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An Extended Method for Analytical Evaluation of Distribution Coefficients on Selective Inorganic Ion Exchangers

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Abstract

A mathematical formulation has been developed for an analytical evaluation of distribution coefficients (K_d) in the whole range of exchange ($0 < \bar{X}_M < 1$) in the M^{n+}/Na^+ exchange system. The present method allows the numerical evaluation of K_d values as a function of exchanging ion and/or total electrolyte concentration.

I. INTRODUCTION

The ion-exchange isotherm (Fig. 1) of a binary ion pair is important in at least two ways: 1) primarily for the thermodynamic interpretation of the ion-exchange phenomena (*1–3*) and 2) for designing separations through chromatography (*4*). In the former, the so-called Kielland plot (the conjugate expression of the ion-exchange isotherm) plays a central part, while in the latter the distribution coefficients (K_d) in an infinitesimal exchange are used for the conventional location of the elution peak (*5*).

Recently, synthetic inorganic ion exchangers with very high selectivity, i.e., high K_d values for several ions, have been reported by several authors (*6–9*). The situation prompted us to develop a simple and useful method for an analytical evaluation of K_d at an infinitesimal exchange based on the Kielland plot. It was exemplified by evaluation of K_d values for Cs^+ on Al^{3+}-substituted tobermorite which is known to exhibit high selectivity toward Cs^+ (*10*).

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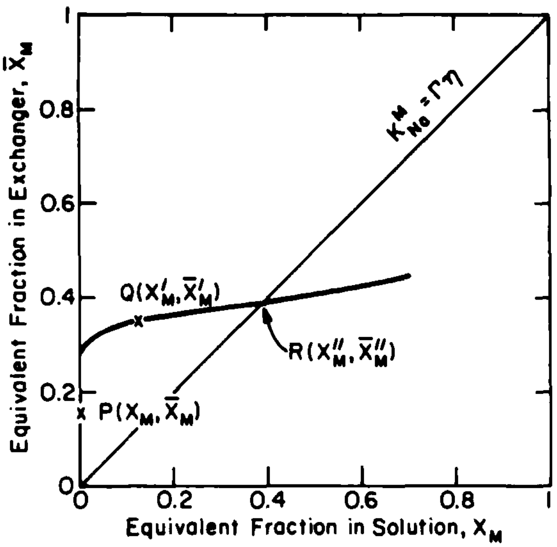

FIG. 1. Typical ion-exchange isotherm of a selective inorganic ion exchanger at a constant total normality for $n\overline{Na^+} + M^{n+} \leftrightarrows \overline{M^{n+}} + nNa^+$.

The present paper describes an extended evaluation method of K_d in the whole range of fractional exchange as a function of the bulk concentration of electrolyte and exchanging ions.

II. THEORETICAL

The ion-exchange process on the Na$^+$ form exchanger can be expressed by

$$n\overline{Na^+} + M^{n+} \leftrightarrows \overline{M^{n+}} + nNa^+ \qquad (1)$$

The thermodynamic equilibrium constant, K, for the ion-exchange process by Eq. (1) is defined by

$$K = \frac{\overline{X}_M[Na^+]^n f_M \gamma_{Na}^n}{\overline{X}_{Na}^n[M^{n+}] f_{Na}^n \gamma_M} \qquad (2)$$

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

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

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

The total normality (TN) and the total capacity (TC) are kept constant throughout the ion-exchange process:

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

By using these definitions, Eq. (2) becomes

$$K = K_{Na}^{M} \frac{f_M}{f_{Na}^{n}} \tag{7}$$

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

$$K_{Na}^{M} = \frac{\bar{X}_M X_{Na}^{n} \gamma_{Na}^{n}}{\bar{X}_{Na}^{n} X_M \gamma_M} \cdot n(\mathrm{TN})^{n-1} \tag{8}$$

This is independent of the total normality only in the special case of $n = 1$. By using the $\gamma_{\pm NaY}$ and $\gamma_{\pm MY_n}$ where Y denotes the common anion, we can calculate the ratio of the activity coefficient:

$$\frac{\gamma_{Na}^{n}}{\gamma_M} = \frac{\gamma_{Na}^{n}\gamma_Y^{n}}{\gamma_M \gamma_Y^{n}} = \frac{\gamma_{\pm NaY}^{2n}}{\gamma_{\pm MY_n}^{n+1}} \tag{9}$$

The activity coefficient $\gamma_{\pm NaY}$ of an electrolyte NaY in the presence of another electrolyte MY_n is given using those of the pure solutes at the same total ionic strength (μ), γ^{NaY} and $\gamma^{\mathrm{MY}n}$, by Glueckauf (*11*):

$$\log \gamma_{\pm \mathrm{NaY}} = \log \gamma^{\mathrm{NaY}} - \frac{[\mathrm{M}^{n+}]}{4\mu} \times \left[K_1 \log \gamma^{\mathrm{NaY}} - K_2 \log \gamma^{\mathrm{My}n} - \frac{K_3}{1 + \mu^{-1/2}} \right] \tag{10}$$

where $K_1 = 2n^2$, $K_2 = (n + 1)^2/2$, $K_3 = (1 - n)^2/2$, and $\mu = (1/2)\Sigma$ $Zi^2[m_i]$. A similar equation is given for $\log \gamma_{\pm \mathrm{MY}n}$ of another electrolyte MYn in the presence of an electrolyte NaY. Thus, we can calculate $\gamma^n_{\mathrm{Na}}/\gamma_{\mathrm{M}}$ in any arbitrary concentration of an electrolyte mixture.

The application of the Gibbs–Duhem equation to the ion-exchange system gives K as follows:

$$\ln K = (1 - n) + \int_0^1 \ln K^{\mathrm{M}}_{\mathrm{Na}}\, d\overline{\mathrm{X}}_{\mathrm{M}} + \Delta \tag{11}$$

The third term on the right, Δ, of Eq. (11) is negligible when compared with the experimental accuracy in measuring the equilibrium (*2*, *3*). A plot of $\log K^{\mathrm{M}}_{\mathrm{Na}}$ vs $\overline{\mathrm{X}}_{\mathrm{M}}$ (Kielland plot) (*12*) often produces a straight line with a slope of $2C$ for a single-site ion exchanger (Fig. 2) and then can be expressed by

$$\log K^{\mathrm{M}}_{\mathrm{Na}} = 2C\overline{\mathrm{X}}_{\mathrm{M}} + \log (K^{\mathrm{M}}_{\mathrm{Na}})_{\mathrm{X}_{\mathrm{M}}, \overline{\mathrm{X}}_{\mathrm{M}} \to 0} \tag{12}$$

where C refers to the Kielland coefficient. Generally, the C value is a negative constant, depending on the exchanger and the ion-exchange system. It means that the ion exchange becomes difficult with progressive exchange.

Equations (11) and (12) are combined to give the thermodynamic constant K:

$$\ln K = (1 - n) + 2.303C + \ln (K^{\mathrm{M}}_{\mathrm{Na}})_{\mathrm{X}_{\mathrm{M}}, \overline{\mathrm{X}}_{\mathrm{M}} \to 0} \tag{13}$$

That is, the thermodynamic equilibrium constant is determined by the valence of the exchanging cation, the Kielland coefficient (C), and the intercept of the Kielland plot, $\ln (K^{\mathrm{M}}_{\mathrm{Na}})_{\mathrm{X}_{\mathrm{M}}, \overline{\mathrm{X}}_{\mathrm{M}} \to 0}$. By tracing the above process in reverse, the ion-exchange isotherm at the total normality (TN) can be determined if these parameters are given.

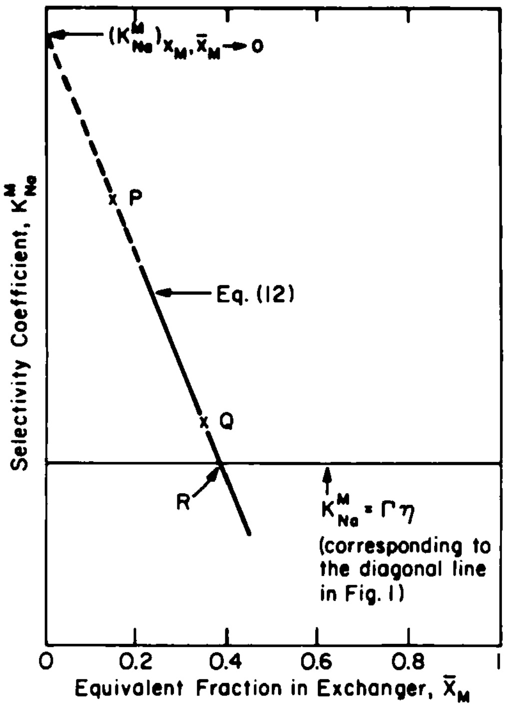

FIG. 2. Kielland plot for M^{n+}/Na^+ exchange. The dashed line shows the region where the exchanging ion concentration is very low in the solution and cannot be determined with high accuracy.

Evaluation of K_d Values

The K_d value at any $\bar{X}_M$ can be calculated as follows. It is defined by

$$K_d = \frac{[\overline{M^{n+}}]}{[M^{n+}]}$$

Using Eqs. (3), (4), and (6), we can get

$$K_d = \frac{TC\ \bar{X}_M}{TN\ X_M} \tag{14}$$

Hence, the K_d value at an intermediate value of $\bar{X}_M/X_M$ can be graphically determined from an ion-exchange isotherm (Point Q of Fig. 1). But it is much better to use the Kielland equation (12) and the selectivity coefficient K^M_{Na} (Eq. 8). First, $\bar{X}_M$ is specified and inserted into Eqs. (8) and (12). This process gives X_M, and then the K_d value can be determined. In the special case of $n = 1$,

$$K_d = \frac{TC}{TN}\left\{\bar{X}_M + (1 - \bar{X}_M)K^M_{Na}\cdot\frac{\gamma_M}{\gamma_{Na}}\right\} \tag{15}$$

The procedure is especially useful when the K_d value is too large to determine or X_M cannot be graphically obtained from the isotherm (Point *P* of Fig. 1).

The K_d value at infinitesimal loading (very small $\bar{X}_M$ is very important for interpreting the chromatographic behavior of metal ions. It can be calculated as follows (*10*). Equations (5) and (8) are combined to give

$$K^M_{Na} = \frac{\bar{X}_M(1 - X_M)^n}{(1 - \bar{X}_M)^n X_M}\,\Gamma\eta \tag{16}$$

where

$$\eta = n(TN)^{n-1}, \qquad \Gamma = \gamma^n_{Na}/\gamma_M$$

Therefore,

$$(K^M_{Na})_{X_M,\bar{X}_M\rightarrow 0} = \left(\frac{\bar{X}_M}{X_M}\right)_{X_M,\bar{X}_M\rightarrow 0}\cdot(\Gamma\eta)_{X_M,\bar{X}_M\rightarrow 0} \tag{17}$$

On inserting Eq. (14) into Eq. (17).

$$(K^M_{Na})_{X_M,\bar{X}_M\rightarrow 0} = \left(\frac{TN}{TC}\,K_d\right)_{X_M,\bar{X}_M\rightarrow 0}(\Gamma\eta)_{X_M,\bar{X}_M\rightarrow 0}$$

Therefore:

$$(K_d)_{X_M,\bar{X}_M\rightarrow 0} = \left(\frac{1}{TN}\right)^n\cdot\frac{TC}{n}\left(\frac{1}{\Gamma}\,K^M_{Na}\right)_{X_M,\bar{X}_M\rightarrow 0} \tag{18}$$

In reverse, we can calculate the equilibrium point $(X_M, \overline{X}_M)$ on the ion-exchange isotherm once the Kielland plot is given. Equations (12) and (16) are put together into one and rearranged.

$$\log \frac{\overline{X}_M(1 - X_M)^n}{(1 - \overline{X}_M)^n X_M} + \log \Gamma \cdot n(\mathrm{TN})^{n-1} = 2C\overline{X}_M + \log (K^{M}_{Na})_{X_M, \overline{X}_M \to 0} \qquad (19)$$

where X_M is given by

$$X_M = \frac{n[M^{n+}]_0 \upsilon - \overline{X}_M(\mathrm{TC})W}{\upsilon(\mathrm{TN})}$$

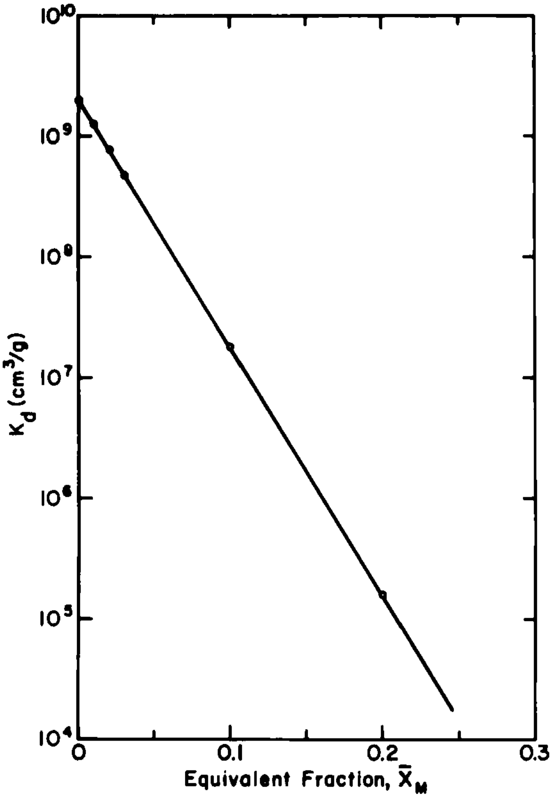

FIG. 3. K_d values calculated on the basis of Kielland plot with $\log (K^{M}_{Na})_{X_M, \overline{X}_M \to 0} = 8$, $C = -10$, $n = 1$, TC = 2 meq/g, TN = 0.1 N, $W = 0.10$ g, $\nu = 10$ cm³.

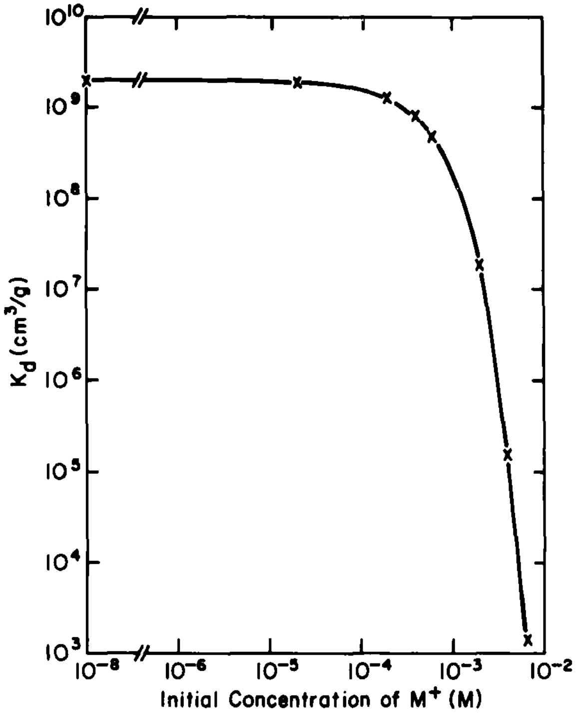

FIG. 4. Change in K_d values as a function of the initial concentration of exchanging ion.

Hence, if the initial concentration of the exchanging ions ($[M^{n+}]_0$), the weight of exchanger (W), the total normality (TN), and the volume of the solution (υ), are given, we can get $\overline{X}_M$ and X_M using the above equation. This calculation can be exemplified by Figs. 3 and 4 where K_d values are represented as a function of the equivalent fraction and the initial concentration of exchanging ion.

The Kielland plot should not vary depending on the TN. Hence, the above procedure is effective for another TN for the same set of $[X_M, \overline{X}_M)$. Thus, K_d values for the whole range of $\overline{X}_M$ can be calculated as a function of TN and initial concentration of exchanging ions.

CONCLUSION

The above unified treatment is very useful for ion-exchange systems and will allow consideration of the exchange-site occupancy when the theoretical or calculated ion-exchange capacity is used for the expression of the isotherm. The systematic procedure proposed here for K_d determination as a function of the initial concentration and the total normality will serve as an alternative for the tedious individual K_d measurements.

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