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EXCHANGE OF HYDRATED AND AMMINATED SILVER(I) IONS IN SYNTHETIC ZEOLITES X, Y AND MORDENITE

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SUMMARY

Equilibrium isotherms have been determined for the exchange of silver(I) and diamminesilver(I) ions into the sodium forms of three synthetic zeolites of differing silica:alumina ratios, namely mordenite, Y and X. Careful tests proved that all systems were reversible, even in X, which is contrary to that which was observed with many other transition metal ions previously examined in this work programme. Complete exchange of sodium by hydrated silver ions was observed in both X and Y, but the addition of ammonia to the systems reduced the maximal exchange levels to nearly half that seen initially. These phenomena are interpreted in terms of the standard model of a crystalline exchanger with more than one set of exchange sites, differentiated primarily by restriction of access due to different channel sizes in the crystals. Ion migration, which was discussed recently from a statistical mechanical view-point, is also considered and discussed.

Mass action quotients were also calculated for all systems, and values of the standard free energy of exchange ΔG^\ominus were determined for the systems involving hydrated silver ions. Absence of available solution activity coefficient data for the diamminesilver salt precluded similar calculations of ΔG^\ominus for the amminated silver exchange processes. Selectivity and thermodynamic affinity trends are compared and contrasted, and discussed in terms of simple dielectric theory, which is shown to be inadequate to explain all the observed behaviour without modification of the original assumptions that were made regarding the permittivity of the crystal phase.

INTRODUCTION

As part of a general study of ion exchange involving transition metals in zeolites, the exchange of hydrated and ammine-complexed silver ions into the sodium forms of three well-known synthetic zeolites X, Y and mordenite (MOR) have been studied. Earlier systematic studies by Sherry on the $\text{Ag} \rightleftharpoons \text{Na}$ ion exchange equilibrium have involved the hydrated ion only in X and Y¹ and in A². The object of this present study was to examine the effects on the overall exchange equilibrium of different framework charge densities, and silver ion complexation. Previous studies in

this series³⁻⁶ have shown that complexation of other transition metal ions with ammonia generally increases the selectivity of a zeolite for that ion.

Zeolites X and Y are isostructural, but differ in their framework silicon to aluminium ratios. Y is the more siliceous of the two, and hence has the lower charge density. The framework structure of X and Y consists of sodalite units or β cages⁷, which are tetrahedrally linked through hexagonal prisms, to enclose larger cages. Full descriptions of the structure are available in the literature^{7,8}. Mordenite is more siliceous than Y, with a framework silicon to aluminium ratio of approximately five. The structure of mordenite, first deduced by Meier⁹, is very different to X and Y, and is primarily characterised by one-dimensional channels with free dimensions of 0.68 nm, but both sides of the main channels are lined by side pockets with entrances (from the main channels) of 0.39 nm free diameter. Half the exchangeable cations in sodium mordenite are situated in these side pockets⁹, in eight-ring windows that link side pockets between neighbouring main channels, whilst the remaining sodium ions are in the main channels. In X and Y, there are at least six different sets of cation sites⁷, and the cation site distributions are complex¹⁰⁻¹².

EXPERIMENTAL

Materials

Zeolites X and Y were supplied by Union Carbide (New York, NY, U.S.A.). Mordenite (sodium "Zeolon") was provided by the Norton Company (Worcester, MA, U.S.A.). All the chemicals, for both analysis and exchange purposes, were of AnalaR grade.

Selectivity measurements

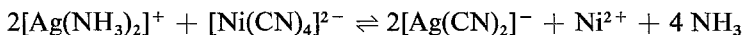
All three zeolites were initially treated with 0.5 mol dm⁻³ solutions of sodium chloride in order to ensure that the starting materials were the homoionic sodium forms. Samples of each zeolite were also exhaustively exchanged with aquosilver(I) or diamminesilver(I) ions, and kinetic tests were undertaken in order to determine the times necessary for ion exchange equilibria to be established. Details are given elsewhere^{3,4,13}.

All ion exchange isotherms were constructed at 25°C using solutions of total normality of 0.1 g.equiv. dm⁻³ using conventional methods^{3,13}. In the case of exchange equilibria involving the $[\text{Ag}(\text{NH}_3)]^+$ ion, in addition, the pH was maintained at a value > 10. Extensive checks on reversibility were carried out, using a method¹³ which avoided drying the samples at any time, since this has previously been shown³ to cause irreversible ion migrations. All equilibrations were undertaken in a dark-room as it was observed that exposure to sunlight reduced the silver, causing the zeolite samples to darken progressively.

Analyses

Both zeolite and solution phases were analysed chemically using spectroscopic and conventional "wet" methods. Full experimental details of the procedures involved in analysing the zeolite phase are given elsewhere^{3,4,13}. For the solutions, the method employed to analyse the silver content depended on the concentration of silver salt present. Where concentrations were high, to each aliquot of solution was added

10 cm³ of 880 ammonia solution and about 0.2 g of K₂Ni(CN)₄, which resulted in the reaction:



The liberated nickel(II) was then determined by back-titration with ethylenediamine-tetraacetic acid (EDTA) using Eriochrome Black T indicator. Where silver was present only in very low concentrations, atomic absorption spectroscopy was employed.

RESULTS

The results of the chemical analyses of the nine zeolites prepared are shown in Table I, in terms of both their unit cell compositions and oxide formulae. The samples of X and mordenite were both found to contain a small quantity of iron impurity, which is shown in the oxide formulae in Table I. It is apparent from the analytical data that stoichiometry of exchange was obtained in all cases; this was a further confirmation, in addition to powder X-ray data, that structure breakdown had not occurred to a significant degree in any of the three zeolites during exchange with either aquated or amminated silver ions.

Ion exchange isotherms, obtained by direct analysis of solutions before and after equilibration with zeolite, and plotted in terms of the equivalent fraction of silver in solution phase (Ag_s) against crystal phase (Ag_c), are shown for the aquated ion in Fig. 1, and for amminated silver in Fig. 2. Complete exchange was only effected with aquosilver(I) in sodium X and Y. All systems were tested and found to be reversible within the limits of experimental uncertainty. Where exchange was incomplete, the maximal levels of exchange indicated by the isotherms were in close agreement with those found on direct analysis of exhaustively exchanged zeolite samples (see oxide formulae in Table I).

DISCUSSION

General comments

Figs. 1 and 2 show the following selectivity sequences, even after "normalisation"^{3,14} of the isotherms is carried out [*i.e.*, after dividing exchange levels throughout by the maximum level of exchange attained, so that Ag_c(max.) in all cases is adjusted to unity]. For the hydrated silver ion, the sequence is X > MOR > Y. In the case of the diamminesilver(I) ion, the selectivity of X for silver is very markedly reduced, to give a sequence MOR > Y > X. These results may be explained using a modification of the original dielectric theory of Barrer and Falconer¹⁵ (see below).

A comparison of the isotherms in Fig. 1 with those obtained by Sherry¹ for the exchange of the hydrated silver ion in X and Y shows good agreement. In addition, it is of interest that Sherry, both in his work on X and Y¹, and on A², explains the high selectivities observed for silver exchanges in terms of the high polarisability of the aquo Ag⁺ ion¹. He assumed that in A (which has an even higher charge density than X) the "Ag⁺ ions coordinate directly to lattice oxygen atoms and thereby free the intracrystalline water"². Such a suggestion is in conformity with the analytical data in Table I, where the water contents of the silver zeolites are seen to be higher than the sodium forms, suggesting that tight binding of silver ions at

TABLE I
CHEMICAL ANALYSES OF ZEOLITES

Sample	Unit cell composition	Oxide formula
Na-X	$\text{Na}_{64.6}(\text{AlO}_2)_{84.7}(\text{SiO}_2)_{107.3} \cdot 251.7\text{H}_2\text{O}$	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.53\text{SiO}_2 \cdot 5.94\text{H}_2\text{O}$
Na-Y	$\text{Na}_{61.3}(\text{AlO}_2)_{61.4}(\text{SiO}_2)_{130.6} \cdot 242.5\text{H}_2\text{O}$	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.25\text{SiO}_2 \cdot 0.002\text{Fe}_2\text{O}_3 \cdot 7.89\text{H}_2\text{O}$
Na-MOR	$\text{Na}_{7.5}(\text{AlO}_2)_7.4(\text{SiO}_2)_{40.6} \cdot 25.6\text{H}_2\text{O}$	$1.01\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 11.03\text{SiO}_2 \cdot 0.005\text{Fe}_2\text{O}_3 \cdot 6.93\text{H}_2\text{O}$
Ag-X	$\text{Ag}_{64.8}(\text{AlO}_2)_{84.8}(\text{SiO}_2)_{107.2} \cdot 261.6\text{H}_2\text{O}$	$\text{Ag}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.53\text{SiO}_2 \cdot 6.18\text{H}_2\text{O}$
Ag-Y	$\text{Ag}_{61.5}(\text{AlO}_2)_{61.5}(\text{SiO}_2)_{130.5} \cdot 290.6\text{H}_2\text{O}$	$\text{Ag}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.25\text{SiO}_2 \cdot 0.004\text{Fe}_2\text{O}_3 \cdot 9.45\text{H}_2\text{O}$
Ag-MOR	$\text{Na}_{61.8}\text{Ag}_{6.6}(\text{AlO}_2)_{7.4}(\text{SiO}_2)_{40.6} \cdot 27.0\text{H}_2\text{O}$	$0.89\text{Ag}_2\text{O} \cdot 0.11\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 11.00\text{SiO}_2 \cdot 0.006\text{Fe}_2\text{O}_3 \cdot 7.33\text{H}_2\text{O}$
Ag(amm)-X	$\text{Na}_{36.5}\text{Ag}_{48.2}(\text{AlO}_2)_{84.4}(\text{SiO}_2)_{107.6} \cdot 159.6\text{H}_2\text{O} \cdot 49.3\text{NH}_3$	$0.57\text{Ag}_2\text{O} \cdot 0.43\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.55\text{SiO}_2 \cdot 3.78\text{H}_2\text{O} \cdot 1.17\text{NH}_3$
Ag(amm)-Y	$\text{Na}_{27.5}\text{Ag}_{53.7}(\text{AlO}_2)_{61.4}(\text{SiO}_2)_{130.6} \cdot 176.5\text{H}_2\text{O} \cdot 61.7\text{NH}_3$	$0.55\text{Ag}_2\text{O} \cdot 0.45\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.25\text{SiO}_2 \cdot 0.003\text{Fe}_2\text{O}_3 \cdot 5.75\text{H}_2\text{O} \cdot 2.01\text{NH}_3$
Ag(amm)-MOR	$\text{Na}_{1.85}\text{Ag}_{5.55}(\text{AlO}_2)_{7.4}(\text{SiO}_2)_{40.6} \cdot 17\text{H}_2\text{O} \cdot 5.4\text{NH}_3$	$0.75\text{Ag}_2\text{O} \cdot 0.25\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 11.04\text{SiO}_2 \cdot 0.005\text{Fe}_2\text{O}_3 \cdot 4.61\text{H}_2\text{O} \cdot 1.46\text{NH}_3$

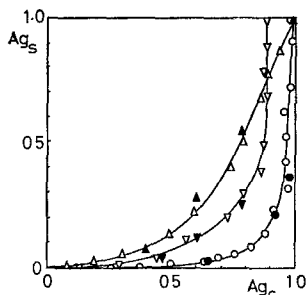


Fig. 1. Equilibrium isotherms for exchange of hydrated silver(I) ions in X (○), Y (△) and MOR (▽). Filled symbols are reverse points.

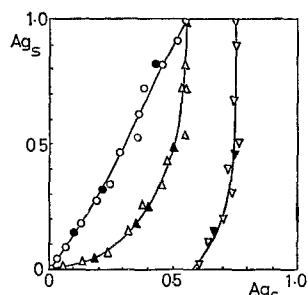
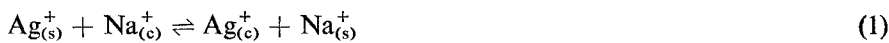


Fig. 2. Equilibrium isotherms for exchange of amminated silver(I) ions in X (○), Y (△) and MOR (▽). Filled symbols are reverse points.

anionic sites within the zeolite framework has occurred, thus yielding more space for intracrystalline water. In contrast, samples containing amminated silver have a total “guest” population (*i.e.*, water plus ammonia molecules) which is lower than that seen in the corresponding sodium zeolite.

Thermodynamic treatment of data

The exchange reaction is



where subscripts *s* and *c* refer to solution and crystal (*i.e.*, zeolite) respectively. The mass action quotient is then

$$K_m = \frac{A_{\text{Ag}_c} \cdot m_{\text{Na}_s}}{Na_c \cdot m_{\text{Ag}_s}} \quad (2)$$

where A_{Ag_c} , Na_c are the equivalent fractions of silver and sodium respectively in the zeolite, and m_{Ag_s} , m_{Na_s} their concentrations (mol dm^{-3}) in solution. Corrections for non-ideality enable the calculation of the thermodynamic equilibrium constant K_a

$$K_a = K_m \Gamma \frac{f_{\text{Ag}}}{f_{\text{Na}}} \quad (3)$$

where Γ is the ratio of single ion activity coefficients in solution and may be related³ to the mean molar stoichiometric activity coefficients for the relevant salts in the *mixed* binary salt solution. f_{Ag} , f_{Na} are activity coefficients for the two ions in association with their equivalents of anionic framework within the zeolite phase, and may be evaluated using the Gibbs–Duhem equation.

The general relationship between Γ and the mean molar stoichiometric activity coefficients for the salts in mixed solution is¹⁶

$$\Gamma = \left\{ \frac{[\gamma_{\pm \text{BX}}^{(\text{AX})}]^{Z_A(Z_B + Z_X)}}{[\gamma_{\pm \text{AX}}^{(\text{BX})}]^{Z_B(Z_A + Z_X)}} \right\}^{1/Z_X} \quad (4)$$

where $\gamma_{\pm AX}^{(BX)}$ and $\gamma_{\pm BX}^{(AX)}$ are the activity coefficients for salt AX in the presence of BX, and the converse respectively. Z_A , Z_B , Z_X are the charge magnitudes of cations A, B and the common anion X. Values of $\gamma_{\pm AX}^{(BX)}$ and $\gamma_{\pm BX}^{(AX)}$ are generally derived from the mean molar stoichiometric activity coefficients of the single salt solutions $\gamma_{\pm AX}$ and $\gamma_{\pm BX}$ using Glueckauf's¹⁷ extension of Guggenheim's¹⁸ treatment. Recent more sophisticated treatments^{19,20} do not significantly affect derived values at the ionic strengths used in this work.

For the uni-univalent exchanges under consideration here, insertion of Glueckauf's relationships into eqn. 4 gives

$$\Gamma = \left[\frac{\gamma_{\pm BX}}{\gamma_{\pm AX}} \right] \left\{ 2 - \left[\frac{m_A + m_B}{I} \right] \right\} \quad (5)$$

since a common univalent anion (nitrate) was used in the experiments. For this case only, $(m_A + m_B)$ equals the ionic strength I , and it is evident that eqn. 5 reduces to just the ratio of the mean molar stoichiometric activity coefficients of the separate salts. Since all solutions used had a constant normality, it follows that I , and hence Γ also, were invariant with the equivalent fraction of silver ion in solution A_{g_c} .

After evaluation of Γ , the thermodynamic equilibrium constant K_a may be obtained using the Gaines and Thomas²¹ treatment, from:

$$\ln K_a = \int_0^1 \ln K_c dA_{g_c} = \int_0^1 \ln K_m dA_{g_c} + \int_0^1 \ln \Gamma dA_{g_c} \quad (6)$$

Since, as noted above, Γ is invariant with solution composition for uni-univalent exchange in the presence of a common univalent anion, the third integral in eqn. 6 is a constant at a given solution normality, irrespective of the exchanger involved. The importance of this is that for uni-univalent exchange, the thermodynamic affinity, related to K_a , and defined in terms of a reaction under *standard* state conditions, can be directly correlated with experimentally observed selectivity trends, as described by K_m . The significance of this is further discussed in the next section. Great care should be exercised in correlating selectivity and affinity trends in the case of exchange involving multivalent ions, since the function $\int_0^1 \Gamma dA_c$ is then no longer a constant for the same pair of ions in different exchangers. This is demonstrated in Fig. 3, where the constancy of Γ for the aquosilver-sodium exchanges being considered here is compared with data for exchanges involving the cupric ion in X, Y and MOR⁶.

Absence of available activity coefficient data for the diamminesilver(I) nitrate salt in solution precluded the calculation of free energy of exchange (ΔG^\ominus) values for exchanges involving the amminated silver ion. Free energy values were determined for the exchanges involving the hydrated silver ion after normalisation^{3,14} of the $Ag \rightleftharpoons Na/MOR$ isotherm. Plots of the so-called Kielland quotient K_c (see eqn. 6) against A_{g_c} were best-fitted using polynomial equations of different orders. Suitable polynomial expressions were chosen on the basis of the residual variance of smoothed data points. The best-fitting equations were then integrated analytically between the prescribed limits.

This procedure is not totally unambiguous. Considering, for example, the silver-sodium exchange in X depicted in Fig. 1, the isotherm shows only minimal

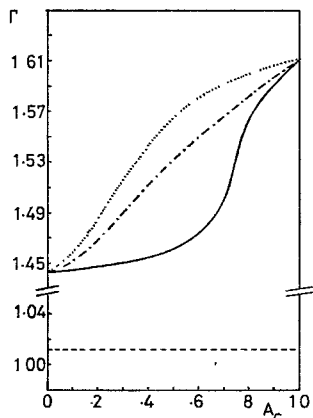


Fig. 3. Plots of the ratio of solution single ion activity coefficient ratios Γ against equivalent fraction of metal ion in crystal A_c . Copper/ammonium Γ ratios in X (—), Y (·—·—·) and MOR (·····); Γ for Ag/Na (- - -).

experimental scatter of data. However, the high selectivity of X for the silver ion made it nearly impossible to obtain accurate isotherm points for low values of A_{g_c} , and at high values of A_{g_c} , only small experimental errors caused large variations in computed values of K_c . The consequences are seen in Fig. 4; there is a paucity of data as $A_{g_c} \rightarrow 0$, and substantial scatter at $A_{g_c} \rightarrow 1$. On the basis of the summation of residuals, a cubic fit was taken as best, yielding a value for ΔG^\ominus of $-12.38 \text{ kJ (equiv.)}^{-1}$. The quadratic fit gave a value for ΔG^\ominus of $-11.31 \text{ kJ (equiv.)}^{-1}$. Although the cubic equation fitted better than the quadratic, the inclination is nevertheless to take the quadratic value, since the extra lack of constraint on the higher order polynomial for $A_{g_c} < 0.2$ makes the higher ΔG^\ominus value of doubtful validity (Fig. 4).

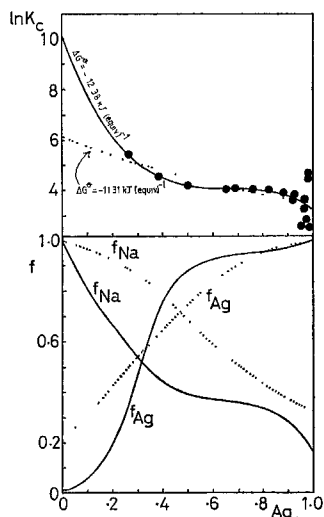


Fig. 4. Plots of the logarithm of the Kielland quotient K_c against A_{g_c} in X, together with corresponding activity coefficients f_{Ag} and f_{Na} . Quadratic fit (·····) and cubic fit (—).

The same problem was encountered to a lesser degree for the $\text{Ag} \rightleftharpoons \text{Na}$ exchange in synthetic mordenite. Fig. 5 shows the results obtained for quadratic and cubic best fits, and also a curve obtained by "smoothing" the data from the isotherm by eye. Calculated ΔG^\ominus values were respectively -8.31 , -7.97 and -8.16 kJ (equiv.) $^{-1}$, a variation of $\pm 2.5\%$. There was little ambiguity with Y (Fig. 6); a quadratic fit gave a value for ΔG^\ominus of -4.33 kJ (equiv.) $^{-1}$.

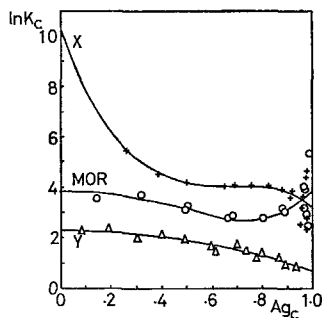
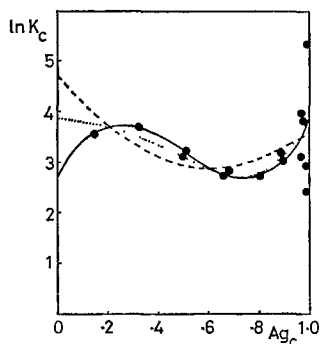


Fig. 5. Plots of the logarithm of the Kielland quotient against Ag_c in mordenite. Quadratic fit (---), cubic fit (—) and "smoothing" isotherm by eye (·····).

Fig. 6. Trends in affinity for the hydrated silver ion as observed in zeolites X, Y and mordenite.

Three comments may be made on these data:

(i) In accord with the comments made above regarding X, on the problems of obtaining very high experimental accuracy at the extrema of a highly selective isotherm, the uncertainty in calculated ΔG^\ominus values is seen to decrease with decreasing selectivity of the exchange system. The importance of appreciating the degree of uncertainty in a given ΔG^\ominus value is obvious. Surprising variations in exchange levels, isotherm shapes and thermodynamic data for a given system have been discussed recently by Cremers²².

(ii) Although the uncertainty in the value of ΔG^\ominus is large in the case of the $\text{Ag} \rightleftharpoons \text{Na}/\text{X}$ system, the *trend* in affinity is quite unambiguous (Table II), and this affinity trend mirrors the isotherm selectivity trend, as expected (compare Fig. 6 with Fig. 1, and see the comments following eqn. 6 above).

TABLE II

STANDARD FREE ENERGIES OF EXCHANGE FOR AQUOSILVER IONS IN SODIUM ZEOLITES

Zeolite	Fit of experimental data	ΔG^\ominus [kJ (equiv.) $^{-1}$]
X	Quadratic	-11.31
X	Cubic	-12.38
Mordenite	Quadratic	-8.31
Mordenite	Cubic	-7.97
Mordenite	"Smoothing" isotherm data by eye	-8.16
Y	Quadratic	-4.33

Affinity sequence: X > MOR > Y

(iii) The values of ΔG^\ominus for silver exchange in Na-X and Na-Y obtained here [-11.31 and -4.33 kJ (equiv.)⁻¹ respectively] are in reasonable agreement with those of Sherry¹ [-10.53 and -4.60 kJ (equiv.)⁻¹].

Application of dielectric theory

Barrer and Falconer¹⁵ interpreted zeolite ion exchange processes in terms of "an interchange of ions between two dielectric media, otherwise inert". In their discussion, and in subsequent extensions of the theory^{4,23,24} it was assumed that the permittivities of the pure A and pure B forms of the zeolite were "sensibly the same"²³. A similar assumption was made regarding the two standard solutions. These assumptions lead to the simple relationship⁶

$$\Delta G^\ominus = \frac{Le^2}{8\pi} \left(\left[\frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right] \left[\frac{1}{\epsilon_c} - \frac{1}{\epsilon_s} \right] \right) \quad (7)$$

where L is the Avogadro constant, e the charge on the electron, r_A , r_B the ionic radii of the incoming (A^{Z_A}) and outgoing (B^{Z_B}) ions respectively and ϵ_c , ϵ_s the permittivities of the crystal and solution phases. Since for systems involving zeolites and aqueous solutions, $\epsilon_c < \epsilon_s$ ²⁴, and for the exchanges considered here $Z_A = Z_B = 1$, it follows that the condition for ΔG^\ominus to be negative is $r_{Ag} > r_{Na}$, which is indeed the case²⁵. The observed negative free energy values for the Ag \rightleftharpoons Na exchanges in X, Y and MOR, calculated as described in the previous section (Table II), are therefore in agreement with theory.

Although no standard free energies were calculated for the Ag(amm) \rightleftharpoons Na exchanges because of the absence of available solution activity coefficient data, eqns. 4-6 above show that for exchanges involving only univalent cations (in association in solution with univalent common anions), there is a direct correlation between selectivities (expressed as the mass action quotient K_m and determined from the experimental isotherms —Figs. 1 and 2) and the standard free energies ΔG^\ominus . It is therefore of interest that application of inequality theory to eqn. 7 predicts an affinity sequence for the Ag(amm) \rightleftharpoons Na exchanges which agrees exactly with the observed selectivity sequence (*viz.*, MOR > Y > X). The detailed argument is given elsewhere¹³.

However, simple dielectric theory also predicts the above affinity sequence for the exchanges involving the hydrated silver ions in X, Y and mordenite¹³. This prediction is not in agreement with experiment (Table II). Sherry¹ has commented on the importance of taking into account the high polarisability of the Ag⁺ ion when seeking to interpret ion exchange selectivities. Molar refractivity data²⁶ enable the calculation of the polarisability α of the silver and sodium ions; α values for these ions are calculated to be $2.41 \cdot 10^{-30}$ m³ and $2.54 \cdot 10^{-31}$ m³ respectively. The increase in the polarisability of the silver over the sodium ion (approximately an order of magnitude) casts doubt on the common assumptions discussed above regarding the constancy of permittivities of the two phases during exchange¹³. Removal of these assumptions leads to:

$$\Delta G^\ominus = \frac{Le^2}{8\pi r_{Ag} r_{Na}} \left(\left[\frac{r_{Na}}{\epsilon_{Ag(c)}} - \frac{r_{Ag}}{\epsilon_{Na(c)}} \right] - \left[\frac{r_{Na}}{\epsilon_{Ag(s)}} - \frac{r_{Ag}}{\epsilon_{Na(s)}} \right] \right) \quad (8)$$

The second term in braces must have the same value irrespective of which zeolite is involved in the exchange process since this term is only a function of the permittivities of the hypothetical ideal molar solutions of the silver and sodium salts respectively. Since $\alpha_{\text{Ag}} > \alpha_{\text{Na}}$, it would be expected that $\varepsilon_{\text{Ag(c)}} > \varepsilon_{\text{Na(c)}}$ and as it is also true²⁵ that $r_{\text{Na}} < r_{\text{Ag}}$ it follows that the first term in braces is negative. The *magnitude* of this term however will depend upon which zeolite is involved in the exchange process; the higher the charge density within the zeolite crystal, the greater will be the enhancement of $\varepsilon_{\text{Ag(c)}}$ over $\varepsilon_{\text{Na(c)}}$ and hence the more negative will the first term be. This *differential* degree of enhancement can explain the affinity trend shown in Table II, as shown elsewhere in detail¹³.

Maximum levels of exchange

None of the exchanges involving the amminated silver ion proceeded to complete replacement of sodium ion (Fig. 2). In addition, in the case of the aquo-silver-sodium exchange in mordenite, approximately 10% of the sodium ions could not be removed, a phenomenon noted before²⁷.

Limits to exchange within zeolites are explained frequently in terms of ion sieving^{1,28,29} or in terms of the less well-known volume steric effect³⁰, when ions are partially excluded, not because they cannot pass through the channel windows, but because they fill all the intracrystalline voids before 100% exchange is achieved. Occasionally ion-sieve and volume steric effects appear to operate together⁵. In cases where ion exclusion is observed, correlations are often drawn between levels of exchange and ion populations in different site sets within the zeolite^{1,2,4,31}. Other studies³² have shown that such correlations should be undertaken with caution²². This is partly due to the fact that ion redistributions may occur throughout all the site sets within a zeolite framework as exchange of one ion for another takes place (as recently demonstrated by Costenoble and Maes³³ in a structural study on mixed Ag/Na-Y zeolite samples) and also, naturally, because it cannot be assumed that an entering ion necessarily takes the same site position as that of the leaving ion²².

In the case of the Ag(amm)-Na exchanges (Fig. 2), and in accord with previous studies on the effect of complexing transition metal ions with ammonia^{4,6} or amines⁵, ion exclusion, probably due to ion sieving, has occurred. However, the levels of exchange do not simply correlate with exchange into just the main cages within X and Y. With mordenite, substantial exchange with sodium ions in the side pockets occurred (although, as emphasised above, this does not simply mean that the amminated ions are *situated* within the side pockets after exchange). The case of hydrated Ag-Na exchange in mordenite is especially interesting. Costenoble and Maes³³ showed that aquosilver ions exchanged readily into the Type I positions in Y, which entails them passing through six-oxygen windows in the sodalite cages, of free diameters⁷ ≈ 0.22 nm. Therefore the ion sieve effect cannot be the explanation for the partial exchange limit seen with hydrated Ag⁺ ions in mordenite (Fig. 1), since the entrances to the side pockets in mordenite have free diameters of ≈ 0.39 nm. Steric effects do not in themselves appear to be an adequate explanation for the observed phenomena.

In a recent statistical mechanical treatment of ion exchange in zeolites, Barrer and Klinowski³⁴ defined some criteria for partial exchange. They considered cation exchange when two kinds of exchange site are present, but where only site group 1 is available to both incoming (A^{Za}) and leaving ions (B^{Zb}), site group 2 being available

only to B^{Z_B} ions. In effect, therefore, an ion exclusion process is operative with respect to A^{Z_A} ions in site 2. However, although this ion sieve effect is operative, the statistical mechanical treatment shows that full exchange for A^{Z_A} is still possible. The absolute limit to exchange with respect to the incoming ion A^{Z_A} is found³⁴ to be the smaller of the two quantities

$$\begin{aligned} A_c(\text{max.}) &= Z_A \eta_1 \\ A_c(\text{max.}) &= 1 \end{aligned} \quad (9)$$

where $\eta_1 = N_1/N_0$, N_1 being the total number of sites of type 1, and N_0 being the total number of charges in the same quantity of zeolite, irrespective of whether these charges are found in type 1 or type 2 sites. It is obvious therefore that η_1 may be greater than, less than or equal to unity. Implicit in this treatment is, therefore, the possibility of ion rearrangements occurring, concurrent with ion sieve exclusion effects, the determinant for the degree of exchange being the magnitude of η_1 .

Elsewhere³⁴, values are given for the activity coefficients f_A and f_B in terms of η for all site sets (*i.e.*, $\eta = \sum N_i/N_0$) and also an energy interaction term between pairs of entering ions, ω_{AA} . f_A and f_B are identical to the phenomenological activity coefficients as obtained using the Gibbs–Duhem equation, and defined in eqn. 3 above. If the siting of entering A^{Z_A} ions is random, these expressions are:

$$\ln f_A = (Z_A \eta - 1) \ln \left(\frac{Z_A Z_B \eta - Z_B A_c - Z_A B_c}{Z_A Z_B \eta - Z_B} \right) - \left(\frac{\omega_{AA}}{Z_A \eta k T} \right) B_c^2 \quad (10)$$

and

$$\ln f_B = (Z_B \eta - 1) \ln \left(\frac{Z_A Z_B \eta - Z_B A_c - Z_A B_c}{Z_A Z_B \eta - Z_A} \right) - \left(\frac{Z_B \omega_{AA}}{Z_A^2 \eta k T} \right) A_c^2 \quad (11)$$

Other expressions are also given³⁴ in which the siting of the ions is assumed to be non-random. For uni-univalent exchange, which is the case in all the silver–sodium exchanges, the first terms in eqns. 10 and 11 reduce to zero, since $(A_c + B_c)$ is equal to unity. The activity coefficients, in agreement with the early semi-empirical treatment of Kielland³⁵, are therefore predicted to be second order polynomials in B_c and A_c respectively and also inverse functions of η . Simultaneous solution of eqns. 10 and 11 can therefore yield values for ω_{AA} and η .

Unfortunately, the problem of experimental error makes the significance of such estimates problematic at present. An examination of Fig. 4 shows that the activity coefficients f_{Ag} and f_{Na} are far more sensitive to the curve-fitting procedure than are the standard free energy values. The same was found to be true for mordenite. In Fig. 7 are shown values of f_{Ag} and f_{Na} corresponding to the curve-fits depicted in Fig. 5. Although eqns. 10 and 11 seem to preclude (for the uni-univalent case) curves for $\ln f_A$ and $\ln f_B$ which are not described by a quadratic fit, the situation is again not so simple. In X, Y and mordenite, more than one set of sites exist within the zeolite, so that the thermodynamic equilibrium constant K_a is found¹⁴ for n site sets, to be

$$K_a = \prod_{i=1}^n K_i \quad (12)$$

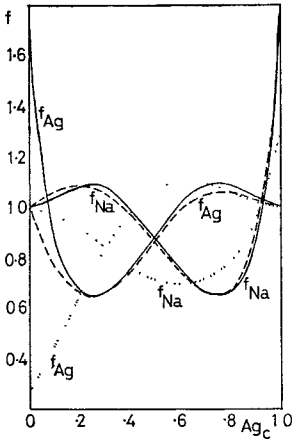


Fig. 7. Plots of the activity coefficients f_{Ag} and f_{Na} for the exchange of hydrated silver(I) ions in sodium mordenite. Curves correspond to the Kielland plots shown in Fig. 5.

where

$$X_i = \frac{Z_A m_{A,i} + Z_B m_{B,i}}{\sum_{i=1}^n (Z_A m_{A,i} + Z_B m_{B,i})} \quad (13)$$

and K_i refers to the i th site set¹⁴. Factorising f_A and f_B gives, from eqn. 12,

$$K_a = \frac{m_B^{Z_A}}{m_A^{Z_B}} \cdot \Gamma \cdot \prod_{i=1}^n \left[\frac{A_{c,i}^{Z_A} f_{A,i}^{Z_A}}{B_{c,i}^{Z_B} f_{B,i}^{Z_B}} \right]^{X_i} \quad (14)$$

and $f_{A,i}$, $f_{B,i}$, referring to the i th site set, must then be expressed in terms of η_i to obtain expressions corresponding to eqns. 10 and 11. Plots of (for example) $\ln f_{Ag}$ against Ag_c which contain several maxima and minima are not precluded therefore, even in this very simple uni-univalent exchange case.

Final remark

In conclusion, careful experimentation can lead to the derivation of values for the standard free energy of exchange where the level of uncertainty may be realistically assessed, and with which good correlations employing simple, or modified, dielectric theory are possible. In contrast, although the understanding of the causes of partial exchange within zeolites has advanced substantially in the last few years, mathematical modelling procedures attempting to correlate experimental data with advances in the statistical thermodynamic theory of ion exchange are still severely limited by experimental uncertainties.

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