Properties of Ion-exchange Resins in Relation to Their Structure. Part VII. Cation-exchange Equilibria on Sulphonated Polystyrene Resins of Varying Degrees of Cross-linking.*

By D. REICHENBERG and D. J. McCAULEY.

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A study has been made of the relative affinities of various pairs of univalent cations for ion-exchange resins consisting of monosulphonated polystyrenes of various degrees of cross-linking. Results are presented for all the possible combination of the four cations, H, Li, Na, and K with resins of 5, 10, 15, and 25% (nominal) divinylbenzene content. Examination of the results suggests a " natural " order of affinities: K > Na > H > Li. Inversions of affinity occurred only with systems involving hydrogen, and these inversions have been shown to be a true effect of the sulphonic groupings and not due to any " polyfunctionality " of the resins. It is concluded that the simplified form of Gregor's theory of ion-exchange affinity (*J. Amer. Chem. Soc.*, 1951, **73**, **643**) does not account completely for the experimental results obtained. It is suggested that any further developments of the theory must take into account the statistical variation of cross-linking in ion-exchange resins and the relative ease with which the hydration shells of ions may lose some water molecules.

REICHENBERG, PEPPER, and McCAULEY (*J.*, 1951, **493**) investigated the sodium–hydrogen equilibria on a number of monosulphonated styrene–divinylbenzene copolymers with varying degrees of cross-linking. This work has now been extended to elucidate some of the fundamental factors governing ion-exchange equilibria by studying various pairs of cations. Since it was desired to eliminate as far as possible such complicating factors as ion-pair and complex-ion formation, the study was confined to the hydrogen ion and ions of the alkali-metals. (However there are grounds for believing that in some respects the hydrogen ion behaves anomalously.) The ion-exchange equilibria of all the possible pairs of ions arising from the series hydrogen, lithium, sodium, and potassium have been studied on sulphonated cross-linked polystyrene resins of 5, 10, 15, and 25% (nominal) divinylbenzene contents. All measurements were made at 25° and from solutions of virtually infinite dilution (with one exception).

EXPERIMENTAL

Determination of Relative Affinity Coefficients.—The method used was essentially the same as that described previously (Reichenberg, Pepper, and McCauley, *loc. cit.*), but whereas the previous work was carried out at 22—25°, in the present study the conditioning process was carried out in an air-thermostat at 25·0° ± 0·1°. The conditioning solution (initially in a vessel outside the thermostat) flowed to the column of resin through coils of glass tubing which even with the highest flow rate used and the highest temperature difference between the inside and the outside of the thermostat ensured that its temperature was within 0·1° of that required.

In the previous work, and also for the sodium–hydrogen equilibria reported in the present work, all conditioning solutions had a concentration of 0·1125N, and after conditioning, the excess of liquid was drained off, a correction being applied for the electrolyte in the small amount of liquid left. For all other equilibria reported in the present paper, the resin was first conditioned with a 0·1N conditioning solution, then with a further amount diluted to 0·05N, then 0·02N, then 0·01N, and finally the resin was washed with water. The amounts of the diluted conditioning solutions and the flow rates used were such as to try to ensure that the ion-exchange equilibrium, if it was dependent on the total concentration, would not be " frozen " at a position corresponding to a concentration greater than 0·01N. It has been assumed that variation of solution concentration below 0·01N has no further effect on the resin composition. As in the earlier work, completeness of conditioning and the absence of hysteresis effects have been demonstrated by approaching the equilibrium from both directions.

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* Part VI, *J.*, 1953, 4097.

In systems involving the hydrogen ion, this ion alone was determined, the amount of the other ion on the resin being obtained by difference from the total ion-exchange capacity of the resin sample (about 2·5 m.-equivs.). With other pairs of ions, both ions were eluted from the resin with 2N-hydrochloric acid, and the total volume made up to 50 ml. with 2N-acid. The amounts of the two ions in the eluate were then determined with a Beckman DU Flame Spectrophotometer, made-up standard solutions containing hydrochloric acid and the chlorides of the two ions being used. The composition of these standard solutions was adjusted so that (*a*) the total chloride ion concentration was 2N, (*b*) the sum of the concentrations of the two cations was the same as in the made-up eluate solution; (*a*) and (*b*) being kept fixed, standards were made up containing various amounts of the two cations. This enabled the exact amounts of the two ions in the eluate solution to be determined separately. It was found in all cases that their sum agreed within experimental error (±2%) with the known total exchange capacity of the sample of resin used.

In the first part of this work, the analyses for the sodium–potassium equilibria were carried out by determining the sodium gravimetrically by means of zinc uranyl acetate and obtaining the potassium concentration by difference. These results were later checked by use of the flame photometer.

Materials.—Resins. The resins used were similar to, but not identical with, those used in the previous work. A brief account of this difference has been given in another paper (Pepper, Reichenberg, and Hale, *J.*, 1952, 3129). The resins of the present work were prepared from the commercial (approximately 50%) divinylbenzene. Differences between these resins and corresponding resins of the other series are small. The properties of the resins used are given in Table 1.

TABLE 1.

Nominal divinyl-benzene content (%)	Particle diameter (swollen in water) (μ)	Specific capacity (m-equivs. per g. dry H-form resin)			Weight swelling (g. of H_2O absorbed per amount of resin equivalent to 1 g. dry H-form resin)			
		(1) Found	(2) Calc.[a]	(3) Calc.[b]	H-form	Li-form	Na-form	K-form
5½	200—250	5·40	5·38	5·37	1·49	1·48	1·26	1·11
10	150—250	5·30	5·30	5·31	0·84	—	0·73	0·62
15	130—220	5·24	5·25	5·25	0·60	—	0·53	0·45
25	100—250	*	4·83	5·11	0·38	0·36	—	—

[a] Calculated from the sulphur content. [b] Calculated assuming monosulphonation of each benzene ring.

* This resin was polyfunctional and its specific capacity increased with increasing pH. In 0·1N-NaCl solution, the specific capacity of 4·83 (calculated from the sulphur content) was realised at pH 3·8, but at pH 12 the capacity was nearly 5·1.

The weight swellings were determined with the centrifuge (Pepper, Reichenberg, and Hale, *loc. cit.*). While absolute values of the weight swellings cannot be relied upon to better than ±0·01, the difference in weight swelling of two different cationic forms of the same resin can be determined to within ±0·003.

Conditioning solutions. All the conditioning solutions were made from appropriate mixtures of 2N-HCl, -LiCl, -NaCl, and -KCl. The last two solutions were made up by weighing out appropriate quantities of "AnalaR" materials which had been dried overnight at 110°. The lithium chloride solution was made by precipitating the carbonate, washing and drying it, and then decomposing a known weight with concentrated hydrochloric acid, followed by evaporating to dryness twice and redissolving. The concentrations of the chloride solutions were checked by using standard ion-exchange procedures described by Samuelson ("Ion Exchangers in Analytical Chemistry," John Wiley and Sons, Inc., New York; Almquist and Wiksell, Stockholm, 1953, Chapter VIII). For use, known volumes of two of the standard 2N-solutions were accurately made up together and diluted to approximately 0·1N total cation concentration.

DISCUSSION

The relative affinity coefficient $K_{\mathrm{A}}^{\mathrm{B}}$ of two ions A and B (of the same valency) for a resin is defined as

$$K_{\mathrm{A}}^{\mathrm{B}} = \frac{[\mathrm{B_R}]}{[\mathrm{A_R}]} \cdot \frac{[\mathrm{A_S}]}{[\mathrm{B_S}]} \cdot \frac{(f_{\mathrm{A}})_{\mathrm{S}}}{(f_{\mathrm{B}})_{\mathrm{S}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[A_R]$ and $[B_R]$ are the amounts of A and B on the resin, $[A_S]$ and $[B_S]$ are the concentrations in solution, and $(f_A)_S$ and $(f_B)_S$ are the activity coefficients of the ions in solution. $[(f_A)_S$ and $(f_B)_S$ cannot of course be evaluated separately though their ratio is determinate.$]$ If the final equilibration is done in solutions of virtually infinite dilution, the activity coefficient ratio in solution may be taken as unity. In 0·1N-solutions, however, this ratio usually differs from unity by a few percent.

For convenience, our results are given as plots of log K_A^B against $(X_B)_R$, where $(X_B)_R$ is the equivalent fraction of B on the resin (Figs. 1—6).

It will be observed that the present results on the Na–H system agree quite well with those previously reported (Reichenberg, Pepper, and McCauley, *loc. cit.*). Such differences as occur increase with increased cross-linking and are undoubtedly due to differences in the preparation of the resins (see above). Where comparison is possible, the present results agree roughly with those of Bonner and his co-workers (Bonner and Rhett, *J. Phys. Chem.*, 1953, **57**, 254; Bonner and Payne, *ibid.*, 1954, **58**, 183; Bonner, *ibid.*, p. 318), but there are more marked differences in the case of the Li–H system. Gregor and Bregman's results (*J. Colloid Sci.*, 1951, **6**, 323) do not agree well with either those of Bonner or our own. These differences are probably mainly due to differences in the resins used, though differences of experimental technique in the determination of relative affinities may also play some part.

In general, for a given pair of ions and a given resin, the relative affinity coefficient varies with the cationic composition of the resin. In nearly all cases, log K_A^B decreases with increasing $(X_B)_R$, *i.e.*, the affinity of the resin for a given ion decreases with increase in the amount of that ion on the resin. Some apparent exceptions are of interest: (1) In the sodium–lithium system, minima are found with the 5% and 10% divinylbenzene resins. These are very shallow and may be within experimental error. (2) In the sodium–hydrogen system, a maximum is found with the 5% divinylbenzene resin. The sodium–hydrogen equilibria were the only ones examined in 0·1N-solution; all the others were studied in solutions of virtually infinite dilution.

These considerations suggest that, in the alkali-metal series, all equilibria in solutions of infinite dilution may conform to the pattern of decreasing K_A^B with increasing $(X_B)_R$.

Both the relative affinity differences themselves and their variation with the cationic composition of the resin increase markedly with increase in the degree of cross-linking. Separate experiments have shown that a resin of only ½% divinylbenzene has K values which are always unity.

It will be observed that the six systems may be divided into two types: (*a*) Those in which an inversion of log K can occur, *i.e.*, log K changes sign with variation of cationic composition. This occurs only in the systems involving the hydrogen ion, Li–H, Na–H, and K–H (Figs. 1, 2, and 3), and only with resins of high cross-linking (15 and 25% divinylbenzene). (*b*) Those in which no inversion occurs. This group comprises the systems Li–Na, Li–K, and K–Na (Figs. 4, 5, and 6).

It was suggested earlier (Reichenberg, Pepper, and McCauley, *loc. cit.*) that inversions might be due to " polyfunctionality " in the resins of high cross-linking rather than a " true " effect of the sulphonic acid groups. This explanation is, however, disproved by the results on the lithium–hydrogen system, for on this basis in Fig.1, the preference for hydrogen should occur at lower values of $(X_{Li})_R$ for the 25% divinylbenzene resin than for the 15% resin, but the reverse is found. This can only be explained by supposing either that the carboxyl groups have an exceptionally high affinity for the lithium ions, higher even than for hydrogen ions, or that the inversion is a true effect of the sulphonic acid groups. The latter explanation is far more probable, and it is clear that the inversion phenomenon is bound up with the unique character of the hydrogen ion.

Among the systems of type (*b*) log K_A^B keeps the same sign for a given pair of ions not only with varying cationic composition but also with varying cross-linking. Thus, log K_{Li}^{Na}, log K_{Li}^{K}, and log K_{Na}^{K} are always positive, so that we may, in a loose sense, write down a " natural " order of affinities K > Na > Li. In Figs. 4—6, A and B have been so chosen as to make log K_A^B positive. With this convention, log K_A^B increases continually with increasing cross-linking at low values of $(X_B)_R$. This is not so at high values of

FIG. 1. *Hydrogen–lithium exchange.*

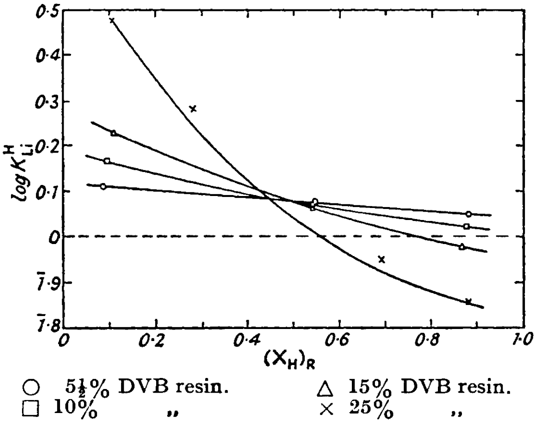


FIG. 2. *Sodium–hydrogen exchange.*

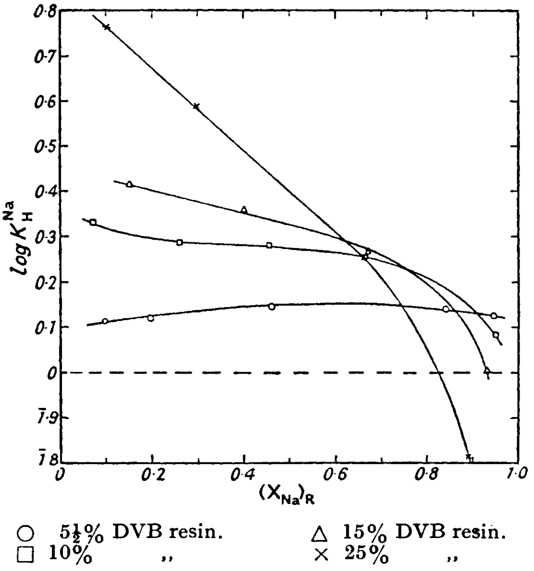


FIG. 3. *Potassium–hydrogen exchange.*

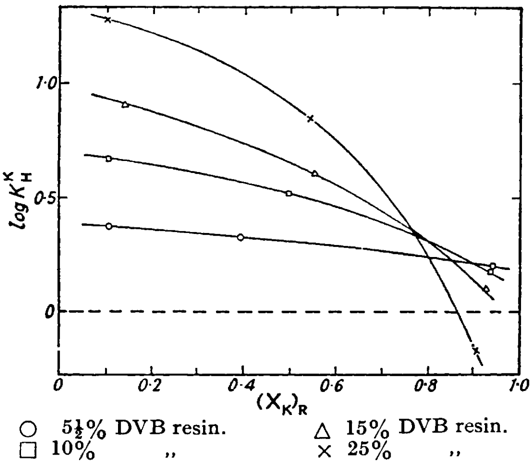


FIG. 4. *Sodium–lithium exchange.*

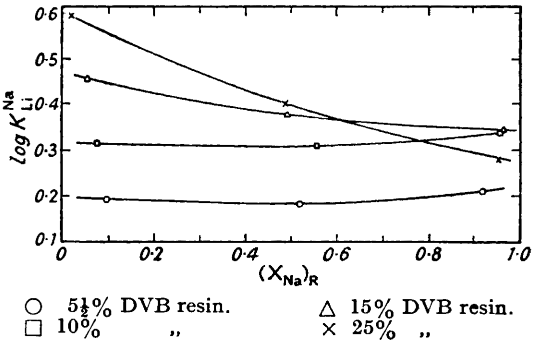


FIG. 5. *Potassium–lithium exchange.*

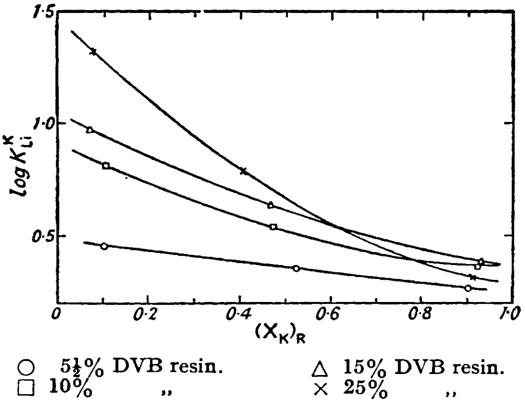
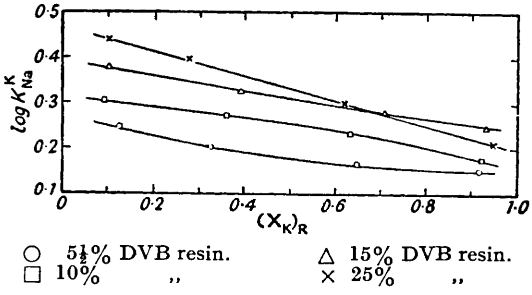


FIG. 6. *Potassium–sodium exchange.*



$(X_B)_R$ since some of the curves cross. (This irregularity appears to be primarily centred in the 25% divinylbenzene resin whose curve in each case crosses at least one of the other curves.) Thus there is a regular effect of cross-linking on the relative affinity provided that the resin is predominantly in the form of the ion of lower " natural " affinity.

For systems of type (*a*) we cannot apply the simple criterion of the sign of log K_A^B to find which ion has the higher " natural " affinity for the resin. However, three regularities may be noted : (1) At low and intermediate degrees of cross-linking, no inversion occurs and log K keeps the same sign with varying cross-linking. On the basis of the sign of log K_A^B within this restricted range of cross-linking, we obtain the order of affinities K > Na > H > Li. (2) If we assume (in accordance with this order) that lithium has a lower " natural " affinity than hydrogen, then to conform to our previous convention log K_{Li}^H should be plotted against $(X_H)_R$ (Fig. 1) rather than log K_H^{Li} against $(X_{Li})_R$. It is then found (Figs. 1, 2, and 3) that at low values of $(X_B)_R$, log K_A^B increases continually with increase of cross-linking *over the whole range of cross-linking.* (3) Provided this convention be adopted, we find that in all cases where inversion occurs, it does so at a lower value of $(X_B)_R$ for the 25% divinybenzene resin than for the 15% one, B being the ion of higher " natural " affinity.

Thus, despite the complication of inversions, there appears to be a " natural " order of affinities K > Na > H > Li.

The order K > Na > Li is also the order of decreasing ionic mobilities and of numerous other physicochemical properties, all of which are agreed to depend on the size of the *hydrated* cation. These results confirm the view (Boyd, Schubert, and Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818) that ion-exchange affinity (at least with these simple cations) is determined primarily by the size of the hydrated ion, ions of small hydrated volume being preferred to large ions. It is also accepted that the hydrated hydrogen ion is larger than that of sodium. However, some doubt attaches to the implication that the hydrated lithium ion is larger than that of hydrogen. This point is discussed later.

THEORETICAL DISCUSSION

Gregor (*J. Amer. Chem. Soc.*, 1948, **70**, 1293; 1951, **73**, 643) represents the behaviour of ion-exchange resins in terms of a model involving an outward swelling pressure due to the osmotic activity of the ion-exchange groups and an inward counter-pressure due to the elastic forces of the cross-linked network. At equilibrium the two pressures are balanced. From this model, Gregor derived the general expression

$$\boldsymbol{R}T \ln K_A^B = \boldsymbol{R}T \ln \left(\frac{f_A}{f_B}\right)_R + \pi (V_A - V_B) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K_A^B is as previously defined and π is the swelling pressure in the resin. π may be obtained unambiguously from the swelling isotherm of the resin if this is compared with that for a resin of low cross-linking or correlated with the osmotic properties of solutions of the corresponding linear polyelectrolyte. V_A and V_B are the volumes of the ions in the resin and $(f_A/f_B)_R$ is the ratio of the activity coefficients of these ions in a hypothetical resin identical in composition with the real one but not acted upon by the elastic counter-pressure. Gregor's general formulation has been widely adopted. The actual magnitudes of V_A, V_B, and $(f_A/f_B)_R$, and hence the relative magnitudes of the two terms on the right-hand side of equation (2), are affected markedly by the convention adopted in defining the components A and B. If A and B are the unhydrated ions, V_A and V_B will be very small and $(f_A/f_B)_R$ will differ greatly from unity. Hence the first term on the right-hand side of equation (2) will greatly outweigh the second. To proceed with this treatment it is necessary to develop a theoretical or semi-theoretical treatment which will enable values of $(f_A/f_B)_R$ to be predicted. This presents considerable difficulties though theories of this type have been developed and are discussed below (Glueckauf, *Proc. Roy. Soc.*, 1952, *A*, **214**, 207; Davies and Yeoman, *Trans. Faraday Soc.*, 1953, **49**, 968, 975).

The difficulty of predicting values of $(f_A/f_B)_R$ theoretically lies, of course, in the fact that all purely theoretical attempts to account quantitatively for the activity coefficients of electrolyte solutions fail even at quite moderate concentrations. Stokes and Robinson however (*J. Amer. Chem. Soc.*, 1948, **70**, 1870; *Ann. New York Acad. Sci.*, 1949, **51**, 593) have shown that if one assigns to each " molecule " of electrolyte an appropriate hydration number and assumes that the *hydrated* ions interact in accordance with the Debye–Hückel approximation, an expression is obtained which gives remarkable agreement with experimental values up to quite high concentrations. In place of the convention of unhydrated ions, Gregor adopted an alternative convention whereby A and B are defined as the hydrated ions in the form in which they exist inside the resins. Equation (2) then becomes

$$\boldsymbol{R}T \ln K_{\mathrm{A}}^{\mathrm{B}} = \boldsymbol{R}T \ln \left(\frac{f_{\mathrm{A}}'}{f_{\mathrm{B}}'}\right)_{\mathrm{R}} + \pi\,(V_{\mathrm{A}}' - V_{\mathrm{B}}') \quad . \quad . \quad . \quad . \quad (3)$$

where $(f_{\mathrm{A}}'/f_{\mathrm{B}}')_{\mathrm{R}}$ is the ratio of the activity coefficients of the hydrated ions in the hypothetical resin, and V_{A}' and V_{B}' are the volumes of the hydrated ions in the resin. The significance of equation (3) is that the first term on the right-hand side corresponds to the Debye–Hückel term in the Stokes–Robinson equation, while the second term on that side corresponds to the " solvent " term. The success of the Stokes–Robinson theory when applied to concentrated solutions encourages the hope that, provided appropriate values of V_{A}' and V_{B}' are chosen and a suitable solution of the appropriate Poisson–Boltzmann equation can be obtained, it will be sufficient to take only the first few terms of this solution to obtain a suitable value for $\boldsymbol{R}T \ln (f_{\mathrm{A}}'/f_{\mathrm{B}}')_{\mathrm{R}}$. Such a solution has not yet been obtained but the work of Katchalsky and Lifson (*J. Polymer Sci.*, 1953, **11**, 409) appears very promising.

Pending such a solution, Gregor has made the provisional assumption that the first term on the right-hand side of equation (3) is of less importance than the second, and that in discussions of the qualitative effects of various factors, the first term may be ignored. This corresponds to the fact that in the Stokes–Robinson equation, the Debye–Hückel term is very much smaller than the " solvent " term. Equation (3) then becomes

$$\boldsymbol{R}T \ln K_{\mathrm{A}}^{\mathrm{B}} = \pi\,(V_{\mathrm{A}}' - V_{\mathrm{B}}') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We will call this equation the expression of the simplified Gregor theory. From it a number of deductions may be made : (1) If $V_{\mathrm{A}}' > V_{\mathrm{B}}'$ then $K_{\mathrm{A}}^{\mathrm{B}} > 1$ and *vice versa.* (2) If $V_{\mathrm{A}}' - V_{\mathrm{B}}'$ does not change sign, then $\ln K_{\mathrm{A}}^{\mathrm{B}}$ should undergo no inversion since π is always positive. (3) If $V_{\mathrm{A}}' > V_{\mathrm{B}}'$, then as $(X_{\mathrm{B}})_{\mathrm{R}}$ increases the resin contracts and π decreases. Hence, provided $(V_{\mathrm{A}}' - V_{\mathrm{B}}')$ does not change to an extent to nullify the effect, $K_{\mathrm{A}}^{\mathrm{B}}$ will decrease. In other words, Gregor's theory predicts unambiguously the decrease of affinity of the resin for an ion with increase in the amount of that ion on the resin. (4) At a given $(X_{\mathrm{B}})_{\mathrm{R}}$, increase of cross-linking causes an increase of π. Hence, provided $(V_{\mathrm{A}}' - V_{\mathrm{B}}')$ does not change to an extent to nullify the effect, $K_{\mathrm{A}}^{\mathrm{B}}$ should increase with increasing cross-linking.

The first prediction is, as we have seen, in fair agreement with what is known of the order of the sizes of the hydrated ions of the alkali-metal series (with the possible exception already mentioned).

The natural deduction from (2) is that $(V_{\mathrm{A}}' - V_{\mathrm{B}}')$ does not change sign in resins of cross-linking up to 10% divinylbenzene. According to equation (4), inversions must be due to a change of sign of $(V_{\mathrm{A}}' - V_{\mathrm{B}}')$.

The third prediction is in accord with nearly all our results and may be generally valid for equilibria in solutions of virtually infinite dilution.

The fourth prediction holds over the greater range of values of $(X_{\mathrm{B}})_{\mathrm{R}}$ in most cases, but in all cases it fails when the resins are predominantly in the form of higher " natural " affinity. With systems not involving hydrogen (*i.e.*, showing no inversion) the failure is confined to the 25% divinylbenzene resin whose curve crosses that of one or more of the other resins. With systems involving hydrogen the intersection of curves is more wide-spread and all the curves cross one another, so that with resins predominantly in the form of higher natural affinity, the order of the log $K_{\mathrm{A}}^{\mathrm{B}}$ values for the different degrees of cross-linking is exactly the opposite of that found when the resins are predominantly in the form of lower natural affinity.

A great merit of Gregor's theory is its simplicity. Thus equation (4) would be of little practical use quantitatively if, in the majority of cases, one had to allow for variation of $(V_A' - V_B')$. It would then be impossible to base quantitative predictions upon equation (4) unless one knew also the variation in $(V_A' - V_B')$. The question therefore arises whether, in the simplest systems, equation (4) holds quantitatively with $(V_A' - V_B')$ assumed constant. It has been seen that equation (4) fails qualitatively with resins of high cross-linking or with systems involving hydrogen. For a simple test of the quantitative applicability of equation (4), the potassium–sodium systems with resins of 5%, 10%, and 15% divinylbenzene have been chosen.

Now π, the internal osmotic pressure of the resin, may be obtained from swelling isotherms. It has been shown (Glueckauf, *loc. cit.*; Boyd and Soldano, *Z. Elektrochem.*, 1953, **57**, 162) that for a given resin (*i.e.*, a given degree of cross-linking), π is a unique function of the swollen volume irrespective of its cationic state. Unpublished calculations by the authors based on data of Pepper (*J. Appl. Chem.*, 1951, **1**, 124) and Boyd and Soldano (*loc. cit.*) indicate that, for a given resin, π is proportional to the weight swelling (provided this is always expressed in terms of a given amount of resin in any one cationic form), *i.e.*,

$$\pi_X = a(G_X)_H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In equation (5), $(G_X)_H$ is the weight of water absorbed by an amount of resin (in form X) equivalent to 1 g. of dry hydrogen-form resin and a is a constant characteristic of the degree of cross-linking of the resin.

It has been shown (Reichenberg, *Research*, 1953, **6**, 9s) that the simplified form of Gregor's theory itself provides a method of obtaining a value for $(V_A' - V_B')$ from swelling data alone and quite independently of any relative-affinity data. If the change in swollen volume which 1 equiv. of a resin undergoes when converted from one cationic form into another is plotted against the degree of cross-linking and extrapolated to zero cross-linking, the value obtained should be equal to one-half the difference in volume of the two hydrated ions per equiv., *i.e.*, $\frac{1}{2}(V_A' - V_B')$. If this procedure is followed with the sodium and potassium forms of the 5%, 10%, and 15% divinylbenzene resins, the value of the intercept is 0·033 l. per equiv. Hence, according to Gregor's simplified theory, the value of $(V_{Na}' - V_K')$ is 0·066 l. per equiv., corresponding to a difference of hydration number of about 4. We may now substitute this value in equation (4) and obtain calculated values of log K^K_{Na}. In Table 2, these values are compared with experimental values.

TABLE 2.

Divinylbenzene (%)	a (atm.)	$X_K = 0{\cdot}1$				$X_K = 0{\cdot}9$			
				log K^K_{Na}				log K^K_{Na}	
		$(G_{0\cdot1})_H$	π (atm.)	Calc.	Found	$(G_{9\cdot0})_H$	π (atm.)	Calc.	Found
5½	61	1·24	76	0·09	0·25	1·13	69	0·08	0·15
10	278	0·72	200	0·23	0·30	0·63	175	0·21	0·18
15	728	0·52	379	0·44	0·38	0·46	335	0·39	0·25

It will be seen that the calculated values of log K^K_{Na} agree in order of magnitude with the experimental values though there is no quantitative agreement. In the case of the 5½% divinylbenzene resin, at least, the discrepancy is quite outside any possible experimental error.

The work of Gregor and Bregman (*loc. cit.*) indicates that the matrix volumes of swollen resins in the potassium forms may be as much as 0·07 ml./g. higher than in the sodium forms (Pepper, Reichenberg, and Hale, *loc. cit.*). The value of 0·066 l. per equiv. for $(V_{Na}' - V_K')$ may therefore be too high by 0·028 l. per equiv. However, adoption of a lower value for $(V_{Na}' - V_K')$ would increase the discrepancy in the case of the 5½% and 10% resins.

It is noteworthy that, for all three resins, the calculated values show only a slight decrease of log K^{K}_{Na} with increase of X_K and fail to reflect the very marked decrease found experimentally. Again, this discrepancy is quite outside experimental error in all three cases. We conclude, therefore, that even in the most favourable case, the simplified form of Gregor's theory is inadequate as a quantitative representation of the behaviour of resins, and in other cases it fails even in its qualitative predictions.

We now discuss possible alternative ways of explaining these phenomena. Consider the intersection of the other curves by those for the 25% divinylbenzene resin. There are two possibilities—either the volumes of the hydrated ions must be considered to vary, or equation (4) is inadequate and the interaction term in equation (3) is essential. Consider the former possibility first. Gregor and Bregman (*loc. cit.*) put forward the view that at high degrees of cross-linking there is some removal of water molecules from the hydration shells of the ions. We assume, with these authors, that the more highly hydrated ions (*e.g.*, lithium and sodium) yield more readily to this "stripping." However, this explanation, taken by itself, is inadequate, since it would predict a decrease of log K over the whole range of cationic composition but without intersections. It is necessary to make, in addition, the plausible assumption that the ion-exchange sites in a resin are not all identical (Walton, *J. Phys. Chem.*, 1943, **47**, 371; Spinner, Ciric, and Graydon, *Canad. J. Chem.*, 1954, **32**, 143). The most plausible cause of variation would appear to be the extent of cross-linking in different parts of the same resin particle, some sulphonic acid groups being situated in regions of a lower degree of cross-linking than others. In principle, there will be a wide and continuous variation of the degree of localised cross-linking, but for a qualitative discussion, we may divide the exchange sites into three groups: (1) Those situated in regions of a very low degree of effective cross-linking: the fully hydrated ions of both A and B are available to the exchange groups but the selectivity is low. (2) Those situated in regions of a medium degree of cross-linking: if B is the ion of higher "natural" affinity (*i.e.*, of smaller volume when fully hydrated), then the fully hydrated B ions (and perhaps also the fully hydrated A ions) may still approach the exchange groups and the selectivity is much greater than for type (1) sites. (3) Those lying in regions of a very high degree of cross-linking: neither type of ion when fully hydrated can approach the exchange groups and clearly that ion will be preferred whose hydration shell can more readily be stripped to a point where the partially stripped ion is small enough to approach the exchange sites. According to our postulates, the A ions will be preferred for this reason.

We can now explain many of the qualitative features of the experimental curves which are not explained by Gregor's theory. If we imagine the resin to be initially completely in the A form, the A ions in sites of the first type will be fully hydrated and those in sites of the third type will be partially stripped. If we start to introduce B ions into the resin, these will initially be taken up preferentially on sites of type (2) (which have the greatest affinity for them) and the value of K^{B}_{A} will be accordingly high. As an increasing fraction of the type (2) sites is filled, more of the B ions will have to go on to type (1) sites and hence K^{B}_{A} will decrease. If there were no sites of type (3) there would be no intersection of the curves for resins of different degrees of cross-linking, since increase of overall cross-linking will increase the proportion of type (2) sites and thus increase the selectivity at all cationic compositions. This, in fact, occurs with resins of low or medium overall cross-linking. However, with resins of a high overall degree of cross-linking, there will be an appreciable fraction of type (3) sites. Since the hydrated B ions are not readily stripped, they cannot readily approach the type (3) sites and their affinity for groups in these sites will be less than that of the A ions already there in a partially stripped state. At sufficiently high values of $(X_B)_R$, therefore, the affinity curve for this kind of resin will intersect those of resins of lower degrees of cross-linking. How far this intersection proceeds depends on the proportion of type (3) sites and the relative ease with which the fully hydrated ions of the two kinds can be stripped. It may be noted that, in accordance with expectation, this intersection occurs at a lower value of $(X_B)_R$ and proceeds farther in the potassium–lithium and the sodium–lithium system than in the potassium–sodium system.

It is clear that, if a sufficient number of type (3) sites are present, the factors discussed should give rise not only to intersections but ultimately to inversions. However, one difficulty is immediately apparent. If, in accordance with the general assumption, the series Li > H > Na > K is taken as the order of decreasing hydrated ionic size, it must be supposed that the hydrated hydrogen ion can be stripped to a smaller volume than those of either sodium or potassium; and the lithium ion to a smaller volume than that of hydrogen. Since with resins of up to 25% divinylbenzene neither the sodium–lithium nor the potassium–sodium systems show inversions, we would expect, with the same resins, neither the sodium–hydrogen nor the potassium–hydrogen systems to show inversions. We would also expect any intersections to be less pronounced. Neither of these expectations is fulfilled in practice.

The difficulty may possibly be resolved by recalling that the hydrogen ion exhibits anomalous ion-exchange behaviour. Kressman and Kitchener (*J.*, 1949, 1190) demonstrated a regular relationship between the affinity of an ion for a given resin and the (best agreed) value for the distance of closest approach of that ion (when hydrated) to the sulphonate group. However, the hydrogen ion had a higher affinity than indicated by this relationship. We suppose, therefore, that the hydrogen ion, *particularly when partially stripped*, may interact with sulphonic acid groups in type (3) sites in some special way (*e.g.*, by some form of loose covalent bonding) that is denied to the other cations. This enables the sodium–hydrogen and potassium–hydrogen systems to show inversions while the sodium–lithium and potassium–lithium systems do not, despite the fact that the partially stripped lithium ion must be smaller than that of hydrogen. These views are supported by the weight swellings of the lithium and hydrogen forms of the 5% and 25% divinylbenzene resins (Table 1). These results show that, whereas the difference between the swellings of the hydrogen and sodium forms of resins decreases with increasing cross-linking at least up to 15% divinylbenzene (Reichenberg, *loc. cit.*), yet in the case of the lithium and hydrogen forms the difference is actually *greater* for the 25% than for the 5% resin. This points to greater stripping of the lithium ion than of the hydrogen ion. The fact that, even with the 5% divinylbenzene resin, the hydrogen form swells somewhat more than the lithium form again indicates that the affinity for the hydrogen ion is not determined by hydrated ionic size alone.

In the foregoing discussion, certain necessary modifications to any simple " ionic hydration " theory of ion exchange have been indicated. Glueckauf (*loc. cit.*) and Davies and Yeoman (*loc. cit.*) have put forward alternative theories based, not on the concept of hydrated ions, but on the application of Harned's rule (Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Rheinhold, New York, 1950, p. 459) to the resins in the mixed A–B cationic forms. Unfortunately, an adequate test of either theory against experimental affinity data is not yet possible since supplementary data are required—in particular, values of the Harned coefficients in electrolyte solutions of the same ionic strength as the resins—but such data are lacking. However, it is quite probable that in any theory the existence of exchange sites of varying properties and the special behaviour of the hydrogen ion would have to be recognised.

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HIGH POLYMERS GROUP, CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX.

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