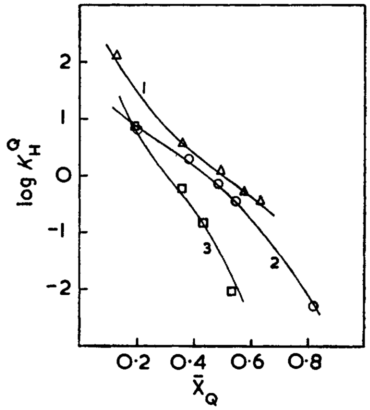

FIG. 7. Tetraethylammonium–hydrogen exchange equilibria (25°).

(1) 4½ × 4½ Resin, (2) Zeo-Karb 225, (3) 15% DVB resin (replotted from ref. 7). (Q = NEt_4^+.)

The only published data for NEt_4^+–H^+ exchange are those of Hale, Packham, and Pepper [7] for a 15% divinylbenzene resin. Both the Zeo-Karb 225 and the 4½ × 4½ resin show less marked variation in K_H^Q with $\bar{X}$. However, as before, there is a characteristic steepening of the curve for the latter resin at low $\bar{X}$, giving very high values indeed for K_H^Q; further, the selectivity for the tetraethylammonium ion is everywhere higher than in either Zeo-Karb 225 or even the 15% divinylbenzene resin.

The characteristic shapes of the equilibrium curves for the 4½ × 4½ resin can both be explained as the result of an increase in " type 2 sites " (see Reichenberg and McCauley [9]). Normally in a 4·5% divinylbenzene resin and indeed even in a 7·0% resin, the proportion of these sites is small, as shown by the values of the relative affinity coefficient K_H^{Na} which do not differ greatly from unity. However, as a result of the interpenetration and entanglement of the second network, the local concentration of polymer chains is increased,[1] giving rise to a decrease in local dielectric constant in the sulphonated matrix.[10] This results in

---

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

[9] Reichenberg and McCauley, *J.*, 1955, 2741.

[10] " Report of National Chemical Laboratory, 1958," H.M.S.O., London, 1959, p. 36.

an increased Coulomb binding energy and a consequential increase in selectivity for the hydrated Na^+ ion in preference to the larger hydrated H^+ ion. This increased concentration of polymer chains also enhances the van der Waals forces on the larger organic ions, which are thus even more tightly bound to the exchange sites, and results in an even more marked increase in the selectivity of the resin for the NEt_4^+ ion. On the other hand, since diffusion of ions in a resin is a function of general rather than local network structure, it is perhaps not surprising that the average coefficients of interdiffusion are higher in a resin with an overall divinylbenzene content of only 4·5% than in one containing 7·0%, irrespective of its equilibrium moisture content.

The $4\frac{1}{2} \times 4\frac{1}{2}$ resin, therefore, shows some of the characteristics of a highly cross-linked resin in its selectivity, but with the high rate of reaction characteristic of a more lightly cross-linked one.

We thank Dr. R. E. Kressman for his advice and criticism, and the Directors of The Permutit Co. Ltd. for permission to publish this paper.

RESEARCH LABORATORY, THE PERMUTIT CO. LTD.,
PONTCYLUN, GLAMORGAN.

[*Received, November* 6*th*, 1961.]