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Am^{3+} and Eu^{3+}/alkali cation exchange selectivity on mordenite and zeolite L

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Am^{3+} and Eu^{3+}/alkali cation exchange selectivity was studied on mordenite and zeolite L at 25 to 60 °C to examine the effect of their openings of ion-exchange sites. The corrected selectivity coefficient at the infinitesimal exchange increased in the order of Eu^{3+} < Am^{3+} on mordenite and Am^{3+} < Eu^{3+} on zeolite L. The selectivity reversal did not reflect the effect of the ionic form, but reflected the dimension of the opening of the ion-exchange site and charge of trivalent cations, since the crystal ionic radii of alkali cations were much smaller than the openings of these zeolites (7–8 Å).

I. INTRODUCTION

A systematic evaluation method of the ion-exchange process on zeolites and other inorganic materials has been developed on a basis of the corrected selectivity coefficient.[1–6] A reversible ion exchange occurs at normal conditions where hydrolysis and precipitation reactions do not take place. The ion-exchange process can be well described by the selectivity plot, i.e., plot of the corrected selectivity coefficient versus the charge fraction in the exchanger ($\overline{X}_M$), where the theoretical or maximum ion-exchange capacity is used for the calculation of $\overline{X}_M$. However, even at present, ion-exchange processes are often evaluated in terms of distribution coefficients, isotherms, and Langmuir plots. The selectivity plot allows (i) evaluation of distribution coefficient as a function of ion concentration in aqueous phase of the exchanging metal ions and (ii) ion-exchange isotherm at various salt concentrations.[2,3] Hence, time-consuming work for determination of distribution coefficients (K_d) at different concentrations can be avoided. Thus, the selectivity plot takes a central role for prediction and interpretation of the ion-exchange process. Crystallographic data coupled with the selectivity plot will help understand the selectivity in inorganic ion-exchange materials. Recently, micro x-ray analysis methods, e.g., EXAFS and XANES, have been used for understanding the local environment of the exchanged species.[7,8]

Cation selectivity of inorganic ion-exchange materials is closely related with the dimension of channel for entering ions.[9–14] It can be exemplified by a number of zeolites. Zeolite L in the K$^+$ form with the unit cell composition of K$_9$[(AlO$_2$)$_9$(SiO$_2$)$_{27}$] · 22H$_2$O gives a theoretical ion exchange capacity (IEC) of 3.10 mequiv/g. The main channel consists of the 12 rings with the opening of 7.1–7.8 Å. The K$^+$ ions are located at four different crystallographic sites, and exchangeable K$^+$ ion is considered to reside on the wall of the main channel.[15] Synthetic mordenite has a unit cell composition of Na$_8$[(AlO$_2$)$_8$(SiO$_2$)$_{40}$] · 24H$_2$O with the channel opening of 6.7–7.0 Å and a theoretical IEC of 2.29 mequiv/g. The former has a ca. 1-Å wider opening available for cation exchange.

Ion exchange of actinides and lanthanides has been described in terms of K_d values on titanium antimonate cation exchangers,[16,17] zeolites,[18,19] and clays.[20,21] The K_d values on these aluminosilicates have been determined in solutions containing H$^+$ ions, and hence the M^{3+}–M$^+$–H$^+$ exchange is involved in these determinations. These complicated ternary exchange systems have not yet been studied analytically. It will be important first to basically understand the feature of ion exchange on these materials.

The objective of the present paper is to study the effect of the channel dimension on Am^{3+} and Eu^{3+}/alkali cation exchange on mordenite and zeolite L in terms of the selectivity plot and the Langmuir plot.

II. EXPERIMENTAL

A. Zeolites and chemicals

Mordenite in the Na$^+$ form (Zeolon 900Na, 100–200 mesh) and zeolite L in the K$^+$ form (TSZ-500, 100–200 mesh) were supplied by Norton (PQ Corp., Philadelphia, PA) and Toso (Minato-ku, Tokyo, Japan), respectively. These were used without further processing. The carrier free ^{241}Am was supplied by Amersham International (Amersham, Pharmacia Biotech, Chalfont, UK). Other chemicals were of analytical grade and supplied by Kanto Chemical Co., Inc.

B. Distribution coefficient (K_d) and selectivity

1. K_d determination of Am^{3+} and Eu^{3+}

A portion of zeolite (0.100 g) was equilibrated at 25–60 °C, with an aliquot of the sample solution (10.0 cm^3) of 0.1–0.5 N with respect to KNO$_3$ or NaNO$_3$. The initial concentrations of Am^{3+} and Eu^{3+} were 2.1×10^{-9} and 1×10^{-4} M, respectively. A period of 1 week was required to attain the steady-state concentration in the supernatant solution. After the equilibration, the supernatant solution was separated and analyzed for Eu^{3+} using a Seiko Instruments ICP-AES model SPS15000 (Mihama-ka, Chiba, Japan) and for Am^{3+} using a well-type scintillation counter. The K_d value was calculated using the following equation:

$$K_d = \frac{[\overline{M^{3+}}]}{[M^{3+}]} \ (\text{cm}^3/\text{g}) \quad . \tag{1}$$

Here $[\overline{M^{3+}}]$ and $[M^{3+}]$ denote the amount of metal ions exchanged in mequiv/g and the equilibrium concentration of metal ions in mequiv/cm^3, respectively.
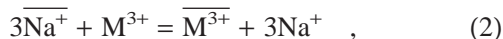
2. Selectivity

A portion of zeolite (0.100 g) was equilibrated at 25–60 °C, with an aliquot of the sample solution (10.0 cm^3) of 0.05 N with respect to Eu(NO$_3$)$_3$ and KNO$_3$ for zeolite L in the K$^+$ form or Eu(NO$_3$)$_3$ and NaNO$_3$ for mordenite in the Na$^+$ form. A period of 2 weeks was required to attain steady-state concentration in the supernatant solution. After the equilibration, the supernatant solution was separated and analyzed for Eu^{3+} as above. The adsorbed amounts were determined from the difference between the initial concentration and the equilibrated concentration.

III. RESULTS AND DISCUSSION

A. Formulations

The M^{3+}/Na$^+$ exchange reactions on zeolites in the Na$^+$ form

$$3\overline{\text{Na}^+} + \text{M}^{3+} = \overline{\text{M}^{3+}} + 3\text{Na}^+ \quad , \tag{2}$$

can be uniquely defined by the thermodynamic equilibrium constant, K. Using the conventional notations for solution and solid phases, it is given by[1,11,22]

$$K = \frac{\overline{X}_M [\text{Na}^+]^3 \gamma_{Na}^3 f_M}{\overline{X}_{Na}^3 [\text{M}^{3+}] \gamma_M f_{Na}^3} \tag{3}$$

$$= K_{Na}^M \frac{f_M}{f_{Na}^3} \quad ,$$

where K_{Na}^M refers to the corrected selectivity coefficient:

$$K_{Na}^M = \frac{\overline{X}_M X_{Na}^3}{\overline{X}_{Na}^3 X_M} \frac{\gamma_{Na}^3}{\gamma_M} 3c_t^2 \quad . \tag{4}$$

Here $\overline{X}_i$ is the charge fraction of ion i in the exchanger, X_i is the charge fraction of ion i in solution, f_i and γ_i are their activity coefficients in exchanger and solution, respectively, and c_t is the total charge concentration in solution, equating $3[\text{M}^{3+}] + [\text{Na}^+]$. The activity coefficients in the nitrate media were calculated with the mean salt method using the following relation:[23]

$$\frac{\gamma_{Na}^3}{\gamma_M} = \frac{\gamma_{Na}^3 \gamma_{NO_3}^3}{\gamma_M \gamma_{NO_3}^3} = \frac{\gamma_{\pm NaNO_3}^6}{\gamma_{\pm M(NO_3)_3}^4} \quad . \tag{5}$$

The mean activity coefficient of La(NO$_3$)$_3$ was used for that of each single electrolyte Am(NO$_3$)$_3$ and Eu(NO$_3$)$_3$.[24] The mean activity coefficient of Eu(NO$_3$)$_3$ in the presence of NaNO$_3$ and that of NaNO$_3$ in the presence of Eu(NO$_3$)$_3$ were calculated using the following Glueckauf's relations:[3,25]

$$\log \gamma_{(NaNO_3)_3}^{Eu(NO_3)_3} = \log \gamma^{Eu(NO_3)_3} + \frac{[\text{Na}^+]}{4\mu} \left(3 \log \gamma^{NaNO_3} \right.$$
$$\left. + \frac{1.5}{1 + \mu^{-1/2}} \right) \quad , \tag{6}$$

$$\log \gamma_{(Eu(NO_3)_3)}^{NaNO_3} = \log \gamma^{NaNO_3} + \frac{[\text{Eu}^{3+}]}{4\mu} \left(18 \log \gamma^{NaNO_3} \right.$$
$$\left. - 8 \log \gamma^{Eu(NO_3)_3} - \frac{2}{1 + \mu^{-1/2}} \right) \quad , \tag{7}$$

where μ is the ionic strength given by $(1/2)\Sigma z_i^2 m_i$, in which z_i and m_i are the formal charge of ions and molality of ions in the solution phase. Temperature dependence was taken into consideration using the Debye–Hückel equation.

The selectivity plot (plot of $\log K_{Na}^M$ versus $\overline{X}_M$) was represented by the following polynomial equation:[3,4]

$$\log K_{Na}^M = \log(K_{Na}^M)_{X_M, \overline{x}_{M} \to 0} + \sum_{m=1}^{n} (m+1) C_m \overline{X}_M^m \quad , \tag{8}$$

where C_m is the coefficient of the polynomial.

A very low concentration of Am^{3+} can be used due to limitation of our experimental facility. In this situation, one can evaluate the corrected selectivity coefficient at infinitesimal exchange, $(K_{Na}^M)_{X_M, \overline{x}_{M} \to 0}$, by using the distribution coefficient, K_d, at the carrier-free tracer experiment.[3]

$$(K_{Na}^M)_{X_M, \overline{x}_{M} \to 0} = \frac{3(c_t)^3}{C_t} \frac{\gamma_{Na}^3}{\gamma_M} (K_d)_{X_M, \overline{x}_{M} \to 0} \quad , \tag{9}$$

where C_t is the total ion-exchange capacity in mequiv/g. The logarithm of both sides is taken to get the following equation, because the total charge concentration, c_t, equals [NaNO$_3$] in case of very low M^{3+} concentration.[11]

$$\log K_d = \log C_t (K_{Na}^{M})_{X_M, \bar{x}_{M \to 0}} \gamma_M / 3 \gamma_{Na}^3 - 3 \log [\text{NaNO}_3] \quad . \tag{10}$$

Hence, plot of $\log K_d$ versus $\log[\text{NaNO}_3]$ will show a straight line with a slope of -3. As long as the activity coefficient does not depend on the total charge concentration, the first term on the right-hand side may be approximated as a constant at any total charge concentration of electrolyte. This relation has been often used for evidence of stoichiometric ion exchange at low concentration.

The hypothetical thermodynamic constant when the C_m values are zero can be determined by integrating from $\bar{X}_M = 0$ to 1. This may be used as an index of the ion-exchange selectivity for the hypothetical exchange with the least steric hindrance.[26]

$$\ln K_{\text{hypo}} = -2 + \ln(K_{Na}^{M})_{X_M, \bar{x}_{M \to 0}} \quad , \tag{11}$$

$$\Delta G^{\circ}_{\text{hypo}} = -RT \ln K_{\text{hypo}} \quad . \tag{12}$$

This equation can be combined with van't Hoff's equation to determine the standard enthalpy change, $\Delta H^{\circ}_{\text{hypo}}$, and the standard entropy change, $\Delta S^{\circ}_{\text{hypo}}$.
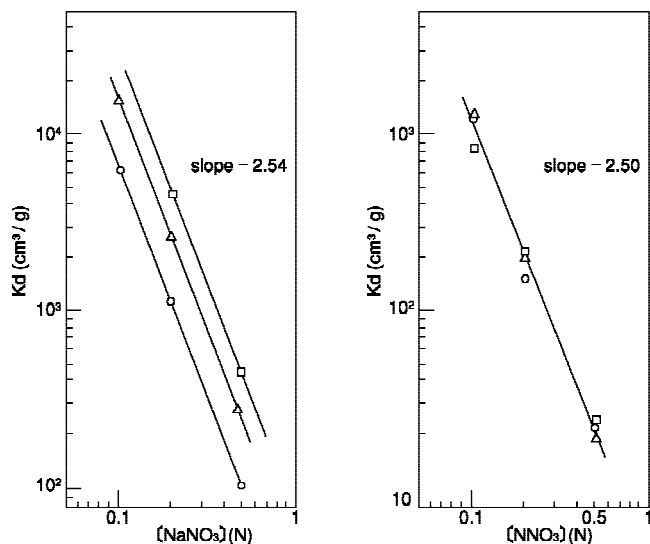
B. Stoichiometry of ion exchange in low metal concentration

Plot of $\log K_d$ of trivalent cations versus $\log [\text{NaNO}_3]$ or $\log [\text{KNO}_3]$ showed a straight line with slope of -2.5 for Am^{3+}/Na$^+$ exchange on mordenite and Am^{3+}/K$^+$ exchange on zeolite L at reaction temperatures of 25, 45, and 60 °C (Fig. 1). Temperature dependence of K_d value is much larger on mordenite than zeolite L. It will be due to narrower opening of the ion-exchange site on mordenite. Even though zeolite L in the Na$^+$ form and mordenite in the K$^+$ form were used in the K_d determination, similar results will be observed because the dimension of the opening is sufficiently large in comparison with the crystal ionic radius of Na$^+$ and K$^+$ ions.[27]

The K_d values of Eu^{3+}/K$^+$ and Eu^{3+}/Na$^+$ exchanges were determined on zeolite L and mordenite, respectively, in the initial concentration of 0.001 N (N = mequiv/cm^3) Eu^{3+} at 25 °C (Fig. 2). The slopes were -2.11 and -2.45, respectively. The larger deviation from the theoretical slope observed on the zeolite L will be ascribed to (i) insufficient correction of activity coefficients in the total charge concentration range used for K_d determination and (ii) large K_d dependence on the metal ion concentration. This extent of
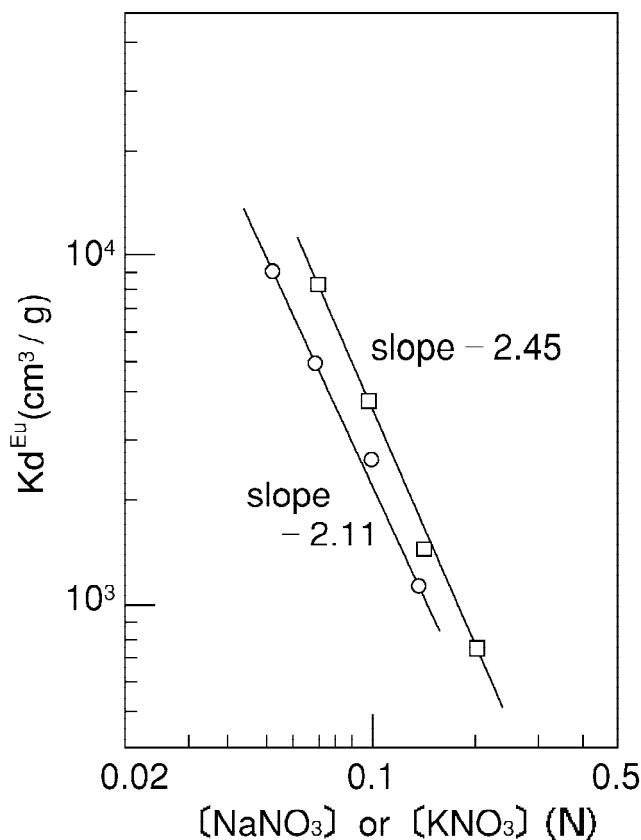

FIG. 1. Plots of K_d versus [NaNO$_3$] (left) or [KNO$_3$] (right) in logarithmic scale for Am^{3+}/Na$^+$ on mordenite in the Na$^+$ form and Am^{3+}/K$^+$ exchange on zeolite L in the K$^+$ form, respectively. Equilibration temperature: (○) 25 °C, (△) 45 °C, and (□) 60 °C.

FIG. 2. Plots of K_d versus [NaNO$_3$] (□) or [KNO$_3$] (○) in logarithmic scale for Eu^{3+}/Na$^+$ on mordenite in the Na$^+$ form and Eu^{3+}/K$^+$ exchange on zeolite L in the K$^+$ form, respectively, at 25 °C.

deviation has been often found in other inorganic ion exchange materials.[2,16,28,29] These considerations indicate that Eu^{3+} or Am^{3+}/alkali cation exchanges on these two zeolites can be described by the ion exchange reaction shown by Eq. (1).

C. Langmuir plots

The Langmuir equation has been used extensively for the description of the adsorption phenomena of molecules and ions,[19,30,31] as well as the ion-exchange isotherm.[32,33] It is given in the familiar form.

$$Q_M = \frac{K_L Q_{max} C_M}{1 + K_L C_M} \qquad \frac{1}{Q_M} = \frac{1}{K_L Q_{max} C_M} + \frac{1}{Q_{max}} \quad . \tag{13}$$

For a one-adsorbate system described by Eq. (2), where C_M and Q_M are the equilibrium concentrations of adsorbate, M, in solid and in solution, respectively, Q_{max} is the maximum value of Q_M and K_L is called the Langmuir constant which is a fitting parameter. The chemical meaning of K_L is ambiguous in the ion-exchange process of inorganic ion exchangers, because the process can occur not only on the surface but also in the crystal lattice. This expression of adsorption can be derived in the ion-exchange process by rearranging the corrected selectivity coefficient, Eq. (4).

$$\frac{1}{Q_M} = \frac{c_t}{m C_t C_M} + \frac{m-1}{m C_t} \qquad \frac{C_M}{Q_M} = \frac{c_t}{m C_t} + \frac{m-1}{m C_t} C_M \quad , \tag{14}$$

where C_t and c_t are the total charge concentration in solid (i.e., so-called total ion-exchange capacity) and in solution, and

$$m = K_{Na}^{M} \frac{\gamma_M}{\gamma_{Na}^{3} 3 c_t^{2}} \quad . \tag{15}$$

The m value is nearly constant in limited extent of exchange, because the corrected selectivity coefficient and the ratio of the activity coefficients are constant for small X_M and $\overline{X}_M$ values.[26] Thus, a plot of C_M/Q_M versus C_M will show a straight line as long as the above conditions are satisfied. When the m value is sufficiently large, comparison of Eq. (14) with Eq. (13) gives

$$C_t = Q_{max} \qquad K_L = K_{Na}^{M} \frac{\gamma_M}{\gamma_{Na}^{3} 3 c_t^{3}} \quad . \tag{16}$$

Therefore, in the ion-exchange process, the Langmuir constant K_L depends on the total charge concentration c_t of solution. The change of K_L with the c_t value cannot be predicted, and hence, one cannot evaluate the Langmuir

plot in a different c_t value. Figures 3 and 4 show the Langmuir plots for Eu^{3+}/K$^+$ and Eu^{3+}/Na$^+$ exchanges on zeolite L in the K$^+$ form and mordenite in the Na$^+$ form, respectively, at 25, 45, and 60 °C. The C_{Eu} and Q_{Eu} values denote equilibrium concentrations of Eu^{3+} in the solution and solid phases, respectively. The former exchange system indicated concave upper curves, and the latter showed more linear relation. These curves can be represented by the second-order polynomial

$$Y = a + bX + cX^2 \quad , \tag{17}$$

where Y and X are $C_{Eu}/Q_{Eu} \times 1000$ and $C_{Eu} \times 1000$, respectively. The coefficients, a, b, and c, are represented in Table I. All smaller uptake points fell around the origin and could not be differentiated from each other. By extrapolation of these points, one should have a maximum uptake or theoretical ion-exchange capacity according to the Langmuir plot. But it is difficult to precisely locate it from these figures and to reveal profile of exchange in a small fractional exchange. These difficulties can be eliminated using the selectivity plot, as described below.

D. Selectivity plot for Eu^{3+}/alkali cation exchanges

The corrected selectivity coefficient for Eu^{3+}/K$^+$ exchange on the zeolite L decreased about linearly with the charge fraction in exchanger, $\overline{X}_{Eu}$, irrespective of temperature (Fig. 5). It will be due to uniform opening of the ion-exchange site. With increase in temperature, increase in selectivity was observed. With an increase in reaction temperature, the hydration shell will become small, causing an increase in the surface charge density of entering
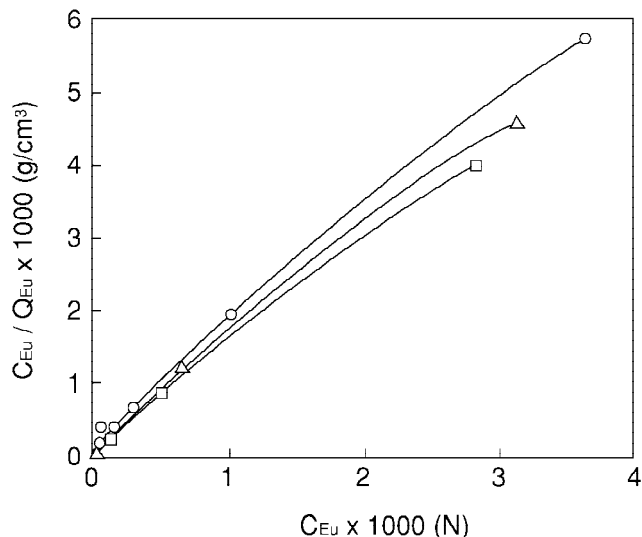

FIG. 3. Langmuir plot of Eu^{3+}/K$^+$ exchange on zeolite L in the K$^+$ form. Equilibration temperature: (○) 25 °C, (△) 45 °C, and (□) 60 °C. Total charge concentration: 0.05 N.

cation. It will increase the selectivity of Eu^{3+} due to enhancement of electrostatic interaction with the negatively charged framework in the ion-exchange site. The corrected selectivity coefficients in the reverse reaction at 45 °C were determined as a representative example. These agreed with that of the forward reaction. Thus, the reversibility of Eu^{3+}/K^{+} exchange was corroborated.

The corrected selectivity coefficient for Eu^{3+}/Na^{+} exchange on mordenite was determined, which is different from that on zeolite L (Fig. 6). Small change in the corrected selectivity coefficient was observed at the small fractional exchange, and then a steep drop of the K_{Na}^{M} took place in large fractional exchange ($\overline{X}_{Eu} > 0.2$). These results will be ascribed to stronger electrostatic repulsion between exchanged Eu^{3+} ions in smaller opening of the exchange site in mordenite. The atomic configuration and charge distribution in the ion-exchange cavity need to be elucidated for better understanding the change in the selectivity with the fractional exchange. The reversibility could be confirmed by determination of the corrected selectivity coefficient at 45 °C as a representative example. Therefore, these selectivity plots can be used for evaluation of thermodynamic quantities and separation parameters.
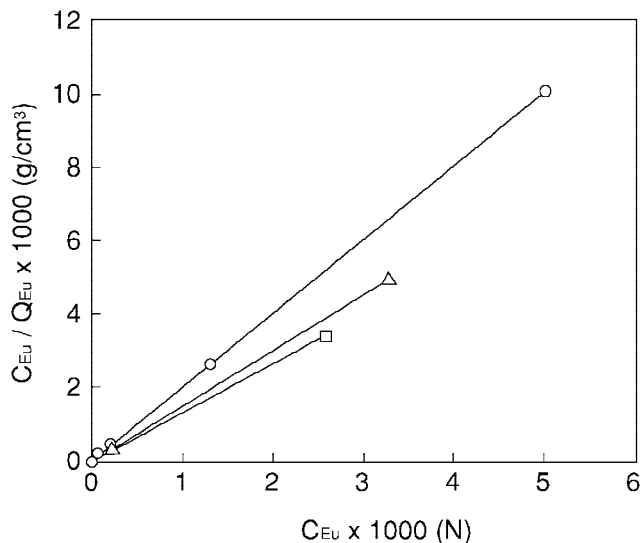

FIG. 4. Langmuir plot of Eu^{3+}/K^{+} exchange on mordenite in the Na^{+} form. Equilibration temperature: (○) 25 °C, (△) 45 °C, and (□) 60 °C. Total charge concentration: 0.05 N.

These plots were used for evaluation of K_{d}^{Eu} values using Eq. (9) to compare them with that of Am^{3+} at 0.05 N KNO$_3$. The K_{d}^{Eu} values at an infinitesimal exchange are summarized in Table II. The K_{d}^{Eu} value evaluated using the selectivity plot at 25 °C is larger than the empirical value shown in Fig. 2. Generally speaking, the K_{d} value becomes large with decrease in the initial concentration of exchanging ion. In this exchange system, a maximum K_{d}^{Eu} value was not obtained even at 0.001 N Eu(NO$_3$)$_3$. It is due to dependence of K_{d}^{Eu} value on metal ion concentration. This feature of inorganic ion-exchange materials is clearly different from that of organic ion-exchange resin. The K_{d}^{Eu} values increased to 2.7×10^4 and 4.7×10^4 at 45 and 60 °C, respectively. Am^{3+} selectivity was lower than Eu^{3+}. Thus, the small separation factor, 0.5–0.13, was found. This level of selectivity may be useful for the binary separation. But it is not easy to separate a small amount of actinide from relatively concentrated lanthanide solution using zeolite L. Another adsorbent with much higher selectivity will be required.

Table III summarized separation parameters evaluated using the selectivity plot on mordenite in the Na^{+} form. The K_{d}^{Eu} value evaluated (3.08×10^4 cm^3/g at 25 °C) was larger than that determined at the initial concentration of 0.001 N (1.8×10^4 cm^3/g at 25 °C). However, the difference is small, because the concentration dependence of the corrected selectivity is small, as Fig. 6 shows. One will be able to precisely predict the K_{d} value if it is possible to evaluate more precisely activity coefficients of components in mixed electrolyte and to eliminate an error by an extrapolation to zero charge fraction. Even in the Am^{3+} concentration lower than 10^{-9} M, very large dependence of the corrected selectivity coefficient on the charge fraction has been reported on an inorganic ion exchanger.[17]

The van't Hoff plots for trivalent metal ions/alkali cation exchange showed that all other exchange reactions except Am^{3+}/K^{+} exchange on zeolite L were endothermic (Fig. 7). The slope of the plot gave approximately the same hypothetical standard enthalpy change, ca. +11 kJ/equiv (Table IV). The Am^{3+}/K^{+} exchange on zeolite L in the K^{+} form gave 0 kJ/equiv for the hypothetical standard enthalpy change. This means no temperature dependence for this exchange system. It may be ascribed to more open ion-exchange site in zeolite L.

TABLE I. Coefficients of Langmuir polynomials for Eu^{3+}/Na^{+} and Eu^{3+}/K^{+} exchanges on mordenite and zeolite L, respectively.

| Temp. (°C) | Coefficient (Eu^{3+}/Na^{+} exchange) | | | Coefficient (Eu^{3+}/K^{+} exchange) | | |
	a	*b*	*c*	*a*	*b*	*c*
25	0.07934	2.092	−0.01983	0.2334	1.848	−0.09295
45	0.01872	1.677	−0.05404	0.07079	1.859	−0.1347
60	0.01145	1.539	−0.07315	0.04676	1.801	−0.1490

The hypothetical standard entropy changes ΔS° for Eu^{3+}/K$^+$ and the Eu^{3+}/Na$^+$ exchange systems were about the same on these two zeolites. But the Am^{3+}/K$^+$ exchange is less selective than other exchanges, giving much smaller standard entropy change. These results will reflect the chemical environment around the exchange site. The dimension of opening is 6.7–7.0 Å for mordenite and 7.1–7.8 Å for zeolite L. The entering cation, Am^{3+}, is strongly hydrated with the large diameter of 9.04 Å. The hydration number is 13.[34] The hydration shell is liable to break at higher temperatures. As a result, it is exchanged more strongly with increase in temperatures favorable for dehydration of hydrated cations in both zeolites.

The Am^{3+} ion is more selectively exchanged by mordenite. It is ascribed to the more limited space, causing larger electrostatic attraction between the entering ions and the negatively charged zeolite framework. The change in hydration structure of Am^{3+} ions associated with ion exchange in zeolites could be estimated when the thermodynamic quantities about hydration of Am^{3+} are available, as has been reported for lanthanides.[35] More detailed study on the electronic structure around the ion-exchange site is required for quantitative inter-
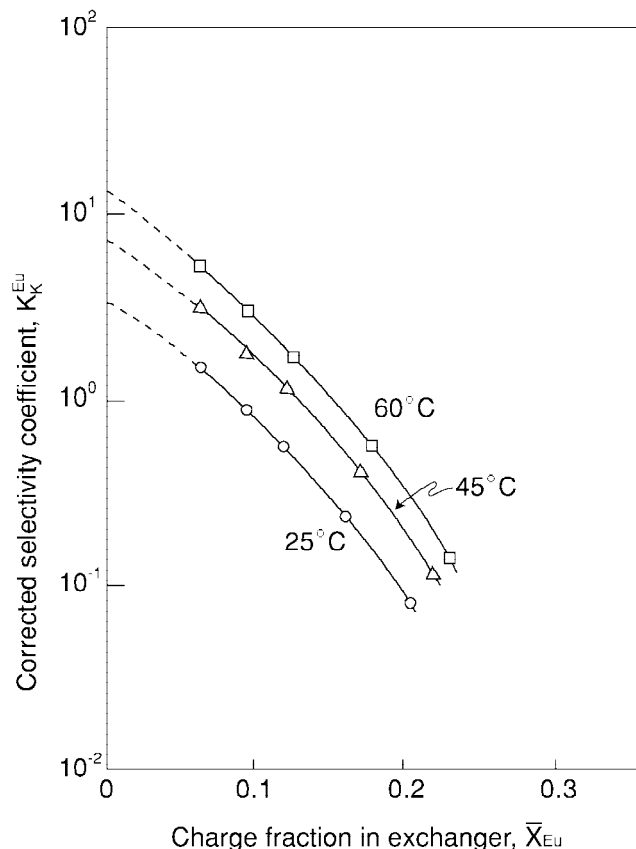
pretation of the ion selectivity. The DV-Xα method for evaluating the chemical environment in metal oxides will be an attractive procedure.[36] The local environment such as the charge distribution in metal oxides will be helpful to simulate the ion-exchange selectivity of inorganic solids. Prior to implementation of these, coordinates of cations in the ion exchange crystal need to be collected as a
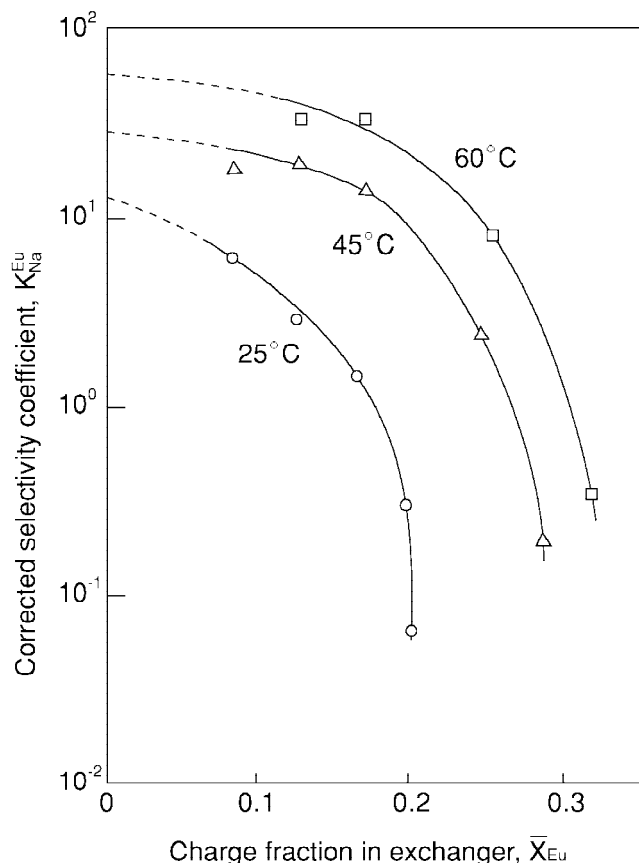

FIG. 6. Selectivity plot of Eu^{3+}/Na$^+$ exchange on mordenite in the Na$^+$ form. Equilibration temperature: ($\bigcirc$) 25 °C, ($\triangle$) 45 °C, and ($\square$) 60 °C.

TABLE II. Separation parameters for Eu^{3+} and Am^{3+} at infinitesimal exchange on zeolite L in the K$^+$ form.

Temp. (°C)	$(K_K^{Eu})_{\overline{X}_{Eu}\to 0}$	K_d^{Eu} (cm^3/g)	K_d^{Am} (cm^3/g)	α_{Eu}^{Am}
25	3.4	1.2×10^4	6.4×10^3	0.53
45	7.6	2.7×10^4	6.4×10^3	0.24
60	13.5	4.72×10^4	6.4×10^3	0.13

TABLE III. Separation parameters for Eu^{3+} and Am^{3+} at infinitesimal exchange on mordenite in the Na$^+$ form.

Temp. (°C)	$(K_{Na}^{Eu})_{\overline{X}_{Eu}\to 0}$	K_d^{Eu} (cm^3/g)	K_d^{Am} (cm^3/g)	α_{Eu}^{Am}
25	13.2	3.08×10^4	3.65×10^4	1.18
45	28.0	6.55×10^4	9.00×10^4	1.37
60	58.0	1.35×10^5	1.60×10^5	1.18

FIG. 5. Selectivity plot of Eu^{3+}/K$^+$ exchange on zeolite L in the K$^+$ form. Equilibration temperature: ($\bigcirc$) 25 °C, ($\triangle$) 45 °C, and ($\square$) 60 °C.

function of the fractional exchange, $\overline{X}_M$. In this respect, the selectivity plot described above will be the first step of the selectivity simulation. Unfortunately this way of research has not actively been carried out in zeolites and other ion-exchange materials. Furthermore, the pre-

cision of chemical analysis was often low to use for theoretical consideration of ion-exchange selectivity on inorganic solids.

IV. CONCLUSION

The hypothetical thermodynamic quantities (ΔY^o_{hypo}) for Eu^{3+} and Am^{3+}/Na^+, and Am^{3+} and Eu^{3+}/K^+ exchanges, the distribution coefficients (K_d) of Am^{3+} and Eu^{3+} on mordenite and zeolite L, and separation factors defined by the ratio of K_d values have been evaluated on a basis of the selectivity plot and tracer experiment. The selectivity plot and the evaluated K_d values of Am^{3+} and $Eu^{3+}/alkali$ cation exchange systems have been found to sensitively reflect the difference of the opening of cation-exchange sites for these two zeolites. The selectivity plot of $Eu^{3+}/alkali$ cation exchange systems will be used for evaluation of $Am^{3+}/alkali$ exchange systems if the selectivity plot for the latter exchange assumes the similar dependence on the fractional exchange, $\overline{X}_{Eu}$. This method can avoid the use of a large amount of α activity to evaluate the ion-exchange behavior in concentrated Am^{3+} solution. However, in this case, more precise information of the mean activity coefficients for each actinide and lanthanide ions is needed.

FIG. 7. van't Hoff's plot of Am³⁺ and Eu³⁺/alkali cation exchanges. Symbols for exchange system: (△) Eu³⁺/K⁺, (▲) Am³⁺/K⁺, (○) Eu³⁺/ Na⁺, and (●) Am³⁺/Na⁺.

TABLE IV. Hypothetical thermodynamic quantities for Eu³⁺ and Am³⁺/M⁺ exchanges on mordenite in the Na⁺ form and zeolite L in the K⁺ form at 298 K.

Zeolite	Exchange system	ΔG° hypo[a]	ΔH° hypo[a]	ΔS° hypo[b]
Mordenite	Eu³⁺/Na⁺	−1.66	+11.7	+44
	Am³⁺/Na⁺	−0.61	+11.7	+41
L-type	Eu³⁺/K⁺	−0.64	+10.9	+38
	Am³⁺/K⁺	+1.15	0	+3.8

[a]kJ/equiv.
[b]J/(K equiv).

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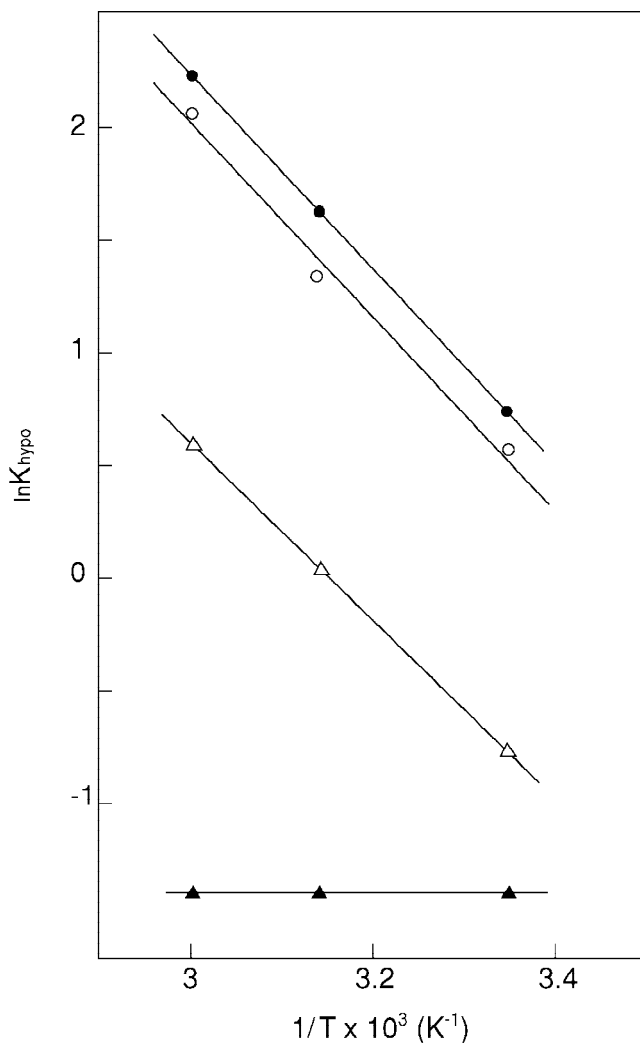15. D.W. Breck, *Zeolite Molecular Sieves* (Robert E. Krieger Publishing Co., Malabar, FL, 1974), p. 156.

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