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An Evaluation Method of Chromatographic Parameters from the Ion-Exchange Isotherm of Al^3-Substituted Tobermorite Cation Exchanger

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An Evaluation Method of Chromatographic Parameters from the Ion-Exchange Isotherm of Al^{3+}-Substituted Tobermorite Cation Exchanger

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Abstract

A new and useful method has been developed for analytical evaluation of the distribution coefficient (K_d) at an infinitesimal exchange. K_d values have an important role for the chromatographic separation of ions. This method is based on the extrapolation of the Kielland plot from an ion-exchange isotherm to zero loading. The usefulness of this method is exemplified by evaluation of K_d values for Cs^+ on Al^{3+}-substituted tobermorite which is known to exhibit high selectivity toward Cs^+.

I. INTRODUCTION

Aluminum and sodium-substituted tobermorites with Ca/(Al + Si) = 0.83 may be represented as follows: $Ca_5[Na_x(Al_xSi_{6-x})]O_{16}(OH)_2 \cdot nH_2O$. The deficient charge coming from the Al substitution is compensated by Na^+ which is located in the interlayers and is exchangeable. These substituted tobermorites constitute a new family of inorganic cation exchangers and are characterized by their high selectivity for Cs^+ (*1*). Some Al^{3+}-substituted tobermorites are stable at 300°C, i.e., the 1.13 nm (002) *d* spacing does not collapse to 0.97 nm at this temperature. This stability can be ascribed to the presence of extensive $\equiv$Si—O—Si$\equiv$ bridges between $Si_3(O/OH)_9$ chains are evidenced by ^{29}Si MAS NMR (*2–4*). The ion-exchange cavity formed from the bridges and the chains is about 4.69 Å in diameter along the *c*-axis and thus imposes steric limitation for the exchange of highly hydrated cations but not for less hydrated Rb^+ and Cs^+ (*1*).

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The ion-exchange isotherms were used for the thermodynamic treatment of ion exchange. The present paper demonstrates a new evaluation method of the distribution coefficient (K_d) at infinitesimal loading and the separation factor by using the ion-exchange isotherm. A few examples are presented.

II. EXPERIMENTAL

Hydrothermal Synthesis of an Anomalous Al^{3+}-Substituted Tobermorite

An anomalous 15% Al^{3+}-substituted tobermorite was prepared by the method reported previously (5). The starting materials (CaO 4.275 g, aluminosilicate gel of Si/Al = 5.6 mol ratio, 5.9489 g, NaOH 1.0971 g, H_2O 38 mL) were mixed in a Teflon vessel and treated hydrothermally at 175°C for 2 weeks in a Parr bomb. After cooling, the product mass was ground in the vessel and washed with deionized water to remove soluble components. Then it was dried at 60°C. The supernatant solution and the washings were collected for chemical analyses. It was identified by the powder x-ray diffraction (XRD) method by using a Philips x-ray diffractometer with Ni-filtered CuK_α radiation. The chemical composition was determined from the difference between the initial amounts used and the remaining amounts in the above solution collected for chemical analysis. Water and OH group contents of the tobermorite were determined from the weight loss after heating at 900°C. The chemical composition was determined to be $Ca_5Na_{0.75}Al_{0.9}Si_{5.1}O_{16}(OH)_2 \cdot 6.03H_2O$.

Distribution Coefficient (K_d)

A 0.025-g portion of the tobermorite was equilibrated with 25 mL of different concentrations of NaCl or $CaCl_2$ solution containing 10^{-4} N CsCl at 25°C. After equilibration, the supernatant solution was analyzed for the Cs^+ and Na^+ or Ca^{2+} as above. The K_d for Cs^+ was calculated by

$$K_d = \frac{\text{amount of } Cs^+ \text{ exchanged (meq/g)}}{\text{equilibrium concentration of } Cs^+ \text{ (meq/mL)}}$$

Cation-Exchange Isotherm

A 0.025-portion of the tobermorite was equilibrated with 25 mL of the mixed solution having different mol ratios of Na^+/Cs^+ or Ca^{2+}/Cs^+ with intermittent shaking at 25°C. The total normality was 0.001 N for $Na^+ \leftrightarrows Cs^+$ exchange and 0.01 N for $Ca^{2+} \leftrightarrows 2Cs^+$ exchange. After equilibration, the supernatant solution was analyzed for the metal ions by atomic emission spectrometry (AES) by using a SpectraMetrics SpectraSpan III instrument or atomic absorption spectroscopy (AAS) by using a Perkin-Elmer PE 703 instrument with an electrodeless discharge lamp. The amounts of metal ions exchanged or released by the tobermorite were determined from the difference in the concentration between the sample and the reference. The calculated capacity based on the expected substitution (1.14 meq/g) was used for representing the ion-exchange isotherm.

III. THEORETICAL

Calculation of Isotherms and Kielland Plots at Different Total Normalities (TN) from a Reference Isotherm at a TN

The cation-exchange reactions between Na^+ and M^{2+} are represented by

$$n\overline{Na^+} + M^{n+} \leftrightarrows \overline{M^{n+}} + nNa^+ \tag{1}$$

The thermodynamic equilibrium constant, K, is defined in the reversible system by

$$K = \frac{\bar{X}_M [Na^+]^n f_M \gamma_{Na}^n}{\bar{X}_{Na}^n [M^{n+}] f_{Na}^n \gamma_M} \tag{2}$$

In these equations, the bar on the character denotes the exchanger phase, $\bar{X}_M$ and $\bar{X}_{Na}$ are equivalent ion fractions in the exchanger, and f_M and f_{Na} are the activity coefficients for the ions in the exchanger. $[M^{n+}]$ and $[Na^+]$ are molalities of the above two exchanging ions in solution, where they have activity coefficients γ_M and γ_{Na}. The standard states chosen are such that f_M and f_{Na} are unity when the exchanger is in its pure M^{n+} and pure Na^+ forms, respectively, and γ_M and γ_{Na} are unity when $[M^{n+}]$ and $[Na^+]$ approach zero.

Molalities $[M^{n+}]$ and $[Na^+]$ are replaced by the equivalent ion fractions:

$$X_M = \frac{n[M^{n+}]}{n[M^{n+}] + [Na^+]}, \qquad X_{Na} = \frac{[Na^+]}{n[M^{n+}] + [Na^+]} \tag{3}$$

$$\bar{X}_M = \frac{n\overline{[M^{n+}]}}{n\overline{[M^{n+}]} + \overline{[Na^+]}}, \qquad \bar{X}_{Na} = \frac{\overline{[Na^+]}}{n\overline{[M^{n+}]} + \overline{[Na^+]}} \tag{4}$$

and

$$X_M + X_{Na} = 1, \qquad \bar{X}_M + \bar{X}_{Na} = 1 \tag{5}$$

By using the total normality (TN) and the total capacity (TC), which are kept constant in the ion-exchange process,

$$n[\mathrm{M}^{n+}] + [\mathrm{Na}^+] = \mathrm{TN}, \qquad n[\overline{\mathrm{M}^{n+}}] + [\overline{\mathrm{Na}^+}] = \mathrm{TC} \tag{6}$$

Then Eq. (2) becomes

$$K = \frac{\overline{\mathrm{X}}_{\mathrm{M}}\mathrm{X}_{\mathrm{Na}}^{n}}{\overline{\mathrm{X}}_{\mathrm{Na}}^{n}\mathrm{X}_{\mathrm{M}}}\cdot\eta\Gamma \tag{7}$$

where

$$\eta = n(\mathrm{TN})^{n-1}, \qquad \Gamma = \frac{\gamma_{\mathrm{Na}}^{n} f_{\mathrm{M}}}{\gamma_{\mathrm{M}} f_{\mathrm{Na}}^{n}} \tag{8}$$

The application of the Gibbs-Duhem equation to the ion-exchange system gives for K:

$$\ln K = (1 - n) + \int_0^1 \ln K_{\mathrm{Na}}^{\mathrm{M}} d\overline{\mathrm{X}}_{\mathrm{M}} + \Delta \tag{9}$$

where $K_{\mathrm{Na}}^{\mathrm{M}}$, the selectivity coefficient, is defined as

$$K_{\mathrm{Na}}^{\mathrm{M}} = \frac{\overline{\mathrm{X}}_{\mathrm{M}}\mathrm{X}_{\mathrm{Na}}^{n}\gamma_{\mathrm{Na}}^{n}}{\overline{\mathrm{X}}_{\mathrm{Na}}^{n}\mathrm{X}_{\mathrm{M}}\gamma_{\mathrm{M}}}\eta \tag{10}$$

The third term on the right of Eq. (9), Δ, is negligible when compared with the experimental accuracy in measuring the equilibrium (*6, 8*). A plot of log $K_{\mathrm{Na}}^{\mathrm{M}}$ vs $\overline{\mathrm{X}}_{\mathrm{M}}$ (Kielland plot) often produces a straight line with a slope of $2C$ for a single-site ion exchanger and then can be expressed by

$$\log K_{\mathrm{Na}}^{\mathrm{M}} = 2C\overline{\mathrm{X}}_{\mathrm{M}} + (\log K_{\mathrm{Na}}^{\mathrm{M}})_{\mathrm{X}_{\mathrm{M}},\overline{\mathrm{X}}_{\mathrm{M}}\to 0} \tag{11}$$

where C refers to the Kielland coefficient.

When $n = 1$ or mono-monovalent exchange, Eq. (7) can be reduced to

$$\frac{K}{\Gamma}\frac{\overline{\mathrm{X}}_{\mathrm{Na}}}{\overline{\mathrm{X}}_{\mathrm{M}}} = \frac{\mathrm{X}_{\mathrm{Na}}}{\mathrm{X}_{\mathrm{M}}} \quad \text{or} \quad \frac{K}{\Gamma}\frac{1 - \overline{\mathrm{X}}_{\mathrm{M}}}{\overline{\mathrm{X}}_{\mathrm{M}}} = \frac{1 - \mathrm{X}_{\mathrm{M}}}{\mathrm{X}_{\mathrm{M}}} \tag{12}$$

where $\gamma_{\mathrm{Na}}/\gamma_{\mathrm{M}}$ and $f_{\mathrm{M}}/f_{\mathrm{Na}}$ vary little from unity. Therefore, a value of $\overline{\mathrm{X}}_{\mathrm{M}}$ is uniquely defined for any fixed value of X_{M} irrespective of the TN. Thus, the ion-exchange isotherms for mono-monovalent exchange is independent of TN. This is well demonstrated by the ion-exchange isotherm for the NO_3^-/Cl^- exchange system in ASB-2 resin (*9*) and the Na^+/Cs^+ exchange system in tobermorite (*10*).

In the case of $n \neq 1$:

$$\frac{K}{\Gamma\eta}\frac{\overline{X}^n_{Na}}{\overline{X}_M} = \frac{X^n_{Na}}{X_M} \tag{13}$$

for a given value of X_M. Two different $\overline{X}_M$ values could be found for a chosen value of X_M when two different TNs were used, because the change in the TN cannot be compensated by the change in η (*6*). Thus, the shape of the ion-exchange isotherm, i.e., plot of $\overline{X}_M$ vs X_M, will change depending upon the total normality. On the other hand, the Kielland plot should not be dependent on the total normality because the Gibbs standard free energy change given by $\Delta G° = -RT \ln K$ does not change. In Eq. (13), the change in η will be compensated mostly by the change in X^n_{Na}/X_M. This is well demonstrated for the Na^+/Cu^{2+} exchange in Dowex 50W-X8 (*11*) and for the Na^+/Mg^{2+} and Na^+/Ca^{2+} exchanges in zeolite A (*8*). Thus, the selectivity coefficient K^M_{Na} and the Kielland coefficient, C will remain the same, irrespective of the TN. It means, in turn, that we can calculate an ion-exchange isotherm at different TN from a reference isotherm at a given total normality by using Eqs. (10) and (11).

Evaluation of Distribution Coefficient (K_d) and Separation Factors (α) from the Kielland Plot

The important factors in column chromatographic separation are the distribution coefficient and the mutual separation factor. They are defined by

$$K_d^M = \frac{[\overline{M^{n+}}]}{[M^{n+}]}, \qquad \alpha\left(\frac{M_2}{M_1}\right) = \frac{K_d^{M_2}}{K_d^{M_1}} \tag{14}$$

The former is related to the equation showing the elution volume, V_{max}, when a Na^+ salt solution was used as an eluent (*12*):

$$V_{max} = I + mK_d^M \tag{15}$$

where V_{max} is the volume of the eluent up to the elution peak of the ion M^{n+}, I is the dead volume of the chromatographic column, and m is the weight of the exchanger in the column. The latter, α value, indicates the extent of mutual separation between M_2 and M_1 ions. The K_d^M values are given by the relation using Eqs. (3), (4), and (6):

$$K_d = \frac{[\overline{M^{n+}}]}{[M^{n+}]} = \frac{TC\overline{X}_M}{TNX_M} \tag{16}$$

Hence, K_d value at intermediate value of $\overline{X}_M/X_M$ can be graphically determined from an ion-exchange isotherm. But it is difficult to estimate K_d value at infinitesimal loading (very small $\overline{X}_M$), which is important for interpreting the chromatographic behavior.

The expression of K_d value at the infinitesimal loading can be derived from the Kielland plot as follows. Equations (5) and (10) are combined to give

$$K_{Na}^{M} = \frac{\overline{X}_M(1 - X_M)^n \gamma_{Na}^n}{(1 - \overline{X}_M)^n X_M \gamma_M}\eta$$

Therefore,

$$(K_{Na}^{M})_{X_M,\overline{X}_M \to 0} = \left(\frac{\overline{X}_M}{X_M}\right)_{X_M,X_M \to 0} \cdot \frac{\gamma_{Na}^n}{\gamma_M}\eta \tag{17}$$

On inserting Eq. (16) in Eq. (17),

$$(K_{Na}^{M})_{X_M,\overline{X}_M \to 0} = \left(\frac{TN}{TC}K_d\right)_{X_M,\overline{X}_M \to 0} \cdot \frac{\gamma_{Na}^n}{\gamma_M}\eta$$

Therefore

$$(K_d)_{X_M,\overline{X}_M \to 0} = \rho(K_{Na}^{M})_{X_M,\overline{X}_M \to 0} \tag{18}$$

where

$$\rho = \left(\frac{1}{TN}\right)^n \frac{TC}{n} \cdot \frac{\gamma_M}{\gamma_{Na}^n}$$

The quantity ρ can be calculated based on the experimental parameters. The total normality is kept constant throughout the ion-exchange process, and the separation factor for two ions, M_1 and M_2, is given by

$$\alpha\left(\frac{M_2}{M_1}\right) = \frac{(K_{Na}^{M_2})_{X_{M_2},\overline{X}_{M_2} \to 0}}{(K_{Na}^{M_2})_{X_{M_1},\overline{X}_{M_1} \to 0}} \tag{19}$$

Thus, the separation factor at infinitesimal loading is given here. From Eq. (18).

$$\log (K_d^{\mathrm{M}})_{\mathrm{X_M},\bar{\mathrm{X}}_\mathrm{M}\to 0} = \log \frac{\mathrm{TC}}{n} + \log (K_{\mathrm{Na}}^{\mathrm{M}})_{\mathrm{X_M},\bar{\mathrm{X}}_\mathrm{M}\to 0}$$

$$+ \log \frac{\gamma_\mathrm{M}}{\gamma_{\mathrm{Na}}^{n}} - n \log (\mathrm{TN}) = \text{constant} - n \log (\mathrm{TN}) \quad (20)$$

The ratio of the activity coefficient will not change very drastically even though TN decreased tenfold when neutral salt media was used (*6*).

In addition, K_d measurements at the micro-loading (very small $\bar{\mathrm{X}}_\mathrm{M}$) will show that the slope of plot of $\log (K_d^{\mathrm{M}})_{\mathrm{X_M},\bar{\mathrm{X}}_\mathrm{M}\to 0}$ vs log (TN) is $-n$. If the valences of the $\mathrm{M_1}$ and $\mathrm{M_2}$ ions are the same, the $\alpha(\mathrm{M_2/M_1})$ value will be an invariant without depending on the TN. Thus, we can calculate the K_d values as a function of the TN from the ion-exchange isotherm.

IV. RESULTS AND DISCUSSION

The ion-exchange rate of $\mathrm{Cs^+}$ was measured in 0.10 N $\mathrm{CaCl_2}$ solution for determination of the equilibrium distribution coefficient (Fig. 1). It took 8 days to reach exchange equilibrium. The exchange of the $\mathrm{Na^+/Cs^+}$ system, $\overline{\mathrm{Na^+}} + \mathrm{Cs^+} \rightleftarrows \overline{\mathrm{Cs^+}} + \mathrm{Na^+}$ (*5*, *13*), attained equilibrium within 3 days. This is ascribed to the steric hindrance for the diffusion of the more

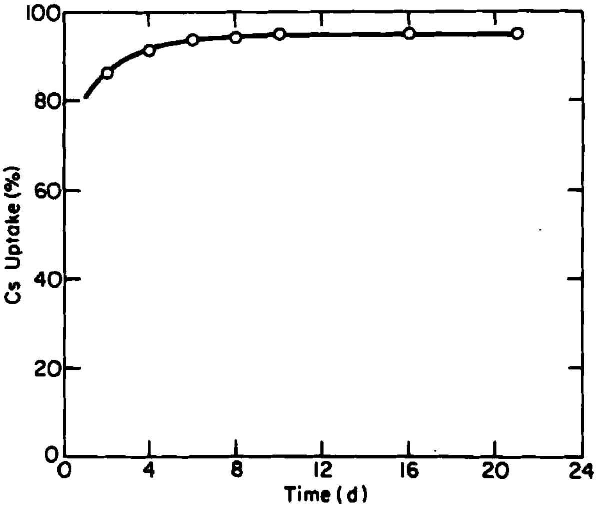

FIG. 1. Ion-exchange rate of $\mathrm{Cs^+}$ in 0.10 N $\mathrm{CaCl_2}$ solution.

strongly hydrated Ca^{2+} than for the hydrated Na^+ in the ion-exchange cavity within the Al^{3+}-substituted tobermorite.

$Na^+ \rightleftarrows \overline{M^+}$ Exchange System

Plots of the K_d for Cs^+ vs the concentration of NaCl showed a slope of −0.87 (Fig. 2). It was very close to the "ideal" slope of −1 in NaCl media as expected by Eq. (20). Thus, the ion-exchange ideality was valid for the Na^+/Cs^+ exchange system.

The K_d values for alklai metal ions in NaCl media were estimated from the ion-exchange isotherm (5) (Table 1). The estimated K_d value of Cs^+, 1.2×10^5 mL/g, is in agreement with the empirical K_d value (2.5×10^5 mL/g). The extent of the discrepancy may be ascribed to the long extrapolation to 0.001 N NaCl.

$2\overline{Na^+} \rightleftarrows \overline{M^{2+}}$ Exchange System

Ion-exchange isotherms and the Kielland plots for Na^+/alkaline earth metal ions are given in Fig. 3. The calculated capacity (1.14 meq/g) was used for normalization. In the small $\overline{X}_M$ region, the $2\overline{Na^+} \rightleftarrows \overline{M^{2+}}$ exchange process is predominant. The Na^+ is rapidly exchanged. In the larger $\overline{X}_M$ (>0.27), the $\overline{Ca^{2+}} \rightleftarrows \overline{M^{2+}}$ exchange process sets in. The Ca^{2+}s in the CaO

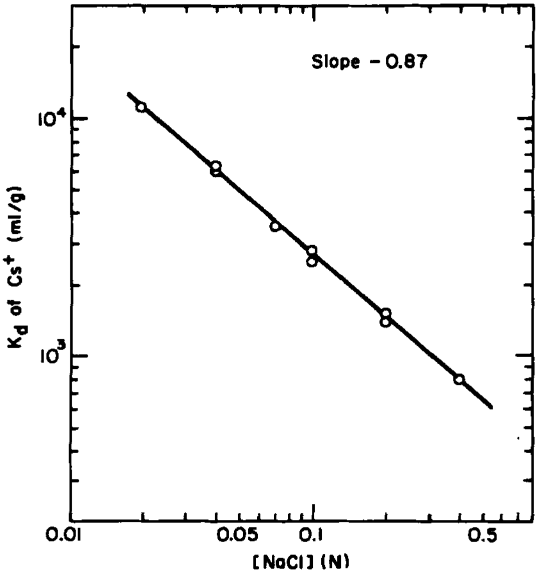

FIG. 2. Plot of K_d values of Cs^+ vs concentration of NaCl.

TABLE 1
Distribution Coefficients (K_d) of Alkali Cations Calculated from the Ion-Exchange Isotherm and Mutual Separation Factor (α)

Parameter	K^+		Rb^+		Cs^+
$(K^{M}_{Na})_{X_M,\bar{X}_M \to 0}$[a]	4.7		66		112
K_d^M(estimated)	5.3×10^3		7.5×10^4		1.2×10^5
K_d^M(empirical)[b]	—		—		(2.5×10^5)
$\alpha(M_2/M_1)$		14		1.7	

[a] Taken from Ref. 5.

[b] Empirical value extrapolated to 0.001 N NaCl.

layer are involved in the exchange at the larger $\bar{X}_M$. The ion-exchange selectivity sequence for 15% Al^{3+}-substituted tobermorite is in the following order: $Mg^{2+} < Sr^{2+} < Ba^{2+}$. K_d values for the alkaline earth metal ions were estimated based on the above treatment from Fig. 3(b) (Table 2). The large K_d value for Sr^{2+} in the 15% Al^{3+}-substituted tobermorite should be stressed. A relatively large separation factor was found.

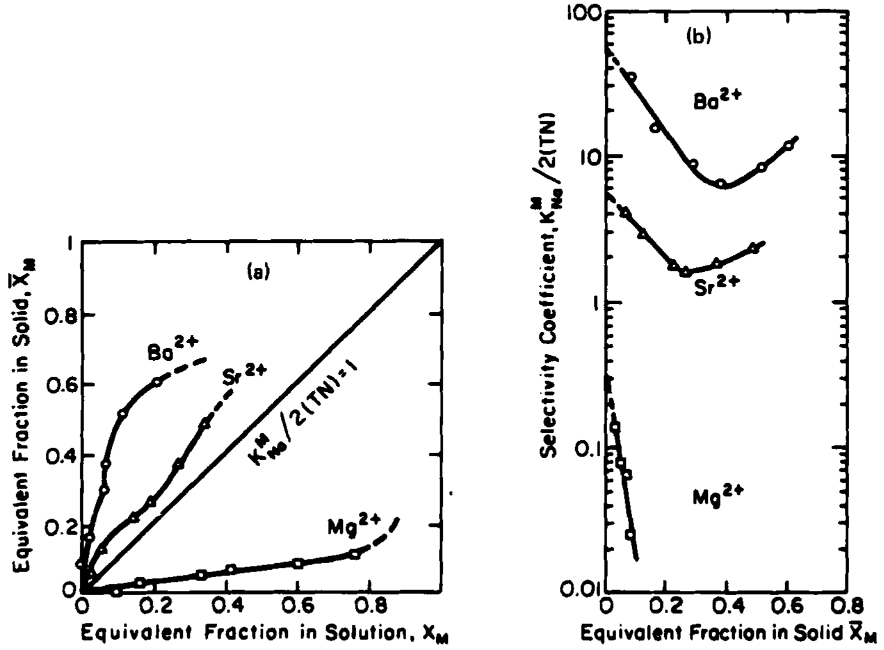

FIG. 3. Ion-exchange isotherms for $\overline{2Na^+} \rightleftarrows \overline{M^{2+}}$ exchange on Al^{3+}-substituted tobermorite.

TABLE 2
Distribution Coefficients (K_d) of Alkaline Earth Cations Calculated from the Ion-Exchange Isotherm and Mutual Separation Factor (α)

Parameter	Mg^{2+}	Sr^{2+}	Ba^{2+}
$(K_{Na}^{M})_{x_M \cdot \bar{x}_M \to 0}$[a]	7.6×10^{-4}	1.16×10^{-2}	1.14×10^{-1}
K_d^M(estimated) (in 0.001 N NaCl)	4.3×10^{2}	6.6×10^{3}	6.5×10^{4}
$\alpha(M_2/M_1)$	15	9.8	

[a] Taken from Ref. *3*.

$Ca^{2+} \rightleftarrows 2Cs^{+}$ Exchange System

The ion exchange of Cs^+ on the Ca^{2+} form is demonstrated in Fig. 4. The slope of −0.50 is equal to the slope for "ideal" ion-exchange, as is clear from the treatment described above. Ca^{2+} replaces Na^+ and will be located in the interlayer cavity made of the $Si_3(O/OH)_9$ chains.

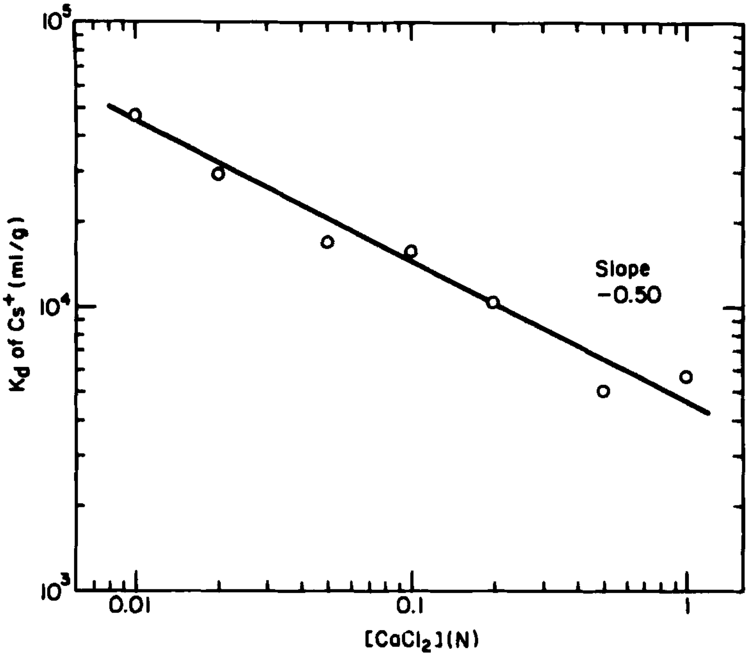

FIG. 4. Plots of K_d values of Cs^+ vs concentration of $CaCl_2$.

A highly selective ion-exchange has been revealed at low loading, similar to that in the Na$^+$/Cs$^+$ exchange (*5*) (Fig. 5). The diagnonal line corresponding to $K_{\overline{\mathrm{Ca}}}^{\mathrm{Cs}}\cdot 2(\mathrm{TN}) = 1$ is shown for comparison. The Kielland plot of the $\overline{\mathrm{Ca}}^{2} \rightleftarrows 2\overline{\mathrm{Cs}}^+$ exchange system gave a straight line up to $\overline{X}_{\mathrm{Cs}} = 0.4$ for the equivalent fraction in the solid state (Fig. 6). This suggests that the ion-exchange sites available for Cs$^+$ are uniformly distributed and single. This is consistent with the structural observations of substituted Al^{3+} responsible for the charge by ^{27}Al and ^{29}Si MAS NMR studies (*3*, *5*).

The K_d value for Cs$^+$ was estimated based on Eq. (18) by using the extrapolated selectivity coefficient $(K_{\overline{\mathrm{Ca}}}^{\mathrm{Cs}})_{X_{\mathrm{Cs}},\overline{X}_{\mathrm{Cs}}\to 0}$, to the zero $\overline{X}_{\mathrm{Cs}}$ in the Kielland plot. The estimated K_d^{Cs}, 3.75 × 10^4 mL/g, is in good agreement with the empirical value of 4.6 × 10^4 mL/g at 0.01 *N* CaCl$_2$. The good agreement of the calculated K_d value with the value determined from ion-exchange ideality clearly shows that the chromatographic parameters (K_d and α) in the small loading can be obtained from the ion-exchange isotherm.

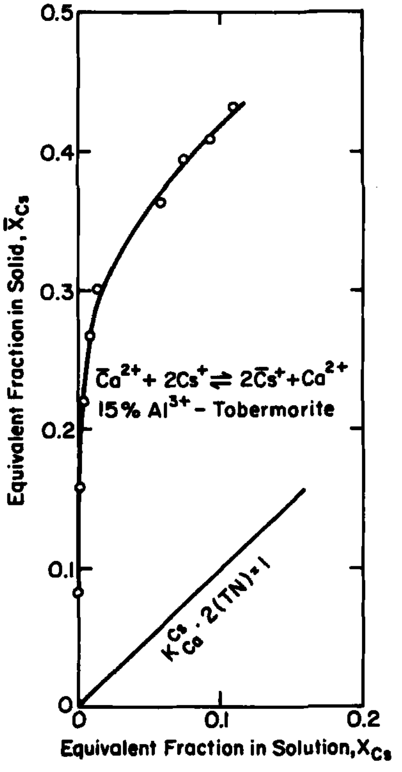

FIG. 5. Ion-exchange isotherm for $\overline{\mathrm{Ca}}^{2+} \rightleftarrows 2\overline{\mathrm{Cs}}^+$ exchange system on Al^{3+}-substituted tobermorite.

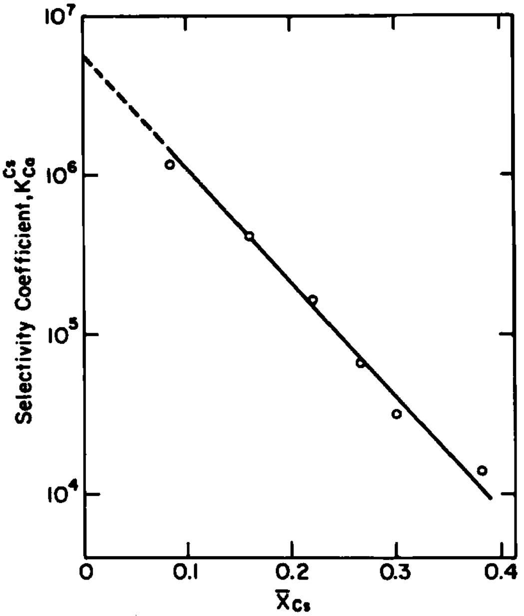

FIG. 6. Kielland plot for $\overline{Ca^{2+}} \rightleftarrows \overline{2Cs^{+}}$ exchange system on Al^{3+}-substituted tobermorite.

The treatment developed above can be applied to any ion-exchange system including anion-exchange systems. It is very useful for estimating the K_d value in micro-loading (very small $\bar{X}_M$) from the Kielland plot.

V. CONCLUSIONS

An evaluation method of K_d based on the ion-exchange isotherm has been successfuly demonstrated for Cs^+ exchange on Al^{3+}-substituted tobermorite. K_d values can be analytically calculated by using the Kielland plot from the ion-exchange isotherm. The calculated K_d value showed good agreement with the empirical K_d value for Cs^+ on Al^{3+}-substituted tobermorite.

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