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Ion-Exchange Reaction of Cs^+ Selective Layered γ-Titanium and γ-Zirconium Phosphates

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The H^+/M_A^+ ion-exchange reaction of layered γ-titanium and γ-zirconium phosphates, $M_T(HPO_4)_2 \cdot nH_2O$, was examined, where M_A is an alkali metal and M_T is Ti or Zr. They showed remarkably high ion-exchange selectivity for Cs^+ and Rb^+ in acidic media. The selectivity for Na^+ was rather low, and Li^+ exchange hardly occurred. The H^+ ion exchange of both γ-phosphates with Cs^+ and Rb^+ apparently occurred in two steps. These ion-exchange reactions occurred first at a pH value of around 2.0 to form a monobasic structure, $M_TM_AH(PO_4)_2 \cdot nH_2O$, accompanied by dehydration of the water of crystallization. The second step occurred at a pH around 8.0 to form a dibasic structure, $M_T(M_APO_4)_2 \cdot nH_2O$, the interlayer space of both γ-phosphates swelled again. The lattice of crystals gradually collapsed corresponding to further progress of the ion-exchange reaction with Cs^+ and Rb^+, and the amorphous phase finally appeared. According to ^{133}Cs NMR study, Cs^+ was found to be rather restricted. The results were compared with those of layered synthetic mica. The high Cs^+ and Rb^+ selectivity was ascribed to the dehydration property and strong interactions of these ions with the host lamella layers. The high selectivity of two γ-phosphates for Cs^+ in acidic media suggested a potentiality as promising materials for the recovery from radioactive waste. The interfering effect of coexisting Fe^{2+} was scarcely observed upon Cs^+ exchange, and was even positive due to the prevention of lattice coagulation.

The phosphates of multivalent metals have been well-known as inorganic ion exchangers. These acid salts have been classified as several different crystal structures, such as α-type, γ-type, a three-dimensional structure, and a fibrous structure.[1,2] Among crystalline titanium phosphates, γ-titanium phosphate $Ti(HPO_4)_2 \cdot 2H_2O$, abbreviated as γ-TiP, has a large interlayer spacing and sorbes cesium ions selectively.[3] On the other hand, inorganic ion exchangers usually show thermal stability and resistance to radiation superior to those of the organic ion-exchange resins. Since γ-TiP has high selectivity for cesium ions, it must be one of the promising materials for the recovery of cesium from radioactive waste, and will definitely contribute as environmental preservation materials, similar to synthetic mica.[4] The structure and general ion-exchange property of γ-TiP have been studied by thermal analysis and powder X-ray diffraction analysis.[3] However, few systematic studies have been carried out concerning the high selectivity for Rb^+ and Cs^+ and stability during the ion-exchange process.

This paper deals with the H^+/M_A^+ (M_A^+: alkali metal ions) ion-exchange reaction of γ-titanium and γ-zirconium phosphates ($M_T(HPO_4)_2 \cdot nH_2O$, where M_T is Ti or Zr) and their high Cs^+ and Rb^+ selectivity. In addition to thermal analysis and X-ray diffraction analysis, ^{133}Cs solid NMR was examined to reveal the origin of the high selectivity. The effect of Fe^{2+} as an interfering ion was examined for the practical recovery of Cs^+ from radioactive waste.

Experimental

Materials. Crystalline γ-titanium phosphate was prepared directly by a hydrothermal reaction of amorphous titanium phosphate in 10 mol dm^{-3} H_3PO_4 at 280 °C for 24 h according to a previously reported method.[5] Thus prepared γ-TiP contained water of crystallization of $n \fallingdotseq 1.6$. In the case of crystalline γ-zirconium phosphate, γ-$Zr(HPO_4)_2 \cdot nH_2O$, γ-ZrP, amorphous sodium zirconium phosphate gel was prepared in advance and crystalline Na^+ type zirconium phosphate was prepared by a hydrothermal reaction at 190 °C for one week. H^+ type γ-ZrP was then prepared by the Na^+/H^+ ion-exchange reaction in 1.0 mol dm^{-3} hydrochloric acid.[6] The prepared γ-ZrP contained water of crystallization of $n \fallingdotseq 1.0$. The appearance and size of two γ-phosphates were quite different.[5] The products were characterized using a powder X-ray diffractometer (MAC Science MO3X-HF, Japan) equipped with monochromized Cu Kα. Thermal analysis was carried out using a TG/DTA system (Rigaku TAS-200, Japan). Before X-ray diffraction or thermal analysis, the samples were stored under a constant humidity over a saturated aqueous NH_4Cl solution for at least three days.

Ion-Exchange Reaction. An ion-exchange reaction of two γ-phosphates with alkali metal ions was carried out similarly as follows. LiCl, NaCl, KCl, RbCl, and CsCl solutions (each 1.0×10^{-4} mol dm^{-3}) were prepared, and a HCl solution was added to vary the solution pH. Each salt solution (20 cm^3) and a γ-phosphate powder (0.2 g) were mixed in a glass ampoule, except for the NaCl solution. A polyethylene vessel was used in the case of the NaCl solution to avoid the contamination of Na^+ from the glass ampoule.

A mixture of 5.0×10^{-5} mol dm^{-3} $FeCl_2$ and CsCl solution was used to examine the interfering effect of Fe^{2+}. The concentration of the alkali metal ions and Fe^{2+} in the supernatant solution was measured by an atomic absorption spectrophotometer (HITACHI 170-30) and an inductively coupled plasma atomic emission spectrophotometer (SHIMADZU ICPS-5000), respec-

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tively. The amounts of sorbed ions were estimated.

pH Titration Curve. Each γ-phosphate (0.1 g) was placed in a glass ampoule and the metal ion solution (10 cm^3) was added. Various pH solutions with an ionic strength of 0.1 were prepared by varying the mixing ratios of 0.1 $mol\,dm^{-3}$ M_ACl and 0.1 $mol\,dm^{-3}$ M_AOH (M_A = Rb, Cs). After equilibrium was reached, the correct pH value was measured using a glass electrode pH meter (TOA HA-60G).

NMR Study. The ^{133}Cs NMR spectra were measured using a 300 MHz FT-NMR spectrometer (JNM-AL300, JEOL, Japan).

Results and Discussion

Ion-Exchange Selectivity. A preliminary study on the ion-exchange study of γ-TiP has already been reported.[7] Figure 1 shows K_d values of two γ-phosphates for alkali metal ions as a function of the pH. The K_d value was defined as follows:

$$K_d = \frac{\text{Concentration of } M_A^+ \text{ in solid phase in mol g}^{-1}}{\text{Concentration of } M_A^+ \text{ in solution phase in mol cm}^{-3}}. \tag{1}$$

K_d values below 1.0 could not be calculated when the amount of sorbed ion was too low. These points were Li^+ at pH 1.0, 1.5, and 2.0 on γ-ZrP, K^+ at pH 1.0 and 1.5, and the whole pH for Na^+ and Li^+ on γ-TiP.

It was found from Fig. 1 that both γ-phosphates showed K_d values of over 10^3 for Rb^+ and Cs^+ in the acidic media; the-observed K_d value for the H^+/Cs^+ ion exchange almost corresponded to that observed in the Na^+/Cs^+ ion exchange on synthetic mica, Na-TSM, in a neutral pH solution.[4] Another fea-

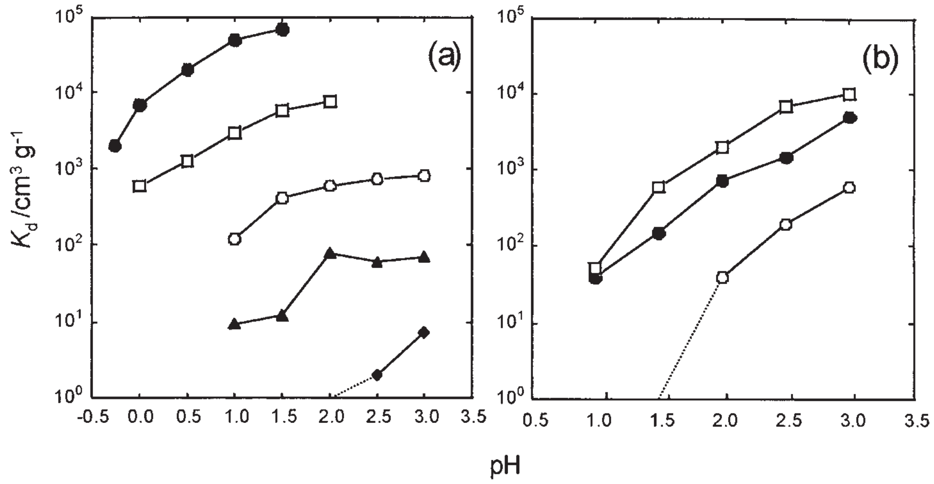

Fig. 1. pH dependence of distribution coefficients K_d for M_A^+/H^+ ion-exchange reaction of alkali metal ions: (a) γ-ZrP and (b) γ-TiP, ●: Cs^+, □: Rb^+, ○: K^+, ▲: Na^+, ◆: Li^+.

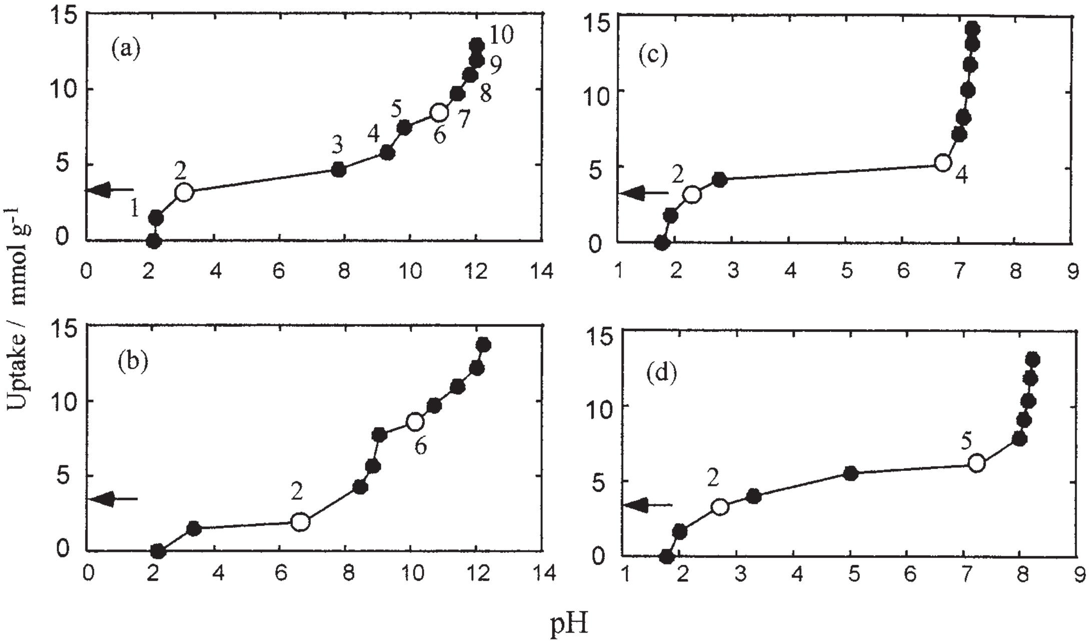

Fig. 2. pH titration curves for Rb^+/H^+ and Cs^+/H^+ ion-exchange reaction on γ-phosphates: (a) Rb^+/H^+ on γ-ZrP, (b) Cs^+/H^+ on γ-ZrP, (c) Rb^+/H^+ on γ-TiP, (d) Cs^+/H^+ on γ-TiP. Arrows indicate uptake of M_A^+ that corresponds to chemical formula of $M_THM_A(PO_4)_2$. Note that accuracy of vertical axis was rather poor.

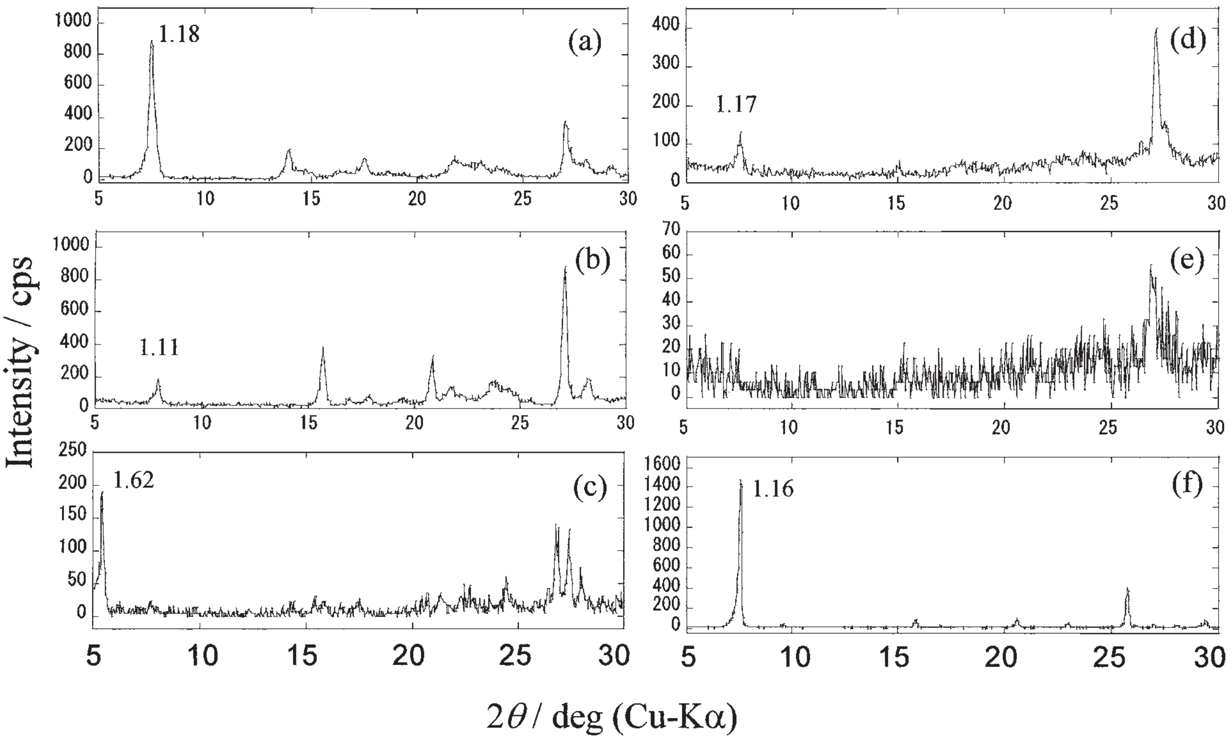

Fig. 3. X-ray diffraction patterns of metal ion sorbed γ-ZrP: (a) γ-ZrP, (b) sample No. 2 for Rb^+, (c) sample No. 6 for Rb^+, (d) sample No. 2 for Cs^+, (e) sample No. 6 for Cs^+. (f) shows X-ray diffraction pattern for ($Cs^+ + Fe^{2+}$) ion-exchanged γ-TiP. Numerals in each figure indicate the basal spacing in nm.

ture was revealed from Fig. 1, that both γ-phosphates seem to favor metal ions with large crystallographic radii. The uptake of Cs^+, Rb^+, and K^+ were rather high, whereas Na^+ was very low and Li^+ was hardly sorbed by both γ-phosphates. Thus, the selectivity sequence was generally $Cs^+ \fallingdotseq Rb^+ > K^+ > Na^+ > Li^+$. This tendency was successfully accounted for based on an analogy of the hydration property of these ions in aqueous solution, as discussed below.

Since both γ-phosphates showed such high Cs^+ selectivity in concentrated acidic media, they must be promising materials for the recovery of cesium ion from radioactive waste, even under strongly acidic conditions.

pH Titration Curves of Cs^+ and Rb^+. Figure 2 shows pH titration curves of Rb^+ and Cs^+ on γ-ZrP and γ-TiP, respectively. It was found from Fig. 2 that both γ-phosphates began to sorb Rb^+ and Cs^+ at a pH value of about 2. The arrow in the vertical axis shows the uptake of $M_A{}^+$ that corresponds to the mono basic chemical formula of $M_THM_A(PO_4)_2$. With an increase in the pH value, the uptake of metal ions increased in consistent with the ion-exchange equilibrium between H^+ and $M_A{}^+$. However, the layer structure at high pH values gave rise to a collapse, as discussed below concerning X-ray diffraction analysis.

X-ray Diffraction Analysis and Stability of Layer Structure. Figure 3 shows the X-ray diffraction patterns of Rb^+ and Cs^+ sorbed γ-ZrP. In sample number 2, the *d*-value of the first peak that corresponds to the basal spacing decreased from 1.18 to 1.11 and 1.18 to 1.17 in nm for Rb^+ and Cs^+ for γ-ZrP, respectively. This result coincided with the thermal analysis, as discussed later, in which the number of water molecules of crystallization decreased after the ion-exchange reaction. The *d*-value of a Rb^+ exchanged sample increased to 1.62 nm, indicating a swelling of the layer structure in sample number 6, which was prepared at a pH value of 11.0. In a Cs^+ exchanged sample, the layer structure collapsed completely to form an amorphous state in sample number 6 at a pH value of 10.0. Similar X-ray diffraction patterns of various Rb^+ and Cs^+ exchanged γ-TiP were observed. Table 1 summarizes the *d*-value of the first peak of each γ-phosphate and its ion-exchanged sample.

Table 1. *d*-Values of γ-Phosphates

Metal ions	*d*-Value/nm			
	γ-ZrP		γ-TiP	
—	1.18		1.15	
Rb^+	1.11[a)]	1.62[b)]	1.12[a)]	1.60[c)]
Cs^+	1.17[a)]	collapsed[b)]	1.14[a)]	1.44[d)]

a) Sample No. 2. b) Sample No. 6. c) Sample No. 4. d) Sample No. 5.

Upon comparing γ-TiP and γ-ZrP, the latter showed 2–3 order higher K_d values than the former at pH = 1.0 either on the H^+/Rb^+ or H^+/Cs^+ ion-exchange reaction. Such a large difference in K_d may be attributed to the appreciable difference in crystallinity and the size of the crystals prepared. γ-ZrP was smaller than γ-TiP, and showed a rather wide line width in the X-ray diffraction pattern, indicating a weak interaction between the host lamellae. However, a definite origin of the difference in K_d could not be verified within the limit of the present study.

It was found through X-ray diffraction analysis that both γ-

phosphates revealed a stable property upon occasion of the Rb^+ and Cs^+ exchange in acidic media.

Mechanism of High Selectivity for Cs^+. So far, many inorganic ion exchangers have been reported concerning the high selectivity for Li^+, which has the smallest crystallographic ionic radius among alkali metal ions. On the other hand, reports on inorganic ion exchangers that are selective for K^+–Cs^+ with a larger crystallographic radius have been rare and, the mechanism of the selectivity has not yet been clarified. Khan et al. have reported the K^+ selective cubic ammonium molybdate and successfully interpreted due to the hydration property of alkali metal ions through a NMR study.[8] In the case of cubic ammonium molybdate, the *B*-coefficient of viscosity was a key parameter to account for the different selectivity among K^+, Rb^+, and Cs^+. The *B*-coefficient reflects the distraction property of the ice-structure in the hydration atmosphere around the metal ions.[9] Accordingly, the hydration/dehydration property was examined by thermal analysis and a NMR study as follows.

Thermal Analysis: The number of water of crystallization was compared between the dibasic structure and the near-monobasic structure. The result is given in Table 2. In the case of γ-ZrP, the 0.76 and 0.50 of water molecules were found to be excluded accompanied by the accommodation of Rb^+ and Cs^+, respectively. In the case of γ-TiP, 1.40 and 0.69 of water molecules were excluded by the accommodation of Rb^+ and Cs^+, respectively. In other words, ion-exchange reactions of H^+/Rb^+ and H^+/Cs^+ occurred together with the excluding of interlayer water molecules in both γ-phosphates. This finding can be explained by the *B*-coefficient of the viscosity. Data of *B*-coefficient are given in Table 3 together with the ionic radii.[9] The negative values of the *B*-coefficient indicate the destructive tendency of the hydrated water. Thus, Rb^+ and Cs^+ tend to exclude their hydrated water molecules.

Table 2. Water of Crystallization of Di- and Mono-Basic Phosphates Prepared

Composition	Number of water of crystallization	Excluded water molecule
γ-Zr(HPO$_4$)$_2$	1.00	—
γ-ZrRbH(PO$_4$)$_2$	—	0.76
γ-ZrCsH(PO$_4$)$_2$	—	0.50
γ-Ti(HPO$_4$)$_2$	1.60	—
γ-TiRbH(PO$_4$)$_2$	—	1.40
γ-TiCsH(PO$_4$)$_2$	—	0.69

Table 3. Ionic Radii and *B*-Coefficients of Viscosity for Alkali Metal Ions[9]

Ions	Ionic radius/nm		*B*-coefficient /kg mol^{-1} (25 °C)
	Crystallographic	Hydrated ([a])	
Li^+	0.068	0.37 (7)	+0.150
Na^+	0.097	0.33 (5)	+0.086
K^+	0.133	0.25 (4)	−0.007
Rb^+	0.152	0.24 (3.5)	−0.030
Cs^+	0.170	0.24 (3.5)	−0.045

a) The average number of hydration estimated for the mobility.

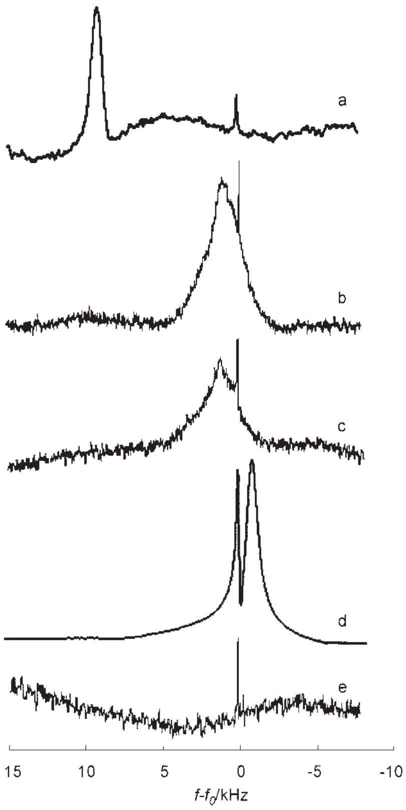

Fig. 4. Static ^{133}Cs NMR spectra: (a) solid CsCl, (b) Cs^+ sorbed γ-ZrP, (c) Cs^+ sorbed γ-TiP, (d) Cs^+ sorbed Na-TSM, and (e) (Cs^+ + Fe^{2+}) ion-exchanged γ-TiP. Each sharp singlet at 0 kHz indicates reference spectrum of aqueous CsCl solution.

NMR Study: ^{133}Cs NMR spectra were measured to clarify the accommodated state of the Cs^+ ion. The results are shown in Fig. 4 together with that in solid CsCl. A sharp signal at 0 kHz indicates the internal standard of an aqueous CsCl solution. Generally, the ^{133}Cs NMR spectrum shows a very narrow signal, like ^{1}H, with a spin angular momentum of 1/2 if the sample is a liquid, as shown in Fig. 4, because of the very small quadrupole moment of -0.003×10^{24} cm^2 although the spin angular moment is 7/2. Accordingly, the increase in the line width of the ^{133}Cs NMR spectrum is attributable either to the motional narrowing or the dipolar broadening.

The ^{133}Cs NMR spectra of Cs^+ accommodated in γ-ZrP and γ-TiP showed a similar line width of about 2.5 kHz. These values were about three times larger than 0.8 kHz of solid CsCl and Cs^+ accommodated in Na-TSM. In case of Cs^+ selective Na-TSM, the line width of ^{133}Cs MAS-NMR of Cs^+ accommodated in Na-TSM was about 0.3 kHz. There are rather large hemispherical holes surrounded by six tetrahedrons of Si–O matrices that are suitable for dehydrated Cs^+ on the surface of Na-TSM lamellae.[10,11] The major part of the line width of Cs^+ accommodated Na-TSM was attributed to dipolar broadening and the effect of motional narrowing was minor. On the other hand, γ-phosphates don't have suitable holes for Cs^+. They have parallel channels[12] that accept Cs^+ on the surface region of the M$_T$–PO$_4$ lamella matrix. If Cs^+ was accommodated in such a channel with a low symmetrical surrounding and a strong interaction between Cs^+ and O$^-$–P, the large

Table 4. Effect of Fe^{2+} on Sorption of Cs^+ by γ-TiP

Cation composition	Amount of ion exchanged /mmol mol^{-1} γ-TiP^{-1}	
	Cs^+	Fe^{2+}
Cs^+ only$^{a)}$	2.40	—
Fe^{2+} only$^{a)}$	—	0.221
$Cs^+ + Fe^{2+b)}$	1.16	0.469

Initial concentrations of reactants: a) 1.0×10^{-4} mol dm^{-3}, b) 5.0×10^{-5} mol dm^{-3}. Volume of reactants: 20 cm^3, γ-TiP: 0.2 g.

dipolar broadening would be expected. In addition, chemical shifts were significantly different between γ-phosphate and Na-TSM indicating the different electric environment. The large line width of 2.5 kHz in γ-phosphates suggests the restricted motion and the absence of motional narrowing.

X-ray diffraction analysis, thermal analysis, and ^{133}Cs NMR clarified the dehydration process and restricted stable state of Cs^+ that caused the high selectivity for Cs^+ as well as that for Rb^+. On the contrary, the strong hydration of Li^+ and Na^+ with a large hydrated ionic radius resulted in the low selectivity to these ions. Thus, the hydrated or Stokes ionic radius as well as the *B*-coefficient must determine the selectivity sequence of $Cs^+ \fallingdotseq Rb^+ > K^+ > Na^+ > Li^+$.

Interfering Effect of Coexisting Fe^{2+}. The interfering effect of coexisting divalent ions was examined from the viewpoint of practical use in the recovery of Cs^+ from nuclear wastes. Fe^{2+} was selected as a model ion. In this case, the pH value of the resultant solution was about 2. Table 4 shows the amount of exchanged ions. Other data have been reported elsewhere.[7] Although the amount of Fe^{2+} ion exchange increased 0.221 mmol mol^{-1} γ-TiP^{-1} to 0.469 mmol mol^{-1} γ-TiP^{-1} by the presence of Cs^+, the ion-exchange reaction of Cs^+ had a slight interference by coexisting Fe^{2+} as shown in Table 4. Figure 3(f) shows the X-ray diffraction pattern of the $H^+/(Cs^+ + Fe^{2+})$ exchanged sample. Very interestingly, the strong and sharp peaks indicated rigid binding between lamellae of the host Ti–PO_4 matrices; and significant swelling was observed. Figure 4(e) shows the ^{133}Cs NMR spectrum of the same sample. The spectrum was broadened significantly, and no detectable peak was observed. This result indicates a strong interaction between Cs^+ and paramagnetic Fe^{2+} in the interlayer gallery space. It was suggested from the figures that the coexisting Fe^{2+} did not disturb the Cs^+ ion exchange but even suppressed the coagulation of the host layer structure, which is preferable for practical use.

In conclusion, it was revealed from the present study and the previous study on Na-TSM[4] that γ-phosphates are preferable ion exchangers for the recovery of Cs^+ in acidic media, especially γ-ZrP, and Na-TSM in a neutral-pH medium. It was suggested that the combination of proper layered materials would be of more suitable materials for the recovery of Cs^+.

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