Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Equilibrium Studies of Sodium-Ammonium, Potassium-Ammonium, and Calcium-Ammonium Exchanges on Clinoptilolite Zeolite

M. A. Jama[a]; H. Yücel[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, MIDDLE EAST TECHNICAL UNIVERSITY, ANKARA, TURKEY

To cite this Article Jama, M. A. and Yücel, H.(1989) 'Equilibrium Studies of Sodium-Ammonium, Potassium-Ammonium, and Calcium-Ammonium Exchanges on Clinoptilolite Zeolite', Separation Science and Technology, 24: 15, 1393 — 1416
To link to this Article: DOI: 10.1080/01496398908050659
URL: http://dx.doi.org/10.1080/01496398908050659

SEPARATION SCIENCE AND TECHNOLOGY, 24(15), pp. 1393-1416, 1989/90

Equilibrium Studies of Sodium-Ammonium, Potassium-Ammonium, and Calcium-Ammonium Exchanges on Clinoptilolite Zeolite

---

M. A. JAMA and H. YÜCEL*

CHEMICAL ENGINEERING DEPARTMENT
MIDDLE EAST TECHNICAL UNIVERSITY
ANKARA 06531, TURKEY

Abstract

Forward and reverse ion-exchange isotherms for the binary sodium-ammonium, potassium-ammonium, and calcium-ammonium systems on clinoptilolite have been measured in aqueous solutions at a total concentration of 0.1 equiv/dm^3 and at 298 K. Prior to exchange experiments it was attempted to prepare homoionic forms of the zeolite by exhaustive treatments with appropriate salt solutions of cations. With no binary exchanges, full replacement of the cation by the ammonium ion is observed, which conflicts with some earlier work on clinoptilolite. Despite the observed partial exchange levels, clinoptilolite shows a very high preference for ammonium ion over sodium and calcium but not over potassium. Thermodynamic values for the exchanges were calculated and compared with data in the literature. Both the selectivity and thermodynamic affinity sequence, in agreement with previous work reported in the literature, are $K^+ > NH_4^+ > Na^+ > Ca^{2+}$.

INTRODUCTION

It has been generally accepted that the presence of ammonia and ammonium ions in wastewaters which subsequently pass into freshwaters

---

*To whom correspondence should be addressed.

may cause a serious water pollution problem. This is mainly due to the facts that ammonia is a toxic hazard to fish and some other forms of aquatic life and, along with phosphate, it promotes algae growth. As a consequence of these concerns it is usually desirable to reduce the ammonia concentrations in wastewaters to a level less than 1 ppm (*1*).

Processes for the removal of ammonium ions from wastewaters include nitrification-denitrification, air stripping, break-point chlorination, and selective ion exchange. The ion-exchange process has several advantages over other methods of ammonia removal including higher efficiency at temperatures below 15°C (*1, 2*).

Among the several ion-exchange materials tested for ammonia removal, a natural zeolite, clinoptilolite, has received much attention because of its favorable selectivity for the ammonium ion in the presence of most of the other cations commonly found in wastewaters and its potential low cost. Clinoptilolite is a silica-rich natural zeolite which occurs in relatively large minable sedimentary deposits of sufficient high purity in many parts of the world (*3*).

Equilibria and kinetic aspects of ammonia exchange on clinoptilolite have been widely studied both in batch and column work (*2, 4–13*). However, there appear to be some conflicting results in the literature about the ammonium exchange capacity and exchange behavior of cations orginally present in the clinoptilolite samples. Some of these discrepancies, such as the difference in exchange capacities, may be partly explained by the inevitable presence of some impurities in these minerals which are difficult to estimate quantitatively. Another complicating factor is the fact that these minerals contain cations: usually Na^+, K^+, Ca^{2+}, and Mg^{2+} in different proportions depending on the mineral's origin, and there is some evidence in the literature that these cations occupy different crystallographic sites (*14*). In a recent study (*15, 16*) it was shown that a clinoptilolite sample that had been maximally exchanged with sodium exhibited partial exchange with ammonium ion, indicating that the estimated theoretical exchange cannot be attained with ammonium ion, contradicting some earlier work. It appears that more information is required on the ion-exchange behavior of clinoptilolite, preferably with parent clinoptilolites of different cationic compositions, to elucidate the factors that influence ammonia exchange on this zeolite.

EXPERIMENTAL

Materials and Pretreatment

The clinoptilolite sample used in the study was from a sedimentary deposit in Western Anatolia. The clinoptilolite was characterized by x-ray diffraction, chemical analysis, DTA and TGA, and adsorption capacities for carbon dioxide, etc. in a previous study, and the details were published elsewhere (*17*).

The original material contained calcium, potassium, magnesium, and sodium as exchangeable cations, and it was attempted to convert the sample into homoionic forms prior to study of the binary exchanges $NH_4^+ \rightleftharpoons Na^+$, $NH_4^+ \rightleftharpoons K^+$, and $2NH_4 \rightleftharpoons Ca^{2+}$. For this purpose, 25 g of the crushed samples (50–100 mesh size fraction) were treated with 400 cm^3 of 1.0 mol/dm^3 solutions of appropriate salts of cations at about 90°C in a stirred vessel for about 2 weeks. This treatment was repeated twice in order to force the clinoptolite into the respective homoionic forms as far as possible. The samples thus treated were washed with deionized water, oven dried at 50°C, and then kept over saturated ammonium chloride solution to provide a constant moisture content prior to chemical analysis and exchange experiments.

Ion Exchange Isotherms

Binary exchange isotherms for $Na^+ \rightleftharpoons NH_4^+$, $Na^+ \rightleftharpoons K^+$, and $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchanges were determined at 298 K and a total solution concentration of 0.1 $equiv/dm^3$. The forward points of the isotherm were obtained by equilibrating accurately weighed amounts of the near homoionic forms of clinoptilolite in a series of solutions containing the two competing ions in different concentration ratios but at a constant normality of 0.1 $equiv/dm^3$. The solutions were shaken in a thermostated shaker for 2 weeks to ensure equilibrium. Kinetic experiments showed that equilibrium was reached at much shorter times. After equilibrium has been established, the mixtures were centrifuged, filtered, and the solutions were analyzed for the cations Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}, as explained below.

The exchange levels were calculated by using the initial and final concentrations during exchange and from the volume of solution with initially known compositions.

The reverse isotherm points were measured in a similar way by using the ammonium form of the clinoptilolite sample as the starting material.

Chemical Analyses of Solid and Solution Phases

The original and near homoionic forms of samples were analyzed after Na_2CO_3 fusion for SiO_2, Al_2O_3, and Fe_2O_3 by wet chemical methods (*18*). Alkali and alkaline earths were determined after volatilization of SiO_2 with $HF_4 + H_2SO_4$ evaporation by atomic absorption spectroscopy and flame photometry. The water content of the sample was determined by vacuum thermogravimetry.

The exchange solutions were analyzed for ammonium ion content by using an ammonia selective electrode (Russel Model 95-5129) and an ion meter (Orion Model 720). Na^+ and K^+ were determined on a Lange 6M flame photometer. Ca^{2+} and Mg^{2+} were analyzed on a Perkin-Elmer Model 2380 atomic absorption spectrophotometer. The instruments were calibrated by using the appropriate standard solutions according to the instrument used and the cation analyzed.

THEORETICAL

The ion-exchange theory of zeolites has been treated in several references (*19–25*).

A binary ion-exchange reaction in zeolites may be represented by

$$Z_A B_z^{Z_B^+} + Z_B A_s^{Z_A^+} \rightleftharpoons Z_A B_s^{Z_B^+} + Z_B A_z^{Z_A^+} \qquad (1)$$

where Z_A and Z_B are the charges of exchanging cations A and B, and the subscripts z and s refer to the zeolite and solution phases, respectively.

The equivalent fraction of the exchanging cation in the solution and zeolite phases are defined respectively by

$$M_A = \frac{Z_A m_{A,s}}{Z_A m_{A,s} + Z_B m_{B,s}} \tag{2}$$

$$N_A = \frac{\text{number of equivalents of exchanging cation A}}{\text{total equivalents of cations in the zeolite}} \tag{3}$$

where $m_{A,s}$ *and* $m_{B,s}$ are the molalities of ions A and B, respectively, in the equilibrium solution. Also $N_A + N_B = 1$ and $M_A + M_B = 1$. The ion-exchange isotherm is a plot of N_A as a function of M_A at a given total concentration and at constant temperature.

The preference of the ion exchanger for one of two counterions may be expressed by a practically important quantity called the separation factor and defined by

$$\alpha_B^A = \frac{N_A M_B}{N_B M_A} \tag{4}$$

If ion A is preferred by the zeolite, α_B^A is greater than unity. The separation factor depends on the total concentration of solution, the temperature, and the solution composition.

The thermodynamic equilibrium constant, K_a, for the binary exchange reaction defined in Eq. (1) is given by

$$K_a = \frac{a_{A,z}^{Z_B} a_{B,s}^{Z_A}}{a_{A,s}^{Z_B} a_{B,z}^{Z_A}} = K_c \frac{f_A^{Z_B}}{f_B^{Z_A}} \tag{5}$$

where

$$K_c = \frac{N_{A,z}^{Z_B} a_{B,s}^{Z_A}}{N_B^{Z_A} a_{A,z}^{Z_B}} = \frac{N_A^{Z_B} m_{B,s}^{Z_A}}{N_B^{Z_A} m_{A,s}^{Z_B}} \cdot \frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} \tag{6}$$

K_c is commonly called the corrected selectivity coefficient since it includes a correction for the activity coefficients of the ions in the equilibrium solution. In these expressions γ and f denote the activity coefficient in the solution and in the zeolite phases, respectively. a denotes the activity. The first subscript on a indicates the type of ion and the second subscript indicates the solution or zeolite phases. $m_{A,s}$ *and* $m_{B,s}$ are related to the total normality N in equiv/dm^3 and the equivalent cation fractions M_A and M_B in the dilute solutions by

$$m_A = \frac{NM_A}{Z_A}, \qquad m_B = \frac{NM_B}{Z_B} \tag{7}$$

since molality and molarity are essentially equal in the dilute solutions.

The activity ration $\Gamma = \gamma_B^{Z_A}/\gamma_A^{Z_B}$ can be evaluated from the mean activity coefficients of salts AY_{Z_A} and BY_{Z_B} in the mixed electrolyte of ionic strength I by

$$\frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} = \frac{\left[\gamma\pm_{BY_{Z_B}}^{Z_B+1}\right]^{Z_A}}{\left[\gamma\pm_{AY_{Z_A}}^{Z_A+1}\right]^{Z_B}} \tag{8}$$

Mean activity coefficients $\gamma\pm$ can be found from the mean molal activity coefficient of each pure salt at the same ionic strength as the mixed electrolyte by Gluekauf's method (*26*). The values of Γ serve to determine the quotient K_c.

By using the Gaines and Thomas approach (*27*), plots of $\ln K_c$ vs N_A can be used to obtain $f_A^{Z_B}$, $f_B^{Z_A}$, and K_a from the relations

$$\ln K_a = Z_B - Z_A + \int_0^1 \ln K_c dN_A \tag{9}$$

$$\ln f_A^{Z_B} = (Z_B - Z_A)N_B - \ln K_c + N_A \ln K_c + \int_{N_A}^1 \ln K_c dN_A \tag{10}$$

$$\ln f_B^{Z_A} = -(Z_B - Z_A)N_A + N_A \ln K_c - \int_0^{N_A} \ln K_c dN_A \tag{11}$$

The standard free energy of exchange per gram equivalent of exchanger is given by

$$\Delta G° = -\frac{RT}{Z_A Z_B} \ln K_a \tag{12}$$

This particular thermodynamic formulation is valid under conditions where imbibition of neutral electrolyte is negligible. A second condition is that the overall contributions made by water activity changes in the zeolite are negligible.

RESULTS AND DISCUSSION

Near Homoionic Forms of Clinoptilolite

Chemical analyses of the parent clinoptilolite and near homoionic Na^+, K^+, Ca^{2+}, and NH_4^+ forms of the clinoptilolite are given in Table 1. It should be noted that despite the stringent conditions used to force the clinoptilolite into its respective homoionic forms, it was not possible to achieve complete exchange in all cases. Some investigators in previous studies (*28–32*) working with clinoptilolites of different origins also noted partial exchange in similar treatments. The cations mostly involved in the exchange process are Na and Ca. K present in the parent material does not exchange significantly with other cations Na and Ca and thus Na- and Ca-exchanged clinoptilolites contained most of the original K. This behavior of K indicates a low mobility of K in the clinoptilolite structure as compared to the other cations. According to Koyama and Takeuchi's (*14*) proposed structure of clinoptilolite, K is located at a specific site M(3) which is situated in an 8-membered ring and has the highest coordination among all the cation sites in the unit cell. K is coordinated with six framework oxygens and three water molecules in this site. In contrast, the M(1) site, which is occupied by Na and Ca, is coordinated by two framework oxygen atoms and five molecules. M(2), also occupied by Ca and Na, is coordinated by three oxygen and five water molecules. Site M(4), which is occupied by Mg, is coordinated only by six water molecules.

The poor ion-exchange ability of K might be attributed to the strong bonding of K at the M(3) site as noted by previous investigators (*28–32*).

TABLE 1
Chemical Analyses of Original and Near Homoionic Clinoptilolites

Sample component	Original clinoptilolite (w/w%)	Na-CLI (w/w%)	K-CLI (w/w%)	Ca-CLI (w/w%)	NH_4-CLI (w/w%)
SiO_2	63.70	62.91	62.91	61.64	67.56
Al_2O_3	11.12	13.92	13.30	13.59	12.64
Fe_2O_3	1.17	0.8791	0.7992	0.77	0.2396
CaO	3.02	0.9529	0.9249	3.99	0.4764
MgO	1.75	0.6811	0.6304	1.77	0.3949
Na_2O	0.30	4.2	0.530	0.24	—
K_2O	2.94	3.05	6.30	2.83	1.71
$(NH_4)_2O$	—	—	—	—	4.42
H_2O	16.00	14.78	14.04	14.26	13.79
Total	100.0	101.4	99.44	99.09	101.2

Isotherms

Equilibrium data for the forward and reverse $Na^+ \rightleftharpoons NH_4^+$, $K^+ \rightleftharpoons NH_4^+$, and $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchanges are given in Figs. 1-3. The experimental isotherms for $NH_4^+ \rightleftharpoons Na^+$ and $2NH_4^+ \rightleftharpoons Ca^{2+}$ conform to type *d* and the isotherm for $NH_4 \rightleftharpoons K^+$ conforms to type *c* in Breck's classification (*19*) with partial maximum levels of exchange. As inferred from the isotherms, clinoptilolite is selective for ammonium ion over Na^+ and Ca^{2+} but not selective for NH_4^+ over K^+.

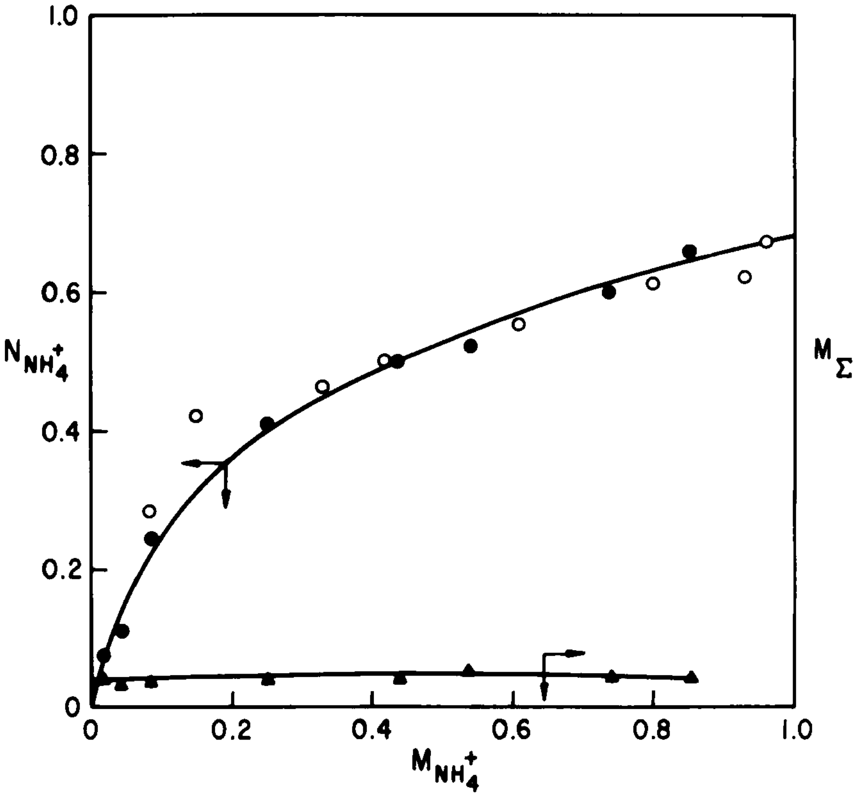

FIG. 1. Experimental isotherm for $Na^+ \rightleftharpoons NH_4^+$ exchange. Forward isotherm point, NH_4^+ exchanged into zeolite (●); reverse point, Na^+ exchanged into zeolite (○); K^+, Ca^{2+}, and Mg^{2+} found in solution in forward exchange (▲).

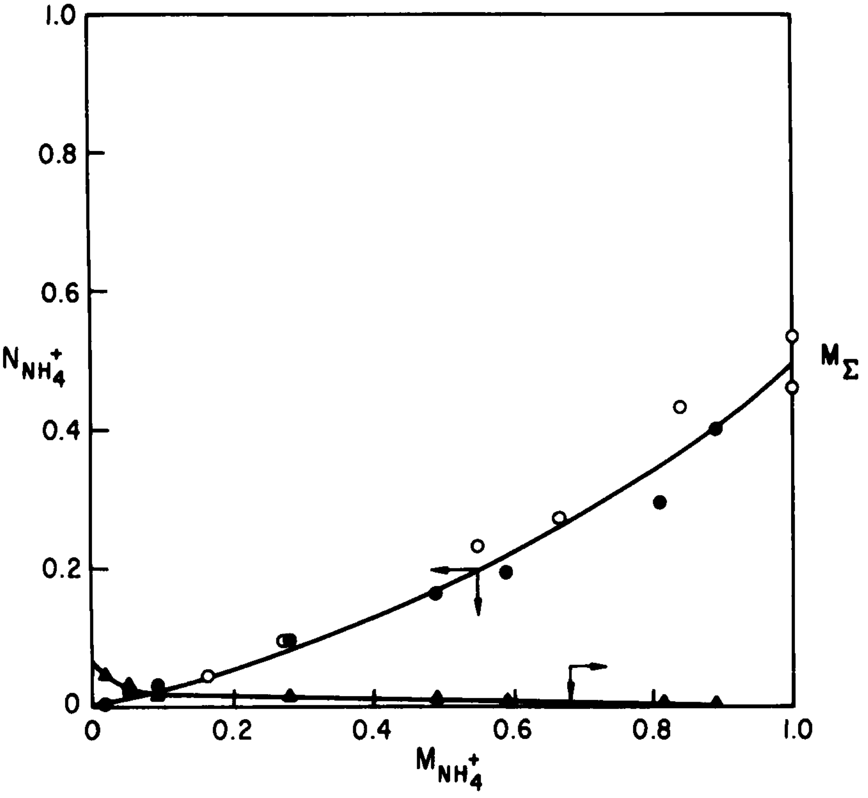

FIG. 2. Experimental isotherm for $K^+ \rightleftharpoons NH_4^+$ exchange. Forward isotherm point, NH_4^+ exchanged into zeolite (●); reverse point, K^+ exchanged into zeolite (○); Na^+, Ca^{2+}, and Mg^{2+} found in solution in forward exchange (▲).

Exchange capacities were estimated by calculations on the basis of aluminum content as found by chemical analysis. Because of the presence of some impurities, this value may give an exchange capacity which is somewhat higher than the actual value. However, because of the difficulty of estimating quantitatively the amounts of impurities, any other method might be more arbitrary.

When clinoptilolite samples which had already been exhaustively exchanged for a particular cation were contacted with the mixed cation/ammonium ion solutions in order to construct the binary isotherm, other cations were also detected in solution after equilibration. For example,

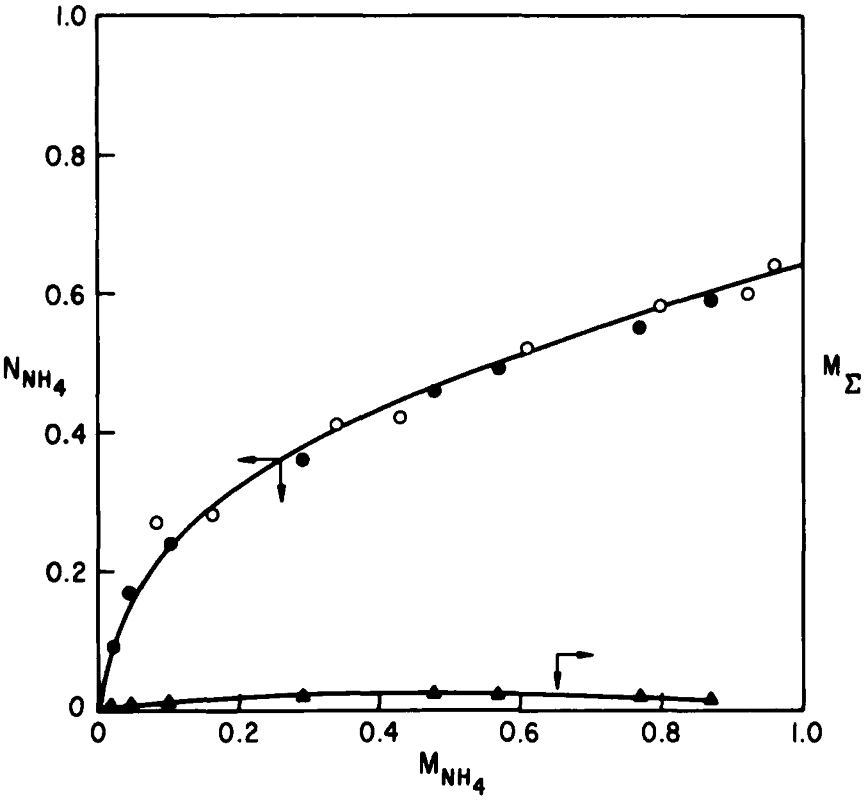

FIG. 3. Experimental isotherm for $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchange. Forward isotherm point, NH_4^+ exchanged into zeolite (●); reverse point, Ca^{2+} exchanged into zeolite (○); Na^+, K^+, and Mg^{2+} found in solution in forward exchange (▲).

when Na-exchanged clinoptilolite was contacted with NH_4^+/Na^+ solutions, some K^+, Ca^{2+}, and Mg^{2+} were also found in solution (see Figs. 1–3). These cations amounted, in equivalent terms, to less than about 5% of the total solution concentration. Generally, the quantity of ammonium ion exchanged into the zeolite balanced closely the cations found subsequently in solution, indicating that only exchangeable cations rather than ions arising from the dissolution of impurities such as calcite were involved in the process.

Apparently some cations which were not replaced during exhaustive ion exchange in the preparation of homoionic forms were accessible to ammonium ions. As a support of this hypothesis, in the reverse $Na_s^+ \rightarrow Na_Z^+$ exchange the amounts of K^+, Ca^{2+}, and Mg^{2+} found in the solution equilibrated were much less than in the forward exchange. In the reverse exchange the starting material was the ammonium form of zeolite which had been prepared by exhaustive exchange of parent clinoptilolite by ammonium chloride solutions. As a result, the forward exchanges were not strictly binary exchanges because of the presence of other cations, and the reverse exchanges approached the binary exchange. However, the reasonable agreement, within experimental accuracy, found between the forward and reverse isotherm points suggests that binary exchange isotherms were not significantly affected by the presence of the other cations under the experimental conditions. This is an expected result if the cations occupy different sites, resulting in little interactions between them. Ames (*9*), too, observed during his study of the selective removal of ammonium ions from agricultural wastewaters that the equilibrium for each cation pair is independent of the other cations.

For the exchanges $Na^+ \rightleftharpoons NH_4^+$, $K^+ \rightleftharpoons NH_4^+$, and $Ca^{2+} \rightleftharpoons 2NH_4^+$ studied, full replacement of all cations by NH_4^+ could not be achieved at the maximum level of exchange. The maximum levels of exchange by ammonium ions were 50% for K-clinoptilolite, 64% for Ca-clinoptilolite, and 68% for Na-clinoptilolite. Limits to exchange within zeolites are frequently explained in terms of ion sieving (*34–36*) when ions are larger than the channel windows so they cannot pass through windows, or in terms of the volume steric effect (*37*), not because they cannot pass through the windows, but because they fill all the intracrystalline voids before 100% exchange is achieved. Occasionally the ion sieve and volume steric effects appear to operate together (*38*).

Another factor that may influence the maximum exchange levels is the ratio of the total available cation sites to charges on the zeolite lattice and the strength of interaction between exchanging cations (*39*). The partial exchange levels observed for ammonia exchange on clinoptilolite suggest that one or more of these factors is operating.

Selectivity Coefficients and Thermodynamic Values

Before any thermodynamic quantity was calculated, the isotherms were normalized (*25*) by dividing all the experimental equivalent fractions by the maximum equivalent fraction of ammonium ion found by extrapolation of the experimental isotherm to $M_{NH_4^+} = 1$.

The separation factors α_B^A defined by Eq. (4) were calculated from the experimental isotherms for the exchanges $Na^+ \rightleftharpoons NH_4^+$, $K^+ \rightleftharpoons NH_4^+$, and $Ca^{2+} \rightleftharpoons 2NH_4^+$, and they are presented in Fig. 4. It is observed that the separation factors for the exchanges studied decrease as the equivalent fraction of ammonia in the zeolite increases.

The activity ratio $\Gamma = \gamma_B^{Z_A}/\gamma_A^{Z_B}$, the solution nonideality correction factor, calculated from Eq. (8), is presented in Fig. 5. It is noted that the solution nonideality correction factor, Γ, is invariant with solution composition and is close to unity for these dilute solutions (0.1 equiv/dm^3) for the uni-univalent exchanges $Na^+ \rightleftharpoons NH_4^+$ and $K^+ \rightleftharpoons NH_4^+$. However, it increases with increasing concentration of NH_4^+ in solution, and varies significantly for the univalent-divalent exchange $Ca^{2+} \rightleftharpoons 2NH_4^+$.

Logarithms of the corrected selectivity coefficients K_c against the equivalent fraction of ammonia in the zeolite phase, usually called Kielland plots (*33*), are presented in Figs. 6–8. The Kielland plots are nearly linear for the exchanges studied. The scatter at the end points of the isotherm is due to poor experimental accuracy at these extrema at which calculations involve the difference between two nearly equal concentration values.

Corrected selectivity coefficients decrease as the equivalent fraction of ammonium ion in zeolite increases for all the exchanges studied.

Plots of activity coefficients of ions in zeolite according to Eqs. (10) and (11) as a function of the equivalent fraction of NH_4^+ in the zeolite phase show a maxima for Na^+ and an S-shaped curve for NH_4^+ for $Na^+ \rightleftharpoons NH_4^+$ exchange (Fig. 9) and a maximum for NH_4^+ and a minima for Ca^{2+} for $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchange (Fig. 10).

The thermodynamic equilibrium constants K_a were evaluated by using Eq. (9). The second term of this equation was determined by graphical integration of the area under the curve ln K_c vs $N_{NH_4^+}$. The free energy of exchange, ΔG°, was calculated by Eq. (12). Values of the thermodynamic equilibrium constants and the standard free energies thus calculated are given in Table 2. The free energies of exchanges indicate that the thermodynamic affinity sequence for the clinoptilolite zeolite is $K^+ > NH_4^+ > Na^+ > Ca^{2+}$.

In Figs. 11 and 12 the normalized selectivity coefficients are given as functions of competing ammonium/cation ratios in solution for the exchanges studied. It is noted that the corrected selectivity coefficients decrease as the ammonium ion/cation ratio in solution increases.

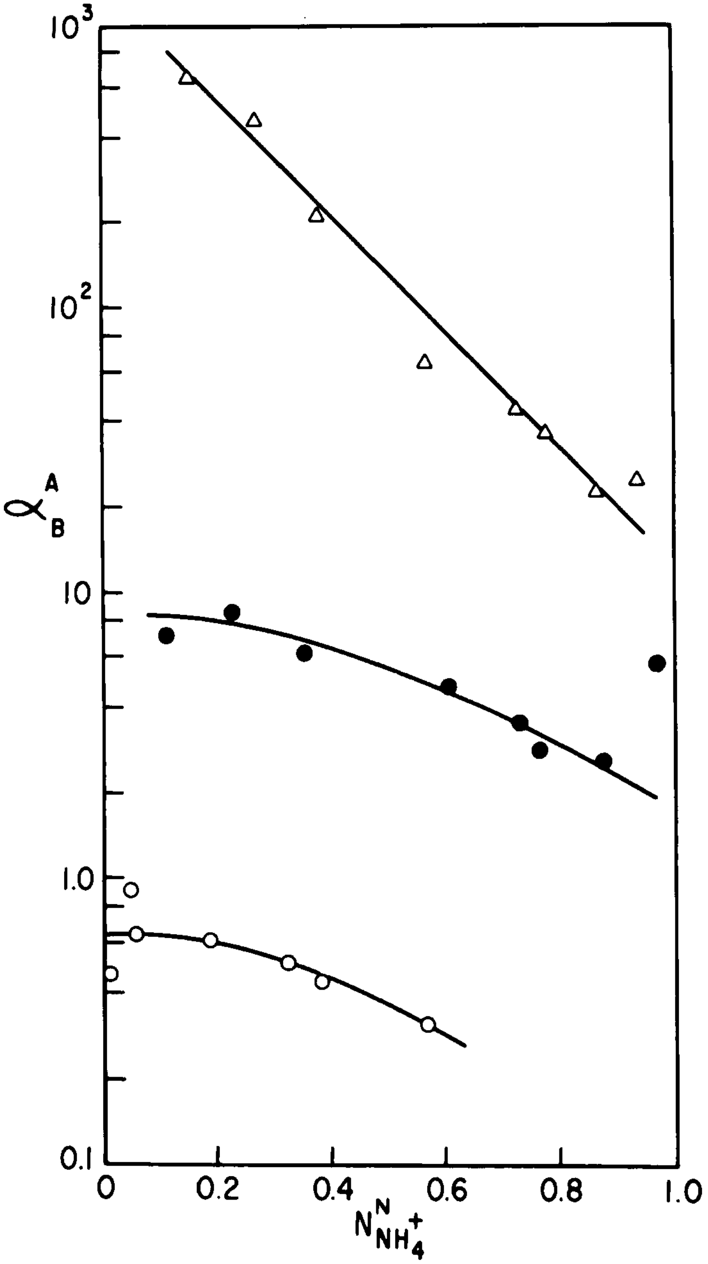

FIG. 4. Values of separation factors α versus equivalent fraction of ammonium ion in zeolite. $Na^+ \rightleftharpoons NH_4^+$ exchange (●); $K^+ \rightleftharpoons NH_4^+$ exchange (○); $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchange (△).

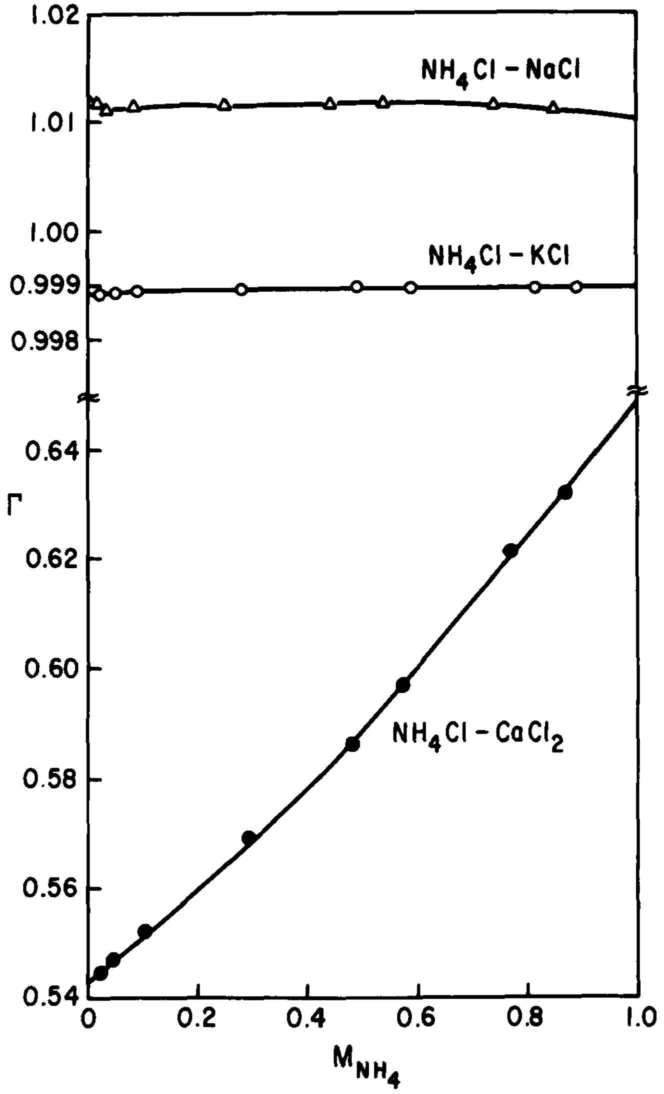

Fig. 5. Values of solution nonideality correction factor Γ versus equivalent fraction of ammonium ion in solution. NH_4Cl-$CaCl_2$ (●), NH_4Cl-KCl (○), NH_4Cl-NaCl (▲).

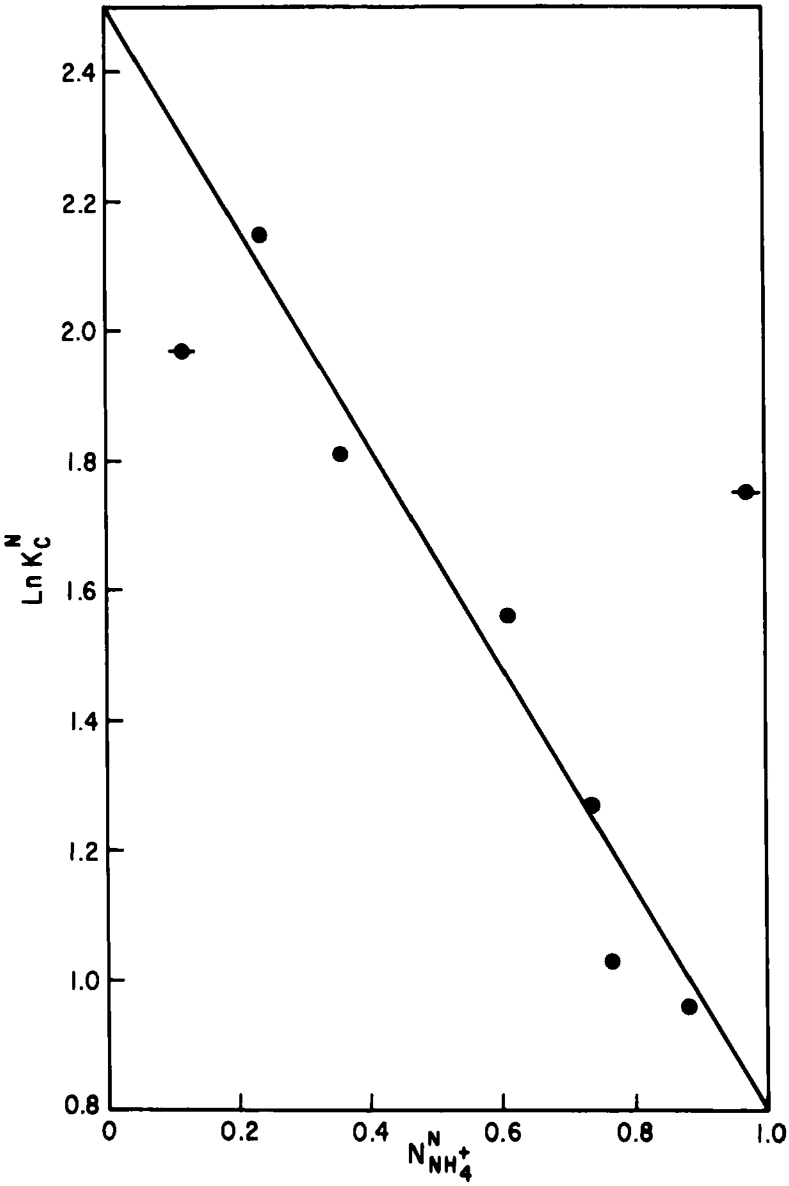

FIG. 6. Normalized Kielland plot for $Na^+ \rightleftharpoons NH_4^+$ exchange versus equivalent fraction of NH_4^+ in the zeolite phase. Points shown as -●- are not considered in the least-square fit of the straight line.

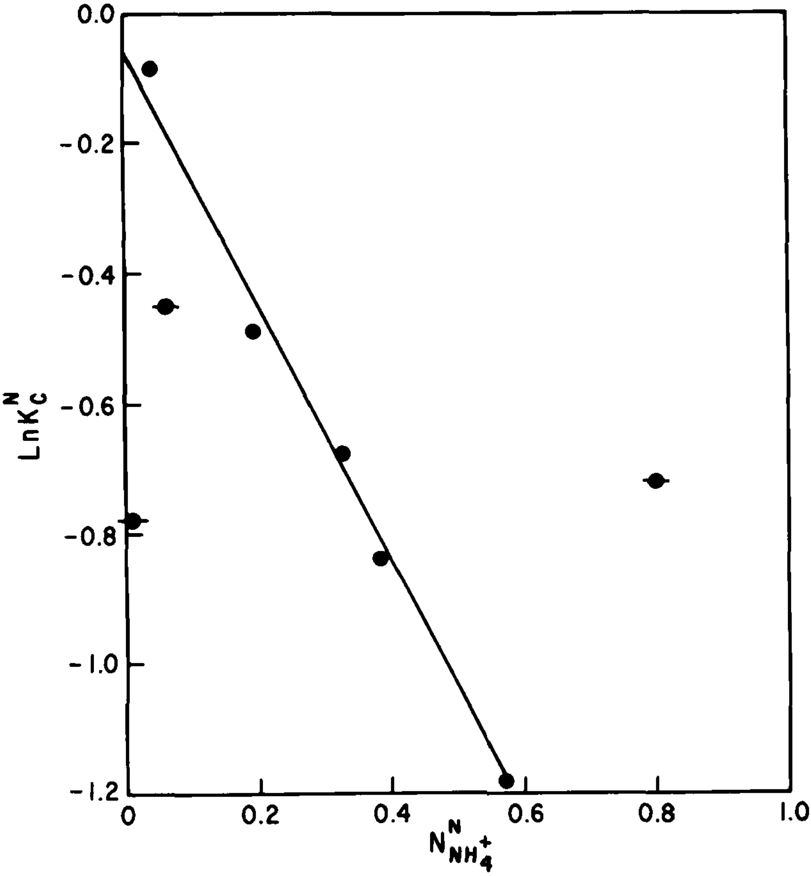

FIG. 7. Normalized Kielland plot for $K^+ \rightleftharpoons NH_4^+$ exchange against equivalent fraction of NH_4^+ in the zeolite phase. Points shown as -●- are not considered in the least-square fit of the straight line.

TABLE 2
Thermodynamic Data for Exchanges $Na^+ \rightleftharpoons NH_4^+$, $K^+ \rightleftharpoons NH_4^+$, and $Ca^{2+} \rightleftharpoons 2NH_4^+$ at 298 K

System	K_a at 298 K	ΔG (kJ/equiv)
NH_4^+-Na^+	5.21	−4.088
NH_4^+-K^+	0.85	+0.413
NH_4^+-Ca^{2+}	145.62	−6.17

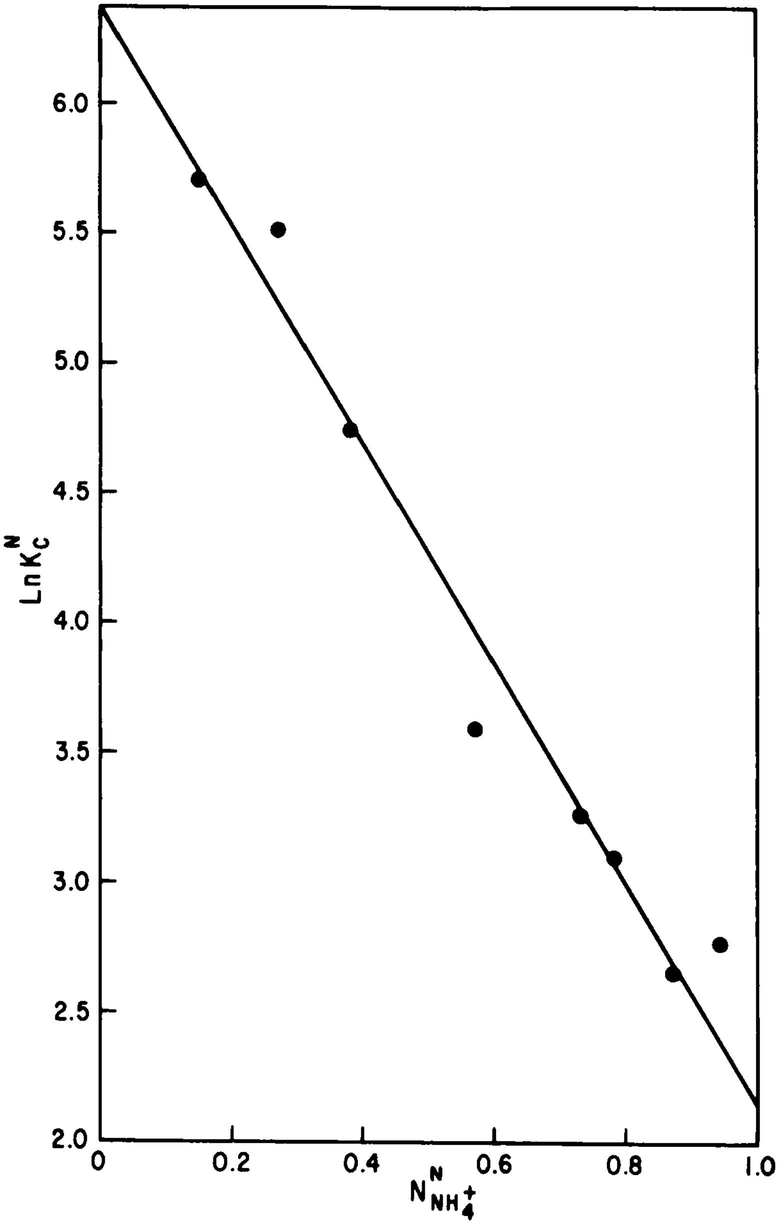

FIG. 8. Normalized Kielland plot for $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchange as a function of NH_4^+ in zeolite phase.

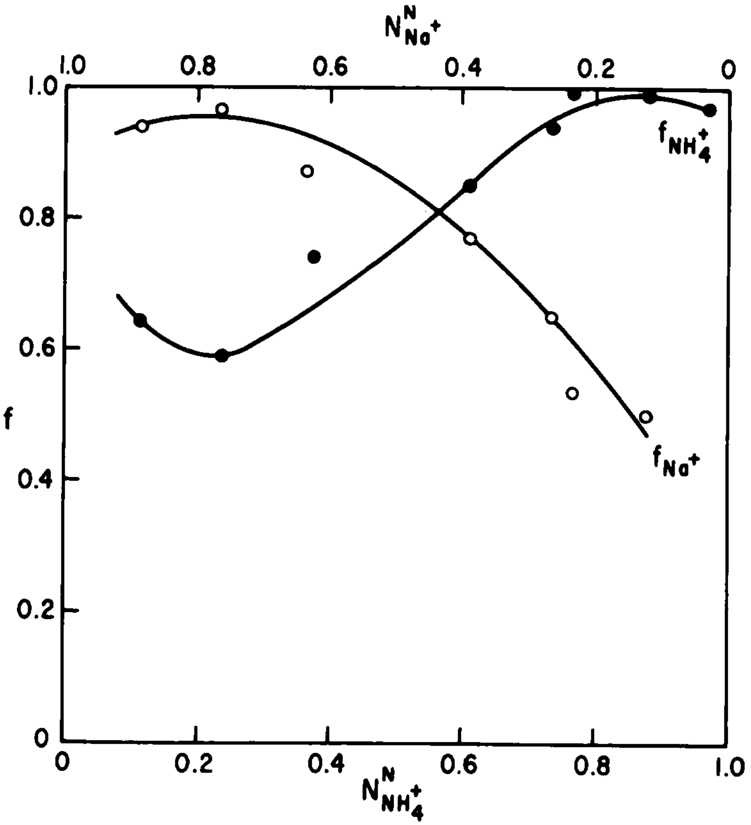

FIG. 9. Activity coefficients of ions in zeolite versus equivalent fraction of NH_4^+ in zeolite for $Na^+ \rightleftharpoons NH_4^+$ exchange.

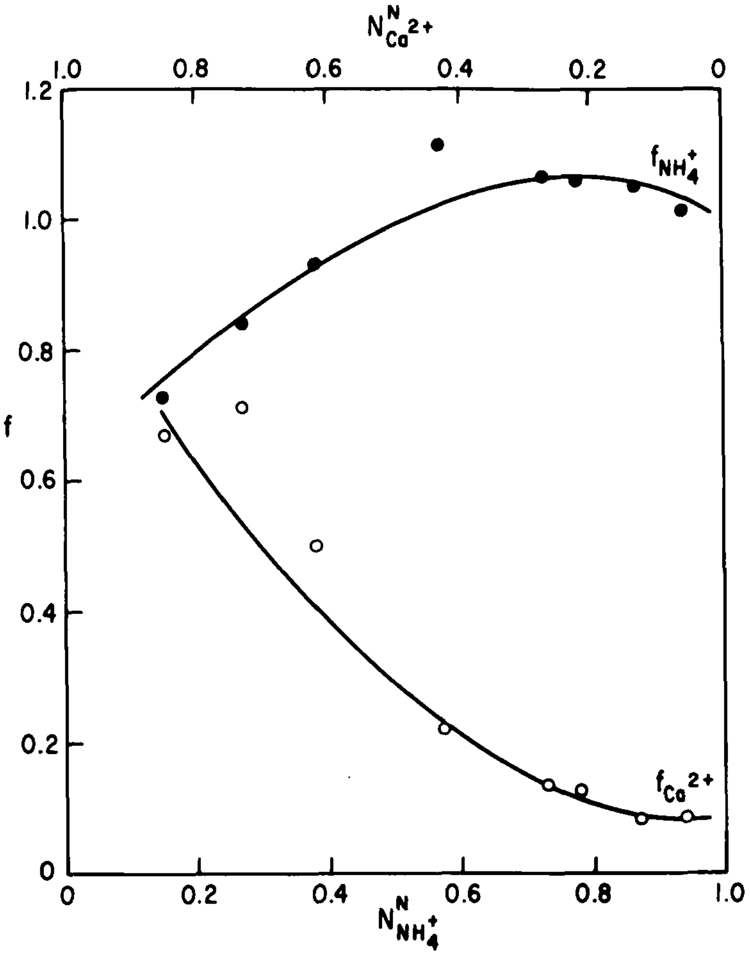

FIG. 10. Activity coefficients of ions in zeolite versus equivalent fraction of NH_4^+ in zeolite for $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchange.

CONCLUSIONS

Despite the observed partial exchange levels, clinoptilolite shows a very high preference for the ammonium ion over sodium and calcium ions. The higher selectivity of clinoptilolite for the potassium ion over the ammonium ion indicates the strong preference of this zeolite for this ion

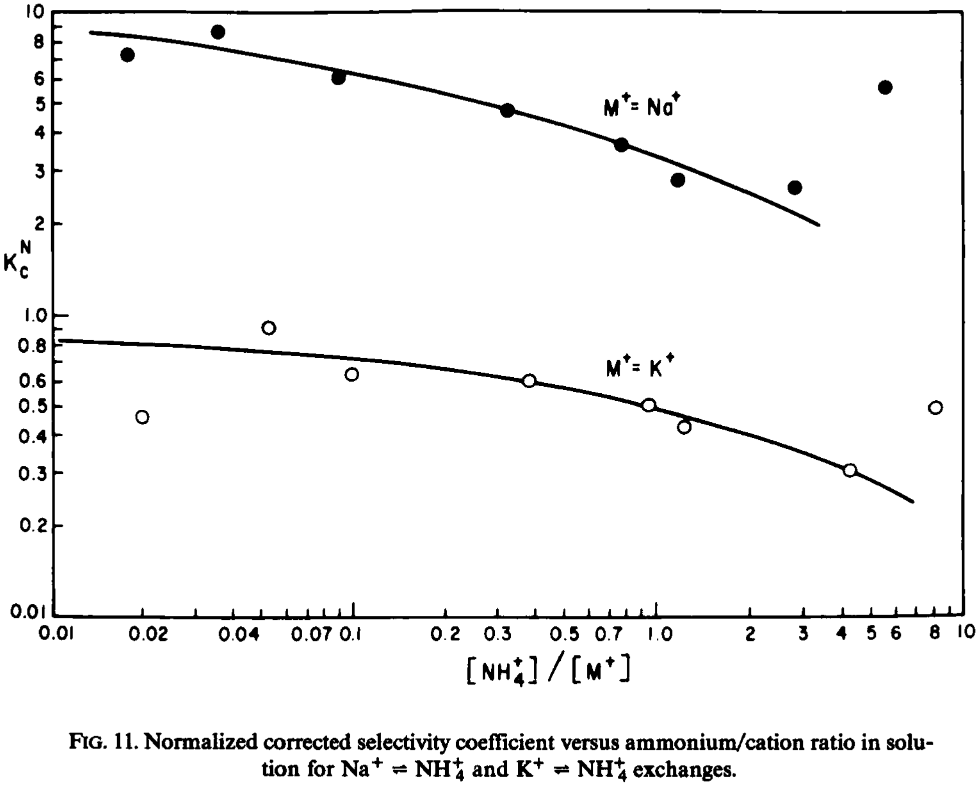

FIG. 11. Normalized corrected selectivity coefficient versus ammonium/cation ratio in solution for $Na^+ \rightleftharpoons NH_4^+$ and $K^+ \rightleftharpoons NH_4^+$ exchanges.

since the potassium ion originally present in the clinoptilolite could not be removed in the preparation of homoionic forms despite the stringent conditions used.

The thermodynamic affinity sequence for the exchanges studied on clinoptilolite was determined as $K^+ > NH_4^+ > Na^+ > Ca^{2+}$. This sequence confirms previous investigations (*9, 10*).

Thermodynamic data for the $Na^+ \rightleftharpoons NH_4^+$ exchange are compared with some data available in the literature (Table 3). Table 3 shows that the values obtained in this study agree closely with those of Townsend et al. (*15*) which were carried out at the same temperature (298 K). The value of Barrer et al. (*37*) which was determined at a higher temperature of 333 K and the value of Howery et al. (*40*) at 303 K seem to be a little larger than the free energy of exchange determined in this work.

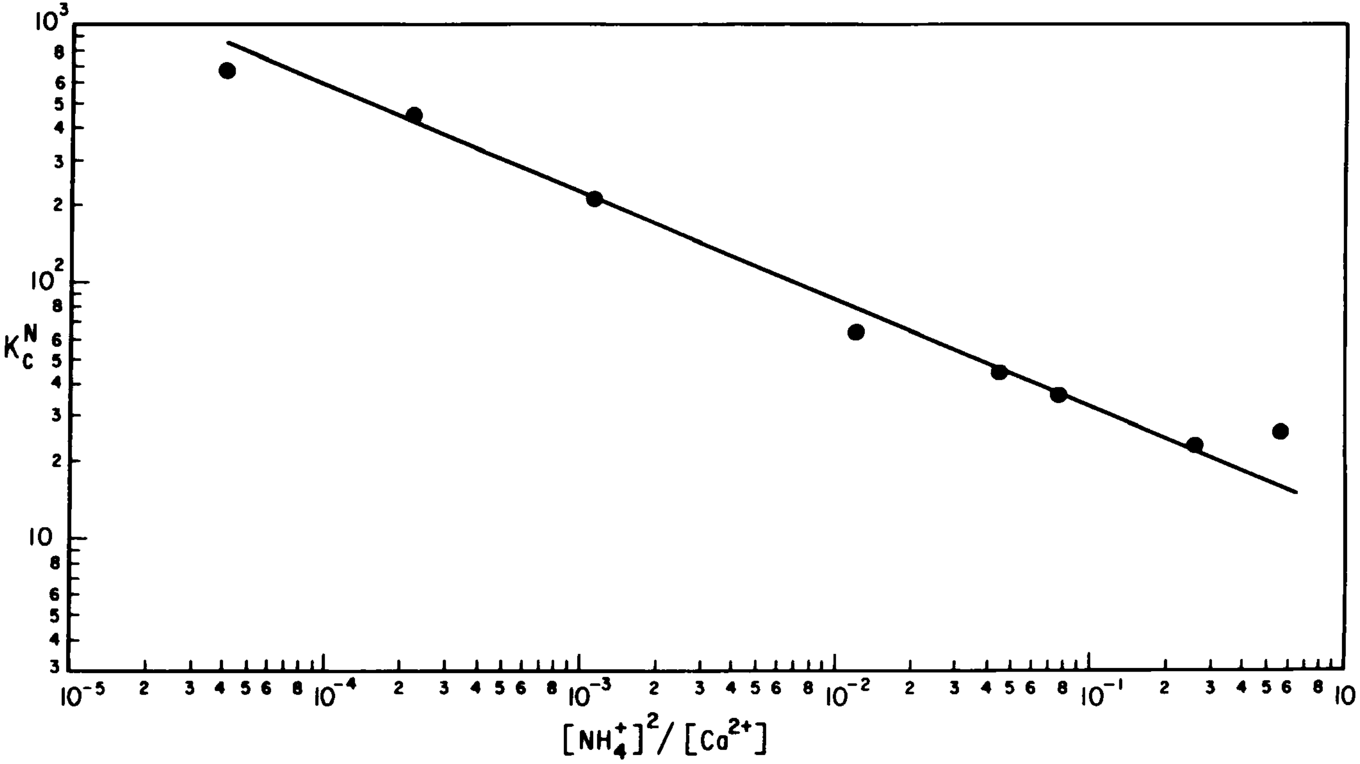

FIG. 12. Normalized corrected selectivity coefficient versus $[NH^+{}_4]^2/[Ca^{2+}]$ in solution for $Ca^{2+} \rightleftharpoons 2NH_4^+$ exchange.

TABLE 3
Comparison of Thermodynamic Data for $Na^+ \rightleftharpoons NH_4^+$ Exchange

Work	Temperature (°K)	K_a	$\Delta G°$ (kJ/equiv)
Townsend et al. (*15*)	298	5.12	−4.03
Barrer et al. (*37*)	333	7.9	−5.75
Howery et al. (*40*)	303	—	−5.39
This work	298	5.21	−4.08

REFERENCES

1. *Process Design Manual for Nitrogen Control*, U.S. Enviromental Protection Agency, Technology Transfer, October 1975.
2. J. R. McLaren and G. J. Farquhar, *J. Environ. Div., Am. Soc. Civ. Eng., 99*, 429 (1973).
3. F. A. Mumpton, in *Natural Zeolites Occurrence Properties and Use* (L. B. Sand and F. A. Mumpton, eds.), Pergamon, New York, 1976, p. 449.
4. L. Liberti, B. Gianfranco, D. Petruzzelli, and R. Passino, *Water Res., 15*, 337 (1981).
5. M. Semmens, A. C. Booth, and G. W. Tauxe, *J. Environ. Eng. Div., Am. Soc. Civ. Eng., 104*, 231 (1978).
6. M. Semmens, J. Klieve, D. Schonbrich, and G. W. Tauxe, *Water Res., 15*, 655 (1981).
7. S. E. Jorgensen, O. Libor, K. L. Graber, and K. Barkacs, *Ibid., 10*, 213 (1976).
8. M. Suzuki and K. Ha, *J. Chem. Eng. Jpn., 17*, 138 (1984).
9. L. L. Ames, in *Proceedings of the 13th Pacific Northwest Industrial Waste Conference*, Washington State University, Pullman, Washington, 1967, p. 135.
10. B. W. Mercer, L. L. Ames, C. J., Touhill, W. J. Van Slyke, and R. B. Dean, *J. Environ. Eng. Div., Am. Soc. Civ. Eng., 99*, 429 (1970).
11. S. E. Jorgensen, O. Libor, K. Barkacs, and L. Kunal, *Water Res., 13*, 159 (1979).
12. J. H. Koon and W. J. Kaufman, *J. Water Pollut. Control Fed., 47*, 448 (1975).
13. J. R. Klieve and M. J. Semmens, *Water Res., 14*, 161 (1980).
14. K. Koyama and Y. Takeuchi, *Z. Kristall, 145*, 216 (1977).
15. R. P. Townsend and M. Loizidou, *Zeolites, 4*, 191 (1984).
16. M. Loizidou and R. P. Townsend, *Ibid., 7*, 153 (1987).
17. H. Yücel and A. Culfaz, in *Occurrence, Properties and Utilization of Natural Zeolites* (D. Kallo and H. S. Sherry, eds.), Akademiai, Budapest, 1988, p. 99.
18. A. J. Easton, *Chemical Analysis of Silicate Rocks*, Elsevier, New York, 1972.
19. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1976, p. 699.
20. H. S. Sherry, in *Ion Exchange, A Series of Advances*, Vol. 2 (J. A. Marinsky, ed.), Dekker, New York, 1969.
21. R. M. Barrer and J. Klinowski, *J. Chem. Soc., Faraday Trans. I, 68*, 73 (1972).
22. R. M. Barrer and J. Klinowski, *J. Chem. Soc., Faraday Trans. II, 69*, 1669 (1973).
23. E. Helffreich, *Ion Exchange*, McGraw-Hill, New York, 1962, p. 134.
24. R. P. Townsend, in *New Developments in Zeolite Science and Technology* (Y. Murakami, A. Ijima, and J. W. Ward, eds.), Elsevier, Amsterdam, 1986, p. 273.
25. A. Dyer, H. Enamy, and R. P. Townsend, *Sep. Sci. Technol., 16*, 173 (1984).
26. E. Glueckauf, *Nature, 163*, 414 (1949).
27. G. L. Gaines and H. G. Thomas, *J. Chem. Phys., 21*, 714 (1953).

28. I. M. Galabova, *Z. Naturforsch, 34a,* 248 (1979).
29. G. Klopp, J. Süto, and I. Szebenyi, in *Proceedings of the Fifth International Conference on Zeolites* (L. V. C. Rees, ed.), Heyden, 1980, p. 841.
30. D. L. Bish, *Clays Clay Miner., 32,* 444 (1984).
31. A. Araya and A. Dyer, *J. Inorg. Nucl. Chem., 43,* 589 (1981).
32. A. Araya and A. Dyer, *Ibid., 43,* 595 (1981).
33. J. Kielland, *J. Soc. Chem. Ind., 54,* 232T (1935).
34. H. S. Sherry, *J. Phys. Chem., 70,* 1158 (1966).
35. R. M. Barrer and W. M. Meier, *Trans. Faraday Soc.,* 54, 1074 (1958).
36. R. M. Barrer and W. M. Meier, *Ibid., 55,* 130 (1956).
37. R. M. Barrer, R. Papadopoulos, and L. V. C. Rees, *J. Inorg. Nucl. Chem., 29,* 2047 (1977).
38. R. M. Barrer and R. P. Townsend, *J. Chem. Soc., Faraday Trans. I, 74,* 745 (1978).
39. R. M. Barrer and J. Klinowski, *Philos. Trans. R. Soc. London, Ser. A, 285,* 637 (1977).
40. D. G. Howery and H. C. Thomas, *J. Phys. Chem.* *69*(2), 531 (1965).

Received by editor December 5, 1988