Exchange of Cadmium into the Sodium and Ammonium Forms of the Natural Zeolites Clinoptilolite, Mordenite, and Ferrierite

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The selectivity of three different natural zeolites for cadmium has been investigated using either chloride or nitrate as the co-anion in solution. The three zeolites examined (clinoptilolite, mordenite, and ferrierite) were prepared in both the sodium and ammonium forms before exchanges with cadmium were attempted, and the selectivities of these materials for cadmium were measured in terms of experimental ion-exchange isotherms at 298 K. With one exception [$Cd/NH_4(Cl/NO_3)$-clinoptilolite] all systems were shown to be reversible. Differences in selectivity when either chloride or nitrate is the co-anion are discussed, and thermodynamic data are derived for those systems shown to be reversible. In contrast to similar studies on clays, no overexchange of cadmium was observed on any of the zeolites. Of the systems studied, it is concluded that sodium clinoptilolite is the most suitable exchanger for the removal of cadmium from solution.

It is well known that the presence of cadmium in the environment is a potential health hazard. Various methods have been employed therefore to effect its removal, such as chemical precipitation,[1] reverse osmosis,[2] foam separation,[3] and ion exchange.[4] Concerning the last, several studies have concentrated on aluminosilicate zeolites, because of their ubiquity and cheapness.[5] Thus Chelishchev *et al.*[6] were the first to study cadmium exchange using a sample of clinoptilolite from Dzegvi in the Georgian SSR, while in a complementary study Semmens and Seyfarth[7] employed natural clinoptilolite from Buckhorn, New Mexico. Gal and co-workers[8,9] and Dubinin *et al.*[10] examined the ion-exchange behaviour of cadmium in sodium A zeolite, while more recently Hertzenberg and Sherry[11] carried out a more detailed study of the same system, in order to assess what effect the likely presence of traces of this metal would have on the effectiveness of zeolite A as a softening builder in detergent formulations. The cadmium–sodium exchange equilibrium in zeolite X has also been investigated recently, using different co-anions or combinations of co-anions in the external electrolyte solution.[12,13]

Although the exchange process was reported to be both stoicheiometric and reversible in several of the above studies, investigations of the cadmium–sodium exchange equilibrium in some clay minerals[14,15] and perhaps also in zeolites[7,11,13] have shown that apparent non-stoicheiometry of exchange can occur with many aluminosilicate exchangers. This non-stoicheiometry is especially marked in the smectites, where in addition some evidence of irreversibility of exchange was noted.[14] It has been suggested recently[15] that the observed overexchange of the bivalent metals cobalt, nickel, copper, zinc, and cadmium in montmorillonite clay is due to the presence of a substantial quantity of the MCl^+ species in solution in addition to M^{2+}, so that the apparently binary exchange is in reality ternary in nature.[15] This suggestion is supported by chemical speciation calculations, not only on the above five bivalent metal ions,[13,15] but also on others.[16] However, it appears that while observed overexchange in smectite clays may be ascribed to a partial exchange of associated metal complexes with sodium ions at the edges and dislocations of the smectite layers,[16] in zeolites these species are effectively excluded from the exchanger.[13]

For the case of cadmium in particular, the co-anion may have a significant effect on the selectivity characteristics of an exchanger such as zeolite X,[12] even though overexchange is negligible. Also, the efficiency of natural zeolites in removing ammonium ion from sewage effluent has been shown to be affected by the presence of polluting bivalent metal ions.[17] For both these reasons, a careful and detailed study on the selectivity of several readily available natural zeolites for cadmium in the presence of either sodium or ammonium, and using different anionic backgrounds, seemed desirable. The results of this study are reported here.

Experimental

Materials.—The zeolites used were kindly supplied by W. R. Grace, from sedimentary deposits found in the U.S.A. The sources of the minerals were Hector, California for the clinoptilolite, and Lovelock, Nevada for both the ferrierite and mordenite samples. The sodium, ammonium, and cadmium salts used were all of AnalaR grade. Some initial purification of the minerals was carried out before use, and the minerals were then converted as far as possible into the near-homoionic sodium and ammonium forms. Details of this procedure for sodium are given elsewhere;[18] the procedure employed for the preparation of the homoionic ammonium form was similar.

Ion-exchange Isotherms.—Selectivity trends were measured by determining ion-exchange isotherms at 298 K and using a total solution concentration‡ of 0.1 equiv. dm^{-3}. The forward (*i.e.* replacement of sodium or ammonium ions by cadmium) points of the isotherms were obtained by equilibrating accurately known quantities of about 0.3 g of the chosen sodium or ammonium zeolite with aliquots (50 cm^3) of the corresponding solutions containing either sodium or ammonium together with cadmium. Four sets of solutions were used, with all solutions having the same total ionic concentration of 0.1 equiv. dm^{-3}, but within a given set each solution differed from the others in the relative quantities of the two cations present. Thus the four sets of solutions comprised mixtures of the salts Na/Cd(Cl), $Na/Cd(NO_3)$, $NH_4/Cd(Cl)$, and $NH_4/Cd(NO_3)$ respectively. After equilibration and prior to analysis, each solution was separated from the suspended zeolite by centrifugation. Reversibility tests[19] were undertaken also.

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‡ Throughout this paper, the term 'equivalent' refers to 1 mol of unit negative or positive charge.

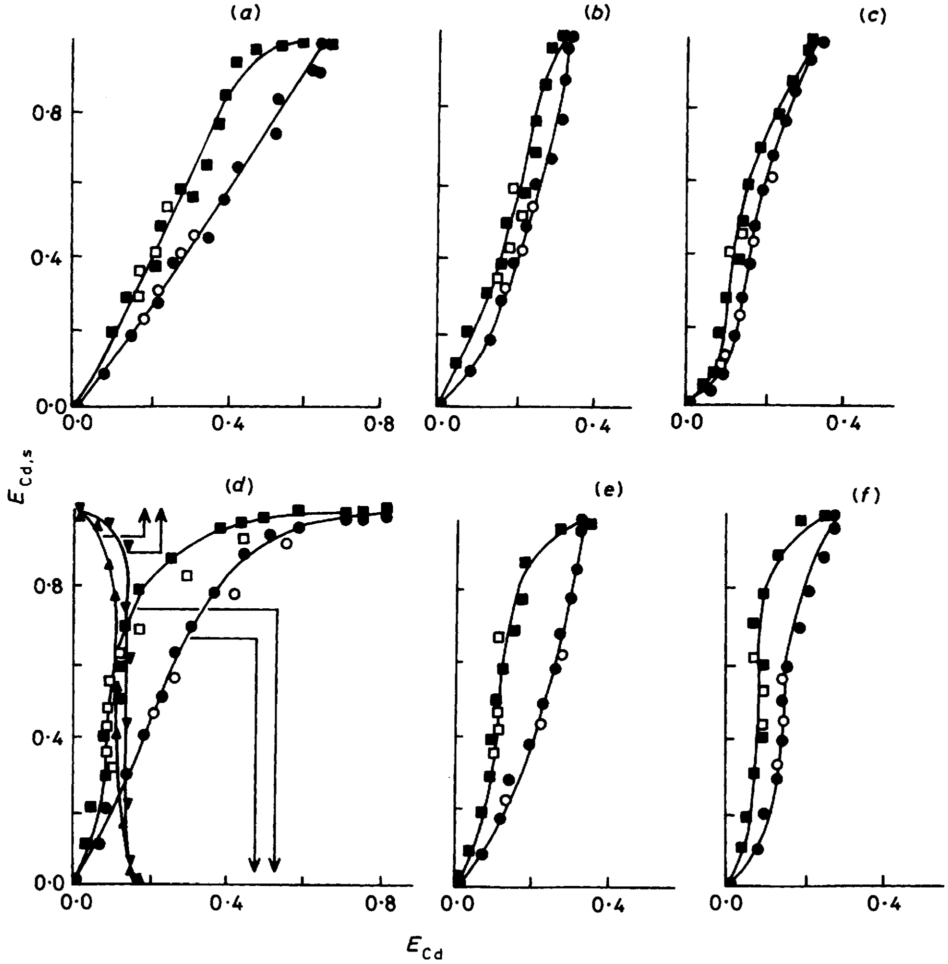

Figure 1. Isotherms obtained at 298 K for the exchange of sodium by cadmium in clinoptilolite (*a*), mordenite (*b*), and ferrierite (*c*); and of ammonium by cadmium in clinoptilolite (*d*), mordenite (*e*), and ferrierite (*f*). In the presence of either chloride (■) or nitrate (●). Filled symbols, forward points; open symbols, reverse points. Extra sodium removed in the presence of chloride (▼) and nitrate (▲)

Analyses.—The isotherm solutions were analysed for cadmium[20] using ethylenediaminetetra-acetate (edta), and also for sodium and ammonium content, both before and after equilibration. In addition, solutions after equilibration were analysed for calcium and potassium. In all cases, the quantity of ammonium present was determined using the Kjeldahl method,[21] and the quantities of sodium and potassium by flame photometry. The calcium content was analysed by atomic absorption spectroscopy.

In addition, analyses of the zeolite phase were undertaken. To determine the composition of maximally exchanged samples of the zeolites with respect to cadmium as well as sodium and ammonium, some samples of the three zeolites were exhaustively exchanged with either cadmium chloride or cadmium nitrate solutions of concentration 0.05 mol dm^{-3}. Finally, the known quantities of zeolite were washed, and digested with nitric acid on a steam-bath for 1 week, in order to dissolve the mineral samples. After centrifugation and washing, the cadmium content in the filtrate was then determined using atomic absorption spectroscopy.

Results

Ion-exchange isotherms for the cadmium–sodium exchange are given for clinoptilolite, mordenite, and ferrierite in Figure 1(*a*)—(*c*) respectively. On each diagram are found two isotherms, corresponding to the data obtained when either chloride or nitrate was present as the co-anion in the external electrolyte solution. Corresponding selectivity data for the cadmium–ammonium exchange equilibrium in the three zeolites are given in Figure 1(*d*)—(*f*).

Three observations are made concerning these results at this point. The first concerns reversibility; with the exception of the cadmium–ammonium exchange in clinoptilolite [Figure 1(*d*)] all systems appeared to be reversible (*i.e.* forward and reverse experimental points coincided within the limits of experimental uncertainty). These observations were in accord with the analyses of the solution phase after exchange; for the cadmium–sodium exchanges in clinoptilolite and mordenite, negligible quantities of either calcium or potassium were found in solution (the presence of these ions is one indication of non-reversibility[18]), while the total quantity of sodium plus cadmium in solution was always close to that expected from a stoicheiometric exchange. In the case of ferrierite [Figure 1(*c*)], traces only of calcium were detected, and again no potassium. Similarly, negligible quantities of calcium and potassium were found in solutions from the cadmium–ammonium exchanges in mordenite and ferrierite.

In contrast, not only were reverse points non-coincident with forward points for the cadmium–ammonium exchange equilibria in clinoptilolite [Figure 1(*d*)], but sodium, in addition to the expected cadmium and ammonium, was detected in the solutions after exchange. Analyses of the total quantities of the three ions in solution indicated that a ternary exchange process was occurring with this system, irrespective of the co-anion present. This system is discussed further below.

The second observation concerns the maximum exchange levels seen for cadmium [*i.e.* $E_{\mathrm{Cd(max.)}}$]. Levels of exchange are defined here in the manner previously described,[18] in terms of *all* the aluminium present in the appropriate zeolite, as based on the chemical analyses (given elsewhere[18]). Undoubtedly this overestimates the exchange capacities of the materials;[22] however, any other assumptions regarding the exchange capacities are likely to be as arbitrary,[18] and in addition may render meaningless any comparisons between maximum exchange levels obtained for different cations (see the Discussion section for further comments on this matter).

Values of $E_{\mathrm{Cd(max.)}}$ for the six exchange systems shown in Figure 1(*a*)—(*f*) were respectively 0.656, 0.334, 0.339, 0.810, 0.327, and 0.280, where $E_{\mathrm{Cd(max.)}}$ is defined in equation (1) and m

$$E_{\mathrm{Cd(max.)}} = 2m_{\mathrm{Cd(max.)}}/m_{\mathrm{Al}} \qquad (1)$$

is the molality (*viz.* mol kg^{-1}) in the zeolite. The important point to note is that in all cases the value of $E_{\mathrm{Cd(max.)}}$ proved to be independent of whether the co-anion in solution was chloride or nitrate (Figure 1). This is in marked contrast to the situation in some other naturally occurring inorganic exchangers such as the smectite group of clay minerals[14,15] (see Discussion section for further comments on this matter).

The third observation, also considered in the discussion below, concerns the relative selectivities exhibited by the three zeolites for cadmium in the presence of either chloride or nitrate. Figure 1 shows that *without exception*, the zeolites show a stronger selectivity for cadmium when nitrate is the co-anion rather than chloride.

Finally, for those systems which proved to be reversible, values of the thermodynamic equilibrium constant K_a were calculated from equation (2); a_{Cd} and $a_{\mathrm{Cd,s}}$ are the activities of the

$$K_a = a_{\mathrm{Cd}}a_{\mathrm{M,s}}^{2}/a_{\mathrm{M}}^{2}a_{\mathrm{Cd,s}} \qquad (2)$$

cadmium species in the zeolite and solution respectively, and a_{M} and $a_{\mathrm{M,s}}$ the activities of sodium or ammonium in the respective phases. Thus K_a corresponds to the exchange reaction (3) where

$$\mathrm{CdX_2} + 2\mathrm{M(L)} \rightleftharpoons \mathrm{Cd(L)_2} + 2\mathrm{MX} \qquad (3)$$

X refers to the co-anion in solution (chloride or nitrate) and L is that quantity of exchanger lattice carrying unit negative charge. Appropriate corrections for non-ideality in solution[13] were carried out, and values of the thermodynamic equilibrium constant were then determined by standard methods.[13,18]

All isotherm data were 'normalized'[23] before the application of thermodynamic procedures, since in all cases (Figure 1) $E_{\mathrm{Cd(max.)}} < 1$. The equilibrium constant K_a was not determined for the cadmium–ammonium system in clinoptilolite, since this had been shown to be non-reversible.

The resulting values of K_a for the reversible systems, and the corresponding standard free energies per equivalent of exchange (*viz.* $-RT\ln K_a/2$), are given in Table 1.

Table 1. Thermodynamic data for the exchange of cadmium on clinoptilolite, mordenite, and ferrierite

Exchange system	ΔG°/kJ mol^{-1}	K_a
Cd/Na(Cl)–clinoptilolite	2.76	0.107
Cd/Na(NO$_3$)–clinoptilolite	2.26	0.160
Cd/Na(Cl)–mordenite	1.11	0.408
Cd/Na(NO$_3$)–mordenite	1.07	0.419
Cd/Na(Cl)–ferrierite	1.68	0.257
Cd/Na(NO$_3$)–ferrierite	2.05	0.190
Cd/NH$_4$(Cl)–clinoptilolite	Irreversible	Irreversible
Cd/NH$_4$(NO$_3$)–clinoptilolite	Irreversible	Irreversible
Cd/NH$_4$(Cl)–mordenite	2.88	0.097
Cd/NH$_4$(NO$_3$)–mordenite	1.23	0.370
Cd/NH$_4$(Cl)–ferrierite	3.66	0.052
Cd/NH$_4$(NO$_3$)–ferrierite	2.98	0.089

Table 2. Chemical analysis of sodium and ammonium clinoptilolite

	Sodium–clinoptilolite		Ammonium–clinoptilolite	
Zeolite	% w/w	Composition*	% w/w	Composition*
SiO$_2$	61.75	9.40	61.99	9.36
Al$_2$O$_3$	11.16	1.00	11.25	1.00
H$_2$O	18.01	9.15	17.86	9.00
Na$_2$O	5.890	0.87	1.096	0.16
K$_2$O	0.392	0.038	0.150	0.015
CaO	1.950	0.31	1.480	0.24
Fe$_2$O$_3$	0.936	0.054	0.950	0.053
(NH$_4$)$_2$O	—	—	5.010	0.87
	100.09		99.79	

* Molar ratio with respect to Al$_2$O$_3$ (= 1).

Discussion

Comparisons with Previous Studies.—In their study on Georgian clinoptilolite, Chelishchev *et al.*[6] give a composition for their material of $\mathrm{Na_{3.66}K_{0.68}Ca_{1.27}Al_{7.07}Si_{28.94}O_{12.0}\cdot 21.5H_2O}$. (The oxygen figure is presumably a misprint, and should read 72.) The silica to alumina and water to alumina ratios of 8.09 and 6.08 respectively are somewhat lower than those observed here (Table 2) and the former value is certainly lower than what is normally regarded as the norm for clinoptilolite.[7] A further difference is that the sum of the sodium, potassium, and calcium contents amounts to a value in equivalents which closely approximates (*ca.* 97%) the theoretical maximum value of the exchange capacity, a value calculated assuming that all the aluminium is present as framework T atoms (*viz.* 246 mequiv. hg^{-1} in this case). Although no mention of any pretreatment of the material is made in their paper[6] it is possible that it was either acid-washed[7] or treated with a concentrated ammonium chloride solution[22] prior to its conversion into the homoionic sodium form, in order to remove excess of calcite.[22] It is well known[7,22] that excess of calcite is normally present, as witnessed in this work by the discrepancy (in equivalent terms, *ca.* 20%) between the total sodium, potassium, and calcium content on one hand and the aluminium content on the other (Table 2). It was a primary purpose of these studies to examine these materials after a minimum of pretreatments and purification procedures since, as Semmens and Seyfarth[7] have observed, 'it is questionable whether selectivities measured with acid-treated zeolites accurately reflect the selectivities which would be observed with the untreated zeolite:' acid washing may well dissolve some of the clinoptilolite. Treating the material with hot concentrated solutions of ammonium chloride also removes the calcite effectively;[22] however, such a process is probably impracticable on a large scale, and therefore again results in a material with properties which do not correspond with general practice. The observed discrepancy (Table 2) between the equivalent cation and the aluminium contents is therefore inevitable in the absence of either of these pretreatments.

The chemical composition differences between the Hector clinoptilolite studied here and the Georgian zeolite[6] makes straightforward comparisons of observed selectivities difficult; qualitatively the data appear similar, especially with respect to the maximum exchange level observed. The Georgian clinoptilolite appears somewhat more selective for cadmium at low values of $E_{\mathrm{Cd,s}}$ [*cf.* Figure 1(*a*) in this paper with the corresponding one in ref. 6]. Semmens and Seyfarth[7] do not give a detailed analysis of their Buckhorn clinoptilolite, nor are their isotherms complete, but again qualitative similarities are observed with respect to both selectivity and maximum exchange levels. However, an important point to note is their discussion regarding the exchange capacity of clinoptilolite. They noted[7] a considerable variation in exchange capacity according to pretreatment, with values ranging from 169 to 223 mequiv. $\mathrm{hg^{-1}}$. The latter value is close to those found here, which were calculated on the assumption that the aluminium content equalled the exchange capacity (see Table 2, exchange capacities for the sodium and ammonium forms are seen to be 219 and 221 mequiv. $\mathrm{hg^{-1}}$). Thus although (as mentioned earlier) it must be overestimating the exchange capacity to some extent to assume that all the aluminium is present as framework T atoms, the overestimate does not seem excessive in the light of the findings of Semmens and Seyfarth.[7] Expressing the capacities in this manner does at least set a basis for comparison against which all the normalizing factors[23] may be set, and it also allows meaningful comparisons of maximum exchange levels for different exchanges in a given zeolite (see following section). An alternative procedure, in which the exchange capacity of the appropriate zeolite is expressed in terms of a maximum exchange level observed with respect to one particular cation, seems far more arbitrary.

Maximum Exchange Levels.—In a series of recent studies, Sposito *et al.*[15,16] studied some overexchange phenomena which were observed by Maes *et al.*[14] when they studied the uptake of various bivalent metal ions on Camp Berteau montmorillonite clay (Morocco). They were able to show that this overexchange was the result of the formation in solution of complexes between the exchanging cations and the co-anions, so that when chloride was the co-anion a substantial quantity of the (ostensibly) bivalent cation was in fact present as $\mathrm{MCl^+}$. When perchlorate was used as the co-anion, the isotherms terminated at an exchange level which was in accord with that expected if the clay was maximally exchanged with the bivalent ion only.[15,16]

Cadmium has been shown[13] to complex far more readily with chloride than it does with nitrate (typically, for *ca.* 0.05 mol $\mathrm{dm^{-3}}$ solutions of cadmium chloride and nitrate, the percentage of cadmium present as $\mathrm{CdX^+}$ was calculated[13] to be respectively >63 and $<6\%$). Thus if the monovalent cadmium complex is also exchanging onto the zeolite or clay, a higher maximum exchange level should be observed for the Cd/Na(Cl) isotherm compared to that for the $\mathrm{Cd/Na(NO_3)}$ system. However, and in contrast to the studies on smectite clays,[14–16] no such effect was observed with the highly aluminous zeolite X.[13] This was attributed to the effective operation in this latter case of Donnan exclusion,[13] which is recognised as being most effective for an exchanger of high charge, such as X.

If this difference between smectite clays and aluminous zeolites is indeed due to the difference in framework charge density,[24,25] one would expect high-silica, low-charge zeolites such as clinoptilolite, mordenite, and ferrierite to behave in a manner intermediate between smectites and zeolite X, thus showing some overexchange when chloride rather than nitrate is used as the co-anion. However, in *all* cases (Figure 1) the maximum observed exchange levels for cadmium [$E_{\mathrm{Cd(max.)}}$] were identical for a given zeolite. It appears therefore that Donnan exclusion is an inadequate explanation for this marked difference in exchange behaviour between smectite clay minerals on the one hand and zeolites on the other. Sposito *et al.*[15] suggest that the monovalent complexes are adsorbed onto external surfaces of the montmorillonite crystals (*viz.* at the edges of the crystals, and at dislocations), whereas the bivalent ionic species are found on the internal (interlayer) sites. This seems a more plausible explanation for the observed difference between clays and zeolites, since, in contrast to clays, very little ($<0.5\%$) of the 'surface' of a zeolite is external.

It seems therefore, from the evidence given in this paper and elsewhere,[13] that with zeolites one may assume that ternary or multicomponent exchange arising from complexation between exchanging cations and some co-anions in solution is not likely normally to be a significant factor. In this respect, zeolites, whether natural or synthetic, are easier materials to study than are smectite clays.

Reversibility of Exchange.—Within the limits of experimental uncertainty, and with the notable exception of the $\mathrm{Cd/NH_4(Cl/NO_3)}$ clinoptilolite systems, all exchange systems appeared to be reversible. Observations of exchange reversibility for cadmium in these systems are in accord with other studies. Thus, although it has been shown from association-constant data that cadmium is on the borderline for stoicheiometric exchange in zeolites,[13] only about 1% of exchanged cadmium was observed to bind irreversibly to X,[13] and even in the highly aluminous zeolite A overexchange was only slightly greater provided nitrate rather than acetate was used as the co-anion.[11] In general, it has been shown that the more siliceous the zeolite, the easier it is to obtain stoicheiometric exchange (*e.g.* compare the exchange of transition metals in synthetic mordenite[26] with exchange of the same metals in zeolites X and Y[27,28]). Thus bearing in mind the near-stoicheiometric exchange of cadmium in A and X, reversible exchange in the siliceous minerals clinoptilolite, mordenite, and ferrierite is to be expected.

The irreversibility of the $\mathrm{Cd/NH_4(Cl/NO_3)}$ clinoptilolite systems is seen to be due to these exchange reactions being ternary in nature, with sodium rather than ammonium ion coming out of the zeolite as the cadmium loading is increased [Figure 1(*d*)]. A comparison of the full chemical analyses of the starting materials (*viz.* sodium and ammonium clinoptilolite) is instructive (Table 2). These materials were prepared by exchange with solutions of either the sodium or ammonium salts at elevated temperature (70 °C), in order to 'force' the clinoptilolite as far as possible into the respective homoionic forms. It is obvious that even under these stringent conditions it was *not* possible to replace all the sodium in the clinoptilolite by ammonium ion. Thus, assuming the sodium is all present in exchangeable form, then in terms of all the aluminium in the zeolite (see Results section) about 16.1% of the sodium remains in the ammonium form of clinoptilolite (Table 2).

Bearing in mind the stringent conditions used to prepare the ammonium clinoptilolite, it is therefore noteworthy that this residual sodium appears to come out readily on treating the ammonium clinoptilolite with cadmium [Figure 1(*d*)]. Even more surprising, if one in addition compares the isotherms for cadmium–sodium exchange [Figure 1(*a*)] with that for cadmium–ammonium exchange, it appears that this extra sodium is *not* removed when the sodium form of the zeolite is similarly treated with cadmium [note that the difference in exchange levels with respect to cadmium for the sodium and ammonium forms (Results section) is also *ca.* 16%]. No explanation can be given for this behaviour at present.

Effect of Co-anion on Selectivity for Cadmium.—In all cases, the three zeolites are seen to be markedly less selective for cadmium when chloride is the co-anion rather than nitrate (Figure 1). This same behaviour was observed by Dubinin *et*

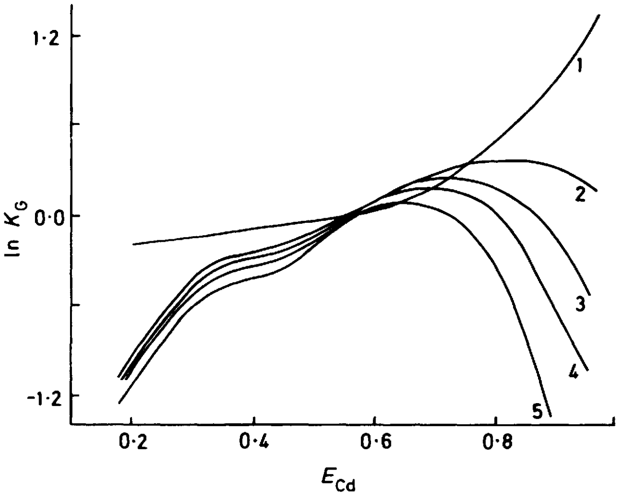

Figure 2. Effect of varying $E_{Cd(max.)}$ on the shape of plots of ln K_G *versus* E_{Cd} for the Cd/Na(NO_3)-mordenite system. Values of $E_{Cd(max.)}$ are (1) 0.334, (2) 0.340, (3) 0.345, (4) 0.350, and (5) 0.360

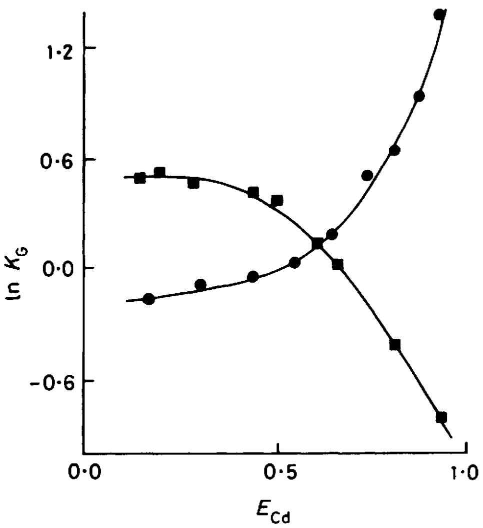

Figure 3. Plots of ln K_G *versus* E_{Cd} for the Cd/Na(Cl, NO_3)-mordenite system. Data for chloride (●) and for nitrate (■)

al.[10] in their studies on cadmium exchange in zeolite A, where the selectivity difference for cadmium in the presence of each of the two anions was especially marked at low E_{Cd} levels. The phenomenon is undoubtedly due to the different levels of complexation of the cadmium ion which occur in the presence of the two different anions; in a thermodynamic formulation the magnitudes of such associations are described adequately in terms of appropriate activity coefficients for the salts in the mixed electrolyte solutions.[29] The means of effecting this correction for solution-phase non-ideality,[13] and its respective magnitude for the cadmium–sodium[12,13] and cadmium–ammonium[30] mixed solutions, are all described elsewhere.

The correction for non-ideality in the solution phase is applied to the mass action quotient K_m [equation (4)] where E_{Cd}

$$K_m = E_{Cd}c_{M,s}^2/E_M^2c_{Cd,s} \qquad (4)$$

and E_M are the equivalent fractions of the appropriate ions in the zeolite, and $c_{Cd,s}$ and $c_{M,s}$ are the molar concentrations (mol dm^{-3}) in solution. A 'corrected selectivity quotient' K_G is then obtained, which for 'dilute' solutions[29] (that is <0.5 mol dm^{-3}) should have the same value for a particular composition of a given exchange system[12] irrespective of the nature of the co-anions in the external electrolyte solution [equation (5)]. In

$$K_G = E_{Cd}a_{M,s}^2/E_M^2a_{Cd,s} \qquad (5)$$

addition, for dilute solutions, if the solution-phase correction has been applied correctly, the thermodynamic equilibrium constant (and therefore the standard free energy of exchange) should also be independent of the nature of the co-anion in solution.[12]

Taking the thermodynamic equilibrium constants first (Table 1), and bearing in mind the sensitivity of a function such as K_a to experimental error[31] [equations (2), (4), and (5)], then the values obtained when a given exchange was carried out in the presence of either chloride or nitrate are seen to be reasonably close to each other. Deviations between pairs of K_a values are most marked in those systems for which the zeolite exhibited poor selectivity for cadmium, and for which in addition the $E_{Cd(max.)}$ values were low [*e.g.* the Cd/NH_4 mordenite and ferrierite systems, see Figure 1(*e*) and (*f*)]. In general, the plots of K_G against composition are extremely sensitive to the exact value chosen for $E_{Cd(max.)}$, especially at the composition extrema. Consider for example the Cd/Na(NO_3) mordenite system (Figure 2). It is obvious that quite small changes in $E_{Cd(max.)}$ have a marked effect on the plot of ln K_G against composition. In addition, when $E_{Cd(max.)}$ is small the normalisation correction exaggerates any differences in curve shape which may have arisen from the fitting procedure used on the experimental isotherm data. For example, the values of $E_{Cd(max.)}$ for both the Cd/Na(NO_3) and Cd/Na(Cl) mordenite systems were identical (0.334), but the curve obtained from best-fitting the chloride results inflects at high $E_{Cd,s}$ values [Figure 1(*b*)] whereas that for nitrate does not. As a consequence the two plots of ln K_G against composition are not coincident as expected by theory[12] but differ markedly (Figure 3). Paradoxically, the two corresponding K_a values are very similar, because K_G is an integral function [equation (6) for

$$\ln K_a = -1 + \int_0^1 \ln K_G dE_A \qquad (6)$$

cadmium–sodium reactions].[13] This serves to emphasise the fact that K_a values can only give a *general* description of relative selectivities for different systems under the prescribed standard-state conditions (*i.e.* affinities).

Despite these reservations, some general conclusions can nevertheless be drawn regarding the selectivity of the three zeolites for cadmium. First, because of the tendency of cadmium to associate strongly with some anions in solution,[13] the selectivity of each zeolite for cadmium is strongly dependent on the nature of the co-anion. Secondly, in accord with data already published on the sodium and ammonium zeolite systems,[18] the sodium zeolites show consistently a higher preference for cadmium than do the ammonium zeolites. Thirdly, the thermodynamic affinities (Table 1) show that cadmium is never preferred over sodium or ammonium, irrespective of which zeolite is chosen.

Conclusions

For a natural zeolite to be useful for the removal of cadmium from an effluent the following properties are desirable. First, it must have a substantial exchange capacity for the cadmium ion. Secondly, it is desirable for the exchanger to be readily capable of regeneration, so that the cadmium can be recovered in concentrated form and the exchanger can be re-used. Thus a zeolite having a very high selectivity for cadmium is not the best choice because of regeneration difficulties; in addition, it is also essential that the exchange reaction be reversible. Taking these requirements into account, sodium clinoptilolite is superior to ammonium clinoptilolite, and it also seems a better choice than either ferrierite or mordenite, whether these latter are in the sodium or ammonium forms.

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