Seventh Symposium on Salt, Vol. II 23–28 (1993)
Elsevier Science Publishers B.V., Amsterdam

Ion-Exchange Selectivity for Alkali Metal Ions on a Hydrous Manganese Dioxide with a Tunnel Structure

Masamichi Tsuji[1], Mitsuo Abe[1], Yasuo Tanaka[2] and Yoshinobu Tanaka[2]

[1]*Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan*
[2]*The Sea Water Science Research Laboratory, Japan Tobacco Inc., 4-13-20, Sakai, Odawara 256, Japan*

ABSTRACT

A cryptomelane-type hydrous manganese dioxide has a 2 x 2 type tunnel structure. The H^+ form has been studied for its ion-exchange selectivity for Li^+, Na^+, K^+, Rb^+ and Cs^+/H^+ exchange at 30°C. The distribution coefficients for each alkali cation were evaluated as a function of the initial concentration of exchanging cations at the total normality of 0.1 N (N = equiv/dm^3) based on the Kielland plot. The separation factors for an Na^+–K^+ pair attained 1.3×10^{13} at $\overline{X}_M \rightarrow 0$. The extremely high selectivity can be attributed to the rigid tunnel structure with an opening which is only accessible to cations with crystal ionic radius of approximately 0.14 nm.

INTRODUCTION

Synthetic hydrous manganese dioxides in various crystal structures have been extensively studied for analytical use of their selective cation-exchange properties for transition metal ions (Ghosh, 1926; Kurbatov et al., 1951; Krauskopf, 1956; Goodall and Moore, 1959; Morgan and Stumm, 1964; Reynolds and Tyler, 1964; Bigliocca et al., 1967; Murray et al., 1968; Ujihira and Suzuki, 1971; Loganathan and Burau, 1973; Gadde and Laitinen, 1974; Murray, 1974; Murray, 1975; Weijden, 1976; Inoue et al., 1978). Recently a synthesized cryptomelane in the H^+ form has been discovered to show interesting ion-exchange selectivity toward cations with crystal ionic radius of approximately 0.14 nm, e.g., K^+, Rb^+, Ba^{2+}. Alkali and alkaline earth metal ions have been demonstrated to be stoichiometrically exchanged with protons in the crystal lattice of this ion exchanger (Tsuji and Abe, 1984a,b; Tsuji and Abe, 1985). Cryptomelane mineral has a 2 x 2 tunnel structure as reported by Byström and Byström (1950). The high selectivity for K^+ can be attributed to the tunnel structure with an opening which is only accessible to cations of this dimension.

The distribution coefficients (Kd) have an important role for the chromatographic separation of ions. The systematic calculation method of Kd determination based on the thermodynamic treatment has been reported (Tsuji and Komarneni, 1989, 1991, 1992; Komarneni and Tsuji, 1989). In those papers, Kd values have been derived as functions of exchanging ions and/or different bulk concentrations of electrolyte on a basis of the Kielland plot determined at one normality. The purpose of the present work was to obtain the Kielland plot for alkali metal ions and Kd values as a function of initial concentration of their cations on a hydrous manganese dioxide with a 2 x 2 type tunnel structure.

EXPERIMENTAL

Synthesis of a hydrous manganese dioxide with a tunnel structure

This was synthesized according to the method reported previously (Tsuji and Abe, 1984a) and described briefly as follows. A precipitate was allowed to form by adding 0.5 M $KMnO_4$ containing 1 M H_2SO_4 to 0.5 dm^3 of 1 M $MnSO_4$ containing 1 M H_2SO_4 at 60°C. The precipitate was aged overnight in the mother solution followed by washing with 6 M HNO_3 (0.5 dm^3) and then with water to remove a large part of the remaining H_2SO_4 and K_2SO_4. The washed product was dried at about 70°C for 3 days, ground and sieved to obtain 100–200 mesh size. The

sieved product was then packed in a glass column (1 cm i.d. x 20 cm) and leached continuously with concentrated HNO_3 to exchange H^+ for K^+ which was incorporated in the crystal structure. The leaching continued until the concentration of K^+ in the effluent became less than 5×10^{-5} M. The treated material was washed thoroughly and air-dried at ambient temperature.

X-ray diffraction and thermal studies

Powder X-ray diffraction study was performed using Mn-filtered Fe–Kα radiation with a RIGAKU Rint diffractometer. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a Rigaku thermoflex-type thermal analyzer, Model 8001, at a heating rate of 20°C/min with α-Al_2O_3 as the reference material.

Ion-exchange study

The exchanger in the H^+ form (0.100 g) was equilibrated with an aliquot of the sample solution (10.0 cm^3) of 0.01 N or 0.05 N with respect to (MNO_3 + HNO_3) where M = Li, Na, K, Rb or Cs. About 4 weeks were required to attain steady-state concentration in the supernatant solution. After the equilibration, the solution was separated from solid and analyzed for alkali metal ions by atomic emission and/or absorption spectrometry by using a Varian-Techtron AA1100 instrument.

Theoretical basis

The calculation method of the distribution coefficient from Kielland plot reported previously (Tsuji and Komarneni, 1992) has been here extended to M^+/H^+ exchange on acid-type cation exchanger. The ion-exchange process on the H^+ form exchanger can be expressed by the following equation:

$$\overline{H^+} + M^+ = \overline{M^+} + H^+ \qquad (1)$$

The thermodynamic equilibrium constant, K, for the ion-exchange process expressed by Equation (1) is defined by (Gaines and Thomas, 1953):

$$K = \frac{\overline{X}_M [H^+] f_M \gamma_H}{\overline{X}_H [M^+] f_H \gamma_M} \qquad (2)$$

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

Molalities $[M^+]$ and $[H^+]$ for solution phase are replaced by the equivalent fractions:

$$X_M = \frac{[M^+]}{[M^+] + [H^+]}, \quad X_H = \frac{[H^+]}{[M^+] + [H^+]} \qquad (3)$$

and for exchanger phase

$$\overline{X}_M = \frac{\overline{[M^+]}}{\overline{[M^+] + [H^+]}}, \quad \overline{X}_H = \frac{\overline{[H^+]}}{\overline{[M^+] + [H^+]}} \qquad (4)$$

and

$$X_M + X_H = 1, \quad \overline{X}_M + \overline{X}_H = 1 \qquad (5)$$

The total normality (TN) and the total capacity (TC) are kept constant throughout the ion-exchange process (Barrer and Klinowski, 1974):

$$[M^+] + [H^+] = TN, \quad \overline{[M^+]} + \overline{[H^+]} = TC \qquad (6)$$

By using these definitions, Equation (2) becomes

$$K = K_H^M \frac{f_M}{f_H} \qquad (7)$$

where K_H^M refers to the corrected selectivity coefficient:

$$K_H^M = \frac{\overline{X}_M X_H \gamma_H}{\overline{X}_H X_M \gamma_M} \qquad (8)$$

The ratio of the activity coefficient, γ_H/γ_M, is nearly equal to unity as long as the electrolyte concentration is low and the Debye–Hückel approximation is valid. Then, the ion-exchange isotherm is almost independent of the total normality. In this special case, the Kielland plot does not almost depend on the TN. However, the ratio will deviate from unity in concentrated solution and as a result the ion-exchange isotherm will be slightly affected because the activity coefficient ratio cannot compensate for the effect of concentration.

The exchange isotherms are all determined in solutions of constant total normality in which only the ratios of X_H and X_M are changed. In this case the simplified form of Glueckauf's equation gives (Glueckauf, 1949)

$$\left\{ \gamma_{(MNO_3)}^{HNO_3} / \gamma_{(HNO_3)}^{MNO_3} \right\}^2 = \gamma^{HNO_3} / \gamma^{MNO_3}$$

$\gamma_{(MNO_3)}^{HNO_3}$ is the activity coefficient of electrolyte HNO_3

in solution with MNO_3 of the given total molality and γ^{HNO_3} is the activity coefficient of electrolyte HNO_3 at the same molality in absence of MNO_3. Also

$$\gamma_H / \gamma_M = \left\{ \gamma^{HNO_3}_{(MNO_3)} / \gamma^{MNO_3}_{(HNO_3)} \right\}^2$$

These equations can be combined to give (Barrer and Sammon, 1955)

$$\gamma_H / \gamma_M = \gamma^{HNO_3} / \gamma^{MNO_3} \qquad (9)$$

The mean activity coefficients, γ^{HNO_3} and γ^{MNO_3}, were calculated or cited from literatures (Kielland, 1935, 1937; Hamer, 1959; Robinson and Stokes, 1965). Generally, the corrected selectivity coefficient is represented by a polynomial function of $\bar{X}_M$ with appropriate coefficients, C_m (Barrer, 1978).

$$\log K^M_H = \log(K^M_H)_{X_M, \bar{X}_M \to 0} + \sum (m + 1) C_m \bar{X}^m_M \qquad (10)$$

where C_m may be called generalized Kielland coefficients. Generally, the C_m value depends on the exchanger and the exchanging ions. It is considered to be related with the exchange energy from statistical treatment. Framework, ion size and shape, charge density on the anionic frame work, ion valency and electrolyte concentration in aqueous phase are involved in determining the coefficient C_m.

Evaluation of the distribution coefficient (Kd) as a function of $\bar{X}_M$ and initial concentration of exchanging cation $[M^+]_o$ can be made as follows. It is defined for the 1:1 exchange by:

$$Kd = \frac{[\bar{M}^+]}{[M^+]}$$

Using Equations (3), (4) and (6), we can get

$$Kd = \frac{TC\ \bar{X}_M}{TN\ X_M} \qquad (11)$$

Hence, the Kd value at an intermediate value of $\bar{X}_M/X_M$ may be graphically determined from an ion-exchange isotherm in case of a low-selectivity exchanger (Breck, 1974). The technique cannot however be used in the rectangular type of ion-exchange isotherm which is characteristic of a highly selective ion exchange. The method will bring a large uncertainty into the value of $\bar{X}_M/X_M$. It is much better to use the Kielland equation. Equations (8) and (11) can be combined to give:

$$Kd = \left\{ \bar{X}_M + (1 - \bar{X}_M) K^M_H\ \gamma_M / \gamma_H \right\} \frac{TC}{TN} \qquad (12)$$

Kd value at infinitesimal exchange is given by:

$$(Kd)_{\bar{X}_M \to 0} = \frac{TC}{TN} \left(\frac{\gamma_M}{\gamma_H} K^M_H \right)_{\bar{X}_M \to 0} \qquad (13)$$

Thus, we can calculate Kd values as a function of exchanger composition, (TC) $\bar{X}_M$ over the whole range of exchange and furthermore as a function of initial concentration of M^+ using the Kielland equation, the corrected selectivity coefficient and given relation

$$[M^+]_o v = v(TN) X_M + w(TC)\ \bar{X}_M \qquad (14)$$

as has been reported (Tsuji and Komarneni, 1991). In the present study, $v = 10\ cm^3$, TC = 2.70 meq/g and w = 0.100 g, as described below.

RESULTS AND DISCUSSION

Ion exchanger

The chemical composition of product and other properties were in good agreement with those reported previously. It belongs to the body-centred tetragonal system $I_{4/m}$ with the chemical composition of $MnO_2 \cdot 0.3H_2O$ or $H_2Mn_8O_{16} \cdot 2.4H_2O$ based on the chemical formula of a cryptomelane. The lattice parameters were a_o 0.977 nm and c_o 0.285 nm. The ion-exchange capacity is calculated to be 2.70 meq/g if $2H^+$ are exchangeable per 8 Mn on a basis of the accepted crystal structure.

Ion-exchange isotherm and Kielland plot

The ion-exchange isotherms for K^+ and Rb^+ showed a rectangular type which indicates the highly selective exchange. Those for Li^+ and Na^+ fell down below the diagonal line (Fig. 1). The reversal of selectivity was found for K^+, Rb^+ and Cs^+ at $\bar{X}_M$ = 0.33, 0.35 and 0.27. In the larger extent of exchange, the equivalent fraction $\bar{X}_M$ increased gradually with

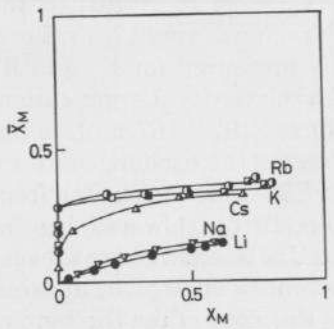

Fig. 1. Ion-exchange isotherms for M^+/H^+ exchange at 30°C. TN:0.01 N for Li^+ and Na^+; 0.05 N for K^+, Rb^+ and Cs^+.

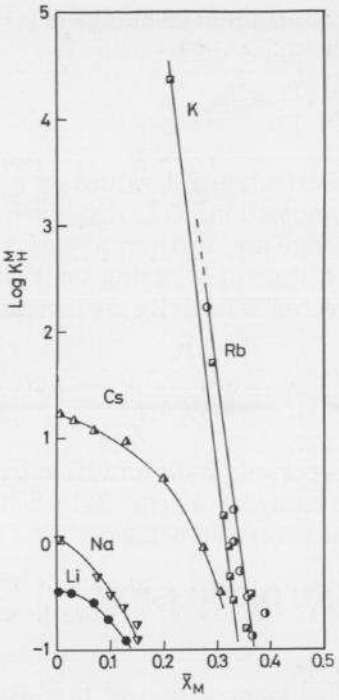

Fig. 2. Kielland plots for M^+/H^+ exchange at 30°C.

an increase in X_M. The profile of exchange can be made clearer on the Kielland plot (Fig. 2). It showed a straight line for K^+ and Rb^+ in a region determined, while those for Li^+, Na^+ and Cs^+ were curved. Extremely large selectivity was revealed between a group of K^+ and Rb^+ and a group of Na^+ and Li^+. No dependence on the total normality was found for the Kielland plots or the ion-exchange isotherms of these cations up to 0.1 N. Moreover, the process has been demonstrated to be reversible (Tsuji and Komarneni, 1992). These findings uniquely define the thermodynamic quantities and allow validity of mutual comparison of the isotherm and the Kielland plot at different concentrations.

The Kielland plot gave a non-linear curve for Li^+, Na^+ and Cs^+. The selectivity increased in the order of $Li^+ < Na^+ < Cs^+ < K^+ < Rb^+$ in the $\bar{X}_M$ value determined. A region of small $\bar{X}_M$ value could not be experimentally measured for K^+ and Rb^+ owing to extremely high selectivity. Larger cation, Cs^+ (effective ionic radius, EIR, 0.167 nm), is less hydrated and easily accesses the exchange site in very small exchange. The EIR values were cited from Shannon's table (Shannon, 1976). However, the framework of exchanger needs to be enlarged to accommodate Cs^+, which requires much energy. In the small extent of Cs^+ exchange, the slope of the Kielland plot is small, but with progressive exchange it becomes very steep and nearly equal to that of K^+ exchange. XRD patterns of alkali cation exchanged forms have revealed single phase of a cryptomelane and a single-site cation exchanger has been obtained. A straight line is therefore expected for the Kielland plot. Those of Li^+, Na^+ and Cs^+/H^+ exchange did not show a straight line, but a curve. This is probably because the exchange site was partially occupied and the tunnel was partially clogged by the exchanged cations. It may be called a self-clogging effect. On the other hand, smaller Li^+ (EIR, 0.074 nm) and Na^+ (EIR, 0.102 nm) are strongly hydrated and have to shake off the hydration water to enter the tunnel site. Thus, limitation of exchange is imposed on these cations, depending on the crystal ionic radius and dimension of hydrated ion. The problem of dehydration of exchanging ion is to be further studied.

Calculation of Kd values

Kd values were calculated using Equations (12)–(14) as a function of the initial concentration of M^+ at the total normality of 0.1 (Fig. 3). At concentrations of $< 5 \times 10^{-3}$ N, a large separation factor α_N^M of $> 10^{13}$ can be found for the Na^+–K^+ pair. The α_N^M for the neighbouring cation pair at "zero" loading was calculated (Table 1). It can be contrasted with that of a strongly acidic cation exchange resin (Strelow et al., 1965). The corrected selectivity coefficient on the organic ion-exchange resin does not change drastically as in inorganic ion exchanger.

Kd values at $\bar{X}_M = 0$ were plotted as a function of effective ionic radius (EIR) (Fig. 4). A large maximum of Kd can be seen at the EIR of approximately 0.14 nm. It agrees well with the openings of the tunnel of the H^+ form exchanger, i.e., 0.135 nm (Tsuji and Abe, 1985). The ion-exchange cavity has almost the same dimension as the crystal ionic radius of K^+ (0.138 nm) and Rb^+ (0.152 nm). In this case, the

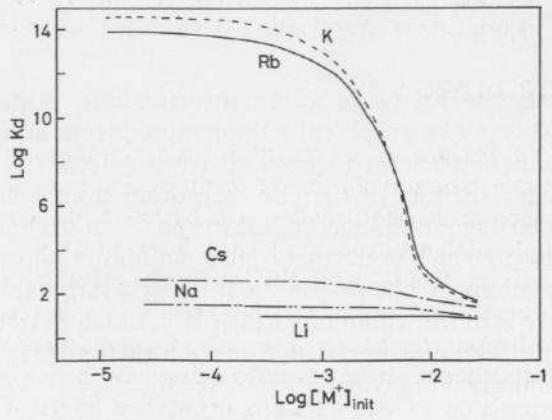

Fig. 3. Calculated log Kd for alkali metal ions as a function of initial concentration in the total normality of 0.1.

TABLE 1

Corrected selectivity coefficients at infinitesimal exchange and Kd values of alkali metal ions at TN 0.10

Exchanger	Parameters	Li^+	Na^+	Cs^+	Rb^+	K^+
This exchanger	$\left(K_H^M\right)_{X_M, \bar{X}_M \to 0}$	0.36	1.20	16	3.16×10^{12}	1.58×10^{13}
	Kd	9.7	32	403	8.53×10^{13}	4.26×10^{14}
	α_N^M	3.3	12.4	2.1×10^{11}	5.0	
		Li^+	Na^+	K^+	Rb^+	Cs^+
BIO-RAD AG50W-X8	$\left(K_H^M\right)_{X_M, \bar{X}_M \to 0}$	0.86	1.40	3.40	3.60	4.10
	Kd	43	70	170	180	205
	α_N^M	1.6	2.4	1.05	1.13	

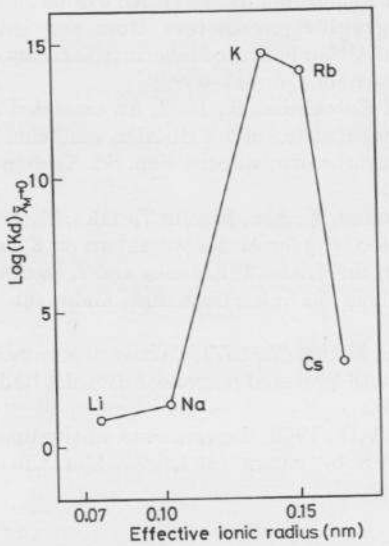

Fig. 4. Plot of log Kd at an infinitesimal exchange vs. effective ionic radius.

electrostatic attraction is extremely large between the negatively charged cavity and these cations.

CONCLUSION

Evaluations of Kd at the infinitesimal exchange and as a function of initial concentration of exchanging ions have been made on a hydrous manganese dioxide with a tunnel structure. The extremely high selectivity for K^+ and Rb^+ with an effective ionic radius of 0.14 nm was revealed. The generalized calculation method of Kd values as a function of initial concentration of exchanging ions and/or ionic composition of ion exchanger on the basis of the Kielland plot is useful for designing chromatographic separation of K^+ in bulk components with this selective cation exchanger along with determinations of the thermodynamic quantities.

REFERENCES

Barrer, R.M. and Sammon, D.C., 1955. Exchange equilibria in crystals of chabazite. J. Chem. Soc., 2838–2849.

Barrer, R.M., 1978. Cation-exchange Equilibria in Zeolites and Feldspathoids. In: L.B. Sand and F.A. Mumpton (Editors), Natural Zeolites, Occurrence, Properties, and Use. Pergamon, New York, pp. 385–395.

Barrer, R.M. and Klinowski, J., 1974. Ion-exchange selectivity and electrolyte concentration. J. Chem. Soc. Faraday 1, 70: 2080–2091.

Bigliocca, C., Girardi, F., Pauly, J., Sabbioni, E., Meloni, S. and Provasoli, A., 1967. Radiochemical separations by adsorption on manganese oxide. Anal. Chem., 39: 1634–1639.

Breck, D.W., 1974. Zeolite Molecular Sieves. Structure, Chemistry, and Use. Wiley, New York, Chap. 7.

Byström, A. and Byström, A.M., 1950. The crystal structure of hollandite, the related manganese oxide minerals and α-MnO_2. Acta Crystallogr., 3: 146–154.

Gadde, R.R. and Laitinen, H.A., 1974. Studies of heavy metal adsorption by hydrous iron and manganese oxides. Anal. Chem., 46: 2022–2026.

Gaines, G.L. Jr. and Thomas, H.C., 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys., 21: 714–718.

Ghosh, B., 1926. Parallelism between the effect of neutral salts on the electrical charge of hydrated manganese oxides and the concentration of hydrogen ions liberated. J. Chem. Soc., 2605–2614.

Glueckauf, E., 1949. Activity coefficients in concentrated solutions containing several electrolytes. Nature, 163: 414–415.

Goodall, C.A. and Moore, R.L., 1959. The co-precipitation of protactinium with the dioxides of manganese, lead and tin. J. Inorg. Nucl. Chem., 11: 290–296.

Hamer, W.J. (Editor), 1959. The Structure of Electrolyte Solutions. Wiley, New York, pp. 120–121.

Inoue, Y., Tochiyama, O. and Hamashima, S., 1978. Removal of ^{233}Pa from ^{237}Np using manganese dioxide or silica gel.

Int. J. Appl. Radiat. Isotopes, 29: 561–565.
Kielland, J., 1935. Thermodynamics of base-exchange equilibria of some different kinds of clays. J. Soc. Chem. Ind., 54: 232T–234T.
Kielland, J., 1937. Individual activity coefficients of ions in aqueous solutions. J. Am. Chem. Soc., 59: 1675–1678.
Komarneni, S. and Tsuji, M., 1989. Selective cation exchange in substituted tobermorites. J. Am. Ceram. Soc., 72: 1668–1674.
Krauskopf, K.B., 1956. Factors controlling the concentrations of thirteen rare metals in sea-water. Geochim. Cosmochim. Acta, 9: 1–32B.
Kurbatov, M.H., Wood, G.B. and Kurbatov, J.D., 1951. Isothermal adsorption of cobalt from dilute solution. J. Phys. Colloid Chem., 55: 1170–1182.
Loganathan, P. and Burau, R.G., 1973. Sorption of heavy metal ions by a hydrous manganese oxide. Geochim. Cosmochim. Acta, 37: 1277–1293.
McKenzie, R.M., 1979. Proton release during adsorption of heavy metal ions by a hydrous manganese dioxide. Geochim. Cosmochim. Acta, 43: 1855–1857.
Morgan, J.J. and Stumm, W., 1964. Colloid-chemical properties of manganese dioxide. J. Colloid Sci., 19: 347–359.
Murray, D.J., Healy, T.W., and Fuerstenau, D.W., 1968. The adsorption of aqueous metal on colloidal hydrous manganese oxide. Adv. Chem. Ser., 79: 74–81.
Murray, J.W., 1974. The surface chemistry of hydrous manganese dioxide. J. Colloid Interf. Sci., 46: 357–371.
Murray, J.W., 1975. The interaction of metal ions at the manganese solution interface. Geochim. Cosmochim. Acta, 39: 505–519.
Reynolds, G.F. and Tyler, F.S., 1964. Studies of the separation of trace metals by the manganese dioxide "collection" method. Analyst, 89: 579–586.
Robinson, R.A. and Stokes, R.H., 1965. Electrolyte Solutions, Butterworths, London, Appendix 8.10.
Strelow, F.W.E., Rethemer, R. and Bothma, C.J.C., 1965. Ion exchange selectivity scales for cations in nitric acid and sulfuric acid media with a sulfonated polystyrene resin. Anal. Chem., 37: 106–111.
Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr., A32: 751–767.
Shannon, R.D. and Prewitt, C.T., 1969. Effective ionic radii in oxides and fluorides. Acta Crystallogr., B25: 925–946.
Tsuji, M. and Abe, M., 1984a. Synthesis of cryptomelane-type hydrous manganese dioxide as an ion-exchange material and their ion-exchange selectivities towards alkali and alkaline earth metal ions. Solvent Extr. Ion Exchange, 2: 253–274.
Tsuji, M. and Abe, M., 1984b. Separation of trace amounts of Ca^{2+} and Sr^{2+} from K^{+} and Rb^{+} with a hydrous manganese dioxide ion exchanger. Radioisotopes, 33: 218–221.
Tsuji, M. and Abe, M., 1985. Acid-base properties of a cryptomelane-type hydrous manganese (IV) oxide and some chromatographic applications. Bull. Chem. Soc. Jpn., 58: 1109–1114.
Tsuji, M. and Komarneni, S., 1989. Alkali metal ion exchange selectivity of Al-substituted tobermorite. J. Mater. Res., 4: 698–703.
Tsuji, M. and Komarneni, S., 1991. An evaluation method of chromatographic parameters from the ion-exchange isotherm of Al^{3+}-substituted tobermorite cation exchanger. Sep. Sci. Technol., 26: 647–659.
Tsuji, M. and Komarneni, S., 1992. An extended method for analytical evaluation of distribution coefficients on selective inorganic ion exchangers. Sep. Sci. Technol., 27: 813–821.
Tsuji, M., Tanaka, Y., Abe, M. and Tanaka, Y., 1991. Ion-exchange Selectivity for Alkali Metal Ions on K^{+} Ion Memory Exchanger. In: M. Abe, T. Kataoka and T. Suzuki (Editors), New Development in Ion Exchange, Kodansha, Tokyo, pp. 627–632.
Ujihira, Y. and Suzuki, Y., 1971. Carrier precipitation of trace elements with hydrated maganese dioxide. Radioisotopes, 20: 427–432.
Weijden, C.H.V.D., 1976. Experiments on the uptake of zinc and cadmium by manganese oxides. Mar. Chem., 4: 377–387.