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Synthetic Inorganic Ion-exchange Materials. XXXVIII. Acid-base Properties of a Cryptomelane-type Hydrous Manganese(IV) Oxide and Some Chromatographic Applications

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The pH titration curves of a cryptomelane-type hydrous manganese(IV) oxide(CRYMO) apparently showed a dibasic Brönsted-acid towards Li^+, Na^+, K^+, and Rb^+ ions and a monobasic Brönsted-acid towards Cs^+ ions, instead of an amphoteric character, using a mixed solution of alkali metal nitrate and nitric acid or each hydroxide with the ionic strength of 0.1. The apparent ion-exchange capacities(meq/g) of alkali metal ions increased in this order: $Li^+(0.50)<Na^+(0.55)<Cs^+(0.85)<Rb^+(1.00)<K^+(1.10)$ at pH 2 and $Cs^+(1.20)<Rb^+(1.72)<Na^+(1.78)<Li^+(1.80)<K^+(1.81)$ at pH 10. The point of zero charge(PZC) of CRYMO was estimated to be much lower than 2. The unusual selectivity for K^+ and Rb^+ ions can be successfully applied to some ion-exchange separations: *e.g.*, the removal of K^+ ions from $NaNO_3$ and $NaMnO_4$ solutions, the removal of Rb^+ ions from a $CsNO_3$ solution, and the selective uptake of K^+ ions from seawater.

An ion-exchange property has been known for a long time in manganese(IV)-oxide minerals.[1-3] Hydrous manganese(IV) oxide is considered to be a multifunctional ion-exchanger with an amphoteric nature.[4] The colloid-chemical properties of synthesized hydrous manganese(IV) oxides have been investigated by many authors.[5-9] The PZC or isoelectric points (IEP) of hydrous manganese(IV) oxides have been reported to change depending on the modifications.:[10] Mn(II)-manganite(1.8 ± 0.5)<δ-type(2.8 ± 0.3)<α-type(4.5 ± 0.5)<γ-type(5.5 ± 0.2)<β-type(7.3 ± 0.2). Of these modifications, α- and γ-type manganese(IV)-oxide minerals exhibit a relatively large ion-exchange capacity (0.6 meq/g of MnO_2 at pH 11).[4] Hydrous manganese(IV) oxides show only cation-exchange properties at $pH>1$.[11]

Recently, much attention has been paid to manganese(IV) oxides as scavengers in analytical chemistry and nuclear-waste processing; they have attracted this attention because of their high selectivities towards certain elements and their stability against various chemicals or the strong fields of various radiations.[11-17]

The present authors have reported that a cryptomelane-type hydrous manganese(IV) oxide behaves as a so-called ion-exchange material. It shows an excellent selectivity towards alkali and alkaline earth metal ions with an effective ionic radius (EIR)[18] of about 1.4 Å (1 Å=0.1 nm).[19] The ion-exchange selectivity for micro-amounts increased in this order: $Li^+<Na^+<Cs^+\ll Rb^+$, K^+ for the alkali metal ions and $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$ for the alkaline earth metal ions. This performance could be successfully utilized for the separation of micro-amounts of Ca^{2+} or Sr^{2+} ions from large amounts of K^+ or Rb^+ ions respectively.[20] This behavior is very different from that of the hydrous manganese(IV) oxides reported by other authors.[4]

This paper will describe the acid-base properties of the CRYMO and some chromatographic applications.

Experimental

Ion-exchange Materials and Characterization. The CRYMO in the H^+ form was prepared as has been described previously.[19] The CRYMO was identified by an X-ray powder analysis and thermal studies (TG and DTA). The X-ray powder diffraction and the thermal studies were carried out by using a JEOL-7E diffractometer and a Rigaku Denki thermal analyzer, Model 8001, with a heating rate of 20 °C/min respectively. The characteristics of the product obtained showed a good agreement with those reported previously:[19] the chemical composition was $MnO_2\cdot0.28H_2O\cdot0.003K_2O$, and the lattice constants (a_o and c_o) were 9.77 Å and 2.85 Å respectively in the tetragonal system.

pH Titration Curve. An aliquot of the sample solution(12.5 cm³), adjusted to the ionic strength of 0.1 with MNO_3 and HNO_3 or MOH (M=Li, Na, K, Rb, and Cs), was equilibrated with the CRYMO in the H^+ form (0.125 g) at 30 ± 0.5 °C. After the equilibration, the metal ion concentration and the pH of the solution were determined. The metal concentration was determined as follows: A 10 cm³-aliquot of the equilibrated solution was neutralized with the standardized 0.05 M (1 M=1 mol dm^{-3}) NaOH or HNO_3; it was then percolated through a Dowex 50W-X8 cation-exchange resin column in the H^+ form. After the column had been washed with demineralized water ($>10^6$ S cm^{-1}) until the effluent was neutral, the amount of H^+ ions liberated by the CRYMO was determined. Thus, the equilibrium concentration of the M^+ ions was deduced by subtracting the amount of NaOH used for neutralization from the amount of H^+ ions titrated. The amount of M^+ ions exchanged was determined from the difference between the initial and equilibrated concentrations.

Preparation of CRYMO in the Na^+ Form. The CRYMO in the H^+ form was converted into the Na^+ form by charging a 0.1 M $NaNO_3$ solution onto the top of a CRYMO column in the H^+ form until the pH of the effluent attained that of the feed (pH 7). The column was washed with water and used in the subsequent experiments.

Column Experiment. A relatively small column (4.6 cm×0.5 cm I.D. or 3 cm×0.4 cm I.D.) of the CRYMO in the H^+ or Na^+ form was used at the ambient temperature. The flow rate was regulated by means of a high pressure pump (Nihon Seimitsu Kagaku, Model NSP-800-5UDX). The effluent was collected by using a drop-counting type fraction collector (Ohtake Works, Model UM-200).

Determination of Alkali and Alkaline Earth Metals. The alkali and alkaline earth metal ions were determined by emission and absorption spectrophotometries respectively by means of a Varian-Techtron atomic absorption spectrometer, Model 1100. The standard addition method was used in both cases.

Optical Spectrophotometry. A Shimadzu double beam optical spectrophotometer, Model UV-150-02, was used for the identification of the Mn(VII) ions.

Reagents. All the chemicals were of an analytical grade from Wako Pure Chemical Ind. Ltd. (Japan), except for Rb_2CO_3, Cs_2CO_3, and $NaMnO_4 \cdot H_2O$. The two carbonates (>99%) and $NaMnO_4 \cdot H_2O$ (>97% purity) were obtained from Soekawa Chemicals (Japan) and Aldrich Chemical Company, Inc. (USA) respectively. They were employed without further purification. Rubidium and cesium hydroxide solutions were prepared by percolating the nitrate solution through a Dowex2-X4 anion-exchange resin column in the OH^- form(2.5 cmϕ×20 cm) with bubbling N_2 gas. The seawater used was collected 1 km off shore at Takamatsu, Kagawa Prefecture, Japan, and filtered through a membrane filter (0.45 μm pore). The chemical composition of the seawater sample was 0.464 M Na^+, 0.00995 M K^+, 0.0492 M Mg^{2+}, and 0.00983 M Ca^{2+} ions.

Results and Discussion

pH Titration Curves. The pH titration curves on the CRYMO in the H^+ form showed a break point at pH 7, except in the case of the Cs^+ ions(Fig. 1). It behaves apparently as a dibasic acid towards these alkali metal ions, while apparently as a monobasic acid for Cs^+ ions. A purple color was observed in a small amount of Mn(VII) ions when the H^+ ions in the CRYMO were exchanged with any alkali metal ions except Cs^+ ions at pH values higher than 10. The CRYMO was broken into fine particles when the H^+ ions in the CRYMO were exchanged with Cs^+ ions at pH values higher than 10. The pH titration curves indicate that there are stronger Brönsted-acid sites in the CRYMO than those of hydrous oxides of other quadrivalent metals, such as Si, Ti, Sn, and Zr.[11]

The amounts of the replaceable protons responsible for the ion-exchange reactions can be estimated by the differences between the blank run (the dotted line) and each titration curve. The apparent capacity thus determined agreed well with the amount estimated from the titration curve (Fig. 2). These results indicate that the cation uptake obeys the ion-exchange reaction in the pH range studied. The ion-exchange capacity increases in this order: $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+$ at pH values lower than 5. The affinity sequence agrees well with our earlier results in acidic media.[19] The apparent capacity of Cs^+ ions almost reaches a saturated value at pH 5. It results in a different sequence of the affinity: $Cs^+ < Rb^+ < Na^+ < Li^+ < K^+$ at pH 10 because of the large steric effect for large cations. The largest ion-exchange capacity (2.4 meq/g) was obtained for Li^+ ions at pH> 11. This value is quite large compared with those of the α- and γ-types hydrous manganese(IV) oxide (0.6 meq/g) reported by other authors.[4]

This ion-exchange behavior can be well understood on the basis of the crystal structure of a cryptomelane.[21] It has been considered that the unit cell contains eight manganese ions (chiefly quadrivalent), with vacancies at two positions of (0, 0, 1/2) and (1/2, 1/2, 0), and sixteen oxygen ions. The two sites are surrounded by eight oxygen ions at a distance of 2.74 Å, forming a cube, and by four oxygen ions at a greater distance of 3.31 Å, forming a square at the same z level as the vaca-

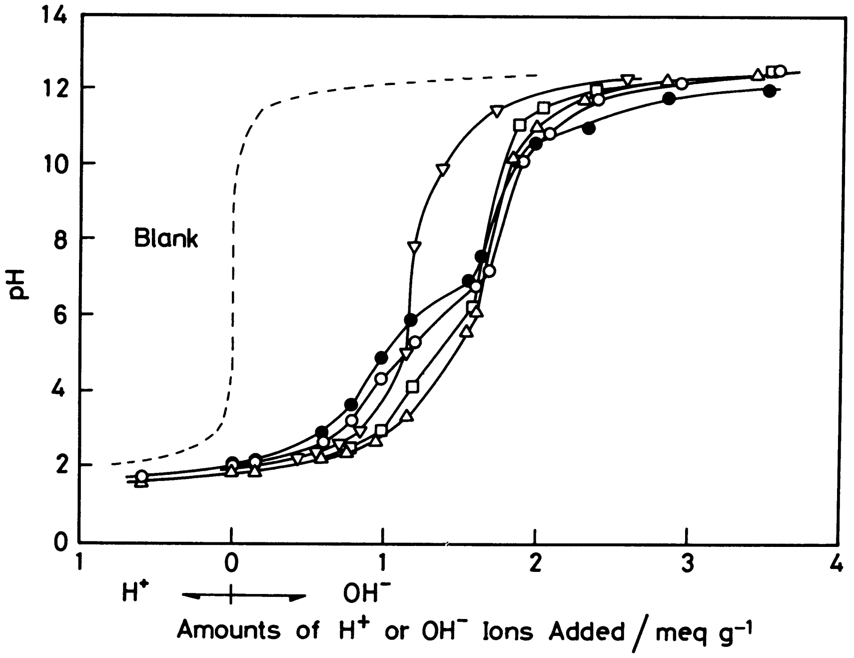

Fig. 1. pH Titration curves of the CRYMO in the H^+ form by various bases. CRYMO: 0.125 g, Soln.: 0.1 mol dm^{-3} (MNO_3+HNO_3) or (MNO_3+MOH) (M=Li(●), Na(○), K(△), Rb(□), and Cs(▽)), Total vol. of soln.: 12.5 cm^3, Temp.: 30±0.5 °C.

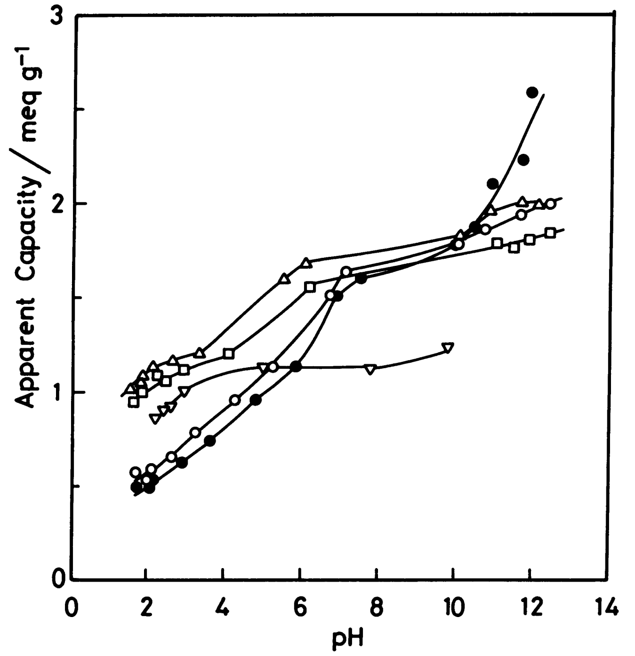

Fig. 2. pH Dependence of the apparent capacity for the alkali metal ions on the CRYMO. The experimental conditions and the marks are the same as in Fig. 1.

ncy. Both ion-exchange sites have the same electrostatic field and are 7.05 Å apart. The sites are estimated to be 2.68 Å long along the a axis and 2.84 Å long along the c axis, based on r ($^{VI}O^{2-}$)=1.40 Å. Hence, because of the electrostatic repulsion, Cs^+ ions with a radius of 1.88 Å cannot occupy all the ion-exchange sites, while Li^+ ions with a radius of 0.74 Å can enter almost all the ion-exchange sites.

The electron configuration of alkali metal ions as well as of alkaline earth metal ions is represented by s^2p^6. The metal ions of this group are less polarized under the influence of the electrical field of the crystal. For this reason, K^+ and Rb^+ ions, with about the same dimentions as the size of the ion-exchange site, are selectively exchanged.

It has been considered that the charges of the entering cations are compensated for by this reaction:[22]

$$V_2Mn_8O_{16} + M^{n+} \rightleftharpoons (V_{2-x}, M_x)Mn^{IV}_{8-y}Mn^{II}_yO_{16}$$

In fact, however, the sorptions of alkali, alkaline earth, and divalent transition-metal ions obey the stoichiometric ion-exchange reaction.[19,23] No such reduction occurs when these metal ions are sorbed. Instead, equivalent amounts of H^+ ions are released. Therefore, H^+ ions lie at the positions of the vacancy considered above.

The strength of hydrous oxide as an acid or base can be well described by the corresponding dissociation constants:[24,25] at a high pH:

$$RH \rightleftharpoons R^- + H^+,$$

$$K_{R^-} = \frac{[R^-][H^+]}{[RH]}$$

and
at a low pH:

$$R'OH \rightleftharpoons R'^+ + OH^-,$$

$$K_{R'^+} = \frac{[R'^+][OH^-]}{[R'OH]}$$

or

$$R'OH + H^+ \rightleftharpoons R'OH_2^+,$$

$$K_{R'OH_2^+} = \frac{[R'OH_2^+]}{[R'OH][H^+]}$$

where R or R′ denote the framework of the exchanger. The densities of the "surface" charges, $[R^-]$, $[R'^+]$, and $[R'OH^+{}_2]$, are often determined by titrating with alkali metal nitrates, and the corresponding hydroxide having less complexing.[6] The PZC is defined by a pH value yielding a zero-charge surface,[25,26] *i.e.*, giving the following relation:

$$[R^-] = [R'^+] + [R'OH_2^+]$$

The pH titration curve shows that the CRYMO releases H^+ ions equal in amount to the alkali metal ions exchanged. Even at pH 2, no appreciable uptake of nitrate ions was observed. Therefore, $[R'^+]$ or $[R'OH^+{}_2]$ is nearly null at a pH value of 2, and the PZC of the CRYMO can be estimated to be considerably lower than 2.

Healy *et al.* have reported that a cryptomelane-type hydrous manganese(IV) oxide showed a PZC value of 4.5±0.5.[10] Their specimen showed an X-ray pattern corresponding exactly with that given by Butler and Thirsk,[27] whose samples have larger lattice constants (a_o 9.85 Å, c_o 2.852 Å) than those reported by the present authors. The K^+ ions in this specimen cannot be removed by washing with water alone. When a considerable amount of K^+ ions is present in the material, increased lattice constants can be observed.[19] Hence, in their sample, a considerable amount of the dissociable protons can be inferred to be replaced by K^+ ions. For this reason, their sample probably showed a larger PZC value.

Selective Uptake of a Small Amount of Alkali Metal Ions from a Large Amount of Alkali Metal Salts by Using the Batch Technique. Generally, the synthetic inorganic ion-exchange materials are more stable against an attack of oxidizing reagents than the organic ion-exchange resins. The CRYMO was stable for a week in such oxidizing reagents as Cr(VI) and Mn(VII) salts solution containing a 1 M H_2SO_4 solution at room temperature. The K^+ impurity in a 0.5 M $NaMnO_4$ solution containing 1 M H_2SO_4 could be removed using the CRYMO (Fig. 3). An X-ray diffraction pattern of the CRYMO used showed no change in the crystalline modification, and repeated use is possible by removing the K^+ ions sorbed.

The uptake of alkali and alkaline-earth metal ions from seawater was determined by changing the ratios of the volume of seawater to the weight of CRYMO (*R* value) (Table 1). The total uptake (Na^+, K^+, Mg^{2+}, and

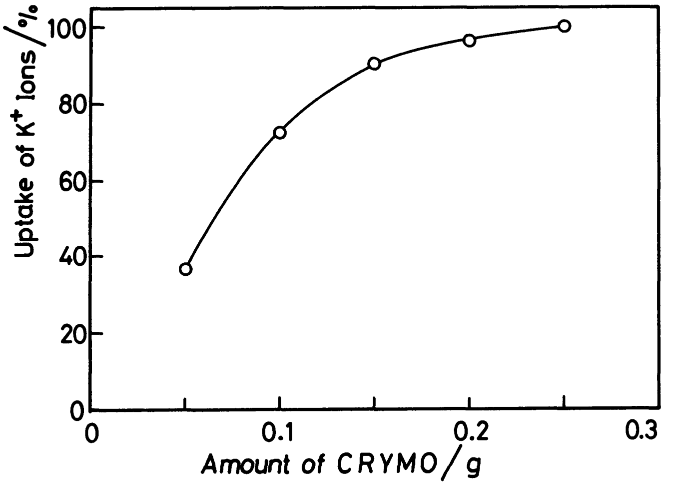

Fig. 3. Selective removal of K^+ ions from 0.5 mol dm^{-3} $NaMnO_4$ containing 1 mol dm^{-3} H_2SO_4 using the CRYMO by the batch technique. Concn. of K^+ ions: 3.65×10^{-3} mol dm^{-3}, Total vol: 25.0 cm^3. Temp: 30±0.5 °C. Immersing time: 4 d.

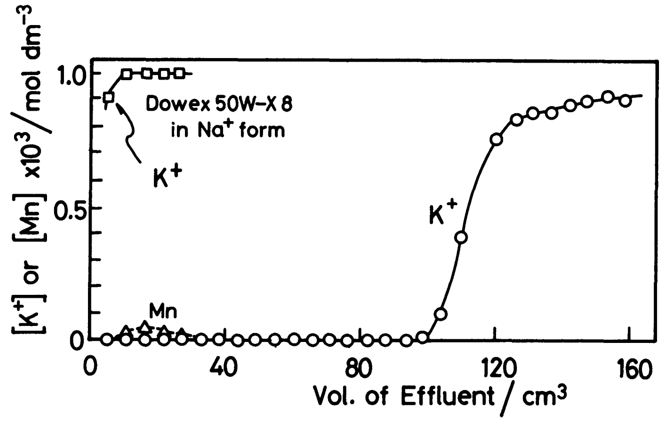

Fig. 4. Selective removal of K^+ ions from $NaNO_3$ solution with the CRYMO column in the Na^+ form. Column: 3×0.4 cm I.D. (100—200 mesh size, 0.50 g), Feed: (1 mol dm^{-3} $NaNO_3$+10^{-3} mol dm^{-3} KNO_3) mixed solution. Flow rate: 0.5—0.6 cm^3/min. □, ○: K^+ ion concn. in the effluent from Dowex 50W-X8 and CRYMO columns, respectively. △: Total manganese ions released to the soln.

Ca^{2+}), 1.3—1.6 meq/g, is nearly equal to the cation content of the CRYMO in the Na^+ form (1.32 meq (Na^++K^+)/g). Hence, a decreased amount of Na^+ ions in the CRYMO is compensated for by the K^+, Mg^{2+}, and Ca^{2+} ions through the ion-exchange process with Na^+ ions. The uptake of K^+ ions increases with an increase in the R values and attains about a constant value of 0.65 meq/g at the R value of 167.

The concentration factor was estimated by using the following equation by Abe and Hayashi[28] (Table 1):

$$f^{M}_{Na} = \frac{[(M)/(Na)]_{CRYMO}}{[(M)/(Na)]_{seawater}}$$

where M denotes K, Mg, and Ca.

The value of f^{K}_{Na} attains about 85 at the R value of 167, while f^{Ca}_{Na} gives the maximum of 55 at the R value of 100. At the pH values and metal concentrations studied, small f^{Mg}_{Na} values were obtained; hence, the selectivity for Mg^{2+} ions is slightly larger than for Na^+ ions. The results are in good agreement with those of our earlier report.[19]

Selective Removal of Alkali Metal Impurities from Salts of Alkali Metals by Using the Column Technique. The frontal chromatographic technique is one of the simplest procedures for the separation of a small amount of an element from a large amount of other elements. However, this technique is not very useful for the separation of a small amount of K^+ ions from a high concentration of Na^+ ions on a Dowex50W-X8 column because of its low selectivity. It is, however, evident from the selectivity studies of the CRYMO in our earlier report[19] that the separation of K^+ ions from Na^+ ions is feasible. The separation can be achieved with a much larger volume of the $NaNO_3$ solution containing 10^{-3} M K^+ ions on the CRYMO than that on Dowex 50W-X8 (Fig. 4).

K^+ ions in the feed solution were retained quantitatively on the column up to 97 cm^3. A faint purple color was observed in the effluent at the early stage of the injection of the feed. The chemical species of the colored component could be assigned spectrophotometrically as Mn(VII) ions. In the final stage, a large gas bubble generated by an unknown cause did not allow the percolation of the feed.

An unusual selectivity for Rb^+ ions on the CRYMO was applied to the separation of a micro-amount of Rb^+ ions from a 1 M $CsNO_3$ solution (Fig. 5). A trace amount of Rb^+ ions (<10^{-6}M) leaked out from the column up to 107 cm^3 of the effluent. The purified cesium nitrate (effluent up to 107 cm^3) showed an impurity level lower than 10^{-6} M for both Rb^+ ions and the total manganese. At 110 cm^3 of the effluent,

TABLE 1. UPTAKE OF METAL IONS FROM SEAWATER[a] BY THE CRYMO[b]

R[c] Value	Equil. pH	Uptake(meq/g) Na^+	K^+	Mg^{2+}	Ca^{2+}	Total uptake (meq/g)	Concentration factor f^{K}_{Na}	f^{Mg}_{Na}	f^{Ca}_{Na}
25	6.33	0.740	0.289	0.206	0.203	1.43	18.2	2.62	13.8
50	6.32	0.501	0.445	0.095	0.439	1.47	41.4	1.78	41.3
100	6.38	0.436	0.612	0.111	0.512	1.67	65.5	2.40	55.6
125	6.70	0.381	0.650	0.088	0.199	1.32	79.7	2.17	24.7
167	6.70	0.361	0.656	0.052	0.220	1.29	84.9	1.35	28.8

a) Initial pH of seawater used: 7.74. b) Cation contents of the CRYMO in the Na^+ form used: Na^+; 1.29 meq/g, K^+; 0.034 meq/g. c) R value: ratio of volume of seawater to weight of exchanger in cm^3/g.

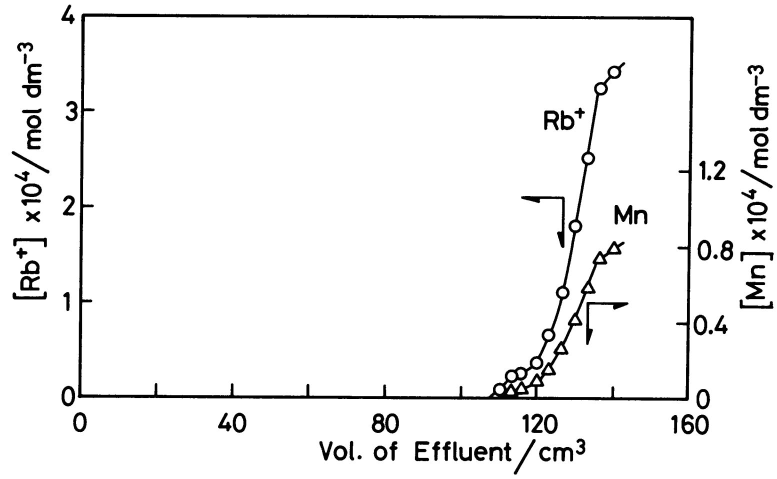

Fig. 5. Selective removal of Rb$^+$ ions from 1 mol dm^{-3} CsNO$_3$ solution by using the CRYMO column in the H$^+$ form. Column: 4.6X0.5 cm I.D. (100—200 mesh size, 1.0 g). Feed: 1 mol dm^{-3} CsNO$_3$+8.8X 10^{-4} mol dm^{-3} RbNO$_3$. Flow rate: 0.2 cm^3/min. Δ: Total manganese ions released to the solution by the CRYMO.

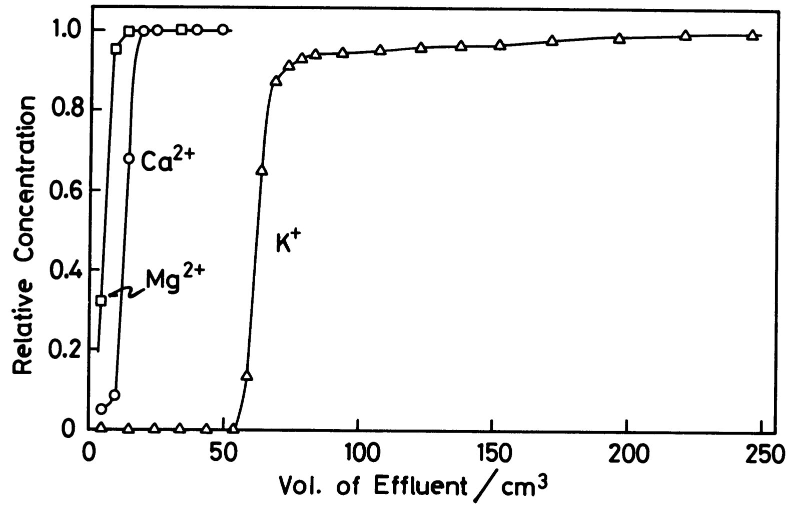

Fig. 6. Breakthrough behavior of metal ions in seawater on the CRYMO column. Column: 4.6X0.5 cm I.D. (100—200 mesh size, 1.0 g). Flow rate: 0.2 cm^3/min. The ordinate shows the concentration in the effluent relative to each metal ion concentration in seawater.

Mn(VII) ions were released from the column. Thus, commercial Cs salts can be very effectively purified by the use of the CRYMO column.

An effective separation of K$^+$ ions from seawater using a commercial cation-exchange resin is usually difficult because of the relatively low separation factor for K$^+$ to Na$^+$ ions, as has been pointed out above. The K$^+$ ions in seawater were collected batchwise as insoluble organic or inorganic compounds.[29,30] However, an effective separation cannot be expected using such a method. The separation technique using the CRYMO may give a better one.

The ion-exchange column technique allows a continuous operation, which is much superior to the batchwise process in terms of time and space. The breakthrough behavior for K$^+$, Mg^{2+}, and Ca^{2+} ions was studied by charging seawater continuously onto the top of the column of CRYMO in the Na$^+$ form (Fig. 6). Metal ions were eluted in this order: Mg^{2+}< Ca^{2+}<K$^+$. The breakthrough capacity showed 0.54 meq/g. The amount (0.65 meq/g) of K$^+$ ions sorbed up to 167 cm^3 of the feed solution is in good agreement with that of K$^+$ ions recovered in the batch equilibration technique at the *R* value of 167 cm^3/g.

By taking advantage of the large difference in the selectivity for K$^+$ and other ions, a more selective concentration of K$^+$ ions in seawater can be achieved by washing out Na$^+$ ions in the CRYMO column with an appropriate eluent. A 30-cm^3 aliquot of seawater was charged onto the column, and the column was washed with 250 cm^3 of a 1 M HNO$_3$ solution at a flow rate of 0.2 cm^3/min. By this operation, less concentration of

K^+ ions than 10^{-6} M was eluted, while almost all of the Mg^{2+} and Ca^{2+} ions and a considerable amount of Na^+ ions were eluted. Then, the K^+ ions exchange-adsorbed could be eluted by 250 cm^3 of a 13 M HNO_3 solution with an average yield of 90—95% in three runs. The concentration factor, $f^{K}_{Na}=480—500$, was obtained in the effluent by this once-through processing. The Mg^{2+} and Ca^{2+} ions in the effluent were less than 10^{-6} M.

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