# BINARY AND TERNARY CATION EXCHANGE IN ZEOLITES

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## SUMMARY

Na–Ca and Na–Mg binary exchange isotherms have been determined in zeolite A at 25 and 65°C and total solution phase normalities of 0.2, 0.1, 0.05, 0.01 and 0.005 equiv./dm³. The concentration–valency effect was shown to be obeyed. The corrected selectivity coefficient data were fitted to polynomial equations and from these thermodynamic parameters were calculated. Na–Ca–Mg ternary isotherms were also determined at 65°C using initial solution phase concentrations of 0.10, 0.05 and 0.01 equiv./dm³ and fixed Ca/Mg ratios of 2:1, 1:1 and 1:2. Finally an attempt has been made to predict ternary exchange data from the corresponding binary isotherms.

## INTRODUCTION

Several papers were published in the period 1960–1970 in which zeolites were used to study some of the more fundamental aspects of cation exchange. Reviews of these papers have been published[1-3]. It was assumed in these studies that zeolites, because of their crystallinity and well-defined anionic frameworks would behave as ideal exchangers. However, these early studies brought to light many problems which showed that zeolite exchangers were not as ideal as originally assumed. Much of this early work was of interest from a fundamental point of view but, commercially, these studies were mainly of interest to petroleum companies in their search for better zeolite catalysts. However, during the past few years the interest in zeolites as cation exchangers has been revived because of their use in large quantities (a) as builders in detergents, (b) to remove $NH_4^+$ ions in sewage treatment plants and (c) to remove radioactive ions in nuclear processing plants.

In this paper emphasis will be placed on the fundamental aspects of ion-exchange processes which are involved in the use of zeolites as builders in detergency.

*Thermodynamics of ion exchange*

When zeolite A is used as a builder in detergents its prime purpose is to replace the $Ca^{2+}$ and $Mg^{2+}$ ions present in hard water with $Na^+$ ions. The reactions to be considered, therefore, are

$$Ca^{2+} + \overline{2Na^+} \rightleftharpoons \overline{Ca^{2+}} + 2Na^+$$
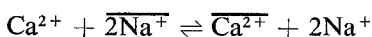
and the corresponding $Mg^{2+}$ case where the bar above the ion indicates the ion present in the zeolite phase. The selectivity coefficient, $K$, can be defined for the $Na^+$–$Ca^{2+}$ exchange (but exactly equivalent equations can be written for the $Na^+$–$Mg^{2+}$ exchange) as

$$K = \frac{Ca_z}{(Na_z)^2} \cdot \frac{m^2_{NaCl}}{m_{CaCl_2}}$$                                                                        (1)

the corrected selectivity coefficient, $K_c$, as

$$K_c = K \cdot \frac{\gamma^4_{\pm NaCl}}{\gamma^3_{\pm CaCl_2}}$$                                                                                (2)

and the thermodynamic equilibrium constant, $K_a$, as:

$$K_a = K_c \cdot \frac{f_{Ca}}{f^2_{Na}}$$                                                                                                 (3)

$Na_z$ and $Ca_z$ are the equivalent cation fractions of $Na^+$ and $Ca^{2+}$ in the zeolite phase and $m_{NaCl}$ and $m_{CaCl_2}$ are the molalities of NaCl and $CaCl_2$ salts in the solution phase respectively. $\gamma_{\pm NaCl}$ and $\gamma_{\pm CaCl_2}$ are the activity coefficients of these salts in the mixed solution phase while $f_{Na}$ and $f_{Ca}$ are the activity coefficients of the respective ions in the zeolite phase. The standard state chosen is one of infinite dilution in the solution phase and the pure $Na^+$ and $Ca^{2+}$ forms of the exchanger phase. $K_a$ is then obtained from $K_c$ from the equation

$$\ln K_a = -1 + \int_0^1 \ln K_c \, dCa_z$$                                                                                       (4)

and $\Delta G^\ominus$ the standard free energy per equivalent of exchange is obtained from the equation:

$$\Delta G^\ominus = -(RT/2) \ln K_a$$                                                                                          (5)

Isotherms are usually represented graphically in terms of equivalent cation fractions in the zeolite and solution phases. The corrected selectivity coefficient, $K_c$, can be expressed more conveniently then as

$$K_c = \frac{Ca_z}{(Na_z)^2} \cdot \frac{(Na_s)^2}{Ca_s} \cdot 2N \frac{\gamma^4_{\pm NaCl}}{\gamma^3_{\pm CaCl_2}}$$                                                (6)

where $Na_s$ and $Ca_s$ are the equivalent cation fractions of Na and Ca respectively in the solution phase and $N$ is the total normality of the equilibrium solution phase. Eqn. 6 quantifies the well-known concentration–valency effect which produces an increasing selectivity for the divalent ion as the total normality of the solution phase decreases.

*Ion exchange in zeolite A*

Because of the renewed interest in zeolite A as a builder in detergency and because of some inadequacies of earlier studies of exchange of $Na^+$ by $Ca^{2+}$ and $Mg^{2+}$ in zeolite $A^4$ we have redetermined these isotherms paying particular attention to the concentration–valency effect and to other factors which were in possible error in previous studies.

The chemical analysis of the zeolite A used in these studies, which was specially prepared by Laporte Industries (Widnes, Great Britain), gave an almost ideal unit cell composition of:

$$Na_{12.05} [12.00 \, AlO_2 \cdot 12.08 \, SiO_2] \, 26.8 \, H_2O$$
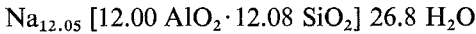
Na–Ca and Na–Mg exchange isotherms were determined at 25 and 65°C with total solution phase normalities of 0.2, 0.1, 0.05, 0.01 and 0.005 equiv./dm³. Exchange was followed for at least 5 days at 65°C and 10 days at 25°C. The resulting isotherms are shown in Fig. 1.
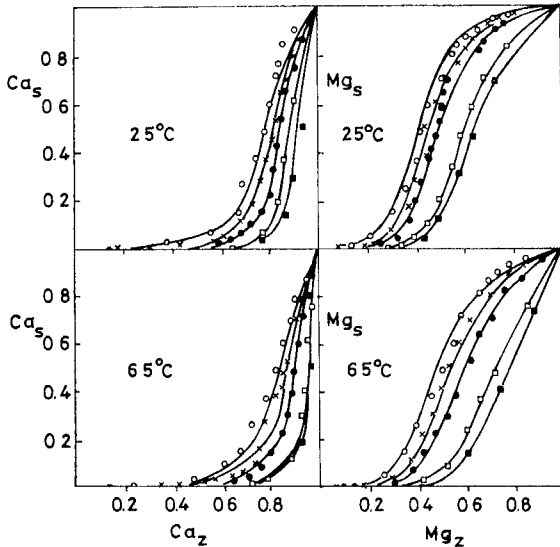


Fig. 1. Na–Ca and Na–Mg binary exchange isotherms: ○, 0.2 $N$; ×, 0.1 $N$; ●, 0.05 $N$; □, 0.01 $N$; ■, 0.005 $N$.

The corrected selectivity coefficients, $K_c$, were calculated from eqn. 6 and the resulting $\log_{10}K_c$ *vs.* $Ca_z$ and $Mg_z$ plots are shown in Figs. 2 and 3 respectively. The activity coefficient ratios, $\Gamma$, where $\Gamma = \gamma^4_{\pm NaCl}/\gamma^3_{\pm CaCl_2}$, were obtained from the experimental data of Moore and Ross[5]. No experimental values of $\Gamma$ are available for mixed Na–Mg solutions so $\Gamma$ values for the corresponding Na–Ca mixtures were used[4].

The experimental points in the $\log_{10}K_c$ *vs.*$A_z$ (where $A_z = Ca_z$ or $Mg_z$) were fitted to a polynomial equation of the form:

$$\log_{10}K_c = C_0 + C_1A_z + C_2A_z^2 + C_3A_z^3 \tag{7}$$
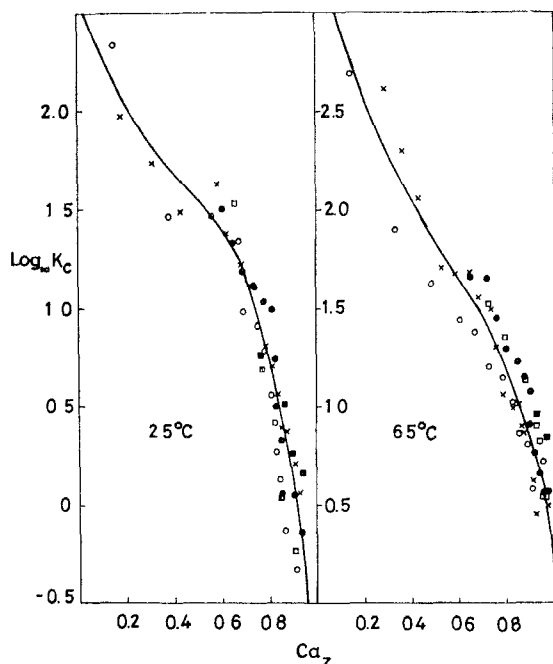
Fig. 2. $\log_{10} K_c$ vs. $Ca_z$. Symbols as in Fig. 1.
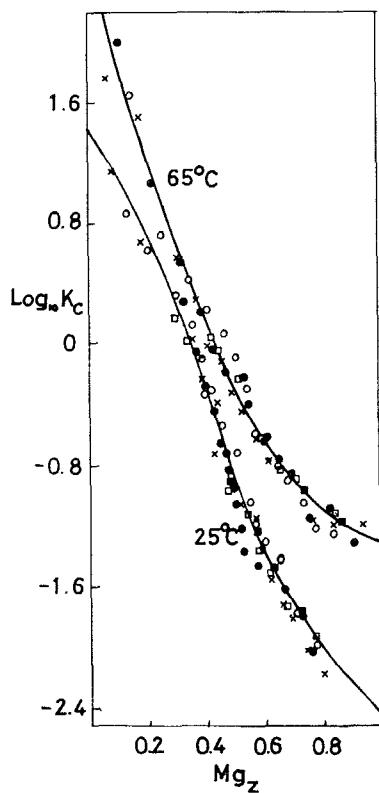
Fig. 3. $\log_{10} K_c$ vs. $Mg_z$. Symbols as in Fig. 1.

The polynominals obtained are given in Table I which also lists the error of the fit, $R$, where $R$ is given by:

$$R = \sqrt{\frac{\Sigma \, (\log K_{c(obs.)} - \log K_{c(calc.)})^2}{N - M - 1}} \qquad (8)$$

$N$ is the number of pairs of $\log K_c$, $A_z$ values and $M$ is the order of the polynomial. The curves derived from these polynomials are drawn as continuous lines in Figs. 2 and 3. The smoothed values of $K_c$ calculated from eqn. 7 were introduced into eqn. 6 to obtain isotherms at the various normalities.

TABLE I

POLYNOMIAL EQUATIONS OF $\log K_c$ vs. $A_z$

| Exchange | Temp. (°C) | Polynomial equation | R |
|---|---|---|---|
| $Na^+ \rightarrow \frac{1}{2}Ca^{2+}$ | 25 | $\log_{10}K_c = 2.83 - 6.03Ca_z + 11.5Ca_z^2 - 9.11Ca_z^3$ | 0.197 |
| | 65 | $\log_{10}K_c = 3.41 - 5.28Ca_z + 6.32Ca_z^2 - 4.01Ca_z^3$ | 0.167 |
| $Na^+ \rightarrow \frac{1}{2}Mg^{2+}$ | 25 | $\log_{10}K_c = 1.46 - 2.66Mg_z - 6.34Mg_z^2 + 5.08Mg_z^3$ | 0.127 |
| | 65 | $\log_{10}K_c = 2.61 - 7.74Mg_z + 3.57Mg_z^2$ | 0.110 |

These predicted isotherms are presented in Fig. 1 as continuous lines where they may be compared with the experimentally determined points. Good agreement is demonstrated indicating that the concentration–valency effect is obeyed and that the $\Gamma$ values chosen for the Na–Mg exchange are not in serious error. These polynomials allow one to predict the isotherms for any normality of solution phase with reasonable confidence.

In Table II $K_a$ values are listed which have been calculated from the integration of the polynomial expressions as in eqn. 4. The $\Delta G^{\ominus}$ values derived from these $K_a$ values are also listed in Table II. The standard enthalpies of exchange, $\Delta H^{\ominus}$, were calculated from the values of $K_a$ at 25 and 65°C and hence, $\Delta S^{\ominus}$, the standard entropy of exchange obtained from $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$. These entropies are also listed in Table II.

TABLE II

THERMODYNAMIC ION EXCHANGE QUANTITIES

| Exchange | Temp. (°C) | $K_a$ | $\Delta G^{\ominus}$ [kJ/(g. equiv.)] | $\Delta H^{\ominus}$ | $T\Delta S^{\ominus}$ | $\Delta S^{\ominus}$ J/(g. equiv.)·K |
|---|---|---|---|---|---|---|
| $Na^+ \rightarrow \frac{1}{2}Ca^{2+}$ | 25 | 8.66 | −2.68 | | 14.9 | 50 |
| | | | | 12.2 | | |
| | 65 | 27.8 | −4.69 | | 16.9 | 50 |
| $Na^+ \rightarrow \frac{1}{2}Mg^{2+}$ | 25 | 0.0717 | 3.26 | | 15.5 | 52 |
| | | | | 18.6 | | |
| | 65 | 0.427 | 1.20 | | 17.4 | 51 |

The value of 12.2 kJ/(g.equiv.) obtained for $\Delta H^{\ominus}$ for the Na–Ca exchange differs from the calorimetrically determined value of 8.8 kJ/(g.equiv.)[6]. Considering the care taken in the determination of the isotherms it is difficult to give a convincing explanation of this considerable difference in these two values.

Table II shows that $\Delta G^{\ominus}$ for the Na–Mg exchange is positive indicating an overall selectivity towards Na ions. Inspection of the Na–Mg isotherms in Fig. 1, especially those obtained at low values of $N$, may suggest the opposite. When the valency of the two ions involved in a binary exchange differ one cannot be certain of the sign of $\Delta G^{\ominus}$ from the shape of the isotherm and this is especially the case when the normality of the solution phase decreases. Secondly, inspection of the isotherms in Fig. 1 shows that the inflexion in the isotherms tends to disappear on dilution of the solution phase. Once again these results indicate that one should not attempt to conclude that only one set of exchange sites exist in an exchanger if the isotherm shows no inflexion when the solution phase is very dilute and the valency of the two ions involved are not equal.

Because the log $K_c$ vs. $A_z$ plots at 25 and 65°C are not parallel the activity coefficients of the two ions in the zeolite phase must change with temperature. The relationship between log $K_c$ and $A_z$ cannot be predicted from $K_a$ and, therefore, isotherms at various temperatures cannot be calculated from $K_a$.

When zeolite A is used as a builder in detergents one is really dealing with a ternary exchange process, i.e., simultaneous exchange of $Na^+$ by both $Ca^{2+}$ and $Mg^{2+}$ ions. Before studying the more complicated ternary exchange systems the

Ca–Mg isotherm at 65°C was determined at a solution phase normality of 0.1 equiv./dm³ as a knowledge of this binary exchange along with the previous Na–Ca and Na–Mg exchanges is essential in the interpretation of the ternary results.

This isotherm, shown in Fig. 4, demonstrates the very high selectivity of $Ca^{2+}$ over that of $Mg^{2+}$ and clearly indicates that zeolite A, although it will accommodate $\approx 2$ $Mg^{2+}$ ions per unit cell (u.c.) greatly prefers $Ca^{2+}$ ions beyond this degree of exchange of 0.33. When $Mg_z$ has a value of 0.42 the $Ca_s$ value is 0.0026 which represents only 5.3 ppm of $Ca^{2+}$ in the solution phase. These results suggest that in hydrated zeolite A $Mg^{2+}$ ions reside in the open eight-membered oxygen rings (site 2) where they can be hydrated with the maximum number of water molecules within the confines of the large cavities ($\alpha$ cages) of zeolite A while $Ca^{2+}$ ions prefer the six-membered oxygen ring sites (site 1) where they can be co-ordinated to three framework oxygens in this puckered ring of oxygens and to water molecules which are present in the cavities ($\alpha$ cage and sodalite cage) either side of this site. Presumably, because of the large amount of energy involved in removing water molecules from the hydrated $Mg^{2+}$ ions, which is not regained on solvation with lattice oxygen $Mg^{2+}$ ions do not replace $Ca^{2+}$ ions in site 1 in at least a time scale of $\approx 10$ days. The differences in solvation energy of $Ca^{2+}$ and $Mg^{2+}$ with the lattice oxygens of site 1 probably arise because of the differences in size of the two ions. With $Ca^{2+}$ we have an ion of diameter 0.198 nm sited in a ring of oxygens of free diameter $\approx 0.24$ nm whereas $Mg^{2+}$ has a diameter of only 0.13 nm and is, therefore, much more loosely associated with these oxygens.
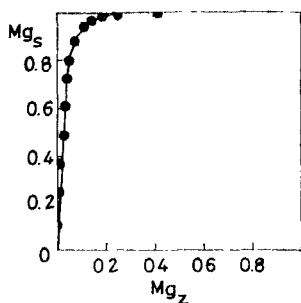


Fig. 4. Ca–Mg binary exchange isotherm at 65°C and 0.1 *N*.

The very interesting Na–Ca–Mg ternary isotherms are shown in Figs. 5–7. The isotherms, all determined at 65°C, were scanned by varying the weight of zeolite used in a fixed volume of solution phase. This initial solution phase always contained a fixed ratio of $Ca^{2+}$ to $Mg^{2+}$ and in most cases was devoid of $Na^+$ ions. In Fig. 5 the Ca/Mg ratio was 2:1 and the total normalities studied were 0.10, 0.05 and 0.01 equiv./dm³. In Fig. 6 the ratio was changed to 1:1 and the normality was 0.05 equiv./dm³ while in Fig. 7 the Ca/Mg ratio was 1:2 and normalities of 0.10 and 0.05 equiv./dm³ were used.

In Fig. 8 the three isotherms at 65°C all determined with a solution phase normality of 0.05 equiv./dm³ but with Ca/Mg ratios of 2:1, 1:1 and 1:2 respectively are plotted to demonstrate the effect of changing the initial Ca/Mg ratio.
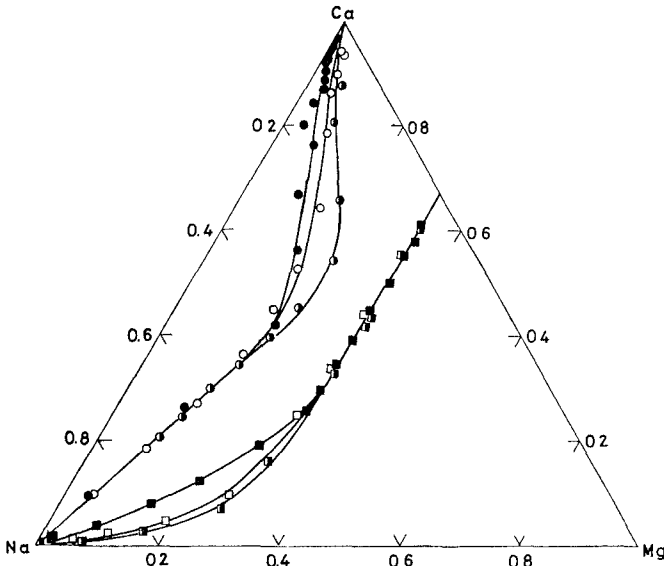
Fig. 5. Na–Ca–Mg ternary exchange isotherms at 65°C. Initial solution phase had constant Ca/Mg ratio of 2:1. ●, ○ and ◗, Zeolite phase; ■, □ and ◪, solution phase; 0.1 $N$, 0.05 $N$ and 0.01 $N$ respectively.
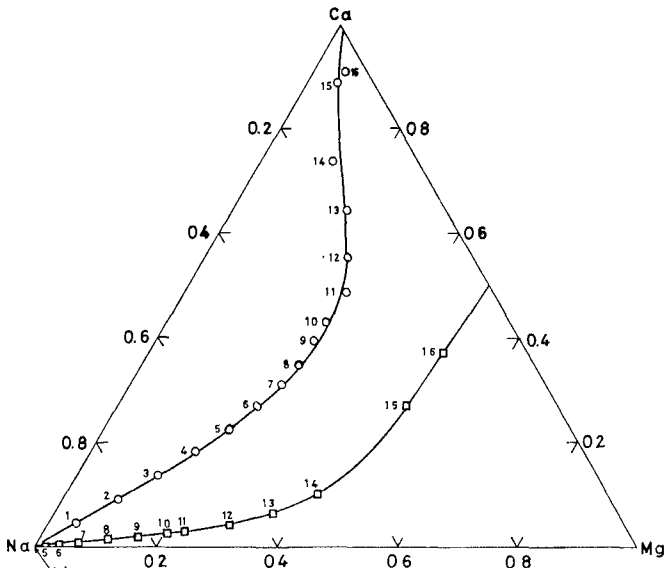


Fig. 6. Na–Ca–Mg ternary exchange isotherm at 65°C and 0.05 $N$. Initial solution phase had constant Ca/Mg ratio of 1:1. Numbers indicate corresponding points in solution (□) and zeolite (○) phases at equilibrium.

Figs. 5 and 7 show that the composition of the zeolite phase is dependent on the normality of the solution phase. The more dilute the solution phase the greater the total divalent ion selectivity becomes. This increase in selectivity towards divalent
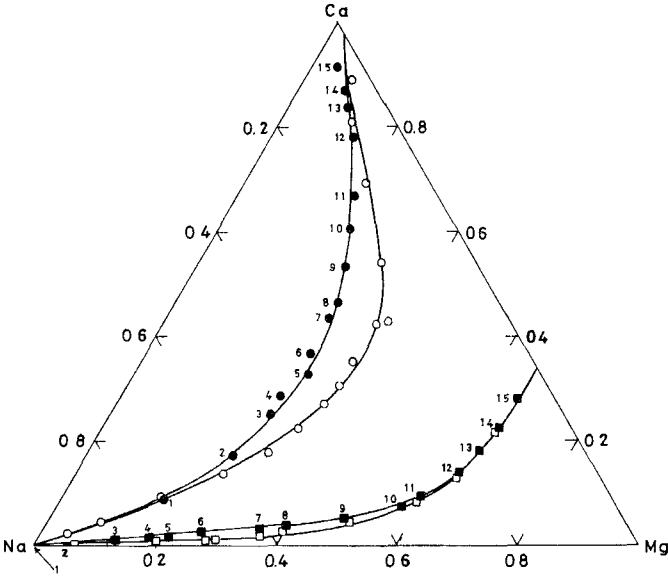
Fig. 7. Na–Ca–Mg ternary exchange isotherm at 65°C. Initial solution phase had constant Ca/Mg ratio of 1:2. ●, ○, Zeolite phase; ■, □, solution phase; 0.1 $N$ and 0.05 $N$ respectively. Numbers indicate corresponding points in solution and zeolite phases at equilibrium in 0.1 $N$ case.
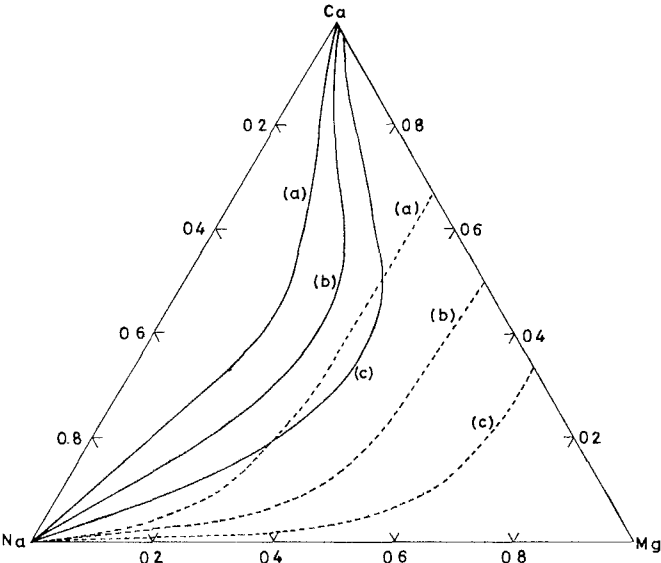


Fig. 8. Na–Ca–Mg ternary exchange isotherms at 65°C and 0.05 N. Initial solution phase had constant Ca/Mg ratio of 2:1 (a), 1:1 (b) and 1:2 (c). Continuous lines, zeolite phase; dashed lines, solution phase.

ion is more clearly demonstrated in Figs. 9 and 10. When $Mg_z$ and $Ca_z$ are plotted against $Mg_s$ and $Ca_s$ respectively then it is easy to observe at a fixed $Mg_s$ or $Ca_s$ value that both $Mg_z$ and $Ca_z$ move to higher values when the normality of the solution phase decreases.
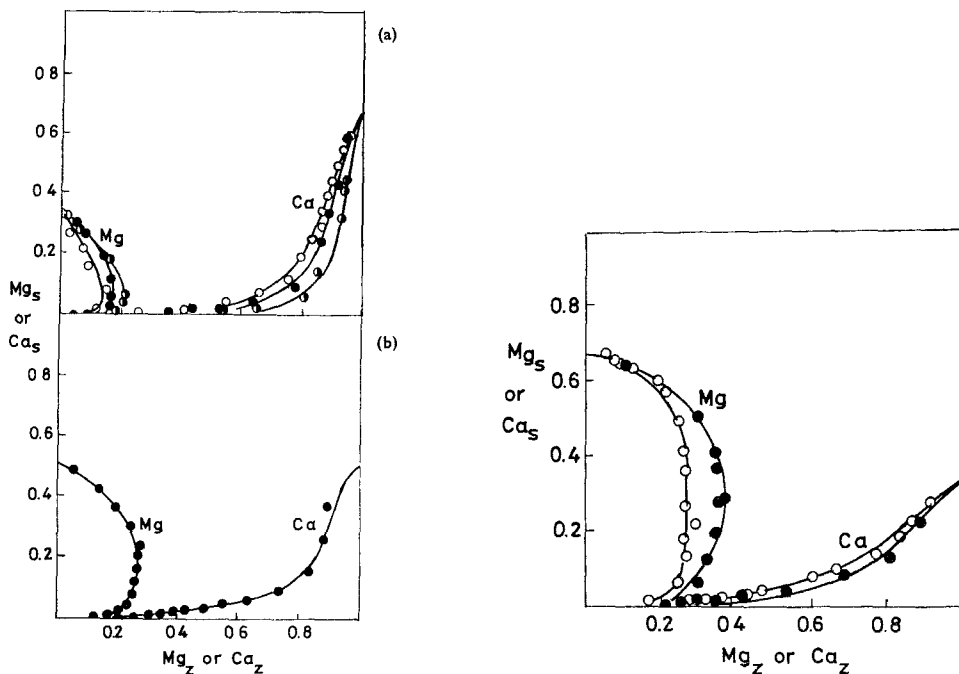


Fig. 9. Plots of $Mg_z$ vs. $Mg_s$ and $Ca_z$ vs. $Ca_s$ data obtained (a) from the ternary exchange isotherms in Fig. 5 (symbols as in Fig. 5), (b) from the ternary exchange isotherm in Fig. 6.

Fig. 10. Plots of $Mg_z$ vs. $Mg_s$ and $Ca_z$ vs. $Ca_s$ data obtained from the ternary exchange isotherm in Fig. 7. Symbols as in Fig. 7.

All isotherms clearly display the very high selectivities for both divalent ions which exist at low $Mg_z$ and $Ca_z$ values. In these regions of low divalent ion loadings in the zeolite little or no divalent ion remain in the solution phase at equilibrium. These initial regions of all the zeolite phase composition curves are near straight lines. When these lines are extrapolated to $Na_z = 0$ they all intersect the Ca–Mg axis at a value equal to the Ca/Mg ratio selected for the initial solution phase. Any trace quantity of divalent ion which existed in the equilibrium solution phase was usually $Mg^{2+}$ with $Ca^{2+}$ being present in concentrations which were often too small to detect (by atomic absorption). The concentration of divalent ion in the solution phase gradually built up with increasing divalent ion loading of the zeolite phase until finally the $Na_s$ value approached zero and the $Ca_s/Mg_s$ ratio approached that of the initial solution phase. The $Mg_s$ values attained their initial solution phase value long before $Ca_s$ attained their initial value, e.g., in Fig. 5, where the Ca/Mg ratio was 2:1 initially, $Mg_s$ attains a value of $\approx 0.33$ when $Ca_s$ is still only $\approx 0.30$ and, thus, only half-way towards its final value of 0.67.

$Mg_z$ passes through a maximum in all the ternary isotherms studied. However, the magnitude of $Mg_z$ at the maximum depends on the ratio of $Ca^{2+}$ to $Mg^{2+}$ and on the total normality in the initial solution phase. In all isotherms the maximum in $Mg_z$ occurs at a $Na_z$ value of $\approx 0.33$ and increases from a value of $\approx 0.19$ in a 2:1 Ca/Mg, 0.10 equiv./$dm^3$ initial solution phase to $\approx 0.38$ in a 1:2 Ca/Mg, 0.05 equiv./$dm^3$ initial solution phase. It is interesting to note that $Mg_z$ never increases above a value of $\approx 0.4$ the maximum value attained in the binary Ca–Mg exchange isotherm illustrating, once again, the difficulty of loading zeolite A with more than two $Mg^{2+}$ ions per u.c. when there are $Ca^{2+}$ ions available to the zeolite.

Since $Mg_z$ passes through a maximum $Ca^{2+}$ ions must replace, not only, $Na^+$ ions but also $Mg^{2+}$ ions during the course of the exchange of the remaining four $Na^+$ ions per u.c. These four $Na^+$ ions which remain in the zeolite at the $Mg_z$ maximum are almost certainly sited in the six-membered oxygen ring sites (site 1). These results suggest, firstly, that $Ca^{2+}$ ions are much preferred to $Mg^{2+}$ ions in site 1 and, secondly, when exchange is pushed towards the complete removal of $Na^+$ ions from the zeolite phase that the system prefers $Ca^{2+}$ ions sited in site 1 to $Mg^{2+}$ ions sited in site 2. Figs. 5–7 indicate that as $Na_z \to 0$ $Ca_z \to 1.0$, i.e., the zeolite phase contains little or no $Mg^{2+}$ ion and this is true even in the extreme case studied where the equilibrium solution phase had a Ca/Mg ratio of 1:2. These results suggest that the zeolite phase much prefers to have six $Ca^{2+}$ ions per u.c. at complete exchange. As there are eight sites 1 available to these six $Ca^{2+}$ ions it would seem, as Fig. 10 clearly demonstrates, that $Ca^{2+}$ ions sited in site 1 is a much preferred situation to one in which $Mg^{2+}$ ions are retained in site 2. However, recent X-ray studies[7] and theoretical calculations[8] suggest that in pure Ca-A zeolite the first five $Ca^{2+}$ ions introduced into the zeolite are sited in site 1 but that the sixth $Ca^{2+}$ ion is sited in site 2. This distribution of $Ca^{2+}$ ions among the eight sites 1 and six sites 2 produces the lowest coulombic repulsion energy. If these findings are proved to be correct then it would seem that $Ca_z > 0.83$ a sixth $Ca^{2+}$ ion sited in site 2 is preferred to the situation where a $Mg^{2+}$ ion is located in this site. However, these recent findings were made with a dehydrated zeolite A and the presence of some 30 $H_2O$ molecules per u.c. may have a significant effect on the location of the sixth cation.

Binary equilibrium data were produced from the ternary data by the method described by Bajpai et al.[9] and Brignal et al.[10]. In this method the sum of the equivalent cation fractions in both solution and exchanger phase of only two of the three ions in the ternary system are normalised to unity. Thus, in effect, the presence of a third ion is ignored in the construction of the binary isotherms. These normalised binary isotherms are shown in Figs. 11–13. The points in these figures were calculated from the ternary data while the curves are the true, experimentally determined, binary isotherms for these systems. The best agreement between the true binary isotherm and the normalised binary data is found for the Ca–Na exchange. These results agree with previous conclusions[9,10] that this method gives the best agreement for the pair of ions which show the highest selectivities.

It is also interesting to note that in the Mg–Na exchange (see Fig. 12) the normalised binary isotherms approach the true binary isotherm more closely when the ratio of Ca/Mg in the initial solution phase decreases suggesting, once again, that $Ca^{2+}$ ions can compete very successfully with $Mg^{2+}$ ions for sites in the zeolite phase.
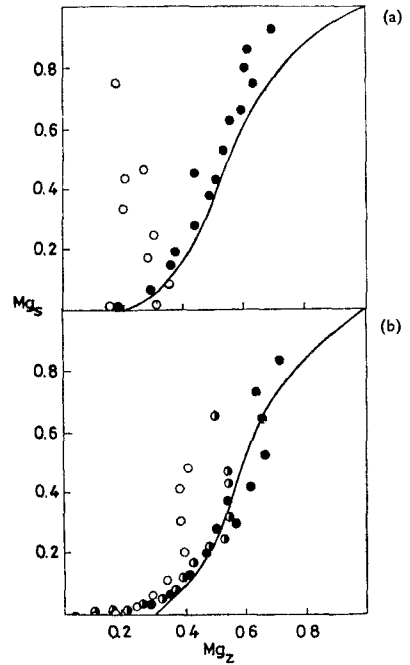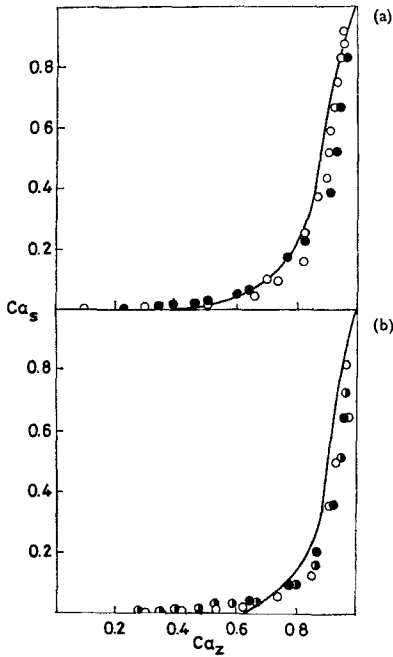
Fig. 11. Na–Ca binary exchange isotherms at 65°C obtained by normalisation of the Na–Ca data of the ternary exchange systems. Ca/Mg ratio = 2:1 (○) or 1:2 (●) in 0.1 $N$ solution phase (a); 2:1 (○), 1:1 (◑) or 1:2 (●) in 0.05 $N$ solution phase (b). The continuous lines are the corresponding binary isotherms from Fig. 1.

Fig. 12. Na–Mg binary exchange isotherms at 65°C obtained by normalisation of the Na–Mg data of the ternary exchange systems. Details as in Fig. 11.
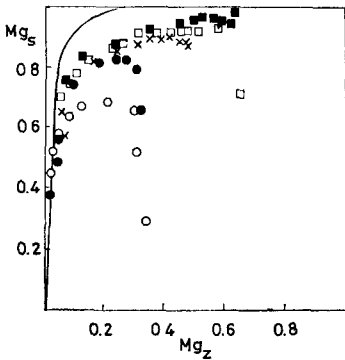


Fig. 13. Ca–Mg binary exchange isotherms at 65°C obtained by normalisation of the Ca–Mg data of the ternary exchange systems. ○, Ca/Mg ratio 2:1 and 0.1 $N$; ●, Ca/Mg 2:1 and 0.05 $N$; ×, Ca/Mg 1:1 and 0.05 $N$; □, Ca/Mg 1:2 and 0.1 $N$; ■, Ca/Mg 1:2 and 0.05 $N$. The continuous line is the corresponding binary isotherm in Fig. 4.

*Prediction of ternary isoterms*

The prediction of ternary isotherms from the respective binary data has been attempted by Brignal *et al.*[10]. This graphical method has been reasonably successful

in a number of examples. However, when the method was tried for the Na–Ca–Mg ternary system it was found to be inadequate. Some contour lines did not intersect and on the occasions when a triangle was formed the triangle was large and the experimental point did not lie at the centroid.

In the Na–Ca–Mg system, as described in this paper, $Na^+$ ions leave the zeolite phase and are replaced by $Ca^{2+}$ and $Mg^{2+}$ ions. The stoichiometric chemical equation describing this reaction is

$$2Na_z^+ + [y\,Mg^{2+} + (1-y)\,Ca^{2+}]_s \rightleftharpoons 2Na_s^+ + [x\,Mg^{2+} + (1-x)\,Ca^{2+}]_z$$
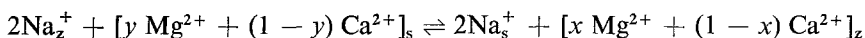
where $1 \geqslant x, y \geqslant 0$. Also a corrected selectivity coefficient $^{Ca,Mg}_{Na}K_c$ can be defined in the same way as in eqn. 6 for the binary system:

$$^{Ca,Mg}_{Na}K_c = \frac{Na_s^2\,[xMg + (1-x)\,Ca]_z}{Na_z^2\,[yMg + (1-y)\,Ca]_s} \cdot 2N \cdot \Gamma \tag{9}$$

When $0 < x,y < 1$ the selectivity coefficient for the ternary system can be obtained from the selectivity coefficients of the Na–Ca and Na–Mg binary systems as follows

$$^{Ca,Mg}_{Na}K_c = [^{Mg}_{Na}K_c]^x \cdot [^{Ca}_{Na}K_c]^{1-x} \tag{10}$$

where $x = \dfrac{Mg_z}{Mg_z + Ca_z}$  and  $(1-x) = \dfrac{Ca_z}{Mg_z + Ca_z}$

Taking logarithms of both sides of eqn. 10 we obtain:

$$\log[^{Ca,Mg}_{Na}K_c] = x\log[^{Mg}_{Na}K_c] + (1-x)\log[^{Ca}_{Na}K_c] \tag{11}$$

For a specific ternary zeolite composition the right-hand side of eqn. 11 can be calculated using the polynomial equations in Table I taking $Mg_z = x$ and $Ca_z = (1-x)$ in the respective polynomials. Having calculated $^{Ca,Mg}_{Na}K_c$ from eqn. 11 the equivalent fraction of sodium in the solution phase, $Na_s$, can be calculated from eqn. 12

$$^{Ca,Mg}_{Na}K_c = \frac{Na_s^2\,(1 - Na_z)}{Na_z^2\,(1 - Na_s)} \cdot 2N \cdot \Gamma \tag{12}$$

assuming $\Gamma$ is equal to the corresponding value for the Na–Ca system at $Ca_s = 0.5$ and normality $N$. This assumption is justified by the fact that these Na–Ca $\Gamma$ values were also used to derive the polynomials for the Na–Mg system and good agreement between calculated and experimental Na–Mg exchange had been obtained. The predicted value of $Na_s$ could be compared with the experimental $Na_s$ value associated with the ternary zeolite phase composition chosen for the calculation. Having obtained $Na_s$ it was then possible to calculate $Ca_s$ and $Mg_s$ since $Ca_z$ and $Mg_z$ and the initial Ca/Mg ratio were known. Very good agreement between predicted and experimental solution phase compositions was frequently found but in a number of points the agreement was not so good. A comparison between predicted and experimental solution phase compositions is shown for one specific ternary isotherm in Fig. 14. In this example the initial Ca/Mg ratio was 2:1 and the total solution phase normality was 0.01 equiv./dm³. For equilibrium zeolite phase compositions numbered
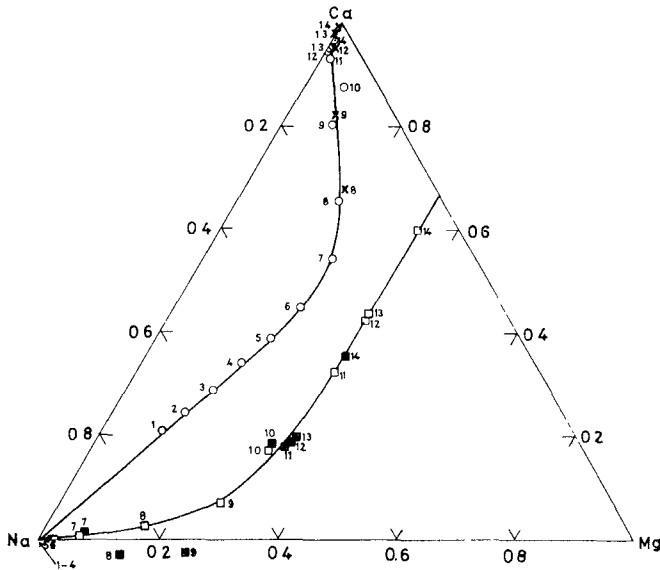
Fig. 14. Comparison of predicted and experimental Na–Ca–Mg ternary exchange isotherm at 65°C. Ca/Mg ratio of 2:1 in initial solution phase of 0.01 $N$. □, Experimental equilibrium solution phase compositions; ■, predicted equilibrium solution phase compositions; ×, adjusted zeolite phase compositions. Numbers indicate corresponding points in solution ( □, ■) and zeolite (○, ×) phases at equilibrium.

1 to 4 the predicted $Na_s$ values decreased from 0.9996 to 0.995 and were in near perfect agreement with the experimental equilibrium $Na_s$ values which decreased from 0.9985 to 0.9944 for these four points. (N.B. these points are not drawn in Fig. 14 as they all lie virtually at the Na apex.) For zeolite phase compositions numbered 5 to 7 agreement between predicted and experimental solution phase composition was still excellent as shown in Fig. 14. However, when zeolite phase compositions numbered 8 to 14 were considered large differences between predicted and experimental solution phase compositions were obtained. In all of these latter cases the predicted $Na_s$ value was always too large, the $Ca_s$ value correspondingly too low while the $Mg_s$ value was, therefore, in near agreement with experiment. In points 8 and 9 these errors in the predicted values result in negative $Ca_s$ values. Although these large differences between predicted and experimental solution phase compositions suggest a serious error in the model this is not really the case. Only the small changes in the zeolite phase compositions shown in Fig. 14 to points 8 to 14 are required to bring the predicted solution phase compositions into perfect agreement with experiment. These adjustments amount to small decreases in the sodium content of the zeolite phase with a corresponding small increase in the calcium content, e.g., in point 8 $Na_z$ is reduced from 0.173 to 0.148 while in point 14 $Na_z$ is reduced from 0.030 to 0.0059. It was found previously during the determination of the Na–Ca binary exchange isotherms that a little over 2% of the total $Na^+$ content of the original zeolite could not be replaced by $Ca^{2+}$. Thus a small amount of $Na^+$ in zeolite A seemed to be unexchangeable and may have been locked in the sodalite cages. When this unexchangeable $Na^+$ is taken into account good agreement between predicted and experimental solution phase composition is obtained.

Other small differences which did arise between the predicted and experimental results can readily be accounted for. In the calculations the respective polynomials given in Table I are used. However, Figs. 2 and 3 show quite a scatter in these log $K_c$ vs. $A_z$ plots. Secondly the experimental determination of solution phase compositions corresponding to points 1 to 4 in Fig. 14 involved the analysis of trace quantities of $Mg^{2+}$ and concentrations of $Ca^{2+}$ which were undetectable by atomic absorption spectroscopy. In points 8 to 14 the $Na^+$ content of the zeolite phase was determined by flame emission spectroscopy. When the scatter in the log $K_c$ values and the errors in the analyses are allowed for the small differences between predicted and experimental data can be explained.

The reasonable agreement found in the above calculations suggests that the binary selectivity coefficients are not significantly affected by the introduction of a third cation, i.e., the activity coefficients of the two ions present in the exchanger phase in the binary system are unchanged in the presence of a third ion. Unfortunately there is no direct method of measuring these activity coefficients. However it has been shown[4] that the activity coefficients of sodium in the zeolite phase calculated from the Na–Ca and Na–Mg binary exchange data are very similar in both systems and the corresponding calcium and magnesium activity coefficients are also very alike. Furthermore the binary and ternary exchange isotherms have suggested that $Ca^{2+}$ ions probably occupy sites 1 while $Mg^{2+}$ ions prefer sites 2. Their interactions on one another, therefore, should be minimal. These factors may explain the good agreement found between the predicted and experimental solution phase compositions. It would be interesting, therefore, to test this method on a ternary system where all three ions compete for the same set of sites.

Finally it must be realised that this new method is still dependent on a knowledge of the composition of the zeolite phase in these ternary exchanges. The prediction of both zeolite and solution phase compositions for a ternary exchange from a knowledge of only binary exchange data still awaits a solution.

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