

# ION-EXCHANGE IN ANALYTICAL CHEMISTRY: PROBLEMS AND PROSPECTS

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## ABSTRACT

An analysis is made of some of the practical problems of ion-exchange chromatography. A comparison is made with gas-liquid chromatography and this leads to the suggestion that improvements can be made in the monitoring system and in the selection of eluents for specific separations. The need for a general purpose gradient elution apparatus is stressed.

Some theoretical aspects of several factors which affect, in particular, the tailing of elution peaks are examined. The desirability of presenting ion-exchange data in the form of complete isotherms is underlined and the type of information that can be derived from such isotherms is indicated by reference to some typical examples of uni-bivalent exchange isotherms. A plea is made for international cooperation in the compilation and collection of such data and in its interpretation in the design of analytical ion-exchange separations.

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The early outstanding successes of ion-exchange in the separations of lanthanides<sup>1</sup>, trans-uranic elements<sup>2</sup> and amino acids<sup>3</sup> led to hopes that ion-exchange would provide a powerful analytical tool. Indeed many papers have been written on the analytical applications of ion-exchange as well as some useful books<sup>4</sup>. Nevertheless, the early hopes have not been fully realized and it might even be considered that ion-exchange is tending to be replaced as a separations technique by gas-liquid chromatography or by solvent extraction. It is also to be noted that, with the development of instrumental techniques, such as atomic absorption and x-ray fluorescence spectroscopy, separation of the components of a material before analysis is often no longer necessary. Such developments are welcome ones, but they do call into question the status of ion-exchange as an analytical technique. It is clear that, in such circumstances, an analytical separation process is likely to be of use only if it can be coupled to an automatic detection and recording process—as is the case with gas-liquid chromatography.

So far ion-exchange has lacked the auxiliary instrumentation that is available in gas-liquid chromatography. A fraction collector connected to an ion-exchange column enables the components of a mixture to be collected separately, but it still leaves the work of analytical determination to be done. By contrast, the detector of a gas-liquid chromatographic column is usually connected to a chart recorder and thus automatically provides a permanent analytical record. Ion-exchange chromatography needs an equally efficient

method of monitoring ions in an aqueous medium which contains a background electrolyte of the ions of the eluting solution.

It is possible that the development of suitable ion-selective electrodes<sup>5</sup> may meet this need. Such electrodes could provide the basis of detection and determination systems that would be more sensitive than those based on pH or conductivity measurements and more convenient than polarographic or spectrophotometric systems where supporting electrolytes or colour-developing reagents have to be mixed with the eluate. The electrodes used would not need to be highly specific in their response. Since at any given stage in the elution, the eluate will, presumably, contain only one component of the mixture being separated, it would be necessary only for the electrode system to distinguish between the eluted ions and the eluent ions. A system that would enable bivalent ions or trivalent ions to be determined in the presence of sodium or ammonium ions, for example, would have many applications. In general, however, ion-selective electrodes could be effective in the determination of the eluted ions only if this were to be done in a medium of either constant ionic background or of an ionic background that is changing uniformly and predictably. Against such a uniform or uniformly varying background it would be possible to draw up calibration curves for varying concentrations of the eluted ions. Progress has been made in the continuous analysis of organic species eluted from ion-exchange columns<sup>3, 6</sup>, but in some cases, at least, the procedures used to date seem rather complicated. It is, therefore, encouraging to note that it is possible to obtain electrodes that respond to organic as well as inorganic ions<sup>7</sup>.

By comparison with the simple carrier-gas system of gas-liquid chromatography, ion-exchange chromatography suffers from the fact that sometimes two, or even three, eluting solutions are used in the course of separating a few ions. Stepwise changes in eluent concentrations are also involved. These inevitably add to the problems of determination of ions by the use of selective electrodes or indeed by any other method. Evidently greater attention needs to be directed to devising chromatographic methods based on one, or at most two, eluting solutions. Whenever possible, gradient elution should be used in place of stepwise elution. Any automatic analytical procedure can be more readily adapted to a continuously changing background than to one that is changing in a discontinuous manner. Systematic studies of systems using single eluents, such as the one involving the separation of the elements as their chloro-complexes<sup>8</sup> are, therefore, particularly valuable. Since most ion-selective electrodes are liable to be sensitive to major changes in hydrogen ion concentration of the eluting solution, the automatic analysis of the eluate is likely to be easier if alkali metal salts (such as chlorides) can be used as eluents in place of free mineral acids (such as hydrochloric acid). Studies with lithium chloride as eluting agent have been reported<sup>9</sup> and there are indications that, despite its lower solubility, solutions of sodium chloride may provide useful complexing eluents for metal ion separations on anion-exchange columns<sup>10</sup>. With such eluents it may be necessary to add small amounts of free acid to prevent hydrolytic reactions, but provided that the amounts so added are controlled and known and the pH is not so low as to interfere with the proposed scheme of automatic analysis no problems should arise. Citrates, EDTA, and other complexometric reagents have

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also been extensively studied in relation to chromatographic separations on both anion—and cation—exchangers<sup>4</sup> and the possibility of their more widespread use, coupled with gradient elution and continuous monitoring of the eluate merits further study. However, it must be remembered that the efficiency of ion-selective electrodes is likely to be impaired by the presence of strongly complexing ligands.

The closer ion-exchange chromatography can approach to gas-liquid chromatography in the simplicity of its monitoring techniques the better. Yet this can only follow from simplicity in the carrier system and it is here that there is much room for improvement. In gas-liquid chromatography a few carrier gases serve for a wide range of uses. By contrast, a very wide range of eluents is used in ion-exchange chromatography. Even when a mixture containing two ions only is to be separated, it would appear, from considerations of *Table 1*, that it is more usual (104 examples cited) to use

*Table 1.* Analysis of separation procedures summarized in Table 6.8<sup>a</sup> in the English edition of *Analytical Applications of Ion Exchangers* by J. Inczedy

Range of eluent types	No. of eluent solutions used	No. of examples quoted where no. of fractions collected is		
		2	3	4 or more
Essentially one species <sup>b</sup>	1	29	5	5
	2	70	4	2
	3	0	11	2
	4	0	0	8
Similar species <sup>c</sup>	2	39	3	1
	3	0	10	1
	4	0	0	8
Different species	2	104	2	1
	3	1	19	3
	4	0	0	11

NOTES: (a) excluding the Lanthanide and Actinide sections.

(b) such as HCl at various concentrations or citrate at various pH values.

(c) such as HCl and NaCl or HCl + HF and HCl alone.

quite different eluents, than to use two very similar ones (70 examples cited) and still less usual to use a single eluent (29 examples cited). Yet in many instances where different eluents are used it is evident that there are often alternative procedures available in which a single eluent is used.

Where it is not practicable to use a single eluent, then it is desirable that gradient rather than stepwise elution should be used. However, even in the use of gradient elution there is a lack of uniformity of practice that is characteristic of ion-exchange chromatography. Thus one standard textbook (the second quoted in ref. 4) illustrates six different forms of apparatus for producing gradients in eluent composition that have been described in the literature. There is a need for an internationally agreed specification for an

apparatus that will produce controlled gradient from a first eluting solution to a second and possibly a third. Some flexibility in the types of gradient and their steepness is important, but lack of it can, to some extent, be offset by flexibility in the column length and flowrates used. Furthermore, a survey of the texts quoted in ref. 4 suggests that in many ion-exchange separations the total volume of eluent used is between 100 ml and 500 ml. Hence it should be possible to design a relatively simple, general purpose apparatus.

Ion-exchange can never approach gas-liquid chromatography in the rate of the basic process that gives rise to the separation process. In gas-liquid chromatography the material sorbed in the column is dissolved in a thin layer of liquid spread on a solid support and the times involved in the diffusion of the solute in and out of the layer are relatively short. By contrast, the film and particle diffusion processes of ion exchange are relatively slow. The mixing processes (due to convection and so on) which take place in the spaces between the ion-exchange beads become significant and can give rise to marked tailing of the elution peaks. It is, therefore, important to speed up the diffusion processes within and around each bead and this can best be done by using small bead sizes. Since this will lead to an increase in the resistance to fluid flow through the column, it may be necessary to use increased hydrostatic pressure to ensure flow at the desired rate through the column. This practice has already been adopted by some workers<sup>11</sup>. A change from glass to plastic columns may also be necessary.

Nothing suggested so far would make ion-exchange chromatography a more complicated procedure than gas-liquid chromatography, but the proposals made would enable it to achieve a comparable flexibility of operation. It ought to be easier to separate organic acid anions on an ion-exchange column than to esterify the acids and then to separate the esters on a gas-liquid column. Furthermore, where an appropriate ion-exchange separation can be devised, this should be a suitable method for the separation of heat-sensitive substances.

To establish ion-exchange chromatography as a procedure comparable with gas-liquid chromatography, there is a need for international agreement on:

(i) the separations that can most profitably be achieved by ion-exchange chromatography; in the field of inorganic chemistry these would include not only the lanthanides and actinides but presumably also the alkali and alkaline earth metal ions, those of the first transition series and such pairs as zinc and cadmium, molybdenum and tungsten, whilst in the field of organic chemistry this would include not only the amino acids but presumably also series of mono- and di-carboxylic acids and other possibilities:

(ii) the choice of the preferred procedure for each of the separations selected in (i);

(iii) the design of a suitable gradient elution apparatus to meet the needs established under (ii);

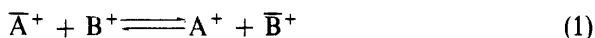
(iv) the selection and design of a monitoring procedure for the continuous analysis of the eluate; preferably only one type, or preferably a very limited range of types of procedure, should be selected.

These would all seem to be matters for a commission of the International Union of Pure and Applied Chemistry to consider.

## THEORETICAL CONSIDERATIONS

Whatever improvements can be achieved in the operation of ion-exchange chromatography, there is yet another problem. It arises from the basic assumption, in any theoretical treatment of elution chromatography, that at every point in the column there prevails a state which closely approaches to an equilibrium one. Unfortunately the implications of this assumption are not always fully considered. In particular, it is difficult to know what the equilibrium state really is.

For an ion-exchange reaction such as



(where barred formulae refer to species in the exchanger phase) the so-called mass-action constant

$$K_{c_A}^B = [\bar{B}] [A] / [B] [\bar{A}] \quad (2)$$

is known not to be a true constant, but to vary with changes in the concentrations of the exchanging ions in each phase. It is, however, a useful quantity in that it relates the ratio of the concentrations of one ion in the two phases to the corresponding ratio for the other ion

$$[\bar{B}] / [B] = K_{c_A}^B [\bar{A}] / [A] \quad (2a)$$

If  $K_{c_A}^B$  is greater than unity then there is a greater uptake of  $B^+$  than of  $A^+$  by the exchanger, relative to their concentrations in the external solution and vice versa. For this reason  $K_{c_A}^B$  is generally known as the selectivity coefficient. However, as the reaction of equation 1 proceeds from left to right the value of  $K_{c_A}^B$  will not be constant, but will vary.

If, initially, the exchanger is entirely in the  $A^+$ -form and the external electrolyte is essentially a (say, decinormal) solution of an  $A^+$  salt ( $AX$ ) with trace amounts only of  $B^+$  ions, then, at equilibrium,  $[A]$  and  $[\bar{A}]$  will not vary significantly from their initial values. Hence

$$[\bar{B}] / [B] = K_{c_A}^B \times \text{const} = K_d \quad (3)$$

where  $K_d$  is known as the distribution coefficient. The variation of  $K_d$  for a series of ions  $B^+$ ,  $B'^+$ ,  $B''^+$  and so on, in their separate exchange reactions with the common reference ion  $A^+$ , will provide a useful indication of the possibility (or otherwise) of a chromatographic separation of the series of ions  $B^+$ ,  $B'^+$ ,  $B''^+$  and so on using  $A^+$  as the eluting ion. However, values of  $K_d$  obtained at concentrations other than trace ones of the ions,  $B^+$ ,  $B'^+$ ,  $B''^+$  and so on will not be strictly comparable with those determined at tracer concentrations of those ions. This point seems to have been overlooked by some workers who have quoted  $K_d$  values at various concentrations.

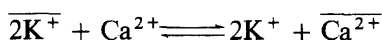
In an elution band of ion  $B^+$  moving down an ion-exchange column, the concentration of  $B^+$  in the exchanger beads within the band will always be finite and in most analytical separations will probably reach saturation. Hence, as the band of  $B^+$  is eluted past that point in the column,  $K_{c_A}^B$  will vary over the whole range of possible values. It is, therefore, useful to know how  $K_{c_A}^B$  varies with respect to, for example, the thermodynamic equilibrium constant  $K_T$ , as  $[\bar{B}]$  changes from its maximum value to zero. One such

semi-empirical relationship with which the author is particularly familiar<sup>12</sup> and which seems to be applicable to a wide range of anion and cation exchange systems is

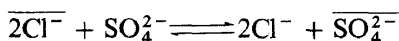
$$\ln K_{c_A}^B = \ln K_T - \frac{1}{2}\bar{x}_B\omega/RT \quad (4)$$

where  $\bar{x}_B = [\bar{B}]/([\bar{A}] + [\bar{B}])$  and  $\omega$  is an interaction term for which positive values correspond to an increase in the energy of the exchanger system when two  $B^+$  ions occupy adjacent exchange sites. It will be noted that if, in equation 4,  $\omega$  is positive, then  $\ln K_{c_A}^B$  becomes less negative or more positive, and hence  $K_{c_A}^B$  increases as  $\bar{x}_B$  tends to zero. This means that, as elution proceeds, the selectivity for ion  $B^+$  would increase. There would thus be an inevitable tendency for tailing of the elution peak to occur, regardless of any operational factors. Hence it is desirable to evaluate  $\ln K_T$  and  $\omega$ . This may be done by plotting  $\ln K_{c_A}^B$  against  $\bar{x}_B$ , which should yield a straight line plot of slope  $\frac{1}{2}\omega/RT$  and with an intercept at  $\bar{x}_B = 0$  of  $\ln K_T$ . For this purpose it is necessary to study the dependence of  $\bar{x}_B$  on  $x_B$  [where  $x_B = [B]/([A] + [B])$ ] over a wide range of values of the latter. This is equivalent to studying the variation of  $\bar{x}_A$  with  $x_A$ , where  $\bar{x}_A = [\bar{A}]/([\bar{A}] + [\bar{B}])$  and  $x_A = [A]/([A] + [B])$ . Since  $A^+$  may be the same reference ion in a whole series of uni-uni-, uni-bi-, and uni-tervalent exchange reactions (and similarly for  $A^-$  in anion exchange reactions), it is sometimes convenient to plot the exchange isotherm for the common reference ion. It is always more convenient to plot the equivalent ionic fraction of one ion ( $\bar{x}_A$  or  $\bar{x}_B$ ) in the exchanger against its corresponding fraction in solution ( $x_A$  or  $x_B$ ) than to plot the concentration of one ion in one place against its concentration in the other, for reasons which will become apparent.

The form of periodic table used by Kraus and Nelson<sup>8</sup> to record the sorbabilities of the elements from hydrochloric acid solutions on to an anion exchanger could provide a convenient model for a table showing the exchange isotherms for the principal ionic forms of the elements. For cationic exchange reactions it is suggested that the potassium ion would be the most suitable reference ion, e.g.



whilst for anionic exchange reactions the chloride ion would be the most suitable reference ion, e.g.



In this way potassium chloride would be the standard reference electrolyte common to both systems. For easily hydrolysed cationic species and for the anions of weak acids it would be necessary to specify an appropriate pH value for the isotherm and in extreme instances to use the hydrogen or hydroxyl ions as secondary reference ions.

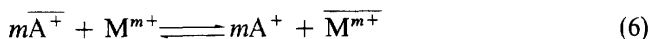
In the first instance a single periodic table referring to systems at 25° with decinormal external electrolyte and with resins of eight per cent nominal crosslinking (or water regain value one, for anion exchangers) would be most appropriate. Later, however, it would be necessary to produce

corresponding tables for other temperatures (up to at least 50°), other external electrolyte concentrations (0.01N to 1N) and other degrees of crosslinking and so on.

Since the selectivity coefficient is essentially the so-called mass action constant, it has a different form for uni-uni-, uni-bi, and uni-tervalent exchange reactions. It is therefore convenient to have a reference term which is the same for all of them. This is the separation factor,  $\alpha$ , which for reaction 1 is given by

$$\alpha_A^B = \frac{[\overline{B}][A]}{[B][\overline{A}]} = \frac{\bar{x}_B x_A}{x_B \bar{x}_A} \quad (5)$$

and is hence, for such uni-univalent reactions, but not for the others, identical with the selectivity coefficient. For the general exchange reaction involving one univalent ion



the separation factor is given by

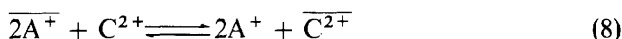
$$\alpha_A^M = \frac{[\overline{M}][A]}{[M][\overline{A}]} = \frac{\bar{x}_M x_A}{x_M \bar{x}_A} \quad (7)$$

The separation factor may thus be regarded as a pseudo uni-univalent selectivity coefficient for the uni-bi- and uni-ter-valent reactions. It must be remembered, however, that  $\bar{x}_M$  is given by  $m[\overline{M}]/(m[\overline{M}] + [\overline{A}])$  and  $x_M$  by  $m[M]/(m[M] + [A])$ , whilst  $\bar{x}_A = (1 - \bar{x}_M)$  and  $x_A = (1 - x_M)$ .

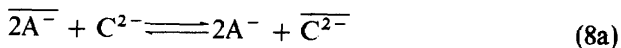
The value of  $\alpha_A^B$  (or  $\alpha_A^M$ , as appropriate) can be obtained directly from a plot of  $\bar{x}_A$  against  $x_A$  (or respectively  $\bar{x}_B$  against  $x_B$  or  $\bar{x}_M$  against  $x_M$ ) as can be seen by reference to *Figure 1*. For the point P lying on the isotherm, the lengths of the vertical and horizontal sides of the shaded area marked Q are given by  $\bar{x}_B$  and  $x_A$  respectively whilst the corresponding sides of area R are given by  $\bar{x}_A$  and  $x_B$  respectively. Hence the value of  $\alpha_A^B$ , at the point P, is given by the ratio of area Q to area R.

Most textbooks on ion-exchange illustrate several uni-univalent exchange isotherms, usually to show the relative affinity series for the alkali metal ions. However, the data given relating to uni-bivalent exchange reactions are generally sparse, consisting usually of a series of isotherms for various bivalent ions at one specified set of conditions and two or three isotherms for one system at two or three levels of external electrolyte concentration. This is unfortunate because several features of uni-bivalent and, incidentally, uni-tervalent exchange reactions are thereby overlooked.

The dependence on external electrolyte concentration of uni-bivalent exchange reactions is, of course, of considerable practical importance in such applications as water softening or demineralizing, as well as in chromatography. It follows directly from the form of the 'mass action constant' or selectivity coefficient for reactions such as:



or



which is

$$K_{c_A}^C = [\overline{C}] [A]^2 / [C] [\overline{A}]^2 \tag{9}$$

Equation 9 may be re-written in a number of ways including

$$[\overline{C}] / [C] = K_{c_A}^C [\overline{A}]^2 / [A]^2 \tag{9a}$$

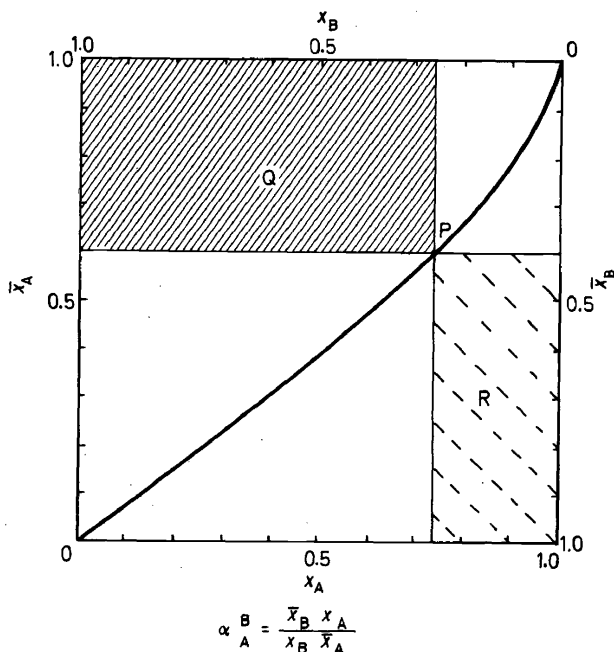


Figure 1. Graphical solution of equation 5

which shows that the ratio  $[\overline{C}]/[C]$  is no longer a simple function of  $[\overline{A}]/[A]$ , even if  $K_{c_A}^C$  is a constant. In the elution of a band of  $C^{2+}$  ions down a column of exchanger by, say, a 0.1N solution of salt AX the value of  $([\overline{A}] + 2[\overline{C}])$  is set by the capacity of the exchanger and that of  $([A] + 2[C])$  at 0.1N. Hence as the main peak of the band passes a given point  $[\overline{A}]$  may be quite low, say 0.5M, and  $[A]$  may be about 0.05M so that  $[\overline{C}]/[C]$  could be about  $100K_{c_A}^C$ , but after the main peak has passed  $[\overline{A}]$  may rise to, say, 2.0M and  $[A]$  to say 0.097M so that  $[\overline{C}]/[C]$  could then be nearer to  $400K_{c_A}^C$ . This factor alone could contribute significantly to the tailing of the peak, but could be offset to some degree by a gradient of increasing concentration of AX.

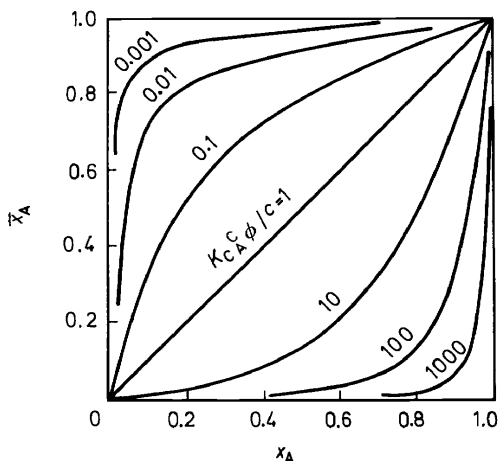
Another form of the equation

$$[\bar{C}]/[C] = \alpha_A^C [\bar{A}]/[A] \quad (9b)$$

shows the dependence of  $[\bar{C}]/[C]$  on  $[\bar{A}]/[A]$  as well as on  $\alpha_A^C$ . The form expressed in terms of equivalent ionic fractions

$$\bar{x}_C/x_C = K_{cA}^C \phi \bar{x}_A^2 / c x_A^2 \quad (9c)$$

where  $\phi = ([\bar{A}] + 2[\bar{C}])$  and is the volume capacity of the exchanger and  $c = ([A] + 2[C])$  and is the total equivalent concentration of exchangeable ions in solution. This last form of the equation 9c which arises directly from substituting the appropriate equivalent fraction terms for the concentration terms in equation 9 shows the dependence of  $[\bar{C}]/[C]$  on the composite term,  $K_{cA}^C \phi / c$ . The isotherms that would arise from certain values of this term are illustrated in *Figure 2*. Since  $K_{cA}^C$  does not vary greatly for a given



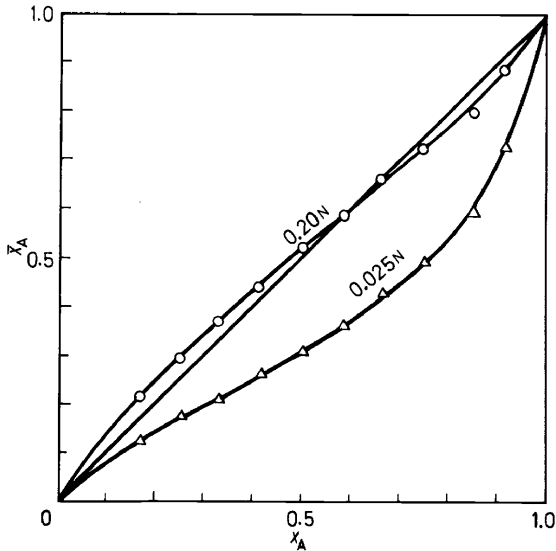
*Figure 2.* Uni-bivalent exchange

system and  $\phi$  is fixed for a given exchanger, the major variations in the composite term arise from variations in the concentration of the external electrolyte. The data for the chloride-oxalate exchange system for specified conditions<sup>13</sup> in *Figure 3* show that the preferential sorption of the bivalent ion from the more dilute solutions gives way at circa 0.2N to preferential sorption of the univalent ion. It is evident that the isotherms shown in *Figure 3* are of a lower symmetry than those shown in *Figure 2*, thus showing that  $K_{cA}^C$  is not constant. In the case of uni-bivalent exchange reactions equation 4 becomes<sup>12</sup>

$$\ln K_{cA}^C = \ln (f_C K_T / f_A^2) - \bar{x}_C \omega / RT \quad (10)$$

(where  $f_C$  and  $f_A$  are activity coefficients of  $C^{2+}$  and  $A^+$  in the external electrolyte). This equation appears to fit the experimental data well for both

anion and cation exchange systems<sup>12-16</sup>. With very few exceptions,  $\omega$  is positive and hence  $K_{cA}^C$  increases as  $\bar{x}_C$  tends to zero and this will cause a further tailing of an elution peak over and above that which would occur with the more symmetrical type of curve shown in *Figure 2*.



*Figure 3.* Effect of total equivalent concentration on the chloride-oxalate exchange isotherm at 25° W.R. 1.19

A typical example of the effect of temperature on the exchange isotherm for a specified system is shown in *Figure 4* from which it can be seen that  $\alpha_A^C$  increases with temperature, hence making the elution of  $C^{2+}$  ions by AX more difficult and, thus, by increasing the volume of eluent required, increasing the effects of random diffusion, and so on, on the tailing of the elution peak.

The value of  $K_T$  derived by plotting  $\ln K_{cA}^C$  against  $\bar{x}_C$  is applicable to a specific exchanger only and will vary from one exchanger to another. The effect of variation in the water regain value (which provides some indication of crosslinking) of a series of similar anion exchange resins on the chloride-sulphate exchange system is shown in *Figure 5*. It should be realized, therefore, that changes in crosslinking designed to speed up the particle diffusion process can produce significant changes in the isotherm and that these can be equivalent to those produced by a change in temperature of about 40 degrees.

For some systems, the exchange process may be particularly sensitive to variations in the degree of crosslinking within the resin beads. In such cases, the plot of  $\ln K_{cA}^C$  against  $\bar{x}_C$  is no longer linear. It is then necessary to apply an empirical correction to allow for the fact that, in an exchanger of variable

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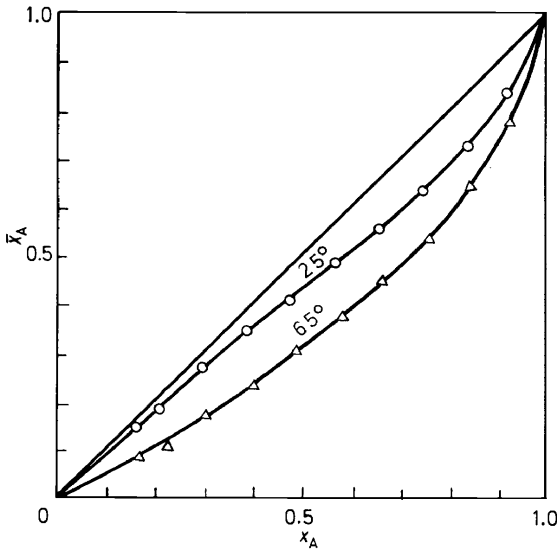


Figure 4. Effect of temperature on the chloride-sulphate exchange isotherm W.R. 0.88 0.1N

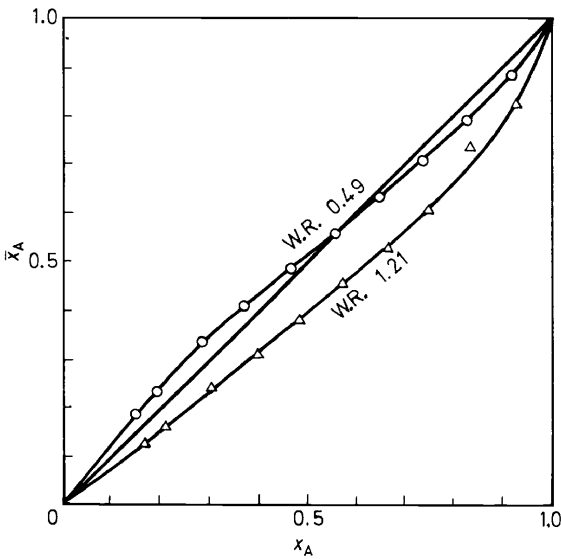


Figure 5. Effect of water regain on chloride-sulphate exchange isotherms at 25° for isoporous resins, 0.1N

crosslinking, pairs of  $C^{2+}$  ions will arise first in regions of crosslinking where  $\omega$  will be lowest and only last of all in regions where  $\omega$  will be highest. Such an empirical correction is incorporated in the equation<sup>12</sup>

$$\ln K_{c_A}^C = \ln K_T - \bar{x}_C \omega [1 + a(\bar{x}_C - x_A) + b(x_C - x_A)^2] / RT \quad (11)$$

where  $a$  and  $b$  are constants. For a number of anion-<sup>13, 15</sup> and cation-<sup>16</sup> exchange systems, this equation 11, with  $a = b = 1$ , seems to fit the experimental data well. In such systems, the increase in  $\ln K_{CA}^C$  as  $\bar{x}_C$  tends to zero is, if anything, enhanced.

It is clear then that it is essential to have more information than a single 'nominal'  $K_d$  value and that to design an efficient chromatographic separation it is desirable to have a fuller knowledge of the factors discussed above. Nevertheless, it is encouraging to note that where these factors have an adverse effect this could probably be counteracted by the use of gradient elution techniques. However, such applications of gradient elution need to be planned in the light of the knowledge of the variation of the selectivity coefficient and separation factor with concentration. There is much information still to be gathered. So far, in addition to our work on univalent anion- and cation-exchange systems, where much remains to be done, we have made a small start on uni-tervalent systems, but have done nothing on the more complex bi-tervalent exchange systems. Research workers from three European countries have helped us to date and two of these have continued such work and extended it to other systems<sup>17, 18</sup> and other exchangers<sup>18</sup> in their own institutions. Another worker from South America is due to join our team soon and will, we hope, continue with the work on returning there. The more that can be done in this direction, the easier it will be to design chromatographic and industrial applications of ion-exchange. Since in preparing this article I have had such practical applications in mind, I have ignored the more theoretical aspects as to the possible theoretical significance of the term  $\omega$  and its variation with crosslinking of the exchanger, and so on, but the unravelling of these and similar points adds considerable interest to the programme of work. However, in view of the vast amount of work to be done in covering the periodic table (in the style of Kraus) and studying organic ions some degree of international cooperation and planning, under IUPAC auspices preferably, seems essential.

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