

## Ion exchange in zeolites: some recent developments in theory and practice

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**Abstract** - Zeolites find relatively few direct applications as ion exchangers and it is perhaps for this reason that the study of their ion exchange behaviour is somewhat neglected in comparison to their other properties. Nevertheless, ion exchange is an essential part of preparative procedures for the manufacture of zeolitic sorbents and catalysts, and there is now increasing recognition of the importance of using strictly controlled conditions during ion exchange in order to avoid hydrolysis and crystal damage. Some practical points concerning ion exchange are therefore considered, and in addition two aspects of the theory of ion exchange are reviewed. Firstly, some recent discussions regarding the propriety of using the Gaines and Thomas thermodynamic formulation to evaluate activity coefficients within the exchanger phase are considered. Secondly, recent progress in the prediction of multi-component exchange equilibria is discussed. Finally, some suggestions are made regarding possible fruitful future areas of research.

### INTRODUCTION

Compared to resins, zeolites have found only very limited application as ion exchangers in the last twenty years. In general, zeolites are used where economic considerations or where a high thermal and/or radiation flux exclude the use of resins. Thus zeolites find application as water softeners in detergency (ref. 1), where the relative cheapness of zeolite A makes it an attractive option in such a "throw-away" application, or in the removal and storage of radionuclides (ref. 2), where the considerable resistance of some zeolites to radiation and thermal damage make them an obvious choice.

The comparatively limited application of zeolites as ion exchangers has meant naturally that research has concentrated on the equilibrium and kinetic properties of those systems of direct interest, especially the sodium/calcium/magnesium-A system (ref. 3, 4, 5, 6) and ammonium exchange in synthetic and natural zeolites (ref. 7, 8, 9). The latter systems are of importance firstly in the use of zeolites to remove ammonia and ammonium ions from fresh-water effluents (ref. 10), and secondly because exchange of ammonium ions into Y (and the removal of sodium) is a normal part of the preparation procedure for cracking catalysts (ref. 11).

In general, however, it must be recognised that the study of ion exchange properties is not a major preoccupation of zeolite chemists. It is natural and only to be expected that synthesis, structure, sorption and catalysis attract more attention, and that compared to these ion exchange is much neglected.

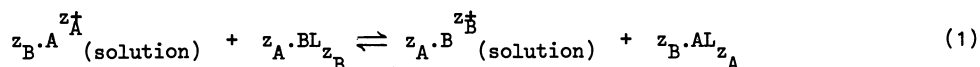
This comparative neglect is perhaps unfortunate for zeolite chemistry as a whole, especially since ion exchange is often an essential procedural component in the preparation and/or manufacture of zeolites for use either as sorbents or catalysts. Indeed, in many such studies it appears that too little attention has been given to the conditions used in the preparation of the materials, with minimal information being provided in many publications. Yet zeolites can be readily hydrolysed, undergoing in the process structural transformations through dealumination. For this and other reasons, a fundamental re-examination of much of the data already published on ion exchange in zeolites appears necessary, and some recent developments in the experimental field which had this end in mind are described below. In addition to the practical aspects of the subject, parts of the background theory (especially the equilibrium aspects) have also had to be re-examined, or developed so that selectivity data obtained experimentally may be employed to predict exchange equilibria over a range of specified conditions. Some of these theoretical aspects are also considered below.

### DEVELOPMENTS IN BACKGROUND THEORY

The development of thermodynamic formulations for ion exchange has occurred in parallel for

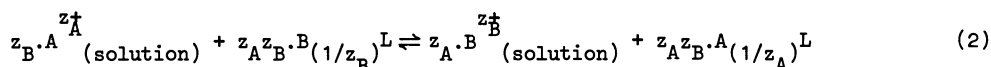
resins, clay minerals and zeolites, with only a limited interchange of information having taken place between the workers concerned. Inevitably therefore, alternative formulations, conventions and concentration scales have been used, which have led on occasion to serious confusion in the literature. Indeed, the approach which has been adopted by all zeolite researchers for the last 30 years has been criticised as being fundamentally incorrect (ref. 12, 13, 14). It is essential therefore to review first these basic theoretical concepts.

There are two alternative and equally valid ways of expressing a binary exchange reaction (and consequently the thermodynamic equilibrium constant). The first of these (most commonly employed) was used by Vanselow (ref. 15):



where  $z_A$  and  $z_B$  are respectively the valencies of the exchanging cations A and B. There are of course present also in the external solution co-anions Y, which maintain electroneutrality in that phase, and these co-anions may be regarded as providing the "exchange capacity" of the electrolyte solution external to the zeolite. L is defined as a portion of zeolite framework holding unit negative charge. Note that the above equation excludes consideration of salt inclusion (ref. 16, 17) within the exchanger, since this would involve a net transfer of some co-anions Y from one phase to the other, resulting in an increase in the exchange capacity of the zeolite at the expense of the solution. However, adequate allowance for the possibility of salt inclusion may be made if required (ref. 18).

A second way of expressing the reaction may be traced to Gapon (ref. 19):



The stoichiometric quantities of A, B, L (and consequently Y) involved in eqn 2 are seen to be the same as in eqn 1, making eqn 2 an alternative (if less familiar) way of expressing the exchange reaction.

From eqn 1, the following (familiar) definition of the thermodynamic equilibrium constant follows:

$$K_a = (a_{B,s}^{z_A} / a_{A,s}^{z_B}) (a_A^{z_B} / a_B^{z_A}) \quad (3)$$

where "a" stands for activity, and a solution phase activity is distinguished by the use of subscript "s". It is evident from eqn 1 that a mole of either homoionic B- or homoionic A-exchanger is defined as  $BL_{z_B}$  and  $AL_{z_A}$  respectively, and thus eqn 3 becomes

$$K_a = (a_{B,s}^{z_A} / a_{A,s}^{z_B}) (X_A f_A)^{z_B} (X_B f_B)^{-z_A} = K_V (f_A^{z_B} / f_B^{z_A}) \quad (4)$$

where  $X_i$  is a cationic mole fraction defined as

$$X_i = n_{iL_{z_i}} / (n_{AL_{z_A}} + n_{BL_{z_B}}) \quad (5)$$

$f_A$ ,  $f_B$  are corresponding rational activity coefficients for the exchange components and the n terms are the number of moles of the appropriate components.  $K_V$  is the Vanselow corrected selectivity quotient (i.e. a quotient which contains within itself the correction for solution phase non-ideality  $\Gamma$  (ref. 20), and which expresses concentrations in the exchanger phase in terms of cationic mole fractions  $X_i$ ). If the exchanger behaves ideally for all values of  $X_A$ ,  $X_B$ , then it follows that  $f_A = f_B = 1$  for all  $X_A$ ,  $X_B$ , and (eqn 4) under such conditions  $K_a = K_V$  for all  $X_A$ ,  $X_B$  as expected.

However, using eqn 2 it is equally correct to define  $K_a$  as

$$K_a = (a_{B,s}^{z_B} / a_{A,s}^{z_A}) (a_A / a_B)^{z_A z_B} \quad (6)$$

where a stands for activity of the appropriate component in the zeolite. The activity terms for the solution phase are seen to be identical in eqns 3 and 6, as expected from reaction

eqns 1 and 2. One mole of either homoionic B- or homoionic A- exchanger is now defined respectively as  $B_{(1/z_B)}^L$  and  $A_{(1/z_A)}^L$ , and eqn 6 becomes

$$K_a = (a_{B,s}^{z_A} / a_{A,s}^{z_B}) (x_A h_A / x_B h_B)^{z_A z_B} = K_H (h_A / h_B)^{z_A z_B} \quad (7)$$

where  $x_i$  is another cationic mole fraction, defined after Gapon's choice of mole (ref. 19) as

$$x_i = n_{i(1/z_i)}^L / (n_{A(1/z_A)}^L + n_{B(1/z_B)}^L) \quad (8)$$

$K_H$  is another corrected selectivity quotient (named after Hogfeldt (ref. 21) who first developed a thermodynamic formulation using Gapon's choice of mole) and  $h_A, h_B$  are corresponding rational activity coefficients. As for eqn 4, it follows from eqn 7 that if the exchanger behaves ideally for all  $x_A, x_B$ , then  $h_A = h_B = 1$  and  $K_a = K_H$  for all  $x_A, x_B$ .

It is most important to note that for the same choice of standard states,  $K_a$  as calculated from eqn 3 must equal  $K_a$  calculated from eqn 6 for a given exchange reaction, whence it follows (ref. 22), that for non-ideal exchangers if  $z_A \neq z_B$  then usually  $a_i \neq a_i, f_i \neq h_i$  and  $K_V \neq K_H$ . Thus eqns 4 and 7 represent two complementary but equally valid ways of expressing  $K_a$  (ref. 22).

However, the thermodynamic formulation which has been employed by all those concerned with ion exchange in zeolites corresponds with neither of the above. This third approach (ref. 18) expresses  $K_a$  as in eqn 3 but expands the exchanger phase activity terms differently:

$$K_a = (a_{B,s}^{z_A} / a_{A,s}^{z_B}) (E_A g_A)^{z_B} (E_B g_B)^{-z_A} = K_G (g_A^{z_B} / g_B^{z_A}) \quad (9)$$

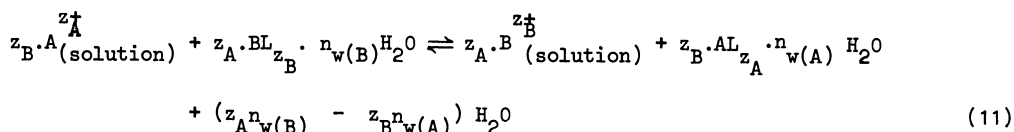
$E_A, E_B$  are cationic equivalent fractions, defined as

$$E_i = z_i n_{iL} / (z_A n_{AL} + z_B n_{BL}) \quad (10)$$

and  $K_G, g_A, g_B$  are the Gaines and Thomas (ref. 18) corrected selectivity quotient and exchanger phase activity coefficients respectively. Then from eqn 9, if the exchanger behaves ideally for all  $E_A, E_B$ , then it should hold that  $g_A = g_B = 1$  and  $K_a = K_G$  for all  $E_A, E_B$ . (Note also that the  $E_i$  are always identical numerically to the Gapon cationic mole fractions  $x_i$ ; nevertheless usually  $g_i \neq h_i$  if  $z_A \neq z_B$ ).

A consequence of expanding the activity terms  $a_i$  in eqn 9 in terms of  $E_i$  rather than  $X_i$  is that the Gaines and Thomas approach (ref. 18), while correct mathematically, mixes two concentration scales ( $X_i$  and  $E_i$ ), and this leads to a more complicated formulation than is seen for either of the others. Ideal behaviour within the zeolite phase is in part defined differently, both for binary (ref. 22) and multicomponent exchangers (ref. 23, 24). It is probably a failure to appreciate this point which has led to suggestions that there is something intrinsically wrong (ref. 12, 13, 14) with the Gaines and Thomas equations. Summaries of the criticisms (ref. 12, 13, 14) and their refutation (ref. 22, 25) are therefore given below.

It was noted earlier that eqns 1 and 2 precluded from immediate consideration the possibility of salt imbibition. Actually, changes in water content in the exchanger are also not taken into account in these equations. If this is done, then (for example) eqn 1 becomes



and

$$K_a = (a_{B,s}^{z_A} / a_{A,s}^{z_B}) (a_A^{z_B} / a_B^{z_A}) a_w^{(z_A^{n_{w(B)}} - z_B^{n_{w(A)}})} \quad (12)$$

where  $a_w$  is the activity of water in the exchanger. To avoid this complication it has been

normal practice to regard the imbibed water as being associated with and partitioned among the exchanging components of the solid solution in fixed proportions. In reality the water is a third independently variable component, but if the two exchange components are regarded as "hydrates" then with varying degrees of inaccuracy the exchanger phase can be treated in an analogous way to a conventional binary solid or liquid solution. The definitions of  $K_a$  given in eqns 3 or 6 may then still be used.

To evaluate  $K_a$ , the Gibbs-Duhem equation is nevertheless expanded with the water as an independently variable term (ref. 18). The resulting complete expressions in terms of the functions  $K_V$ ,  $K_H$  and  $K_G$  respectively are then

$$\ln K_a - \Delta = \int_0^1 \ln K_V dE_A = \int_0^1 \ln K_H dE_A = (z_B - z_A) + \int_0^1 \ln K_G dE_A \quad (13)$$

where  $\Delta$  is the water activity term, comprising three integrals (ref. 20), but readily summarised as

$$\Delta = -z_A z_B \int_{\ln a_w=0(E_B=1, I=0)}^{\ln a_w=0(E_A=1, I=0)} v_{w,AB} d \ln a_w \quad (14)$$

$v_{w,AB}$  is the number of moles of water per equivalent of exchanger, and  $I$  the ionic strength in solution (ref. 18, 23). It has however been common practice when evaluating  $K_a$  and/or activity coefficients to ignore the water term on the basis that its magnitude is normally found to be very small (ref. 20, 26). If  $\Delta$  is assigned a value of zero and the conditions of ideal behaviour with respect to the exchanger components are considered (*vis.* that  $f_A = f_B = h_A = h_B = 1$  for all  $E_A, E_B$ ) then eqns 4, 7 and 13 all show that  $K_V = K_H = K_a =$  constant for all  $E_A, E_B$  as expected. However, with  $\Delta=0$ , the Gaines and Thomas formulation becomes (eqn 13)

$$\ln K_a = (z_B - z_A) + \int_0^1 \ln K_G dE_A \quad (15)$$

Equation 9 shows that when  $g_A = g_B = 1$ , then  $K_G = K_a =$  constant. However, eqn 15 shows that if  $(z_B - z_A) \neq 0$  then  $K_G \neq K_a$ . Thus eqns 9 and 15 are mutually exclusive. It is this paradox, and similar ones concerning expressions for the activity coefficients  $g_A$  and  $g_B$ , which led to suggestions (ref. 12, 13, 14) that the Gaines and Thomas approach was wrong intrinsically.

The solution to this paradox has been demonstrated recently (ref. 22). Using the Gibbs-Duhem equation, ideal behaviour for water in the zeolite has as its criterion for formulations involving  $K_V$  and  $K_H$  that (ref. 22).

$$\begin{aligned} (n_{w,AB} / (n_A + n_B)) d \ln a_w &= 0 & (K_V) \\ v_{w,AB} d \ln a_w &= 0 & (K_H) \end{aligned} \quad (16)$$

so that under ideal conditions  $\Delta$  (eqn 14) is zero by definition. If therefore the water terms are ignored no paradoxes will arise regarding ideal behaviour for the formulations involving  $K_V$  or  $K_H$  in eqn 13. In contrast, for the Gaines and Thomas formulation, the criterion for ideal behaviour with respect to imbibed water is not that  $\Delta$  be zero (ref. 22) but rather that

$$v_{w,AB} d \ln a_w = ((z_A - z_B) / z_A z_B) dE_A \quad (17)$$

whence (eqns 14 and 17)

$$\begin{aligned} \Delta &= -z_A z_B \int_{\ln a_w=0(E_B=1, I=0)}^{\ln a_w=0(E_A=1, I=0)} ((z_A - z_B) / z_A z_B) (dE_A / d \ln a_w) d \ln a_w = (z_A - z_B) \quad (18) \\ \ln a_w &= 0(E_A=1, I=0) \end{aligned}$$

Thus if the  $\Delta$  term is ignored by arbitrarily assigning it a value of zero, a paradox must arise for  $z_A \neq z_B$ . Conversely, inserting eqn 18 into the third of eqns 13 gives for ideal behaviour with respect to zeolitic water and for any values of  $z_A, z_B$  that

$$\ln K_a = \int_0^1 \ln K_G dE_A \quad (19)$$

With eqn 19, for  $g_A = g_B = 1$ ,  $K_G = K_a = \text{constant}$  for all  $E_A, E_B$  as expected for ideal conditions, and no contradiction between eqns 9 and 19 exists. Equation 15 is seen therefore to be an inadmissible approximation when considering ideal behaviour of components in the zeolite phase.

There is therefore nothing intrinsically wrong with the Gaines and Thomas formulation (ref. 18) and workers on ion exchange in zeolites may continue to use it if they so wish. This conclusion is of significance not only to those who have in the past evaluated thermodynamic parameters by this method, but is perhaps especially important for those who have used the activity coefficients  $g_A, g_B$  either in detailed statistical thermodynamic formulations (ref. 27) or in detailed studies on the rates of ion exchange processes (ref. 28, 29).

### DEVELOPMENTS IN THE PREDICTION OF EXCHANGE EQUILIBRIA

The basic principles which underlie the prediction of exchange equilibria at constant temperature over a range of solution phase compositions and total concentrations have been known for some time (ref. 20). They rest on the fact that the ratio of activity coefficients for the exchanging components within the exchanger should hardly change for a given zeolitic composition as the total concentration of electrolytes within the external solution which is in equilibrium with the zeolite is varied. Constancy of this ratio depends on the value of  $\Delta$  being near negligible (ref. 20) (discussed in the previous section) and also on the absence of a significant degree of salt imbibition (ref. 16, 17, 20, 23). If these conditions are fulfilled, then for a given composition  $E_A, E_B$  the appropriate corrected selectivity quotient  $K_V, K_H$  or  $K_G$  should be invariant with changes in total solution concentration. Variations in selectivity of the zeolite for cations in solution then depend only on non-ideal behaviour in the solution phase (ref. 30, 31). The principles underlying prediction for binary exchanges, the required iteration procedures, and examples of such predictions, have all been outlined previously (ref. 32).

More recently, similar prediction procedures have been applied to ternary and multicomponent systems (ref. 6, 33). Two basic requirements for successful prediction of selectivity behaviour in such systems are an adequate means of determining quantitatively the magnitude of the non-ideality correction in solution (ref. 30, 31) and a much more sophisticated iteration procedure (ref. 6). Another desirable requirement is an adequate thermodynamic formulation for the multicomponent exchange equilibrium. For ternary systems a formulation in terms of pseudo-binary Vanselow-type corrected selectivity quotients  $K_V$  has been derived by Chu and Sposito (ref. 34) and another formulation was published simultaneously by Fletcher and Townsend (ref. 23), who used  $K_G$  functions rather than  $K_V$ . Recently, the compatibility of these two separate approaches has been demonstrated (ref. 35) and comparisons with other models have been made (ref. 36).

Unfortunately, as mentioned in the previous section, a multicomponent formulation which uses  $K_G$  functions becomes progressively more complicated as the number of exchanging components is increased. For example, for a ternary exchange reaction formulated in terms of  $K_G$  functions, the requirement for the water to behave ideally in the exchanger is (ref. 24)

$$v_{w,123} d\ln a_w = -(1/z_3)((z_3 - z_1)dE_1/z_1 + (z_3 - z_2)dE_2/z_2) \quad (20)$$

for cations of types 1, 2 and 3 respectively, whereas the requirements if the other formulations are used are (ref. 24)

$$\begin{aligned} (n_{w,123}/(n_1 + n_2 + n_3))d\ln a_w &= 0 & (K_{V,\text{ternary}}) \\ v_{w,123} d\ln a_w &= 0 & (K_{H,\text{ternary}}) \end{aligned} \quad (21)$$

Therefore in the interests of simplicity it seems sensible to abandon formulations based on a Gaines and Thomas (ref. 18) type approach for multicomponent exchange equilibria. Instead, a formulation based on Gapon's choice of mole (ref 19) rather than Vanselow's (ref. 15) seems preferable, since (as emphasised earlier) Gapon's cationic mole fraction  $x_i$  is identical to the cationic equivalent fraction  $E_i$ , and there are sound reasons, based on

statistical thermodynamic considerations (ref. 25, 27), for preferring a formulation using cationic equivalent fractions rather than cationic mole fractions. In addition, a multi-component formulation based on  $K_H$  functions yields the simplest mathematical expressions of all three (ref. 24).

Irrespective of which formulation is used, the important point is whether or not one can thence predict multicomponent exchange equilibria (ref. 32). That such predictions are indeed possible is demonstrated in Fig. 1, which compares predicted and measured data for the Na/Ca/Mg-A and Na/K/Cd-X systems (ref. 6, 33). Note that it was not possible to obtain all crystal phase compositions for the former of these systems (ref. 5); the normalisation procedure used for binary exchanges (ref. 23) cannot be applied to ternary systems (ref. 23), but the prediction procedures employed for the ternary system obviated the need for any such normalisation procedure (ref. 6). For the Na/K/Cd-X system, an increasing systematic error between predicted and measured data was observed as the external solution concentration was changed. The cause of this is not as yet clear, but it is possible that some salt imbibition was occurring at higher concentrations (ref. 33) (see comments at beginning of this section).

In contrast to the above, the means by which accurate prediction of exchange selectivity as a function of temperature can be accomplished must still be regarded as a distant prospect. Not only are many accurate data for activity coefficients of the salts in the external electrolyte solution for a range of temperatures required, but it is also necessary to evaluate accurately the activity coefficients for the exchanging components within the zeolite at one temperature and then predict how these values will change with temperature (ref. 36). This requires detailed knowledge concerning the manner in which the different exchange cations are partitioned amongst the various cation-bearing sub-lattices which the zeolite may provide. Recently, Barrer (ref. 38) has considered cation partitioning between sub-lattices, taking in particular two possible situations. In the first of these, the fraction of total cationic charge  $\epsilon_i$  associated with a given sub-lattice  $i$  was assumed to stay constant as the exchange reaction took place, whereas in the second case no such constraint was placed on the system. In addition, it was recognised that the  $\epsilon_i$  may vary with

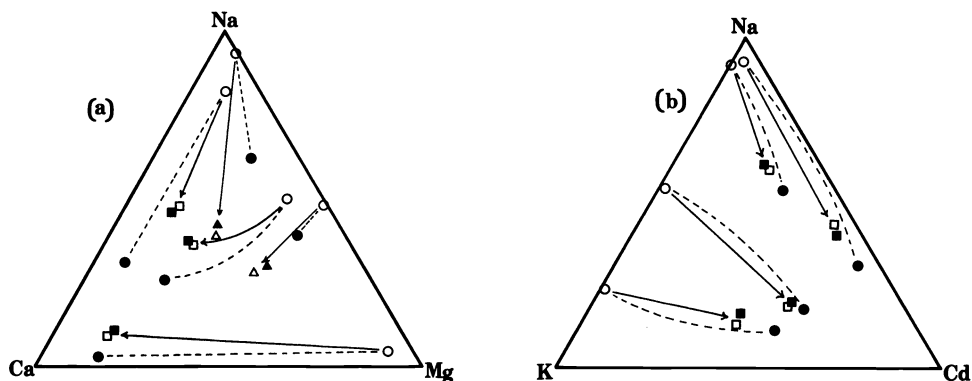


Fig. 1. Examples of predicted compositions for (a) the Na/Ca/Mg-A, and (b) the Na/K/Cd-X systems. O, ●: solution phase and corresponding compositions measured at 0.1 equiv  $\text{dm}^{-3}$  (points joined by a tie-line-----). □, ■: predicted and measured compositions at 0.4 equiv  $\text{dm}^{-3}$  respectively. Δ, ▲: predicted and measured compositions at 0.025 equiv  $\text{dm}^{-3}$  respectively.

temperature (ref. 38). Expressions in terms of the  $\epsilon_{iA}$  and  $\epsilon_{iB}$  were then obtained for the standard thermodynamic functions  $\Delta G^\theta$ ,  $\Delta H^\theta$ ,  $\Delta S^\theta$  and  $\Delta C_p^\theta$ . Two matters of immediate relevance to the current discussion arise out of this study (ref. 38). Firstly in zeolites where cation vacancies occur on sub-lattices, substantial redistributions of cations between sub-lattices may take place as the temperature is altered, resulting in changes not only in the overall  $\epsilon_i$  values but also in the  $\epsilon_{iA}$  and  $\epsilon_{iB}$ , and consequently in the partition equilibrium quotients. As a further consequence, the standard thermodynamic functions can then also vary markedly with temperature. This phenomenon must in part be the explanation for the marked difference between  $\Delta H^\theta$  values obtained calorimetrically or by means of a Gibbs-Helmholtz relation for the Ca/Na-A exchange, as discussed by Rees (ref. 39). Secondly, despite the large amount of information in the literature regarding cation site populations and distributions for different zeolites (ref. 40), few of these data were found to be sufficiently reliable for the evaluation of partition coefficients (ref. 38) because of the uncertainties inherent in the X-ray data and/or because the water content in the crystals was either inadequately controlled or not recorded during determination of cation site populations. (Once more, the water content is seen to be of great importance - see comments regarding ideal behaviour in the previous section). As a result of these problems, evaluation of partition coefficients was only found to be meaningful for some forms of dehydrated A, X and Y zeolites (ref. 38).

## DEVELOPMENTS IN EXPERIMENTAL TECHNIQUE

In a discussion of results obtained by different workers for the Ca/Na-A system, Rees (ref. 39) emphasised the importance of accuracy in analysis, particularly at the extrema of the isotherm plot. Only small errors in the analysis of low concentrations of an ion can have a dramatic effect on the shape of plots of  $\ln K_G$  against composition (ref. 5, 39). This is undoubtedly the primary explanation for the many discrepant results in the literature for a given system; indeed, in the two most recent studies on the Ca/Na-A system (where special attention was paid to analytical accuracy) the resulting  $\ln K_G$  plots agree well (ref. 3, 5). This underlines the need, emphasised elsewhere (ref. 41), to analyse for each exchanging ion in both exchanger phases when constructing exchange isotherms.

It is likely however that this is not the only cause of discrepant data being obtained for different studies on a given exchange. Thus for the Ca/Na-A system, Wiers, Grosse and Cilley (ref. 4) noted that the total ion content (i.e. Na+Ca) recovered from A crystals was low by between 5 and 13% after equilibration. Low recoveries for this exchange were also observed by Franklin and Townsend (ref. 5), and it seems that these must be attributed to hydronium exchange occurring concomitantly during the Ca/Na exchange reaction. Such a conclusion is supported by the kinetic studies of Drummond, De Jonge and Rees (ref. 42) and others (ref. 43).

Knowledge of the phenomenon of hydronium exchange is not new, and was noted some time ago for zeolites A and X by Kuhl *et al* (ref. 44, 45). However, it is the opinion of the author that the full implications of this phenomenon for ion exchange studies are only just being realised. It was common practice in the past for binary exchange measurements to analyse both phases for one ion only, and to infer the concentrations of the other ion by differences. When hydronium exchange occurs also, such a practice must lead to serious errors in the calculation of corrected selectivity quotients and separation factors, especially at the extrema of isotherms. A re-examination of many experimental data on ion exchange equilibria may therefore be necessary.

However, it is not suggested that low total recoveries of exchange cations within the zeolite should be attributed simply to hydronium exchange. Undoubtedly, hydronium exchange is sometimes accompanied by dealumination and partial destruction of the zeolite framework. Damage to the framework, and dissolution of zeolite during ion exchange processes have been discussed by Sherman (ref. 2), and in a recent elegant study on hydronium exchange in Y, mordenite and ZSM zeolites, Chu and Dwyer (ref. 46) sought to minimise any such damage through the use of an acid ion-exchange resin. For the Ca/Na-A system, Drummond *et al* (ref. 42) suggested a mechanism in which hydronium exchange was accompanied by structural breakdown of the zeolite and subsequent release of aluminium species; this implies that it is essential for careful studies to analyse not only all exchanging cations, but also the aluminium content of both phases.

Franklin and Townsend (ref. 5) analysed for aluminium in solution during their studies of the Ca/Na-A exchange, but any aluminium present was always found to be below the level of detection. Such an absence of aluminium in solution does not imply that the above suggestion (ref. 42) concerning structural breakdown is incorrect. After dealumination, the aluminium species may remain occluded within the zeolite channels and cages, a phenomenon commonly observed during the dealumination of heat-treated ammonium Y samples (ref. 47). Indirect evidence substantiating this is shown in fig. 2, where data obtained for the K/Na-Y system as a function of solution pH are given (ref. 43). Binary isotherms were constructed using sets of solutions having initial pH's ranging from near-neutral to 2. With the exception of the latter pH, the isotherms remained near-coincident (fig. 2a) despite the fact that the level of "hydronium exchange" within the zeolite increased markedly (figs. 2b and 2c). Only when the initial pH of the solutions was 2 did the isotherm shape modify (fig. 2a), at a point when the total (Na+K) cation recovery was very low (fig. 2d), and it was only in this latter case that large quantities of aluminium were detected in solution. Details of this work are given elsewhere (ref. 43).

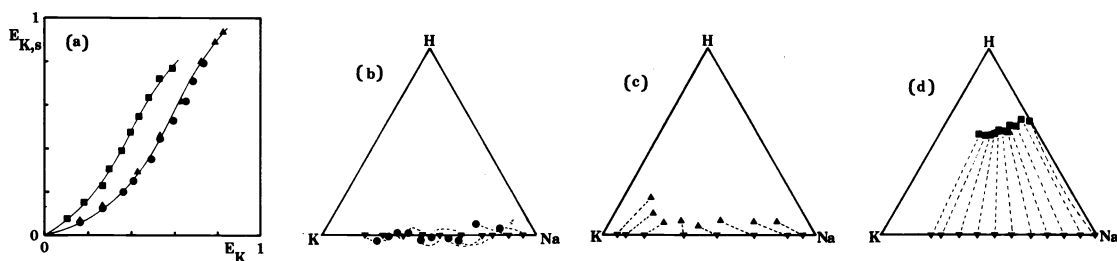


Fig. 2. Exchange isotherms for the K/Na-Y systems. (a) Binary plots (i.e. K/Na only) for initial pH's of 4 (●), 3 (▲) and 2 (■). Taking hydronium exchange into account gives for the three initial pH's (b), (c) and (d) respectively. Solution phase points ▼; crystal phase points as for figure 2(a).

It seems therefore advisable for careful studies of ion exchange equilibria to supplement the full analysis of all exchanging cations plus aluminium in both phases with both strict pH control and the use of other analytical techniques. Of these, a check of the crystallinity of the samples before and after exchange using X-ray crystallography is probably not the best criterion for assessing crystal damage; adsorption capacities and visible damage as observed by electron microscopy have however proved of considerable utility (ref. 48). Undoubtedly, the best approach would be to use routinely  $^{27}\text{Al}$  and  $^{29}\text{Si}$  m.a.s.n.m.r. to monitor levels of framework destruction and dealumination during the exchange process.

### CONCLUDING REMARKS

Throughout this paper the properties of imbibed water within the zeolite have been emphasised. However, the imbibed solvent need not be water, and a fruitful area for future research must be the study of ion exchange processes in zeolites using non-aqueous solvents. In addition, re-examination of other systems of industrial importance should continue, such as the exchange of rare-earth metals in faujasites (ref. 49), and attention is already turning towards the ion-exchange properties of high silica and dealuminated zeolites (ref. 46, 50). It seems likely that for the next few years these areas will be the ones in which research into the ion-exchange properties of zeolites will concentrate.

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