

527. *Solvent-modified Polymer Networks. Part III.¹ Cation-exchange Equilibria with some Univalent Inorganic and Organic Ions.*

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The exchange equilibria, against H^+ , of some univalent inorganic and organic cations have been measured in the sulphonated derivatives of styrene-divinylbenzene copolymers prepared in the presence of toluene. These have been compared with the corresponding equilibria on conventional sulphonic acid resins. The ion-exchange sites within the larger pores of these solvent-modified resins contribute little to the equilibria, the greatest effect being caused by those in the more highly cross-linked regions. This is readily explained in terms of the resin structure postulated previously. While the effect of divinylbenzene content is qualitatively the same as in conventional materials, the lesser entanglement, resulting from modification by solvent, greatly affects the equilibria in both expanded-network and macroporous resins. Exceptionally high electrolyte invasion confirms the macroporous nature of some of the solvent-modified materials.

THE modification by solvent of polymer networks has been shown to produce significant changes in their properties. The effects on the physical properties of the hydrocarbon copolymers and derived cation exchangers² and on the kinetics of cation exchange in the latter¹ have already been reported. This Paper describes the effect of modification by solvent on the cation-exchange equilibria of a number of univalent ions with the hydrogen form of some of these cation exchangers.

For the exchange $\bar{H}^+ + A^+ \rightleftharpoons \bar{A}^+ + H^+$, the ion-exchange equilibria may be represented by the curves of the relative affinity coefficient,³ $K_{\bar{A}}^H$, against \bar{X}_A , the equivalent fraction of the ingoing ion in the resin. Since at the concentrations used (0.05N and less) the ratio of the coefficients of the two ions in solution is practically unity, $K_{\bar{A}}^H$ may be taken simply as the ratio $([\bar{A}^+][H^+]) : ([\bar{H}^+][A^+])$, where the barred symbols relate

¹ Part II, Millar, Smith, Marr, and Kressman, *J.*, 1963, 2779.

² Millar, Smith, Marr, and Kressman, *J.*, 1963, 218.

³ Reichenberg, Pepper, and McCauley, *J.*, 1951, 493.

to quantities in the resin phase. Concentrations are expressed in the resin phase as equivalent fractions, and in solution as equivalents per litre.

The effect of modification by solvent is to change both the magnitude and size-distribution of the pores within the resin, and this will be reflected in a change in the equilibrium curves. The variation of K_H^d with \bar{X}_A , therefore, can be expected to yield information about the pore size and pore-size distribution. In particular, it will provide information about the more highly cross-linked portions of the resins, the larger pores having a progressively smaller proportion of the total ion-exchange sites situated within them. This is in contrast to the kinetics of exchange which provide most information about the more lightly cross-linked areas.¹

Because of the low charge density within the macropores, these will be expected to show a low Donnan exclusion of electrolyte and, indeed, the total volume of the pores in a highly macroporous resin can be so large as to give a very low overall electrolyte exclusion, in spite of the high degree of exclusion from the more highly cross-linked areas.

EXPERIMENTAL AND RESULTS

Materials.—Inorganic salts were AnalaR grade, and the quaternary ammonium salts were identical with those previously used.¹ The resins were made as previously described,² toluene

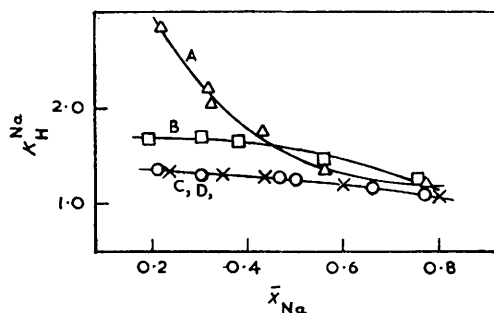


FIG. 1. Effect of divinylbenzene content on $\text{Na}^+\text{-H}^+$ equilibria at essentially constant F_M . (A) 27% tol, $F_M = 0.40$; (B) 20% tol, $F_M = 0.45$; (C) 15% tol, $F_M = 0.40$ (crosses); (D) 10% tol, $F_M = 0.45$ (circles).

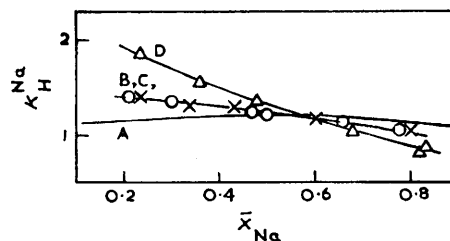


FIG. 2. Effect of divinylbenzene content on $\text{Na}^+\text{-H}^+$ equilibria at essentially constant specific water regain.

(A) Conventional resin, SWR = 0.43 (from Ref. 6); (B) 10% tol, SWR = 0.45 (circles); (C) 15% tol, SWR = 0.47 (crosses); (D) 27% tol, SWR = 0.47.

Characteristics of resins.

Divinylbenzene content (% v/v)	Volume fraction of monomers (F_M)	Toluene regain (ml./g.) of hydrocarbon copolymer	Sulphonated copolymer	
			Capacity (mequiv./g. H^+ -form)	Specific water regain (g./mequiv. H^+ -form)
7	1.00	0.79	4.98	0.21
10	0.45	1.80	4.92	0.45
15	0.62	0.87	4.90	0.20
15	0.40	1.89	4.87	0.47
20	0.45	1.52	4.80	0.30
27	1.00	0.31	4.56	0.08
27	0.60	0.93	4.73	0.17
27	0.51	1.14	4.61	0.22
27	0.40	1.86	4.74	0.29
27	0.27	3.12	4.72	0.47
34	0.50	0.87	4.67	0.19
34	0.33	1.95	4.40	0.40
55	0.33	2.21	3.52	0.54

being used as the solvent. Their constitutions and properties are summarised in the Table. We shall refer to the resins containing $x\%$ of divinylbenzene and made in the presence of toluene as " $x\%$ tol resins," identifying them where necessary by quoting the appropriate volume fraction of monomers.

Equilibria with Inorganic Ions.—These were measured as previously described,⁴ the H⁺ ion being used as the reference ion. To avoid corrections for electrolyte invasion (see below) the resin : solution ratio was kept smaller than 1 : 40, 0.01N-solutions being used where necessary

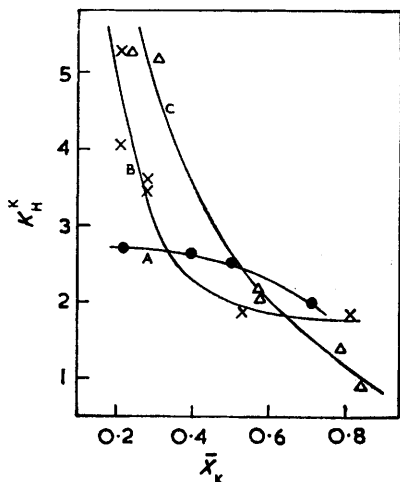


FIG. 3. Effect of divinylbenzene content on K⁺-H⁺ exchange at constant specific water regain.

(A) 7% SWR = 0.21; (B) 15% tol, SWR = 0.20; (C) 27% tol, SWR = 0.22.

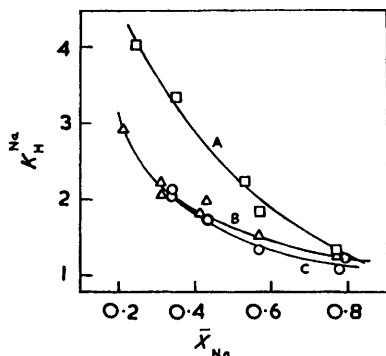


FIG. 5. Effect of F_M on Na⁺-H⁺ equilibria at constant divinylbenzene content of 27%.

(A) $F_M = 1.0$, SWR = 0.08; (B) $F_M = 0.60$, SWR = 0.17; (C) $F_M = 0.40$, SWR = 0.29.

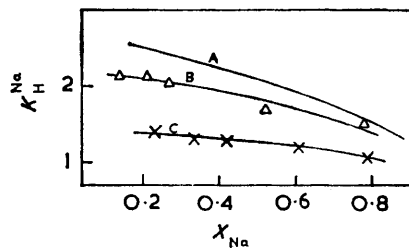


FIG. 4. Effect of F_M on Na⁺-H⁺ equilibria at constant divinylbenzene content of 15%.

(A) $F_M = 1.0$, SWR = 0.11 (from Ref. 8); (B) $F_M = 0.62$, SWR = 0.20; (C) $F_M = 0.40$, SWR = 0.47.

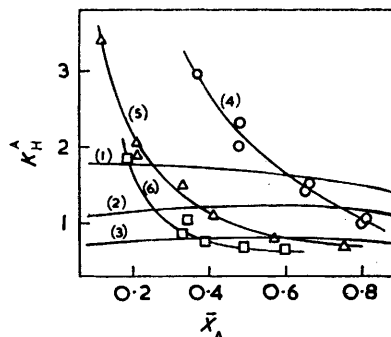


FIG. 6. Li⁺, Na⁺, and K⁺-H⁺ exchange on a conventional and a macroporous exchanger of similar specific water regain.

(1)–(3): conventional resins, SWR = 0.43 (from Ref. 6). (4)–(6): 34% tol, $F_M = 0.33$, SWR = 0.40. (1) and (4), K⁺-H⁺ exchange. (2) and (5), Na⁺-H⁺ exchange. (3) and (6), Li⁺-H⁺ exchange.

to obtain this condition. (Since we are concerned only with uni-univalent exchanges, the equilibria are independent of concentration.) Although equilibrium was established within ten days, at least three weeks were always allowed before analysis.

Fig. 1 shows the Na⁺-H⁺ equilibria for several resins of different divinylbenzene contents but similar values of F_M , the volume fraction of monomers in the initial monomer-diluent mixture. Fig. 2 shows the Na⁺-H⁺ equilibria on four resins of different divinylbenzene contents, all of which have specific water regains (SWR) corresponding to an apparent divinylbenzene

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

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content⁵ of about 3%. Fig. 3 shows, similarly, the K^+-H^+ equilibria on a number of resins of specific water regain *ca.* 0.21, which corresponds to a conventional resin of *ca.* 7% divinylbenzene content.

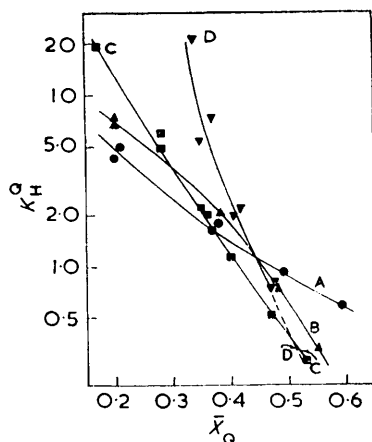


FIG. 7. Quaternary ions on a 7% conventional resin, SWR = 0.21.

(A) NMe_4^+ ; (B) NEt_4^+ ; (C) $NPr^n_4^+$; (D) $NBu^m_4^+$.

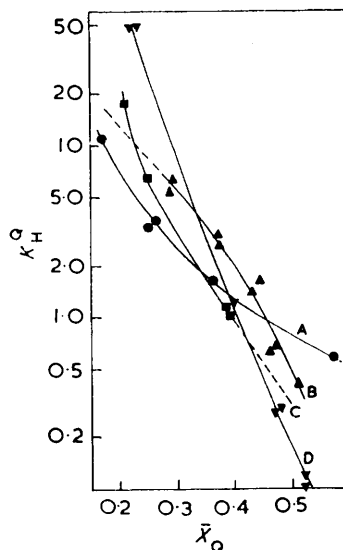


FIG. 8. Quaternary ions on a 15% tol resin, SWR = 0.20.

[Curves (A)–(D) as for Fig. 7.]

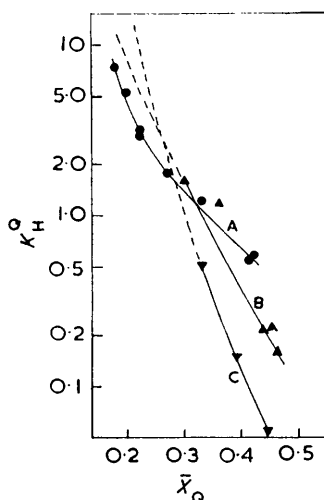


FIG. 9. Quaternary ions on a 27% tol resin, SWR = 0.22.

[Curves (A)–(D) as for Fig. 7.]

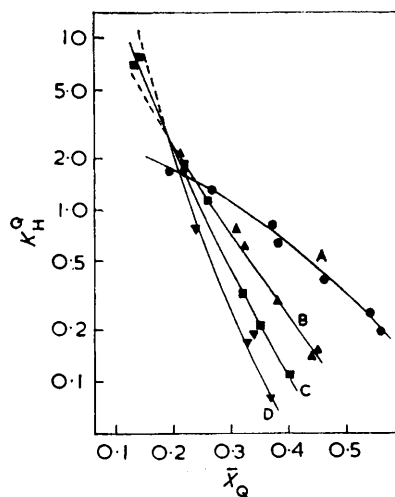


FIG. 10. Quaternary ions on a 34% tol resin, SWR = 0.40.

[Curves (A) and (B) as for Fig. 7; curve C, $NBu^m_4^+$.]

Figs. 4 and 5 show the Na^+-H^+ exchange equilibria on resins containing 15% and 27% divinylbenzene, respectively, prepared with different volume fractions of monomers. The equilibrium behaviour with three inorganic ions is shown for a typical macroporous cation

⁵ Kressman and Millar, *Chem. and Ind.*, 1961, 1833.

exchanger in Fig. 6, and compared with that reported⁶ for a resin of 4% nominal divinylbenzene content of similar specific water regain.

Equilibria with Organic Ions.—These were measured as before,⁴ except that between 2 and 3 weeks were required for equilibrium to be established with the tetra-*n*-propyl- and tetra-*n*-butyl-ammonium ions. The results are shown in Figs. 7–10.

Electrolyte Invasion.—This was measured by the method of Bauman and Eichhorn.⁷ Fig. 11 shows the ratio of internal to external molarity of HCl in the H⁺-form resins as a function of the external molarity.

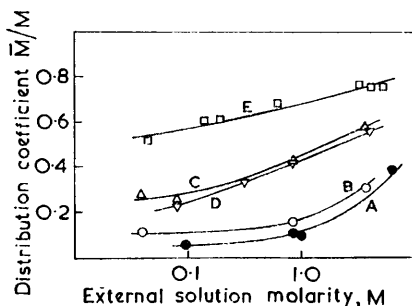


FIG. 11. Electrolyte invasion in a conventional exchanger and in comparable expanded-structure and macroporous resins (H⁺-form, HCl as invading species).

- (A) 7% DVB, $F_M = 1.0$, SWR = 0.21.
 (B) 15% tol, $F_M = 0.62$, SWR = 0.20.
 (C) 27% tol, $F_M = 0.51$, SWR = 0.22.
 (D) 34% tol, $F_M = 0.50$, SWR = 0.19.
 (E) 34% tol, $F_M = 0.33$, SWR = 0.40.

DISCUSSION

The force binding inorganic cations to a cation-exchange resin is purely coulombic, and the selectivity for the preferred of two inorganic cations is greater the higher the local charge density. Since, as the exchanging ions enter a resin, they must first take up positions in regions of highest affinity and then in regions of progressively lower affinity, it follows that low values of exchange (low \bar{X}) correspond to a high local charge density, and high values to a low local charge density. In a conventional resin, made in the absence of diluent ($F_M = 1$), the former can, in general, be identified⁸ with regions of high local cross-linking and/or chain entanglement, and the latter with regions of low local cross-linking and/or entanglement. In solvent-modified resins ($F_M < 1$) the areas of high cross-linking can be identified with the nuclei, and those of low cross-linking with the internuclear regions in the expanded-network resins or with the macropores in the macroporous resins.*

It follows that anything that increases the proportion of the nuclei will increase the selectivity at low values of \bar{X} , and Fig. 1 demonstrates this for the Na⁺-H⁺ exchange on a series of resins at constant F_M and increasing divinylbenzene content. Comparatively little effect is observed at higher values of \bar{X} because, although the volume of the larger pores is increasing correspondingly, the number of ion-exchange groups situated therein must, by their very nature, be small.

An increase in divinylbenzene content with a simultaneous decrease in F_M to give the same apparent degree of cross-linking (the same specific water regain) similarly results in an increase in the proportion of the nuclei, and again the selectivity is increased at low

* In very highly cross-linked and entangled regions where the local dielectric constant is low,^{4, 9} the charge density may also be low¹⁰ owing to ion-pairing of the SO₃H group.^{8, 11} It is also possible that in these regions the nature of the exchanging species may change by their becoming at least partially dehydrated. Both of these effects may change the "natural" order of affinities of the ions.⁸

⁶ Bonner, *J. Phys. Chem.*, 1954, **58**, 318.

⁷ Bauman and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2831.

⁸ Reichenberg and McCauley, *J.*, 1955, 2741.

⁹ "Report of National Chemical Laboratory, 1958," H.M.S.O., London, 1959, p. 36.

¹⁰ Lindenbaum, Jumper, and Boyd, *J. Phys. Chem.*, 1959, **63**, 1924.

¹¹ Bonner and Rogers, *J. Phys. Chem.*, 1960, **64**, 1499.

values of \bar{X} (Fig. 2). As before, the proportion of the larger pores increases correspondingly (which, indeed, is the reason for the identity of the specific water regain values), but the effect of these on the relative affinity coefficient at high \bar{X} is small, for the same reason.

Fig. 3 demonstrates the same effect for the K^+-H^+ exchange. Here, however, the specific water regain of the resins is considerably lower and the exchange sites represented by the higher values of \bar{X} are now situated in pores smaller than those of Fig. 2. This results in a change in relative affinity coefficient with changing divinylbenzene content at these higher \bar{X} values, an effect characteristic of a highly cross-linked resin.⁸

The effect of increasing the proportion of solvent (decreasing F_M) at constant divinylbenzene content is primarily to *decrease* entanglement, particularly of the highly cross-linked regions, with a corresponding reduction in selectivity at low values of \bar{X} (Figs. 4 and 5). The 15% tol resin of Fig. 4, with comparatively small nuclei, contains no macropores but possesses a purely expanded structure,² and the effect of increasing modification by solvent here is a general increase in size of the pores. The result is a steady fall in the relative affinity coefficient at all values of \bar{X} . For the 27% tol resin, in which the nuclei are larger, less toluene is required to give a comparable drop in selectivity (see Fig. 5). In each case, the characteristic concave or convex shape of the equilibrium curve is maintained, irrespective of the degree of modification by solvent.

A divinylbenzene content of 34%, combined with an appropriate degree of modification by solvent, gives a resin with a high proportion of its pore-volume in the form of macropores, yet with well over half its capacity in the region of the nuclei. The relative affinity coefficients on this resin for the exchange with H^+ of K^+ , Na^+ , and Li^+ ions (Fig. 6) can be explained on the same model. Again we see the higher values of K_H^A at low values of \bar{X} , compared with a conventional resin of the same apparent degree of cross-linking. Very marked selectivity reversal is shown by all three ions, increasing in the order $K < Na < Li$. This is the order found by Reichenberg and McCauley⁸ on conventional resins of high divinylbenzene content. Inversion in the macroporous 55% tol resin occurs at still lower values of \bar{X} , the Na^+ ion inverting at $\bar{X}_{Na} = 0.40$ and the K^+ ion at $\bar{X}_K = 0.70$. Since the kinetics of exchange on these resins are quite fast, macroporous resins of this kind would be excellent subjects on which to study selectivity reversal.

When one of the exchanging ions is a large organic ion, an additional (van der Waals) binding force is involved.¹² The low values of \bar{X} now correspond to the regions of *low* local cross-linking (the internuclear regions or macropores in the solvent-modified resins) where the large ion can come sufficiently close to the matrix carrying the fixed charges to result in a high van der Waals interaction. The larger the ion, the greater is this interaction and the greater the affinity coefficient relative to the purely ionically bound hydrogen ion. The high values of \bar{X} correspond to the regions of high local cross-linking (the nuclei in the solvent-modified resins). Here the ion cannot approach within the few Ångstrom units of the matrix essential for van der Waals binding, and indeed the distance between the two charges can become so great that even the coulombic binding force is small and the hydrogen ion is preferred. The larger the ion the smaller is this coulombic force and the smaller, therefore, the relative affinity coefficient. Consequently, on any given resin, the $K-\bar{X}$ curves for a homologous series of organic ions exchanged against H^+ will be steeper the larger the ion, and will intersect somewhere in the middle \bar{X} region. Figs. 7–10 show that this is, indeed, the case for both conventional ($F_M = 1.0$) and solvent-modified resins. The 15% tol resin (Fig. 8), possessing a purely expanded structure, shows a similar $K-\bar{X}$ pattern to a conventional 7% resin of the same specific water regain. There is a similarity in behaviour of the $K-\bar{X}$ curves when either the ion-size on a given resin or the degree of modification by solvent of the resin for the same ion is altered;

¹² Kressman and Kitchener, *J.*, 1949, 1208.

this is to be expected, since the determining factor is the size of the ion in relation to the pore-diameter in a given region of the resin.¹³

As the divinylbenzene content is increased and the expanded structure gives way to the more rigid macroporous structure, progressively greater numbers of ion-exchange groups lie within regions of high cross-linking, and low relative affinity coefficients are thus associated with correspondingly greater proportions of the total exchange. This is reflected in the progressive movement of the $K-\bar{X}$ curves for any ion toward lower values of \bar{X} (Figs. 9 and 10). It occurs in the 34% tol resin despite its higher specific water regain, since the additional water is almost entirely accommodated within the macropores which, as already explained, have little or no influence on the relative affinity coefficient.

These macropores can also accommodate appreciable amounts of electrolyte. While in conventional resins the Donnan membrane effect results in marked exclusion of electrolyte, in larger pores the charge density is lower and electrolyte invasion is facilitated. Curves (A)—(D) in Fig. 11 show the progressive increase in electrolyte invasion, and thus in the proportion of larger pores, as the result of maintaining, by means of modification by solvent, an essentially constant apparent cross-linking, while the divinylbenzene content is increased. The resin of curve (E) has the same divinylbenzene content as that of curve (D), but a reduction in F_M has resulted in a high degree of macroporosity; the greater water content represented by the difference in their specific water regains is again largely accommodated within the macropores. Such a high degree of electrolyte invasion as that represented by curve (E) must reflect the presence of macropores so large that the Gouy layers wholly fail to overlap, and the charge density throughout most of the volume of these pores is essentially zero. Here Donnan exclusion will be wholly absent, even at low ambient concentrations.

The previous Paper¹ demonstrated the remarkably high rate of exchange in solvent-modified resins, a result of their substantially unentangled internuclear regions and macropores which make the areas of higher cross-linking, including the nuclei, more accessible to the exchanging ions. The present work has shown the comparatively small effect of these larger pores on the ion-exchange equilibria, which are almost exclusively determined by the more highly cross-linked regions. Thus, in a single resin, equilibria characteristic of a highly cross-linked resin are combined with kinetics characteristic of a more lightly cross-linked one. This is similar to the effect noted in an earlier Paper,⁴ where the resin concerned was a conventional one of comparatively low cross-linking, the entanglement of which had been deliberately enhanced by the addition of a second interpenetrating styrene-divinylbenzene network. Thus resins of similar "external" characteristics (*e.g.*, exchange capacity, water regain, and apparent cross-linking) can be prepared with internal structures varying from the complexity of the intermeshed copolymers, through the pseudo-homogeneous conventional materials, to the patently heterogeneous macroporous materials described in the present series of Papers.

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[Received, August 2nd, 1963.]

¹³ Ref. 9, p. 39.