105. *Properties of Ion-exchange Resins in Relation to their Structure. Part II. Relative Affinities.*

By D. Reichenberg, K. W. Pepper, and D. J. McCauley.

The relative affinity coefficients ($K_{\mathrm{H}}^{\mathrm{Na}}$) of sodium and hydrogen ions for sulphonated polystyrene resins of different degrees of cross-linking have been determined at 0·1M-cation concentration in solution. For a resin of low cross-linking, $K_{\mathrm{H}}^{\mathrm{Na}}$ is approximately unity and independent of the mole-fraction of sodium ion on the resin ($X_{\mathrm{Na_R}}$). With resins of medium cross-linking, $K_{\mathrm{H}}^{\mathrm{Na}}$ is greater than unity for all values of $X_{\mathrm{Na_R}}$ and shows a flat maximum at a value of $X_{\mathrm{Na_R}}$ of 0·4—0·5. For resins of high cross-linking, the maximum disappears and $K_{\mathrm{H}}^{\mathrm{Na}}$ decreases sharply with increasing $X_{\mathrm{Na_R}}$, becoming less than unity at high values of $X_{\mathrm{Na_R}}$. Within the series of resins, $K_{\mathrm{H}}^{\mathrm{Na}}$ at low values of $X_{\mathrm{Na_R}}$ increases with increasing cross-linking.

In general, these results are consistent with Gregor's theory (*J. Amer. Chem. Soc.*, 1948, **70**, 1293) that ion-exchange resins may be regarded as swelling gels, the swelling pressure due to the osmotic activity and hydration of the ionic groupings being balanced by a counter-pressure exerted by the cross-linked polymeric network. The theory fails to account for the decrease of $K_{\mathrm{Na}}^{\mathrm{H}}$ to values below unity with resins of high cross-linking, and also for the increase in $K_{\mathrm{H}}^{\mathrm{Na}}$ with increasing $X_{\mathrm{Na_R}}$ with resins of medium cross-linking. Tentative explanations for these effects are suggested.

In Part I of this series (Topp and Pepper, *J.*, 1949, 3299) the titration curves of a series of resins of known preparation were correlated with the properties of the ionizable groups present. The advantages of monofunctional resins (*i.e.*, those containing only one type of ionizable group) in ion-exchange chromatography and in studies of their physicochemical properties were emphasized. Among the most important of these properties is the relative affinity of the resin for different ions. With two exchangeable ions, the difference in affinity is manifested by a difference between the ratio of the amounts of the two ions on the resin and that in a solution in equilibrium with the resin. As a result, the relative affinity is the principal factor determining the ease and efficiency of a separation by ion-exchange chromatography. A knowledge of the relative affinities of different ions for various resins should therefore be of immediate practical value, while at the same time helping towards a better insight into the nature of the ion-exchange process and the structure of the resins.

The importance of relative affinity has long been recognised and has been the subject of much study both with synthetic resins and with other types of exchange materials (natural and artificial zeolites, sulphonated coals, etc.). However, only the most recent work with synthetic resins has a direct bearing on the present research. Boyd, Schubert, and Adamson (*J. Amer. Chem. Soc.*, 1947, **69**, 2818) investigated ion-exchange equilibria with a polyfunctional resin containing phenolic and methylenesulphonic groups, under conditions where the phenolic groups might be expected to play little or no part in the exchange. For the sodium–hydrogen exchange in solution of total cation concentration of 0·1M., they concluded that the relative affinity coefficient, $K_{\mathrm{H}}^{\mathrm{Na}}$ (for exact definition of this quantity see below), remained constant within experimental error when the mole-fraction of sodium on the resin ($X_{\mathrm{Na_R}}$) was varied from 0·3 to 0·8. Bauman and Eichhorn (*ibid.*, p. 2830), working with a monofunctional synthetic resin containing nuclear sulphonic groups, investigated the effect of variation of the total cation concentration, using ammonium and hydrogen as cations. They found that $K_{\mathrm{H}}^{\mathrm{NH_4}}$ remained constant at a value of 1·2 for solutions below 1M., but decreased with increasing cation concentration, becoming 0·5 at 4M.* Duncan and Lister (*J.*, 1949, 3285) investigated the sodium–hydrogen exchange on a similar resin in solutions of total cation concentration 0·2M. They found that $K_{\mathrm{H}}^{\mathrm{Na}}$ did not remain constant with varying $X_{\mathrm{Na_R}}$, there being a maximum at a value of $X_{\mathrm{Na_R}}$ of about 0·1. They also found (*Faraday Soc. Discussions*, 1949, No. 7, 104) a similar variation of K when other pairs of cations were used (barium–hydrogen and lanthanum–

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* In these experiments $K_{\mathrm{H}}^{\mathrm{NH_4}}$ was not corrected for activity coefficients in solution.

hydrogen). Cosgrove and Strickland (*J.*, 1950, 1845) investigated the exchange of potassium–hydrogen, ammonium–hydrogen, and potassium–ammonium on two resins, one of which was a sulphonated cross-linked polystyrene prepared in this laboratory. In all cases when the mole-fraction of cation on the resin was increased from 0·2 to 0·8, the relative affinity for that cation fell markedly.

The general aim of the present work was to investigate the effect on affinity of variation in the polymer structure of the resin, in particular the degree of cross-linking. Sulphonated cross-linked polystyrene resins are particularly suitable for such a study, since the degree of cross-linking may be readily controlled and varied by varying the proportion of cross-linking agent—divinylbenzene in the present instance. It is known that the degree of cross-linking markedly affects other properties of these resins, *e.g.*, the swelling in water and the rates of exchange (Pepper, *J. Soc. Chem. Ind.*, in the press). Kunin and Myers (*Faraday Soc. Discussions*, 1949, No. 7, 114) have shown that with anion-exchange resins both the swelling and the effective capacity for large anions decrease markedly with increase of cross-linking, and there was also an increase of affinity for fluoride, chloride, and iodide ions relative to hydroxyl ions. Samuelson (*Ingen. Vetensk. Akad.*, 1944, No. 179), working with a very highly swollen sulphonated polystyrene resin, found that the values of K for the exchange reactions hydrogen–sodium, hydrogen–potassium, and hydrogen–tetramethylammonium were all unity within experimental error.*

Various theoretical treatments have been given of the equilibria of ion-exchange. However, all that can, in fact, be measured in a given system containing two exchangeable ions, A and B (which, for simplicity, we will suppose to be of the same valency), is the quantity K_A^B, defined as follows:

$$K_A^B = \frac{[B_R]}{[A_R]} \cdot \frac{[A_S]}{[B_S]} \cdot \frac{f_{A_S}}{f_{B_S}}$$

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 in solution. K_A^B has been called the "thermodynamic equilibrium constant" of the exchange reaction $A_R + B_S \rightleftharpoons B_R + A_S$. This is permissible provided it is understood that K_A^B may, in principle, vary with X_{B_R}, *i.e.*, $[B_R]/([A_R] + [B_R])$. We prefer, however, the name "relative affinity coefficient" and this term will be used throughout the present work.

The present paper deals with the relative affinity coefficients of sodium and hydrogen ions for sulphonated polystyrene resins cross-linked with varying amounts of divinylbenzene. Experimentally, the problem resolved itself into measuring $[Na_R]/[H_R]$ and $[Na_S]/[H_S]$. The method used in the present work consisted essentially of preparing a series of "conditioning solutions" each having a known value of $[Na_S]/[H_S]$ (but all of the same total cation concentration) and treating a fixed quantity of the resin, of known exchange capacity, with one of the solutions until the resin was in equilibrium with the solution. $[H_R]$ was then determined directly by displacement with excess of neutral sodium chloride, $[Na_R]$ being obtained from the difference between the known exchange capacity of the resin and $[H_R]$. The experiments were all carried out at room temperature (22—25°) and in solutions of total cation concentration 0·1125M.

EXPERIMENTAL.

Materials.—Resins. The preparation of the resins examined, sulphonated cross-linked polystyrenes in bead form, has been described in detail (Pepper, *loc. cit.*). Briefly, a mixture of styrene and divinylbenzene solution with 1% of benzoyl peroxide as catalyst was heated in aqueous suspension at 80° for 18 hours. The resulting copolymer was sulphonated by treatment with concentrated sulphuric acid at 100° in presence of 1% of silver sulphate. The products were washed, treated alternately with 2M-sodium chloride and 2N-hydrochloric acid two or three times, and finally sieved. The divinylbenzene solution was a commercial supply and consisted of divinylbenzene (*ca.* 33%) in ethylstyrene (*ca.* 66%) with a little saturated material. The divinylbenzene contents of resins given in this paper are nominal; the proportions of divinylbenzene solution and styrene were varied systematically but the composition of the divinylbenzene solution was not known accurately and it has not been proved that the three monomers styrene, ethylstyrene, and divinylbenzene copolymerise uniformly in all proportions. Unambiguous evidence of the increase in degree of cross-linking resulting from increase in nominal divinylbenzene content is, however, provided by the marked reduction in swelling shown in Table I. The observed specific exchange capacities of the resins (except that containing 33% of divinylbenzene)

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* After this work had been commenced, we learnt that Dr. W. C. Bauman was engaged on a similar investigation and also had observed the marked influence of the degree of cross-linking on relative affinities.

agree closely with those calculated on the assumption that the monomers copolymerise uniformly and that each benzene ring in the copolymer contains one sulphonic acid group.

TABLE I.

Properties of resins.

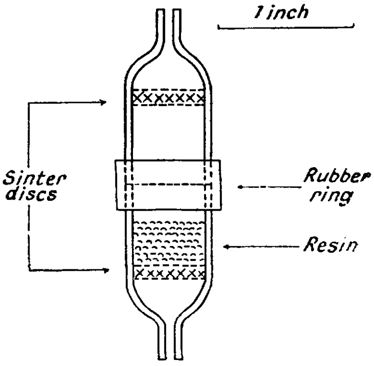
Nominal divinylbenzene content, %.	Particle-diameter, μ. (wet).	Swelling (g. of H_2O per g. of dry H^+ resin).	Specific exchange capacity * (mg.-equivs. per g. of dry H^+ resin): Obs. ($\pm$0·05).	Calc. for monosulphonic acids.
2	250—200	3·35	5·40	5·39
5	400—300	1·45	5·30	5·34
10	500—400	0·80	5·15	5·24
17	400—250	0·57	5·00	5·11
33	200—100	0·55	4·25	4·74

* These specific exchange capacities were obtained on samples of the resins used for the affinity determination by estimation of hydrogen ion displaced from a known dry weight in equilibrium with a solution of $[\mathrm{Na_S}]/[\mathrm{H_S}]$ ratio about 1000. The values quoted previously (Pepper, *loc. cit.*) were the means obtained in alkaline solution for several preparations at each nominal divinylbenzene content. The determinations in alkaline and slightly acid solution agreed within experimental error except in the case of the 17% and 33% resins. In alkaline solution, the latter resins gave values of 5·15 and 4·60 mg.-equivs. per g.

Conditioning solutions. Approx. 2N-hydrochloric acid and 2N-sodium hydroxide solutions were made with AnalaR chemicals, and their relative concentrations obtained by titration. The acid was standardised independently and found to be 2·25N. For each conditioning solution, appropriate volumes of the acid and the alkali solutions were made up to 2 l. with water. These solutions (of total cation concentration 1·125M.) were kept as stock solutions and when required for an affinity determination were diluted ten-fold (*i.e.*, to 0·1125M.). The relative strengths of the acid and the alkali solutions and the volumes of each used in making up a given conditioning solution being known, the ratio $[\mathrm{Na_S}]/[\mathrm{H_S}]$ could be readily calculated. However, for conditioning solutions of high $[\mathrm{Na_S}]/[\mathrm{H_S}]$ a small error in the value for the relative strengths of acid and alkali, or in either of their volumes, would cause an appreciable *relative* error in $[\mathrm{Na_S}]/[\mathrm{H_S}]$. In these cases, the stock conditioning solutions (1·125M.) were themselves titrated against some approx. 0·05N-sodium hydroxide which was in turn standardised against the original 2·25N-acid. These titrations gave directly the ratio $([\mathrm{Na_S}] + [\mathrm{H_S}])/[\mathrm{H_S}]$ for the conditioning solution, from which an accurate value of $[\mathrm{Na_S}]/[\mathrm{H_S}]$ was calculated. This procedure was carried out with conditioning solutions of decreasing $[\mathrm{Na_S}]/[\mathrm{H_S}]$ until the value so obtained agreed exactly with that calculated by the former method. The conditioning solutions used for affinity determinations covered a range of $[\mathrm{Na_S}]/[\mathrm{H_S}]$ from 0·02 to 50.

FIG. 1.

Diagram of apparatus.



When this work was commenced, ordinary distilled water was used for the preparation of solutions and for washing the resin. Later, conductivity-grade water obtained by mixed-bed deionization became available in quantity and was used in preference.

Determination of Relative Affinity Coefficients.—Apparatus. The resin was contained in a small column made from two glass tubes fitted with sealed-in sintered discs (porosity 1). The glass tubes were cut to within 1 in. of the sinters, and the ends ground flat. The tubes were then fitted together with a rubber ring which sealed the joint (Fig. 1). This apparatus permitted agitation and backwashing of the resin without loss of material.

Method. An amount of resin having a capacity of about 2·5 mg.-equivs. (0·5 g. of air-dry material) was introduced into the apparatus, and 250—500 ml. of 0·1M-conditioning solution (*i.e.*, about 10—20 times the capacity of the sample) were passed through the resin at a flow-rate of *ca.* 100 ml./hour. For the more highly cross-linked resins (17% and 33% nominal divinylbenzene content), which exchange more slowly, 1 l. of conditioning solution was passed during 12 hours. To avoid channelling and to ensure complete mixing, the resin was back-washed at about half-hourly intervals. Trouble was sometimes experienced owing to the liberation of dissolved air bubbles which subsequently tended to adhere to the resin and prevent free access of fresh solution. This difficulty was obviated by back-washing the resim (before conditioning) with a 0·1% solution of Lissapol N (a non-ionic detergent), followed by washing with water. After the conditioning, the apparatus was drained by a standard procedure, air being sucked through for 1 minute at 10 ml./second. The resin was then washed to neutrality, the washings being collected and titrated with the standard 0·05N-sodium hydroxide. Finally, the *combined* hydrogen was displaced from the resin with neutral 0·5M-sodium chloride, and the effluent collected and titrated. For all these titrations, the indicator used was a mixture of methyl-red and bromocresol-green in alcohol (Kolthoff and Stenger, "Volumetric Analysis," Vol. II, 1947, p. 58). This had a titration exponent of 5·1 and under the conditions used was virtually unaffected by carbon dioxide.

Careful consideration was given to the removal of conditioning solution left in the apparatus after drainage. The greater part of this residual electrolyte was held in the two sintered discs, but some would be retained between beads of resin and possibly, to a small extent, within the resin itself (Bauman and Eichhorn, *loc. cit.*). The following subsidiary experiments proved that during washing the relative amounts of *combined* sodium and hydrogen remained unchanged. In determining the capacity of a sample, the resin was first converted into the hydrogen form by using 0·1125N-hydrochloric acid. After the standard drainage procedure, the sample was washed and the washings titrated as in an affinity determination. For each sample of resin, this titre (t_w) was closely reproducible. Since washing would not be expected to remove *combined* hydrogen from the hydrogen form of the resin, the titre t_w must represent the amount of hydrogen in the residual electrolyte referred to above. The total amount of residual electrolyte is likely to be dependent only on the total cation concentration and independent of $X_{\mathrm{H_S}}$ and should therefore be the same in an affinity as in a capacity determination. Hence, provided that the amount of combined hydrogen on the resin did not alter during washing, the titre of the washings in an affinity determination ($X_{\mathrm{H_S}}$ of conditioning solution <1) should be equal to $t_w X_{\mathrm{H_S}}$. This was confirmed experimentally in all cases, proving that the only hydrogen removed during washing was that due to residual electrolyte.

The overall accuracy of the determinations of $K_{\mathrm{H}}^{\mathrm{Na}}$ is considered to be $\pm 2\%$ for values of $X_{\mathrm{Na_R}}$ from 0·2 to 0·9; outside this range, it is $\pm 10\%$ for the 17% and 33% divinylbenzene resins and $\pm 5\%$ for those of lower divinylbenzene content. At low $X_{\mathrm{Na_R}}$, $[\mathrm{Na_R}]$ is given by the small difference between two large titres. A small error in either would produce a large relative error which increases as the difference between the titres decreases. To reduce the effect of any systematic error, which would give an erroneous plot for $K_{\mathrm{H}}^{\mathrm{Na}}$ against $X_{\mathrm{Na_R}}$ at low values of $X_{\mathrm{Na_R}}$, the capacity and affinity determinations were carried out by the same method. At high values of $X_{\mathrm{Na_R}}$, the accuracy was limited by the small volume of the hydrogen titre. Any resulting error was reduced by using standardised 0·01N-sodium hydroxide for these titrations.

A slight decrease in the capacity of the resin was observed during a series of experiments; *e.g.*, for a 10% divinylbenzene resin, the loss was 0·7% after 60 cycles. To avoid possible errors due to this effect, capacity determinations were interspersed between affinity determinations; thus the capacity appropriate to each affinity determination was known.

Complete attainment of equilibrium between resin and conditioning solution was checked in at least one of two ways: (*a*) doubling the volume of conditioning solution passed at the same flow-rate, (*b*) starting the conditioning with the resin in the hydrogen instead of the sodium form. In all cases the results were found to be independent of these variations in procedure and no evidence was found of any hysteresis.

Correction for activity coefficients in solution. The values of the ratio $f_{\mathrm{H_S}}/f_{\mathrm{Na_S}}$ for the various conditioning solutions were calculated by using published data on activity coefficients in mixed solutions (Harned and Owen, " Physical Chemistry of Electrolytic Solutions," New York, 1943, p. 450 *et seq.*). Now

$$\frac{f_{\mathrm{H_S}}}{f_{\mathrm{Na_S}}} = \frac{f_{\mathrm{H^+}}f_{\mathrm{Cl^-}}}{f_{\mathrm{Na^+}}f_{\mathrm{Cl^-}}} = \frac{(\gamma_{\mathrm{HCl}\pm})^2}{(\gamma_{\mathrm{NaCl}\pm})^2}$$

the γ terms referring to *mean ion activity coefficients* (which are the quantities usually given in tables of published data).

With NaCl-HCl mixtures of total concentration 0·1125M. (0·1130 molal), we calculate that for $X_{\mathrm{Na_S}} = 0, f_{\mathrm{H_S}}/f_{\mathrm{Na_S}} = 1{\cdot}022$, and for $X_{\mathrm{Na_S}} = 1, f_{\mathrm{H_S}}/f_{\mathrm{Na_S}} = 1{\cdot}029$. For our present purpose, it is sufficiently accurate to take $f_{\mathrm{H_S}}/f_{\mathrm{Na_S}}$ as being a linear function of $X_{\mathrm{Na_S}}$ between these limits.

RESULTS AND DISCUSSION.

In Figs. 2—6, values of $K_{\mathrm{H}}^{\mathrm{Na}}$ have been plotted as functions of $X_{\mathrm{Na_R}}$ for resins containing nominally 2%, 5%, 10%, 17%, and 33% of divinylbenzene. The following conclusions may be drawn. (*a*) With the resin of *low* cross-linking (2% divinylbenzene, Fig. 2) $K_{\mathrm{H}}^{\mathrm{Na}}$ is approximately unity for all values of $X_{\mathrm{Na_R}}$. (*b*) With the resins of *medium* cross-linking (5% and 10% of divinylbenzene, Figs. 3 and 4), $K_{\mathrm{H}}^{\mathrm{Na}}$ increases with $X_{\mathrm{Na_R}}$ at low values of $X_{\mathrm{Na_R}}$ and shows a flat maximum at about $X_{\mathrm{Na_R}} = 0{\cdot}4$—$0{\cdot}5$. In the range $X_{\mathrm{Na_R}} = 0$—$0{\cdot}5$, $K_{\mathrm{H}}^{\mathrm{Na}}$ increases with the degree of cross-linking. With both resins, $K_{\mathrm{H}}^{\mathrm{Na}}$ is greater than unity at all values of $X_{\mathrm{Na_R}}$. (*c*) With the resins of *high* cross-linking (17% and 33% of divinylbenzene, Figs. 5 and 6) the maximum disappears. $K_{\mathrm{H}}^{\mathrm{Na}}$ has a high value at low values of $X_{\mathrm{Na_R}}$ and decreases with increasing $X_{\mathrm{Na_R}}$, becoming less than unity at high values of $X_{\mathrm{Na_R}}$. The higher the cross-linking, the greater is the value of $K_{\mathrm{H}}^{\mathrm{Na}}$ at low $X_{\mathrm{Na_R}}$ and the smaller its value at high $X_{\mathrm{Na_R}}$.

In our view, two important theoretical interpretations of ion-exchange equilibria may be distinguished, *viz.*, Jenny's treatment (*J. Physical Chem.*, 1932, **36**, 2217) as developed by Boyd, Schubert, and Adamson (*loc. cit.*) and by Kressman and Kitchener (*J.*, 1949, 1190), and Gregor's theory (*J. Amer. Chem. Soc.*, 1948, **70**, 1293). According to the former view, the equilibria are governed by the electrical energy gained or lost on replacing one cation by another. For ions of the same valency, this energy change will be determined mainly by the

FIG. 2.

2% *Nominal divinylbenzene content.*

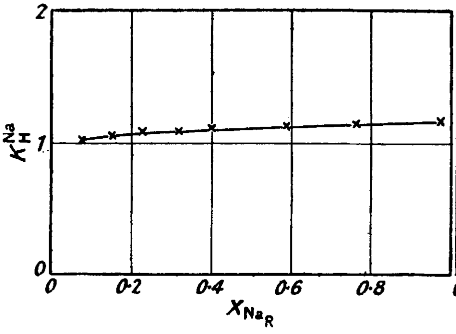


FIG. 3.

5% *Nominal divinylbenzene content.*

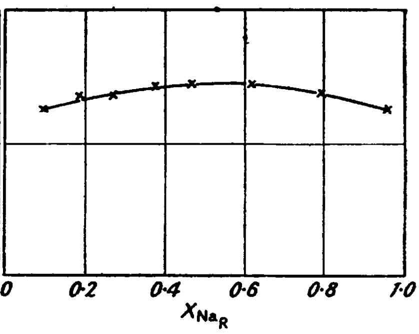


FIG. 4.

10% *Nominal divinylbenzene content.*

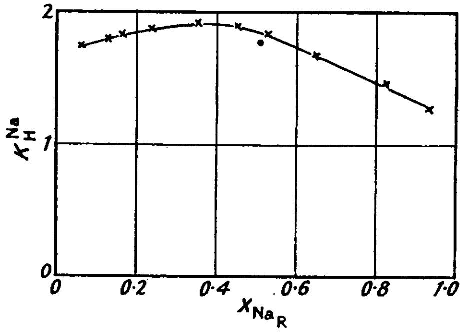


FIG. 5.

17% *Nominal divinylbenzene content.*

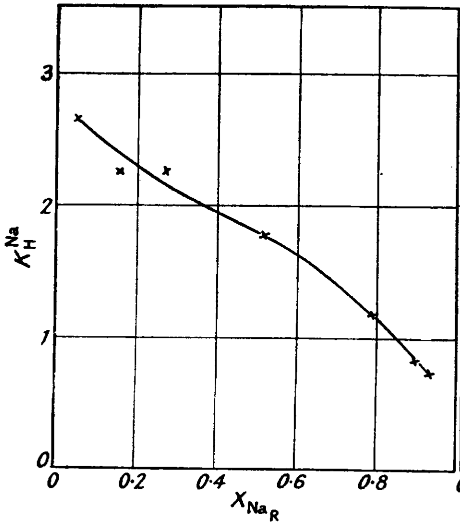
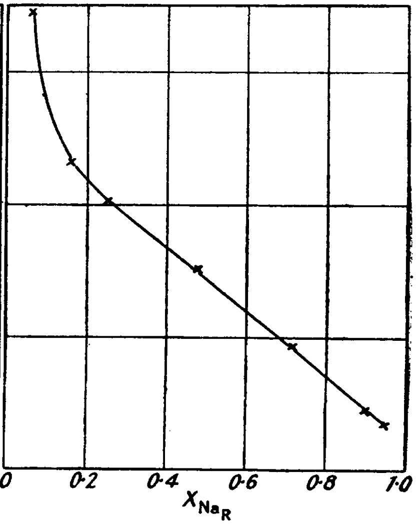


FIG. 6.

33% *Nominal divinylbenzene content.*



" distance of closest approach " of the cation to the bound anionic group, which in turn will depend on the effective radius of the cation. It is important to note that this effective radius is that of the ion in the state of hydration in which it exists in the resin.

Gregor regards an ion-exchange resin as a swelling gel in which swelling of the dry resin (owing to hydration of the ions and their osmotic activity) is restrained by the cross-linked polymeric structure, equilibrium being attained when the swelling pressure and the elastic restraint are balanced. The essence of the theory is to treat the resins in terms of a model in which the elastic counter-pressure is regarded as having the same effect as a normal external pressure on an osmotic system. Making a number of simplifying approximations and assumptions in the equations for osmotic equilibrium, Gregor deduced the relationship

$$\boldsymbol{RT} \ln K^{\mathrm{B}}_{\mathrm{A}} = p(\bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{B}})$$

where $K^{\mathrm{B}}_{\mathrm{A}}$ is the relative affinity coefficient, p is the swelling pressure at equilibrium, and $\bar{V}_{\mathrm{A}}$ and $\bar{V}_{\mathrm{B}}$ are the partial molal volumes of the hydrated cations in the resin. The following deductions may be derived from Gregor's theory.

(1) If $\bar{V}_{\mathrm{A}} > \bar{V}_{\mathrm{B}}$, then $K^{\mathrm{B}}_{\mathrm{A}} > 1$. This deduction, which follows also from Jenny's theory, is in general agreement with experimental results on strongly acidic resins. In the present work, the values of $K^{\mathrm{Na}}_{\mathrm{H}}$ were greater than unity (except with resins of high cross-linking at high $X_{\mathrm{Na_R}}$) in accord with the view that the hydrogen ion in solution is larger than the sodium ion owing to its higher degree of hydration. This is probably true in the resin under normal conditions.

(2) If $\bar{V}_{\mathrm{A}} > \bar{V}_{\mathrm{B}}$, then, as $X_{\mathrm{B_R}}$ increases, the resin contracts and p decreases. If $\bar{V}_{\mathrm{A}}$ and $\bar{V}_{\mathrm{B}}$ remain roughly constant and independent of $X_{\mathrm{B_R}}$, then $K^{\mathrm{B}}_{\mathrm{A}}$ will decrease. The decline in $K^{\mathrm{Na}}_{\mathrm{H}}$ with increasing $X_{\mathrm{Na_R}}$ observed with the 17% and 33% resins (and also with the 5% and 10% resins at high $X_{\mathrm{Na_R}}$) is consistent with this prediction.

(3) For a given ionic composition, the equilibrium value of p depends on the elastic properties of the resin. The greater the degree of cross-linking, the greater will be the elastic modulus and the smaller the volume of the swollen resin at equilibrium. Hence the concentration of osmotically active groups will be greater and p will be greater. Hence, the higher will be the numerical value of $\ln K^{\mathrm{A}}_{\mathrm{B}}$, if $(\bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{B}})$ remains approximately constant for resins of different cross-linking. Conversely, a resin of very low cross-linking should have a value of $K^{\mathrm{B}}_{\mathrm{A}}$ nearly equal to unity for all values of $X_{\mathrm{B_R}}$. This prediction is borne out by the results for the 2% resin.

We now consider those experimental results not satisfactorily covered by this simplified version of Gregor's theory.

(*a*) Although the theory predicts a decline in $K^{\mathrm{Na}}_{\mathrm{H}}$ with increasing $X_{\mathrm{Na_R}}$, it does not predict the drop in $K^{\mathrm{Na}}_{\mathrm{H}}$ below unity at high values of $X_{\mathrm{Na_R}}$ (Figs. 5 and 6). It is considered that this effect may be due to the presence in these two resins of acidic groups other than the sulphonic acid groups. Whilst complete sulphonation of the resins of lower cross-linking was achieved in a few hours, it was necessary to heat the 17% and 33% resins with concentrated sulphuric acid at 100° for 7 days and the possible formation of carboxylic groups cannot be overlooked. The specific exchange-capacity of the 33% resin when determined in alkaline solution $([\mathrm{Na_S}]/\mathrm{H_S}] \sim 10^{11})$ was 6—10% greater than the value obtained in acidic solution $([\mathrm{Na_S}]/[\mathrm{H_S}] \sim 1000)$. The corresponding difference for the 17% resin was 2—3%. These data indicate the presence of small amounts of weakly acidic groups. The amount of sodium ion taken up by such groups would be small from conditioning solutions of $[\mathrm{Na_S}]/[\mathrm{H_S}]$ of 50 or less but, in the analysis of the resins with neutral 0·5M-sodium chloride, hydrogen ion might be displaced to some extent from the weak groups, thus giving higher values of $[\mathrm{H_R}]$ and lower values of $K^{\mathrm{Na}}_{\mathrm{H}}$ than correspond to the sulphonic acid groups alone. The effect would be more pronounced at high values of $X_{\mathrm{Na_R}}$ where $[\mathrm{H_R}]$ becomes very small. It is possible to calculate what amount of hydrogen ion displaced from weak groups is necessary to give the observed values of $K^{\mathrm{Na}}_{\mathrm{H}}$, the true $K^{\mathrm{Na}}_{\mathrm{H}}$ for sulphonic groups being taken as unity. The required amounts (expressed as percentages of the capacities) are 6% for the 33% resin and 2% for the 17% resin. We conclude, therefore, that there may be sufficient weakly acidic groups in these two resins to account for the drop in $K^{\mathrm{Na}}_{\mathrm{H}}$ below unity.

In contrast, for the three resins of lower cross-linking, the difference between the specific exchange capacity in alkaline solution and in acid solution was less than 2%, an amount which can have negligible influence on the observed values of $K^{\mathrm{Na}}_{\mathrm{H}}$.

(*b*) The theory fails to account for those parts of the curves for the 5% and 10% divinylbenzene resins where $K^{\rm Na}_{\rm H}$ *increases* with increasing $X_{\rm Na_R}$ (Figs. 3 and 4). Gregor considers only the effect of the pressure due to the elastic network on the relative affinities of ions. However, there will be also an internal effect due to ionic interactions. In general, we may write :

$$K^{\rm B}_{\rm A} = (K^{\rm B}_{\rm A})_{\rm int.} \cdot (K^{\rm B}_{\rm A})_{\rm ext.}$$

Following Bauman and Eichhorn (*loc. cit.*) we may put

$$(K^{\rm B}_{\rm A})_{\rm int.} = (f_{\rm A_R}/f_{\rm B_R})_{\rm int.}$$

The latter quantity is analogous to the ratio of the activity coefficients of two ions in mixed solutions at normal pressure. The ratio $(f_{\rm H_R}/f_{\rm Na_R})_{\rm int.}$ might be expected therefore to show similar *qualitative* features to the ratio $f_{\rm H}/f_{\rm Na}$ for solutions of mixed salts at total cationic concentration comparable to that in the resin (1·5—8 molal, calculated on the basis of g.-equivs. per 1000 g. of absorbed water, cf. Table I). Values of $f_{\rm H}/f_{\rm Na}$ calculated from published data on solutions of NaCl–HCl mixtures at various concentrations are as given below (Harned and Owen, *loc. cit.*; Robinson and Stokes, *Trans. Faraday Soc.*, 1949, **45**, 612).

Molality.		0·1.	0·2.	1·0.	3·0.	5·0.
$f_{\rm H}/f_{\rm Na}$	$X_{\rm Na} = 0$	1·020	1·033	1·161	1·524	1·951
	$X_{\rm Na} = 1$	1·026	1·050	1·308	2·213	3·715

At all concentrations $f_{\rm H}/f_{\rm Na}$ increases with increasing $X_{\rm Na}$. It may well be that this result holds qualitatively for the ions in the resin, thus accounting for the increase observed in $K^{\rm Na}_{\rm H}$.

In conclusion, it would appear that the experimental results are generally consistent, at least qualitatively, with Gregor's theory, but that a complete interpretation requires consideration of both internal and external effects.* In an attempt to elucidate these effects, a study of equilibria with other pairs of cations is being made.

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