Cation-Exchange Selectivity for K^+, Mg^{2+}, and Ca^{2+} Ions on Sodium-Substituted Taeniolite

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The cation-exchange selectivity for K^+, Mg^{2+}, and Ca^{2+} ions on Na-substituted taeniolite, which is one of the fluormicas with swelling property, has been investigated. The distribution coefficient for each cation was numerically estimated at infinitesimal loading based on the Kielland plots for the $Na^+ \rightarrow K^+$, $2Na^+ \rightarrow Mg^{2+}$, and $2Na^+ \rightarrow Ca^{2+}$ exchanges. The separation factors for K^+–Mg^{2+} and K^+–Ca^{2+} pairs, which are the ratios of the distribution coefficients, were found to be 9.1×10^7 and 1.4×10^8, respectively. The high K^+ ion separation effect on Na–substituted taeniolite was also supported by the experimental results made in the presence of Na^+, Mg^{2+}, and/or Ca^{2+} ions. Na-substituted taeniolite was, therefore, shown to be useful for the separation and immobilization of K^+ ions.

Introduction

Na-substituted taeniolite (NaT), which is one of the fluormicas, is swellable with water, while taeniolite [$KMg_2LiSi_4O_{10}F_2$] is nonswellable.[1] Their structures are built by the stacking of the complex layer made by two SiO_4 tetrahedral sheets and one $(Mg,Li)(O,F)_6$ octahedral sheet.[2] The stacked complex layers are connected through interlayer sheets made by exchangeable Na^+ ions and water molecules in Na-substituted taeniolite (NaT). The chemical composition of NaT is ideally $NaMg_2LiSi_4O_{10}F_2{\cdot}2H_2O$, and its basal spacing is 12.3 Å at room temperature in 70% relative humidity (rh).[1]

NaT has been discovered to exhibit an outstanding K^+ ion sieve effect in the presence of a large excess of Na^+ ions.[3] Namely, NaT selectively takes up K^+ ions from the system which has a large quantity of Na^+ ions and a small quantity of K^+ ions, and the characteristics of K^+ uptake are independent of the concentrations of Na^+ and K^+ ions. The high selectivity for K^+ ions was interpreted as due to stabilization by the structural change from a swelling state to a nonswelling state. It is significant to examine the cation-exchange characteristics of NaT for Mg^{2+} and Ca^{2+} ions in case of utilizing NaT in the separation and immobilization of K^+ ions from seawater (Na^+, 10 500 ppm; K^+, 380 ppm; Mg^{2+}, 1350 ppm; Ca^{2+}, 400 ppm), body fluid, and so on.

In this paper, we report the cation-exchange selectivity of NaT for K^+, Mg^{2+}, and Ca^{2+} ions and obtain the distribution coefficients and separation factors at infinitesimal loading.

Experimental Section

NaT samples (Topy Ind. Co.) were repeatedly washed with distilled water, and small amounts of impurities such as α-cristobalite and other nonswelling particles were removed by centrifugation. After drying at 80 °C under vacuum, the specimens were pulverized and stored in a desiccator with rh = 70%. The characterization of the specimens was carried out by powder X-ray diffraction (XRD), using a Shimazu X-ray diffractometer XD-3 with Cu Kα radiation, and by TG-DTA, using a Rigaku PCT 10A instrument with α-Al_2O_3 as reference material.

The $Na^+ \rightarrow K^+$, $2Na^+ \rightarrow Mg^{2+}$, and $2Na^+ \rightarrow Ca^{2+}$ exchange experiments were conducted by a normal batch method within fixed times in a shaker with 120 rpm at 25 °C, as described elsewhere.[4] The rates of cation-exchange reactions on 0.1-g specimens were measured using 40 cm^3 of 1×10^{-2} N KCl, $MgCl_2$, and $CaCl_2$ solutions with pH = 5.2. The 0.1-g specimens were equilibrated in 40 cm^3 of a binary chloride solution (NaCl + KCl and NaCl + MCl_2; M = Mg and Ca) with various ratios of the two salts for 24 h in order to determine exchange isotherms at a constant total normality of 1×10^{-2} N. The rates of the $(x + 2y)Na^{2+} \rightarrow (xK^+ + yM^{2+})$ exchange reactions on the 0.1-g specimens were also measured, using 40 cm^3 of binary chloride solutions (KCl + MCl_2) with M^{2+}/K^+ ratios of 1, 2, 5, 10, and 20 at K^+ ion concentration of 1×10^{-2} N.

After the reactions, the solid and solution phases were separated by filtration and centrifugation, and a part of the supernatant solution was collected for chemical analyses. The solutions were analyzed for Na, K, Mg, and Ca by atomic absorption spectroscopy, using a Hitachi 180-30 instrument, and by inductively coupled plasma emission spectroscopy (ICP), using a Shimazu ICPS-500 instrument. At least two or more replications were carried out in the cation-exchange experiments.

Results and Discussion

NaT sample was identified as a swelling state with basal spacing of 12.3 Å at room temperature and rh = 70% and confirmed to contain no impurities by XRD as shown in Figure 1a. Each interlayer Na^+ ion in NaT sample was

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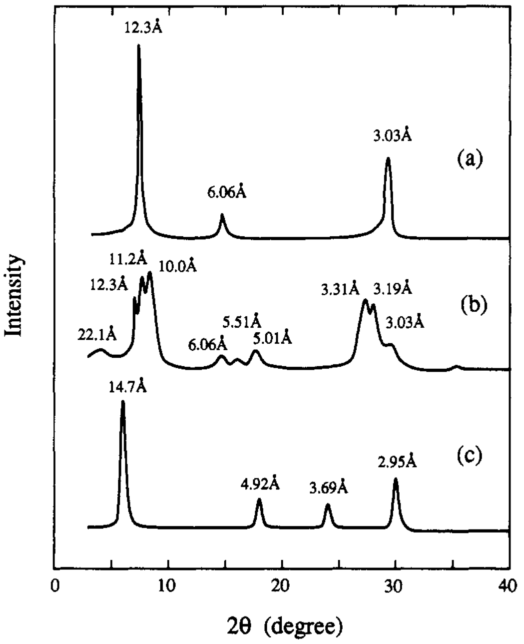

Figure 1. X-ray diffractograms of NaT before and after the cation-exchange reactions: (a) original, (b) after K^+ uptake, and (c) after Mg^{2+} or Ca^{2+} uptake.

estimated to be surrounded by two water molecules from the TG-DTA analysis.

The reaction of NaT with $MgCl_2$ solution attained a steady state within 8 h, while those with KCl and $CaCl_2$ solutions attained steady states within 12 h. The pH values before and after the reactions were hardly altered. The molar ratios between interlayer Na^+ ions released from NaT and cations removed from the solutions were found to be $Na^+/K^+ \cong 1.0$, $Na^+/Mg^{2+} \cong 2.0$, and $Na^+/Ca^{2+} \cong 2.0$ during the reactions, respectively, *i.e.*, the K^+, Mg^{2+}, and Ca^{2+} uptake phenomena are the cation-exchange reactions between interlayer Na^+ ions in NaT and cations in the solutions. K^+ ions of ca. 1.33, Mg^{2+} ions of 1.50, and Ca^{2+} ions of 1.32 mequiv/g were taken up after the cation-exchange reactions for 24 h, respectively. As the theoretical cation-exchange capacities of NaT is 2.35 mequiv/g, the cation-exchanges that occurred were incomplete. This was considered to be attributed to steric hindrance in the interlayer.[5]

XRD revealed that NaT, after K^+, Mg^{2+}, and Ca^{2+} uptakes, maintained the taeniolite structure. Namely, the peak intensities from basal reflections of NaT weakened after K^+ uptake, and new peaks assigned to two layer structures were present as shown in Figure 1b. One is the phase corresponding to KT with a basal spacing of 10.0 Å. The other was considered to be the phase with a basal spacing of 22.2 Å corresponding to a regular interstratified structure of NaT and KT (12.3 + 10.0 Å), because the basal reflections show the rational series, *i.e.*, $d(001) = 22.1$, $d(002) = 11.2$, $d(004) = 5.51$, and $d(007) = 3.19$ Å. The peak positions of basal reflections of NaT shifted toward lower diffraction angles after Mg^{2+} and Ca^{2+} uptakes, and the basal spacing increased from 12.3 to 14.7 Å at room temperature and rh = 70% as shown in Figure 1c. The swelling state of Mg^{2+} ion-exchanged form was more sensitive to humidity than that of Ca^{2+} ion-exchanged form.

The cation-exchange process on mice is represented by

$$A^{z+} + z\text{Na–mica} = z\text{Na}^+ + \text{A-mica} \qquad (1)$$

The corrected selectivity coefficient, K_{Na}^{A}, is given by[6-8]

$$K_{Na}^{A} = \frac{\overline{X_A} X_{Na}{}^{z} \gamma_{Na}{}^{z}}{\overline{X_{Na}}^{z} X_A \gamma_A} z(\text{TN})^{z-1} \qquad (2)$$

In eqs 1 and 2, A is a cation with valence of z; $\overline{X_A}$ and $\overline{X_{Na}}$ are the equivalent cation fractions in the mica; X_A and X_{Na} are the equivalent cation fractions in solution; and γ_A and γ_{Na} are the activity coefficients for the cations in the solution. γ_A and γ_{Na} approach unity when the total normality, TN (mequiv/mL), of exchanging ions, which is kept constant in the cation-exchange process, is low. The equivalent cation fractions and TN are defined by

$$\overline{X_A} = \frac{z\overline{[A^{z+}]}}{z\overline{[A^{z+}]} + \overline{[Na^+]}}, \quad \overline{X_{Na}} = \frac{\overline{[Na^+]}}{z\overline{[A^{z+}]} + \overline{[Na^+]}} \qquad (3)$$

$$X_A = \frac{z[A^{z+}]}{z[A^{z+}] + [Na^+]}, \quad X_{Na} = \frac{[Na^+]}{z[A^{z+}] + [Na^+]} \qquad (4)$$

$$\overline{X_A} + \overline{X_{Na}} = 1, \quad X_A + X_{Na} = 1 \qquad (5)$$

$$\text{TN} = z[A^{z+}] + [Na^+] \qquad (6)$$

where $[A^{z+}]$ and $[Na^+]$ are molalities of the cations in the solution. In eq 2, A^{z+} ions are preferable to Na^+ ions if K_{Na}^{A} is larger than $z(\text{TN})^{z-1}$, whereas Na^+ ions are preferable to M^{2+} ions if K_{Na}^{A} is smaller than $z(\text{TN})^{z-1}$. $K_{Na}^{A} = z(\text{TN})^{z-1}$, which indicates the diagonal line in the ion-exchange isotherm, represents no preference between these cations. Namely, the exchange isotherm lies above the diagonal line when $K_{Na}^{A} > 1$ and below the diagonal line when $K_{Na}^{A} < 1$.

The plot of log K_{Na}^{A} versus $\overline{X_A}$ (Kielland plot) often gives a straight line for a single-site ion exchanger, as described by[9]

$$\log K_{Na}^{A} = 2C\overline{X_A} + \log K_{Na}^{0} \qquad (7)$$

where C is the Kielland coefficient, and log K_{Na}^{A} = log K_{Na}^{0} when $\overline{X_A} = 0$. The thermodynamic equilibrium constant, K, is obtained from log K_{Na}^{A} in eq 7, using the Gibbs–Duhem equation[6-8]

$$\ln K = (1 - z) + \int_0^1 \ln K_{Na}^{A} \, d\overline{X_A} \qquad (8)$$

The distribution coefficient, K_d (g/mL), is estimated from the Kielland plot. It is defined by[10]

$$K_d = \overline{[A^{z+}]}/[A^{z+}] \qquad (9)$$

The K_d is rewritten using eqs 3, 4, and 6:

$$K_d = TC\overline{X_A}/TNX_A \qquad (10)$$

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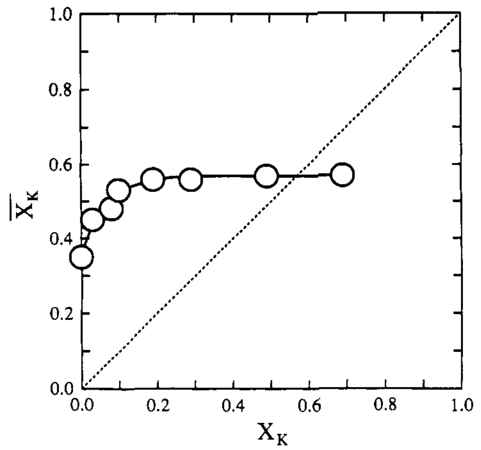

Figure 2. $Na^+ \rightarrow K^+$ exchange isotherm at a constant total normality of 1×10^{-2} N.

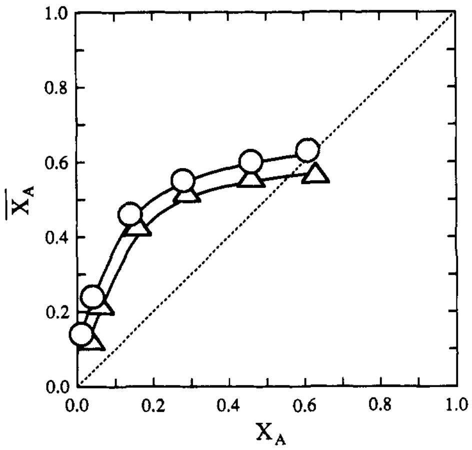

Figure 3. $2Na^+ \rightarrow Mg^{2+}$ (○) and $2Na^+ \rightarrow Ca^{2+}$ (△) exchange isotherms at a constant total normality of 1×10^{-2} N.

$$TC = z[\overline{A^{z+}}] + [\overline{Na^+}] \qquad (11)$$

where TC (mequiv/g) is the total capacity. Although it is difficult to estimate the K_d graphically from the ion-exchange isotherm at very small $\overline{X}_A$, the value is important for explaining the chromatographic behavior. Equation 2 at $\overline{X}_A \cong 0$ can be written as eq 12, using eq 5:

$$K^0_{Na} = \frac{\overline{X}_A \gamma_{Na}{}^z}{X_A \gamma_A} z(TN)^{z-1} \qquad (12)$$

Thus K_d and separation factor, α, at infinitesimal loading ($\overline{X}_A \cong 0$) are derived from eqs 10 and 12 as follows:

$$(K_d)_{A \cong 0} = \frac{TC\gamma_A}{zTN^z \gamma_{Na}{}^z} K^0_{Na} \qquad (13)$$

$$\alpha\left(\frac{A_2}{A_1}\right) = \frac{(K_d)_{A_2 \cong 0}}{(K_d)_{A_1 \cong 0}} \qquad (14)$$

The α value indicates the extent of mutual separation between A_1 and A_2 ions.

The theoretical cation-exchange capacity was employed as the value of TC in this analysis, because the experimental cation-exchange capacity depended on the exchanging cation.[10] The $Na^+ \rightarrow K^+$ and $2Na^+ \rightarrow M^{2+}$ exchange isotherms on NaT are shown in Figures 2 and 3, respectively. The $Na^+ \rightarrow K^+$ exchange isotherm rose steeply and attained a plateau above the diagonal line in the initial stages, which revealed that K^+ ions were extremely preferred over Na^+ ions in the low-concentration region of K^+ ions. The superior preference for K^+ ions over Na^+ ions on NaT was independent of the total normality.[3] The $Na^+ \rightarrow K^+$ exchange isotherm, however, lay below the diagonal line in the range $X_K > 0.58$, which indicated that the cation selectivity is reversed in the high-concentration region of K^+ ions. This was considered to be due to the fact that the cation exchanges were incomplete.

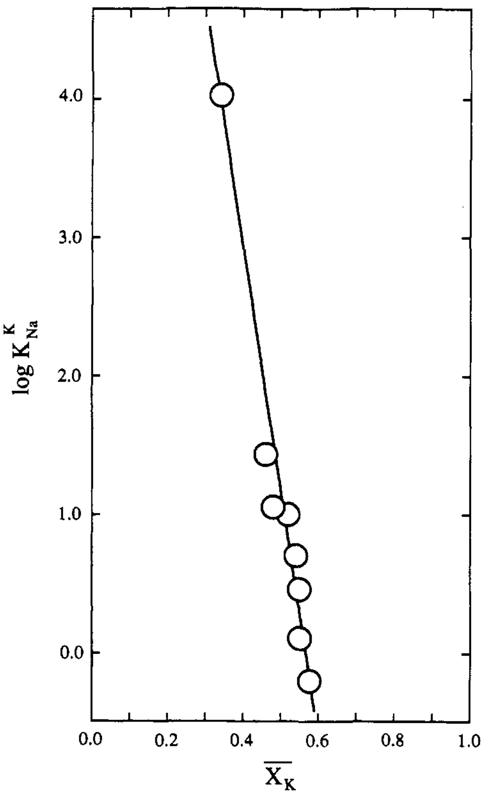

Figure 4. Kielland plot for $Na^+ \rightarrow K^+$ exchange.

The $2Na^+ \rightarrow Mg^{2+}$ and $2Na^+ \rightarrow Ca^{2+}$ exchange isotherms also increased exponentially above the diagonal line in the low-concentration regions. Namely, NaT exhibited preferences for Mg^{2+} and Ca^{2+} ions over Na^+ ions in the low-concentration regions of Mg^{2+} and Ca^{2+} ions. The $2Na^+ \rightarrow Mg^{2+}$ exchange isotherm lay above the $2Na^+ \rightarrow Ca^{2+}$ exchange isotherm in the range $X_A < 0.56$. The order of cation selectivity, therefore, were determined to be $Na^+ < Ca^{2+} < Mg^{2+}$ in the range $X_A < 0.56$. The $2Na^+ \rightarrow Ca^{2+}$ exchange isotherm, however, lay below the diagonal line in the range $X_A > 0.56$, which revealed that Na^+ ions were preferred over Ca^{2+} ions in the high-concentration region of Ca^{2+} ions. The $2Na^+ \rightarrow Mg^{2+}$ exchange isotherm will probably also go across the diagonal line in the range $X_A > 0.64$ because of the incompleteness of the cation-exchange reactions.

The Kielland plots for $Na^+ \rightarrow K^+$ and $2Na^+ \rightarrow M^{2+}$ exchanges are shown in Figures 4 and 5, respectively. The Kielland plot for $Na^+ \rightarrow K^+$ exchange gave a linear plot in the determined $\overline{X}_A$ values, while those for $2Na^+ \rightarrow Mg^{2+}$ and $2Na^+ \rightarrow Ca^{2+}$ exchanges gave curves. These suggested that NaT exhibited the extremely strong selectivity for K^+ ions, as compared with those for Mg^{2+} and Ca^{2+} ions. It is difficult to obtain experimentally the selectivity coefficient at infinitesimal loading due to the high selectivity of NaT. Thus, each Kielland plot was extrapolated to the intercept in order to estimate the

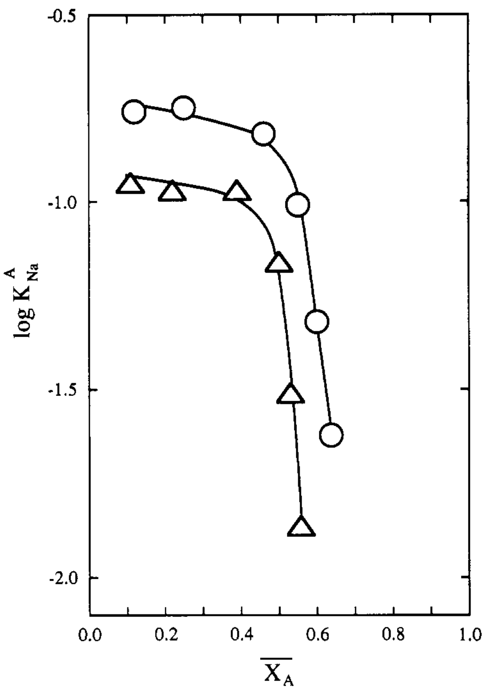

Figure 5. Kielland plots for $2Na^+ \rightarrow Mg^{2+}$ (○) and $2Na^+ \rightarrow Ca^{2+}$ (△) exchanges.

Table I. Selectivity Coefficients, Distribution Coefficients, and Separation Factors between K^+ and M^{2+} Ions on NaT at Infinitesimal Loading, which Are Estimated from Kielland Plots at *TN* = 0.01

	K^+	Mg^{2+}	Ca^{2+}
K_{Na}^0 (mequiv/mL)	8.7×10^{8a}	0.18	0.12
K_d (mL/g)	2.0×10^{11}	2.2×10^3	1.4×10^3
$\alpha(K/M)$		9.1×10^7	1.4×10^8

[a] K_{Na}^0 for $Na^+ \rightarrow K^+$ exchange is dimensionless.

K_{Na}^0 value. The Kielland plot for $Na^+ \rightarrow K^+$ exchange was assumed to show a straight line in the range $\overline{X_K} < 0.58$, according to the relationship between the shapes of exchange isotherm and Kielland plot.[5,10] The K_{Na}^0 values for K^+, Mg^{2+}, and Ca^{2+} ions are given in Table I. The K_d values and α values between K^+ and M^{2+} ions at infinitesimal loading were calculated, using eqs 13 and 14, are also given in Table I. The separation factors for K^+ ions from Mg^{2+} and Ca^{2+} ions were found to be excellent.

The separative ability on NaT was examined in order to experimentally back up these results, using $KCl + MCl_2$ solutions with a large excess of M^{2+} ions. The time dependences of K^+ and M^{2+} uptakes from $KCl + MCl_2$ solutions are shown in Figures 6 and 7. The both results revealed that NaT selectively took up K^+ ions, and amounts of Mg^{2+} and Ca^{2+} uptakes extremely decreased. The cation-exchange reactions of NaT with K^+ ions attained steady states within 24 h in both mixed solution system, while those with Mg^{2+} and Ca^{2+} ions attained steady states within short times. The amounts of K^+ and M^{2+} uptakes from $KCl + MCl_2$ solution with a large excess of M^{2+} ions after the cation-exchange reactions for 24 h are listed in Tables II and III. Although the amount of K^+ uptake slightly decreased with increasing concentrations of Mg^{2+} and Ca^{2+} ions in the solution, about 85% of the actual cation-exchange capacity for K^+ ions (about 1.13 mequiv/g) was taken up from $KCl + MCl_2$ solution with M^{2+}/K^+ ratio of about 20.

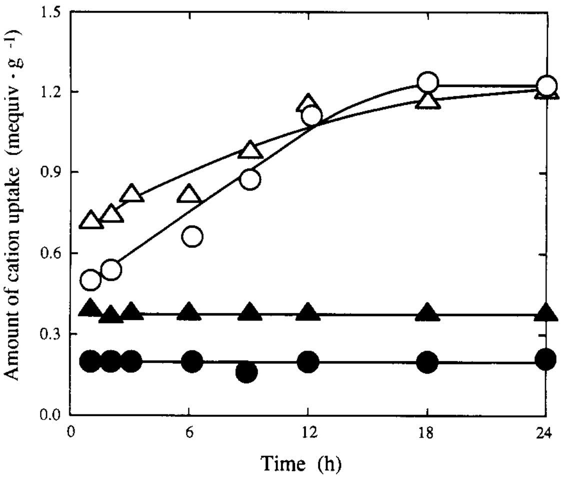

Figure 6. Time dependences of amounts of K^+ (○ and △) and Mg^{2+} (● and ▲) from $KCl + MgCl_2$ solution with $Mg^{2+}/K^+ = 1.0$ (circle) and 4.7 (triangle) as shown in Table II, respectively.

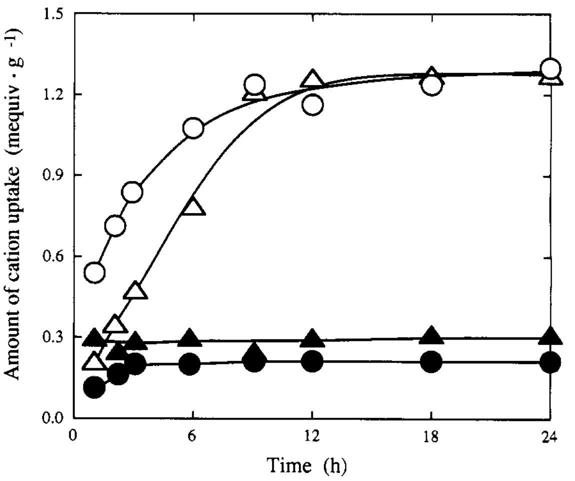

Figure 7. Time dependences of amounts of K^+ (○ and △) and Ca^{2+} (● and ▲) from $KCl + CaCl_2$ solution with $Ca^{2+}/K^+ = 0.9$ (circle) and 4.9 (triangle) as shown in Table III, respectively.

Table II. K^+ Ion Selectivity on NaT (0.1 g) in $KCl + MgCl_2$ Solution (40 cm^3) with an Excess of Mg^{2+} Ions after Cation-Exchange Reaction for 24 h

	initial concn, mequiv/L		amount of uptake, mequiv/g	
Mg^{2+}/K^+	K^+	Mg^{2+}	K^+	Mg^{2+}
1.0	9.97	10.32	1.23	0.22
1.8	10.92	19.56	1.26	0.22
4.7	10.46	49.42	1.21	0.40
9.3	10.63	98.36	1.16	0.30
19.9	9.91	196.98	1.12	0.26

Table III. K^+ Ion Selectivity on NaT (0.1 g) in $KCl + CaCl_2$ Solution (40 cm^3) with an Excess of Ca^{2+} Ions after Cation-Exchange Reaction for 24 h

	initial concn, mequiv/L		amount of uptake, mequiv/g	
Ca^{2+}/K^+	K^+	Ca^{2+}	K^+	Ca^{2+}
0.9	10.51	9.66	1.29	0.22
1.8	10.70	18.86	1.29	0.24
4.9	10.21	50.36	1.26	0.36
10.1	9.68	97.60	1.16	0.20
17.8	10.72	191.18	1.13	0.24

The K^+ ion sieve effect on NaT of 0.5 g was further examined, using the mixed solution system of 200 cm^3 including 4.746×10^{-1} N NaCl, 9.46×10^{-3} N KCl, 1.886×10^{-2} N $MgCl_2$, and 2.236×10^{-2} N $CaCl_2$, which was prepared by referring to the concentration of seawater.

Consequently, K^+ ions of 1.26, Mg^{2+} ions of 0.12, and Ca^{2+} ions of 0.14 mequiv/g were found to be taken up by NaT after the cation-exchange reaction for 24 h, respectively.

In conclusion, the K_d and separation factor, which were evaluated at infinitesimal loading based on the Kielland plots obtained from the $Na^+ \rightarrow K^+$, $2Na^+ \rightarrow Mg^{2+}$, and $2Na^+ \rightarrow Ca^{2+}$ exchange isotherms, revealed that NaT exhibited the superior preference for K^+ over Na^+, Mg^{2+}, and Ca^{2+} ions. These were consistent with the experimental results made in the presence of Na^+, K^+, Mg^{2+}, and/or Ca^{2+} ions. The present basic studies, therefore, suggest that NaT is available for the separation and immobilization of K^+ ions from the system including Na^+, K^+, Mg^{2+}, and Ca^{2+} ions, for example, seawater, body fluid and so on.

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