260. *Cation Exchange with a Synthetic Phenolsulphonate Resin. Part II. Equilibria with Multivalent Cations.*

By T. R. E. Kressman and J. A. Kitchener.

The study described in Part I has been extended to equilibria between an ammonium resin and salts of Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cd^{++}, Cu^{++}, Zn^{++}, Co^{++}, Ni^{++}, Pb^{++}, Hg^{++}, Al^{+++}, Th^{++++}, Zr^{++++}. They obey the law of mass action, concentrations being used instead of activities. This is discussed in relation to activity coefficients in uni-bivalent salt mixtures.

All the sulphonate groups in the resin can be neutralised by an equivalent number of multivalent cations, and this leads to the hypothesis that multivalent ions are not closely associated with their valency number of sulphonate groups. Ionic size (measured by the a° parameter) seems to be a factor determining the affinity of bivalent cations for the resin. These observations can be reconciled by the assumption that the cation is close to one sulphonate group and relatively far from the other. The generally increasing affinity observed with increasing valency is in keeping with this concept.

Incomplete dissociation of the salts of multivalent ions in solution is an important factor in determining the extent of exchange with these ions and gives an explanation also of the effect of the anion.

Part I (preceding paper) dealt with equilibria between a phenolsulphonic acid–formaldehyde resin and various simple univalent cations. The present paper is concerned with equilibria involving chiefly bivalent ions, and these were studied by the same experimental technique as that used in Part I. The ammonium ion was used as the reference ion in the resin, and the reactions are, therefore, of the type

$$2R^-NH_4^+ + M^{++}X^-_2,\ aq. \rightleftharpoons R^-_2M^{++} + 2NH_4^+X^-,\ aq. \qquad (1)$$

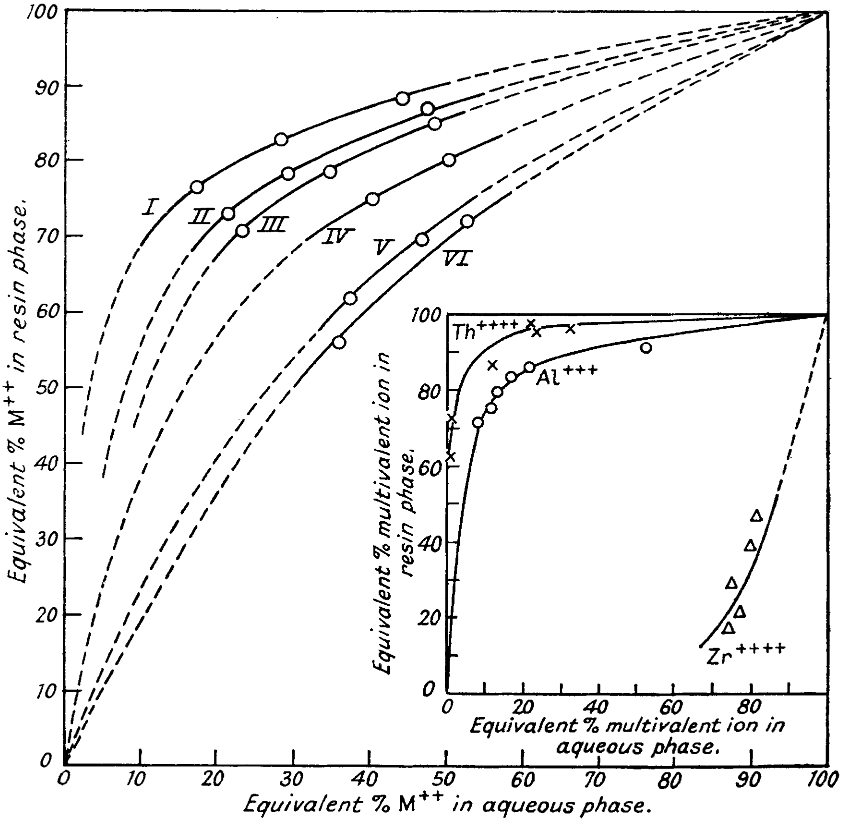
The results are plotted in terms of equivalent percentages in Fig. 1. As discussed in Part I, this method of plotting is the most suitable for comparing the affinities for the resin of ions of different valency, and a comparison of the curves with Fig. 3 of Part I shows clearly the generally higher affinity of the resin for the doubly charged ions than for the singly charged ones. There is, nevertheless, a certain overlap, and Tl^+, in spite of its single charge, is as strongly held to the resin as Ba^{++} in 0·1N-solution.

The curves of Fig. 3 in Part I are symmetrical in form while those of Fig. 1 are unsymmetrical.

This is a reflection of the symmetrical uni-univalent system and the unsymmetrical uni-bivalent system respectively.

The results expressed by Fig. 1 are in accord with the simple law of mass action using concentrations, as is illustrated by Fig. 2, where the appropriate mass-action functions are plotted. In this graph the concentration of each cation in the resin phase is expressed as the ratio of the number of equivalents of that cation to the total number of equivalents of cations in that phase; this ratio is dimensionless. The concentration of each cation in the aqueous phase is expressed as equivs. per l. Alternatively, it is sometimes convenient, especially when it is desired to compare the extent of exchange occurring in solutions of different concentrations, to express the aqueous concentration as a ratio in a manner identical with that used for the solid phase. The corresponding mass-action function, like that for the solid phase, is then dimensionless, and its numerical value will be v times that calculated by the first method (v is the volume of solution, in litres, containing 1 g.-equiv. of total cations or of the anion). The points relating to various initial concentrations of a given cation lie on a common curve in Fig. 2, but each concentration yields a separate curve when plotted by the alternative method. This is illustrated in Fig. 5. Thus a separate constant is obtained, from the slopes of the curves, for each concentration. It is proposed to call the constant so obtained the "exchange constant" and to designate it by K': like that obtained for ions of equal valency, it is dimensionless. The equilibrium constants, K, obtained from the slopes of the curves in Fig. 2 are the true stoicheiometric mass action constants and are independent of dilution. They have the dimensions of concentration and the values are given in the table, where

Fig. 1.



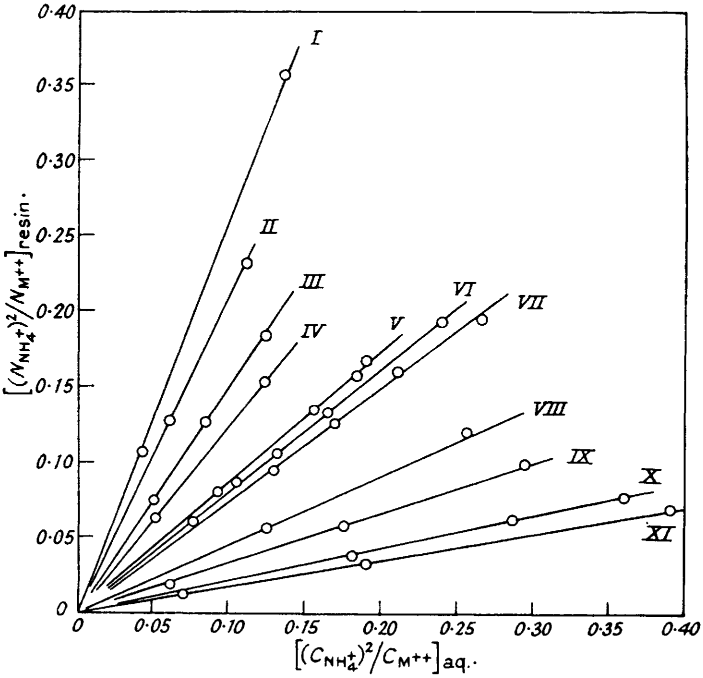
I, $BaCl_2$
II, $SrCl_2$
III, $CaCl_2$
IV, $MgCl_2$; $ZnCl_2$
V, $BeSO_4$
VI, $CdCl_2$

$$K = \left[\frac{(C_{NH_4^+})^2}{C_{M^{++}}}\right]_{aq.} \bigg/ \left[\frac{(C_{NH_4^+})^2}{C_{M^{++}}}\right]_{res.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equilibrium constants for the exchange between NH_4*-resin and various bivalent metal salts.*

Cation (and anion).	Concn. studied, N.	Equilm. constant at 25°.	Cation (and anion).	Concn. studied, N.	Equilm. constant at 25°.
Cd^{++} (chloride)	0·1	0·384	Cu^{++} (chloride)	0·1	1·23
Be^{++} (sulphate)	0·1	0·471	Ni^{++} ,,	0·1	1·23
Mg^{++} ,,	0·1—0·005	0·667	Co^{++} ,,	0·1	1·32
(formate)	0·1	0·912	Ca^{++} ,,	0·1	2·16
(chloride)	0·1—0·005	1·14	Sr^{++} ,,	0·1	3·00
Mn^{++} (sulphate)	0·1	0·82	Pb^{++} (nitrate)	0·1	4·65
(chloride)	0·1	1·00	Ba^{++} (chloride)	0·1	5·64
Zn^{++} ,,	0·1	1·14	Hg^{++} ,,	0·10; 0·05	0·038
UO_2^{++} (nitrate)	0·1	1·00			

FIG. 2.



I, $CdCl_2$.	VII, $CoCl_2$.
II, $BeSO_4$.	VIII, $CaCl_2$.
III, $MgSO_4$.	IX, $SrCl_2$.
IV, $MnSO_4$.	X, $Pb(NO_3)_2$.
V, $MgCl_2$; $Mg(NO_3)_2$; $ZnCl_2$.	XI, $BaCl_2$.
VI, $CuCl_2$; $NiCl_2$.	

The range of variation in resin composition represented by the curves is relatively limited, owing to the strong affinity of the resin for the bivalent ions as compared with that of the reference ion NH_4^+. It is perhaps not surprising, therefore, that the law of mass action should apply over this rather narrow range. The graphs cannot accurately be extended beyond the range illustrated, since large proportions of resin to solution are needed and the experimental error is inevitably large. Nevertheless, by starting with a resin containing bivalent ions, *e.g.*, Mg^{++}, and allowing it to come to equilibrium with solution of ammonium chloride, the equilibrium was approached from the other side and the upper portions of the curve obtained by the use of a low ratio of solid to aqueous phase, thus permitting high accuracy to be achieved.

Fig. 3, obtained in this way, represents an overall variation in resin composition from 100 equivs. % of Mg^{++} to 40 equivs. %. The graph shows clearly that the law of mass action is obeyed over this wide range, and it is remarkable that such agreement should be obtained by the use of concentrations and not activities. This result has several important implications, as described below.

Influence of Activity Coefficients on Bivalent Salt Solutions.—Thermodynamically the following relationship must define the ion exchange equilibrium $2(\mathrm{A}^+)_{\mathrm{res.}} + \mathrm{B}^{++}_{\mathrm{aq.}} \rightleftharpoons \mathrm{B}^{++}_{\mathrm{res.}} + 2(\mathrm{A}^+)_{\mathrm{aq.}}$:

$$K^\circ \left[\frac{(a_{\mathrm{A}^+})^2}{a_{\mathrm{B}^{++}}}\right]_{\mathrm{resin}} = \left[\frac{(a_{\mathrm{A}^+})^2}{a_{\mathrm{B}^{++}}}\right]_{\mathrm{aq.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

i.e.,

$$K^\circ \left[\frac{(N_{\mathrm{A}^+})^2}{N_{\mathrm{B}^{++}}}\right]_{\mathrm{res.}} \left[\frac{(f_{\mathrm{A}^+})^2}{f_{\mathrm{B}^{++}}}\right]_{\mathrm{res.}} = \left[\frac{(C_{\mathrm{A}^+})^2}{C_{\mathrm{B}^{++}}}\right]_{\mathrm{aq.}} \left[\frac{(f_{\mathrm{A}^+})^2}{f_{\mathrm{B}^{++}}}\right]_{\mathrm{aq.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where K° is the thermodynamic equilibrium constant, N_{A^+} and $N_{\mathrm{B}^{++}}$ are the ratios of the number of equivalents of the cations A^+ and B^{++} to the total number of equivalents of the cations in the resin phase, *i.e.*,

$$N_{\mathrm{A}^+} = n_{\mathrm{A}^+}/(n_{\mathrm{A}^+} + n_{\mathrm{B}^{++}}) \text{ and } N_{\mathrm{B}^{++}} = n_{\mathrm{B}^{++}}/(n_{\mathrm{A}^+} + n_{\mathrm{B}^{++}}) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and C_{A^+} and $C_{\mathrm{B}^{++}}$ are the concentrations of the two ions in the aqueous phase. Experimentally, the linear graphs prove that

$$K[(N_{\mathrm{A}^+})^2/N_{\mathrm{B}^{++}}]_{\mathrm{res.}} = [(C_{\mathrm{A}^+})^2/C_{\mathrm{B}^{++}}]_{\mathrm{aq.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Hence

$$(K^\circ/K)[(f_{\mathrm{A}^+})^2/f_{\mathrm{B}^{++}}]_{\mathrm{res.}} = [(f_{\mathrm{A}^+})^2/f_{\mathrm{B}^{++}}]_{\mathrm{aq.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

FIG. 3.

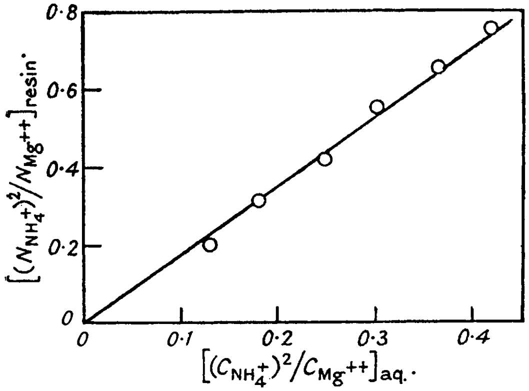
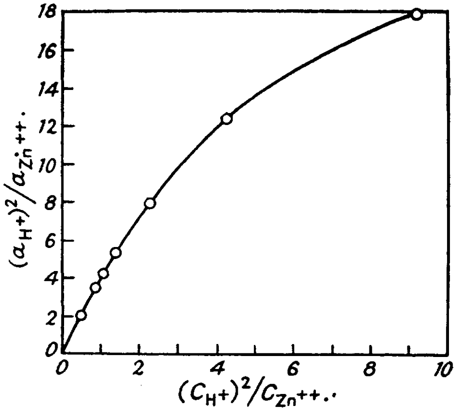


FIG. 4.



It is well known from activity measurements in electrolyte solutions that f_{A^+} and $f_{\mathrm{B}^{++}}$ in solution must vary with the relative proportions of uni- and bi-valent ions in the solution and with the dilution of the mixed uni–bi-salts. Hence the ratio $[(f_{\mathrm{A}^+})^2/(f_{\mathrm{B}^{++}})]_{\mathrm{aq.}}$ cannot in general remain constant with composition or with dilution. As no suitable data are available in the literature on this point, a series of measurements were carried out on the system $\mathrm{ZnCl_2}$–HCl, using an e.m.f. method.

The activity ratios $(a_{\mathrm{H}^+})^2/(a_{\mathrm{Zn}^{++}})$ so obtained are plotted against the corresponding concentration ratios in Fig. 4: the graph is seen to be far from linear. It follows, therefore, that $[(f_{\mathrm{H}^+})^2/f_{\mathrm{Zn}^{++}}]_{\mathrm{aq.}}$ changes over the range of composition involved.

At the same time, the equilibrium curve for the system Zn–resin–HCl, like that of the other uni-bivalent systems, is a straight line when plotted in terms of concentrations (see Fig. 5).

Therefore $$[(f_{\mathrm{H}^+})^2/f_{\mathrm{Zn}^{++}}]_{\mathrm{aq.}} = (K^\circ/K)[(f_{\mathrm{H}^+})^2/f_{\mathrm{Zn}^{++}}]_{\mathrm{resin}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and, consequently, the changes occurring in $[(f_{\mathrm{H}^+})^2/f_{\mathrm{Zn}^{++}}]_{\mathrm{aq.}}$ must be accompanied by proportion ate changes in $[(f_{\mathrm{H}^+})^2/f_{\mathrm{Zn}^{++}}]_{\mathrm{resin}}$.

EXPERIMENTAL.

Measurement of Activities in $\mathrm{ZnCl_2}$–HCl *Mixtures.*—The following cell was used

$$\mathrm{Zn/Hg\ (2\ phase)} \mid \mathrm{ZnCl_2{-}HCl,\ aq.} \mid \mathrm{H_2\ (Pt)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

A two-phase zinc-amalgam electrode has been shown by Clayton and Vosburgh (*J. Amer. Chem. Soc.*, **1936**, **58**, 2093) and by Cohen (*Z. physikal. Chem.*, 1900, **34**, 612) to behave exactly as a pure zinc electrode. The e.m.f. of the cell is accordingly:

$$E_{\mathrm{cell}} = E_{\mathrm{H}} - E_{\mathrm{Zn}} = -E_{\mathrm{Zn/Zn^{++}}} + (\boldsymbol{R}T/2\boldsymbol{F}) \log_e [(a_{\mathrm{H}^+})^2/a_{\mathrm{Zn}^{++}}] \quad . \quad . \quad . \quad . \quad (9)$$

Hence from measurements of the e.m.f. of the cell when the proportions of $ZnCl_2$ and HCl are varied, the total concentration being kept constant, the activity ratio $(a_{H^+})^2/(a_{Zn^{++}})$ corresponding to the known concentration ratio can be obtained. The value used for $E_{Zn/Zn^{++}}$ is that given by Clayton and Vosburgh, *viz.*, +0·7612 v. (American convention) at 25°, at which temperature the measurements were carried out.

The zinc-amalgam electrode was prepared by a modification of the method of Clayton and Vosburgh *loc. cit.*) and that of Tartar, Newschwander, and Ness (*ibid.*, 1941, **63**, 28). A stick of zinc of A.R. purity was dipped in a small pool of mercury beneath a concentrated solution of zinc sulphate slightly acidified with sulphuric acid and contained in a wide test-tube which was heated in a boiling water-bath for several hours. A considerable quantity of the zinc dissolved in the mercury but, at the same time, the stick became thoroughly amalgamated to a depth of 1 mm. or so. When not in use, the amalgamated zinc rod was kept under the zinc sulphate solution with its end in contact with the pool of amalgam. In this way the electrode was found to keep perfectly and to give entirely reproducible results.

The hydrogen electrode was of the Hildebrand type (*J. Amer. Chem. Soc.*, 1913, **35**, 847) and, like the zinc electrode, dipped directly into the $ZnCl_2$–HCl electrolyte which was contained in a bottle having a rubber stopper and an outlet for excess hydrogen. No liquid-junction potentials, therefore, had to be taken into account.

A series of measurements was made with $ZnCl_2$–HCl mixtures of total concentration 0·249N: the e.m.f. readings were steady and reproducible. Erratic and unsteady readings resulted with mixtures of lower concentration (0·1N, 0·05N), and the e.m.f. varied with the rate of flow of the hydrogen. It is known that dissolution occurs at a zinc electrode in dilute acid solutions, and evidently the flow of hydrogen affected this as a result of its stirring action. No evidence of dissolution was detected with the 0·249N-concentration.

DISCUSSION.

An explanation of this proportionality of the activity coefficient ratios can be obtained from a consideration of the ionic atmospheres to which the cations in the resin phase are subjected. According to the Debye–Hückel theory, the activity coefficient of an ion is determined by the ionic atmosphere surrounding it. Now, the cations in the solid phase must be more or less fixed and hence can exert relatively little influence on one another. The ions in the aqueous phase, however, *can* approach close to those in the solid and can readily influence them. Thus a cation in the solid phase may be surrounded by an ionic atmosphere similar to that surrounding a corresponding cation in the aqueous phase, and its activity coefficient may, therefore, vary in a similar manner with the composition of the solution. The activity coefficients would be equal in the two phases only if the cation in the solid phase were completely surrounded by the aqueous ionic atmosphere.

Structure of the Multivalent Metal Salts of the Resin.—Since the sulphonate groups occupy irregular positions in the resin, it might be expected that, while a certain number of these would be in favourable position to be neutralised by the multiple valencies of multivalent ions, the rest would not be in such favourable positions and could not exchange their univalent for bivalent ions. In fact, the whole of the sulphonate groups can be as readily neutralised by multivalent ions as they are by univalent. (This was demonstrated by an experiment in which an excess of ammonium chloride solution was passed over a column of about 7 g. of washed H-resin, liberating 14·55 meq. of H^+. The resulting NH_4-resin was washed and similarly treated with an excess of thorium nitrate solution, liberating 14·60 meq. of NH_4^+, *i.e.*, virtually identical with the liberated H^+.)

This is best explained by supposing each multivalent, if not univalent, cation not to be associated closely with any particular sulphonate groups (two, three, or four, as the case may be), but to be distributed throughout the resin phase in positions of minimum potential energy. The ions will be held in stoicheiometric number by electrostatic forces.

This picture is in keeping with the concept of the resin phase being completely ionised though not dissociated—a structure similar to that of a crystal. Unlike the ions in the crystal, however, those in the resin will be situated in an irregular pattern, as the anions—the resin sulphonate groups—are also in irregular positions.

A similar phenomenon is encountered in the combination of dye anions with wool, where the maximum capacity of the wool for dye combination is found to be a constant whatever the valency of the dye anion (see Speakman and Elliot, *J. Soc. Dyers Col.*, Symposium, 1946; Astbury and Dawson, *ibid.*, 1938, **54**, 6; Gilbert, *Proc. Roy. Soc.*, 1944, **183**, *A*, 167).

The facile and complete exchange of the univalent cations in an organic exchanger by multivalent seems to be a property unique to this type of exchanger. It is found to occur also with a sulphonated-coal exchanger, a phenol-ω-sulphonate resin, and a resin based on sulphonated styrene and divinylbenzene. On the other hand, Patton and Ferguson (*Canadian J. Res.*, 1937, *B*, **15**, 103) showed that 80% only of the total Na^+ in their (inorganic) zeolite was readily exchangeable for Ca^{++}, while the remainder was very difficult to replace and, in fact, they succeeded in exchanging only 90% of the Na^+ even on prolonged contact with a very dilute calcium solution.

It is of interest that a synthetic resin similar to that used in the present study, but deliberately prepared with one-fifth of the number of sulphonate groups, showed a similar and even greater reluctance to exchange H^+ for Mg^{++}, although exchange for Na^+ occurred quite readily.

Patton and Ferguson found that, although their equilibrium results for a single concentration fitted the Rothmund–Kornfeld equation, the effect of dilution was less than would be expected from this equation, and they ascribed this to the uncertain and varying available (total) capacity.

In the light of this evidence it is probable that true equilibrium is rarely reached in " equilibrium " studies made with inorganic exchangers, and the results will depend considerably on time of contact and on dilution. This may well be the reason for the frequent contradictions between the results of different workers using similar materials.

Importance of Dissociation in Solution.—The affinity of the resin for the simpler univalent cations, whose salts are highly dissociated in aqueous solution, is readily obtained from the equilibrium constants, and the values obtained are independent of concentration, anion, etc. The influence of incomplete dissociation on the equilibrium position attained with thallous salts has been dealt with in Part I. It was shown that this, at present, makes it impossible to discover the primary factor determining the affinity of this ion for the resin.

FIG. 5.

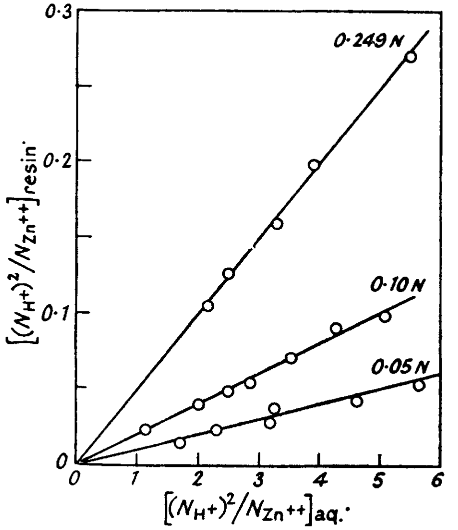
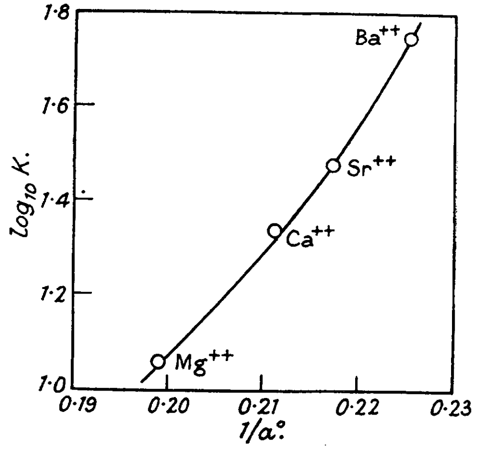


FIG. 6.



Incomplete dissociation is more commonly observed in the salts of multivalent cations, and it plays an important part in determining the extent of exchange with these ions. As with the thallous ion, the primary factor determining their affinities for the resin is largely hidden by this effect. An extreme case of incomplete ionisation is illustrated by the remarkably low affinity of the resin for the mercuric ion, which is taken up by a hydrogen resin and by an ammonium resin to an only just measurable extent from a 0·1 or 0·05N-solution of mercuric chloride (cf. table). The rôle of ionisation in determining the affinity of multivalent cations when associated with different anions in solution will be dealt with later.

The relation, if any, between affinity and ionic size should appear most clearly in the equilibria involving the alkaline-earth chlorides, which are typical strong electrolytes (Scatchard and Tefft, *J. Amer. Chem. Soc.*, 1930, **52**, 2281). Fig. 6 shows the graph of log K against $1/a°$ for this series. The values of $a°$, the distance of closest approach of the ions, are those of Stokes and Robinson (*ibid.*, 1948, **70**, 1870) and are, therefore, comparable with those used for the univalent cations (see Part I). The smooth curve so obtained might be an indication that ionic size does, in fact, play a determining rôle. This can be so if each bivalent ion in the resin phase is situated close to one of its neutralising sulphonate groups and relatively far from the other. Such a position might well be that of minimum potential energy. This arrangement may be reflected in the curvature of the graph as compared with the straight line obtained with the univalent ions, where only one sulphonate group per cation is involved and to which sulphonate group the cation evidently approaches closely.

All the salts of the ions Cd^{++}, Co^{++}, Ni^{++}, Zn^{++}, Mn^{++}, Cu^{++}, and Pb^{++} exhibit ion association to such a marked extent (Scatchard and Tefft, *loc. cit.*) that this becomes a major factor determining the " affinity " of these ions. The measured affinity is the resultant of this secondary effect and the primary determining factor, which may or may not be ionic size, and it is exceedingly difficult to separate the two. This difficulty exists because activity coefficients reflect both degree of dissociation and ionic size (in terms of the a° parameter), and few data exist for the a° values and degrees of dissociation separately of the salts studied here. Knowledge of the latter can alone enable the true activities in the aqueous phase to be calculated and thus permit the primary factor to be studied.

Scatchard and Tefft (*loc. cit.*) calculated a° values for the chlorides of lead and zinc from the respective activity coefficients, taking into account the incomplete dissociation of the salts, and obtained the values 1·9 and 3·5—6, respectively. This, qualitatively, is in keeping with the higher affinity of the resin for lead than for zinc ions. No quantitative conclusions can be drawn, however, for the absence of figures for the respective degrees of dissociation precludes the calculation of the true activities in the aqueous phase.

Boyd, Schubert, and Adamson (*J. Amer. Chem. Soc.*, 1947, **69**, 2828) have suggested that the relative magnitude of a° for bivalent ions may be found directly from activity coefficient–concentration graphs and that, therefore, the " affinities " will be in the opposite order to the activity coefficients. This is, in fact, true only for the salts of the alkaline-earth ions, and it can scarcely apply to those ions whose salts exhibit ion association, since a low activity coefficient could be the result either of high ion association, leading to a low affinity, or of a small a° value, leading to a high affinity.

Using their theory, they predicted the affinities of the transition metals to be $Zn^{++} > Cu^{++} > Ni^{++} > Co^{++} > Fe^{++}$. In fact, the affinities of the first four of these lie in very nearly the reverse order (see Fig. 2 and table), *viz.*, $Co^{++} > Ni^{++} = Cu^{++} > Zn^{++}$.

Influence of the Anion on the Equilibrium Position.—In Part I the conflicting statements appearing in the literature on the influence of the anion have been discussed. It was shown that the dependence on the anion of the equilibria involving the thallous ion, and the corresponding independence of those involving the alkali-metal ions, is consistent with the assumption that the effect of the anion is to change the degree of dissociation of the salts in solution. Those anions which do not change the degree of dissociation of the two salts involved, or change it to the same extent, result in the same equilibrium; while those which cause an unequal change will result in a different equilibrium, the cation associated with the less dissociated salt showing a lesser tendency to pass into the resin phase.

The behaviour of equilibrium systems containing multivalent cations when the anion is changed, lends further support to this concept. As mentioned above, incomplete dissociation is more commonly observed in the salts of multivalent cations than in those of univalent, and this is reflected in a much greater dependence upon the anion of systems containing multivalent cations. In particular, less of the multivalent cation passes into the resin phase from solutions containing bivalent anions, *e.g.*, sulphate, than from solutions containing univalent anions. Thus, a uni–bivalent system of ammonium resin and magnesium salts showed the same equilibrium with the chloride and nitrate, but sulphate and formate caused less bivalent ion to pass into the solid phase. The NH_4^+–Mn^{++} system behaved in an identical manner. A system of bi–bi-valent ions, *viz.*, beryllium resin and magnesium salts, came to the same equilibrium position in the presence of the anions Cl', NO_3', and SO_4''; the system Mg-resin–Mn^{++} behaved similarly. Systems involving tervalent ions were studied, *viz.*, NH_4-resin and Mg-resin, respectively, with the chloride and sulphate of aluminium. Less of the higher-valent cation passed into the solid phase in the presence of SO_4'' than in the presence of Cl'.

Ter- and Quadri-valent Cations.—Because the exchange lies so far to one side, and the third and fourth powers of concentration appear in the mass-action expression, it is difficult to test the law of mass action for these ions. However, assuming its validity, approximate values of the stoicheiometric equilibrium constants are 4·1 for Al^{+++} (sulphate solution) and 0·6 for Th^{++++} (nitrate solution), where

$$K_{Al} = [(C_{NH_4^+})^3/C_{Al^{+++}}]_{aq.}[N_{Al^{+++}}/(N_{NH_4^+})^3]_{resin} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$K_{Th} = [(C_{NH_4^+})^4/C_{Th^{++++}}]_{aq.}[N_{Th^{++++}}/(N_{NH_4^+})^4]_{resin} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

[The N terms are as defined in equation (5), and the C terms are expressed in equivs. per litre.]

Both these values, and particularly that for Th^{++++}, represent a very strong binding of the ion by the resin, as Fig. 1 (inset) shows. In agreement with earlier work, the affinity of the ions is seen to increase with increasing charge.

The general influence of charge has been tacitly assumed, in the past, to be in accordance with Coulomb's law. This is correct only if the multivalent cation is situated close to one of its neutralising sulphonate groups (presumably at the a° distance) and relatively far from the others. The interaction energy between the cation and its nearest sulphonate group is then

$$E = ze^2/Da^\circ \qquad (13)$$

(z = valency of cation and D = dielectric constant), while an additional contribution is provided by the attraction of the more distant sulphonate groups. The total interaction is, therefore, greater than z times e^2/Da°, which is that of z univalent ions of the same size. A comparison of the a° values given in the literature indicates that uni- and bi-valent ions, at least, are very nearly the same size.

If the multivalent cation were situated more or less at the "centre of gravity" of the z negative groups, the interaction energy would be considerably *less* than that of z univalent cations, each situated close to a sulphonate group. This model is consistent with that derived above from other considerations.

In spite of its quadruple charge, the zirconium ion goes on to the resin from a solution of its nitrate to only a very small extent, its equilibrium constant against NH_4^+ being *ca.* 4×10^{-6} (cf. the value for thorium and Fig. 1 inset). This, without doubt, is due to the very small number of free Zr^{++++} ions present in solution, in consequence of the tendency of zirconium to form complex anions (see Hopkins, " Chapters in the Chemistry of the Less Familiar Elements," Stipes Publishing Co., **1939**, Chap. 12, pp. 7 *et seq.*).

Imperial College of Science and Technology,
South Kensington, London, S.W.7.

[*Received, October* 13*th*, 1948.]