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Potassium-ion Exchange on α-Hafnium Phosphate

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Forward and backward pH titration curves were measured for potassium-ion exchange on crystalline α-hafnium phosphate which had been prepared by the direct-precipitation method. Exchange in each direction proceeded in two steps, and the hysteresis was observed in the region of smaller loadings of the potassium ions. Exchange in the ternary H^+–Li^+–K^+ system was also preliminarily investigated, the selectivity of the potassium and lithium ions was what would be expected from the results of the binary hydrogen ion-alkali metal ion systems.

Lithium-ion-exchange behavior on crystalline α-hafnium bis(hydrogenphosphate) monohydrate, $Hf(HPO_4)_2 \cdot H_2O$, was reported in a previous paper[1)], where this compound was considered not to form as many exchanged phases as α-zirconium phosphate because of the single-step lithium-ion exchange.

In contrast to the lithium-ion exchange, the potassium-ion exchange proceeds step-by-step as is the case for α-zirconium phosphate, but considerable difference is observed in the forward and backward titrations. Detailed experiments were thus carried out for K^+– and H^+–ion exchange, as well as for ternary-ion exchange (H^+–Li^+–K^+), and will be reported in this paper. The α-hafnium phosphate employed here had been synthesized by the direct-precipitation method. Comparison between the ion exchangers prepared by the reflux method and by the direct-precipitation method was also made.

Experimental

Ion-exchangers. Alberti and Torracca[2)] prepared α-zirconium phosphate by the direct-precipitation method. Hasegawa and Kuwayama,[3)] and Inoue and Yamada[4)] have further developed methods for α-zirconium phosphate. There has been no data for the direct precipitation of α-hafnium phosphate, but a method similar to α-zirconium phosphate preparation can be expected to be useful. For the preparation of α-hafnium phosphate, the methods adopted by the above-mentioned authors were applied to the hafnium compound with some modifications. Hafnium tetrachloride was dissolved in hydrofluoric acid. To this we then added phosphoric acid, the concentrations of the resulting solutions were 0.13 mol·dm^{-3} in Hf^{IV}, 0.76 mol·dm^{-3} in HF, and 2.5 mol·dm^{-3} in H_3PO_4. The solution was transferred into a polyethylene bottle and placed in a water bath kept at 56 °C; then prehumidified air was passed through for more than 100 h. The crystalline precipitates thus formed were centrifuged and washed with deionized water until the pH of the supernatant solution became 4.5. The product was stored over silica gel, and characterization was made by means of X-ray powder diffractometry and thermal analysis (TG, DTA).

The potassium form of α-hafnium phosphate was prepared from α-hafnium phosphate by the batch method in the presence of 0.033 mol·dm^{-3} KCl and 0.067 mol·dm^{-3} KOH. The potassium salt employed in the backward titration was a monohydrate of the dipotassium salt of α-hafnium phosphate.

Ion-exchange Experiment. This experiment was carried out by the batch method. In the binary K^+–H^+ forward experiment, mixed solutions of 0.1 mol·dm^{-3} KCl and 0.1 mol·dm^{-3} KOH at variable mixing ratios were used to give solutions with differing pH values, while the K^+ ion concentration was kept constant. A weighed amount (150 mg) of α-hafnium phosphate was placed in contact with each of the above-mentioned solutions (15 cm^3) in a stoppered Erlenmeyer flask, and the mixture was shaken for 5 d at 25 °C. After equilibration, the solution was centrifuged, and the supernatant was subjected to pH measurement, as well as to the determination of potassium by means of gravimetry with sodium tetraphenylborate.[5)] The analytical data for potassium were used for the calculation of the K^+ ionic fraction ($\overline{X}_K$) of the exchanger. The solid phase was analyzed by means of X-ray powder diffractomety with a Shimadzu X-ray diffractometer, XD-3A. The samples were either in a slightly wet state before mesurement or in a completely dry state after having been placed over silica gel. Thermogravimetry and differential thermal analysis were carried out with a Shimadzu thermal analyzer, DT-30.

In the backward titration, a 180-mg portion of potassium salt was taken, the amount being equivalent to 150 mg of α-hafnium phosphate. Fifteen-cm^3 portions of the mixed solutions of 0.1 mol·dm^{-3} KCl and 0.1 mol·dm^{-3} HCl at variable mixing ratios were placed in contact with the potassium form for 5d at 25 °C.

In the case of the ternary H^+–Li^+–K^+ system, a 150-mg portion of α-hafnium phosphate was equilibrated with mixed solutions of 0.1 mol·dm^{-3} LiCl, 0.1 mol·dm^{-3} LiOH, 0.1 mol·dm^{-3} KCl, and 0.1 mol·dm^{-3} KOH at 25 °C. The equilibration time was 5 d. The lithium in the supernatant was determined by means of flame photometry with a Hitachi atomic absorption spectrophotometer, 170-50A.

Results and Discussion

Synthesis of α-Hafnium Phosphate by the Direct-precipitation Method. The X-ray powder diffraction data of the α-hafnium phosphate prepared by the direct-precipitation method are given in Table 1, together with those obtained for that prepared by the reflux method.[6)] A very good agreement is seen between the *d*-spacings measured for both specimens. The relative intensities of some diffraction lines differ considerably, however; especially, the reflection from the (002) plane is very strong in the specimen obtained by the direct-precipitation method as compared to that obtained by the reflux method, in which the reflection from the (112) plane is the most intense. The results of TG and DTA are shown for both specimens in Fig. 1. The dehydration of 1 mol of water takes place at about 170 °C in both cases, but the sample prepared by the direct-precipitation method is dehydrated very slowly until it has released 1 mol of water up to 550 °C. The finely powdered specimen gave the same result.

Forward K^+-H^+ Ion Exchange. The pH-titration curve for K^+ ion exchange is shown in Fig. 2. The forward exchange, where H^+ ions of α-hafnium phosphate were replaced by K^+ ions, proceeded in two steps. The first plateau, in the Region I at a pH value of around 2.7, corresponds to the existence of two phases, namely, α-hafnium phosphate and monopotassium salt. Slightly before a half exchange, the pH values increased rather abruptly and attained the second plateau at a pH value of around 7.3. The second plateau is very flat and corresponds to the stage where the mono- and dipotassium salts coexist. The titration curve is completed at approximately the theoretical exchange capacity of 5.15 meq·g^{-1} α-hafnium phosphate. This dibasic feature of the curve has not been observed in the case of Li^+ ion exchange on α-hafnium phosphate.1)

TABLE 1. X-RAY POWDER PATTERNS OF α-HAFNIUM PHOSPHATE

Reflux[a]		Direct Precipitation		hkl[b]
d/Å	I/I_0	d/Å	I/I_0	
7.55	65	7.56	100	002
4.44	54	4.44	16	110
4.40	30	4.40	8	012
4.19	14	4.20	6	$11\bar{2}$, $20\bar{2}$
3.78	9	3.79	11	004
3.54	100	3.55	48	112
3.51	52	3.51	25	$20\bar{4}$
3.21	20	3.21	12	202
3.07	6	3.07	5	014
2.64	20	2.64	15	020
2.63	31	2.62	13	114
2.61	35	2.61	11	$20\bar{6}$
2.40	21	2.40	15	204

a) α-Hafnium phosphate prepared by refluxing in 12 mol·dm^{-3} H_3PO_4 for 245 h. b) The *hkl* indices are tentatively assigned by referring to the powder data of α-zirconium phosphate (JCPDS 22-1022, 1971), with small modifications.

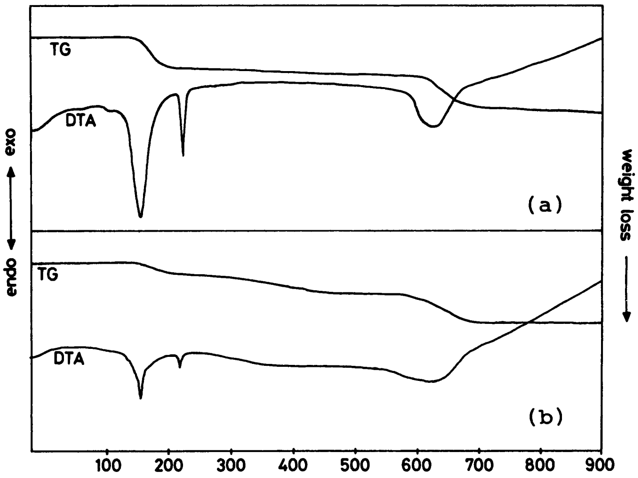

Fig. 1. TG and DTA curves of α-hafnium phosphate prepared by the reflux method and the direct precipitation method. (a): reflux method, (b): direct precipitation method

The X-ray powder patterns of the exchanger at every stage of the forward exchange were measured in the wet and dry states of the sample and are represented in Figs. 3 and 4 respectively. In the case of the exchanger in the wet state, the diffraction line from the (002) plane(d=7.6 Å) decreased in intensity as the K^+-ion exchange proceeded, and the line at 8.1 Å appeared. This indicates the formation of the monohydrate of monopotassium salt. At the ionic fraction ($\bar{X}_{\bar{K}}$) of 0.44, the 7.6 Å peak appears to have increased again, but this is due to the overlapping of the reflection because the anhydride of monopotassium salt has almost the same d value, as will be described later. On the further progress of the K^+-ion exchange, the second plateau of the titration curve started, and the dipotassium salt with the interlayer distance of 10.8 Å soon appeared. This means that the trihydrate of dipotassium salt formed after the half exchange. Figure 4 shows the powder patterns which have been measured on the exchangers dried over silica gel. A considerable variation of the patterns with the drying conditions of the samples can be seen. Thus, the monohydrate of monopotassium salt loses 1 mol of water on standing over silica gel at room temperature, and it gives anhydride with the interlayer distance of 7.6 Å. Similarly, the trihydrate of dipotas-

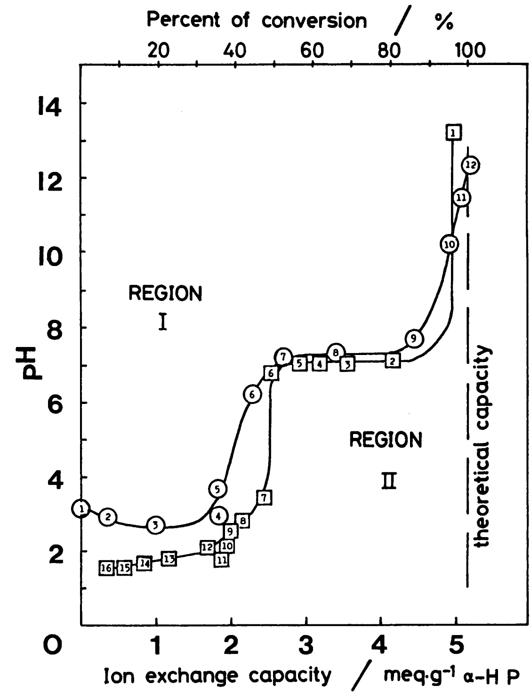

Fig. 2. The forward and backward pH titration curves for K^+ ion exchange on α-hafnium phosphate.
○: Forward, □: Backward.
α-HP stands for α-hafnium phosphate.

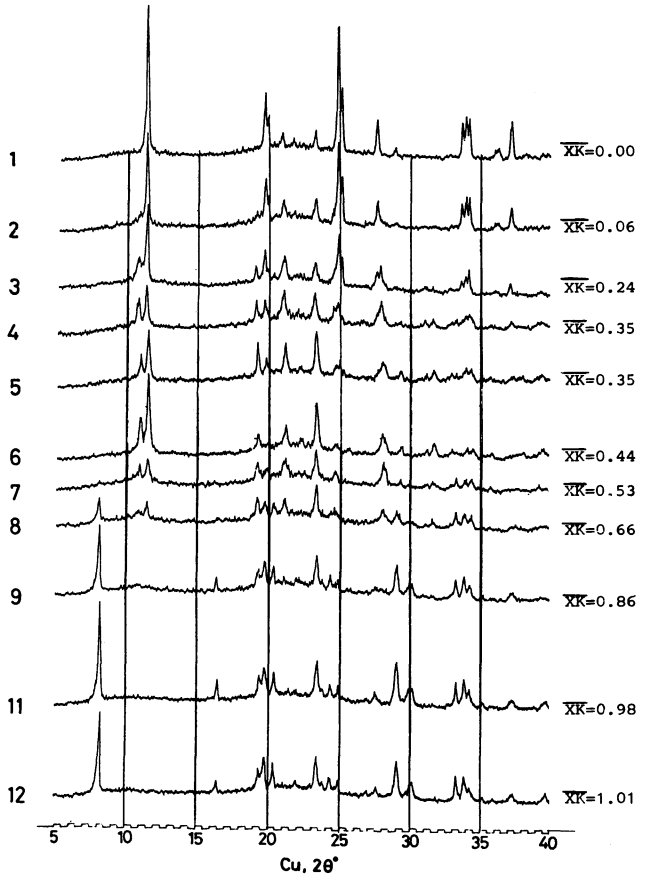

Fig. 3. The X-ray powder patterns of wet exchanged forms of α-hafnium phosphate at several stages of forward exchange.

$\overline{XK}$ denotes the potassium ionic fraction. The numbers 1 to 12 indicate the corresponding points in the titration curve in Fig. 2.

sium salt is converted into monohydrate with the interlayer distance of 9.2 Å. The water content has been confirmed by thermogravimetry. The above results may be summarized as follows:

$$\begin{array}{l} \mathrm{Hf(HPO_4)_2\cdot H_2O} \longrightarrow \\ (7.6\,\text{Å}) \end{array}$$

$$\begin{array}{ccc} \mathrm{Hf(KPO_4)(HPO_4)\cdot H_2O} & \longrightarrow & \mathrm{Hf(KPO_4)_2\cdot 3H_2O} \\ (8.1\,\text{Å}) & & (10.8\,\text{Å}) \\ \downarrow & & \downarrow \\ \mathrm{Hf(KPO_4)(HPO_4)} & & \mathrm{Hf(KPO_4)_2\cdot H_2O} \\ (7.6\,\text{Å}) & & (9.2\,\text{Å}) \end{array}$$

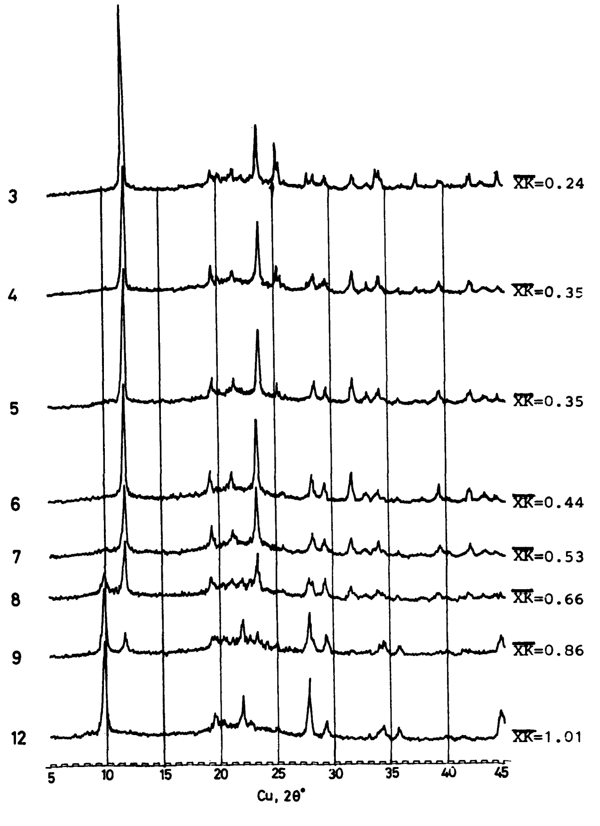

Fig. 4. The X-ray powder patterns of dry exchanged forms of α-hafnium phosphate at several stages of forward exchange. The numbers 3 to 12 indicate the corresponding points in Fig. 2.

Backward K^+–H^+-ion Exchange. The pH titration curve of the backward process is given in Fig. 2. A two-step ion exchange is clearly observed. The plateau at a pH value of around 7.0 corresponds to the coexistence of the dipotassium salt and the monopotassium salt. The forward and backward curves practically coincide in this region (Region II in the figure), indicating that the process is reversible, not only in the ion-exchange reaction, but also in the structural change of the exchanger. An abrupt change in the pH at the half exchange shows the existence of a single monopotassium salt phase. This has been confirmed by the X-ray powder data which will be shown below. As the exchange progressed, the deviation of the backward curve from the forward one became remarkable. This kind of hysteresis can often be observed in alkali-metal ion exchange on α-zirconium phosphate; it suggests that the formation of the dihydrogen form does not always result in a α-type crystal. It is further noted that a small fraction of the K^+ ions could not be released with 0.1 mol·dm^{-3} HCl within 5d.

The X-ray powder patterns of the exchanger at every stage of the backward exchange in wet and dry states are given in Figs. 5 and 6 respectively. The starting exchanger has an interlayer distance of the monohydrate of dipotassium salt of 9.2 Å instead of the 10.8 Å of the trihydrate, because it was necessary to weigh the exchanger in the dry state. As may be seen in Fig. 5, up to $\overline{XK}$=0.57 the 9.2 Å peak disappeared, and the reflection lines from the monopotassium salt appeared. At about a half exchange, two reflections at 2θ=11° amd 11.6° corresponding to the monohydrate (d=8.1 Å) and the anhydride (d=7.6 Å) of monopotassium salt, were observed. The relative intensities of the two peaks depended on how wet the X-rayed specimens were. As K^+ ions in the exchanger were replaced by H^+ ions, however, the position of the lowest-angle reflection remained essentially unchanged, suggesting that the 8.1 Å peak still predominated even if the monopotas-

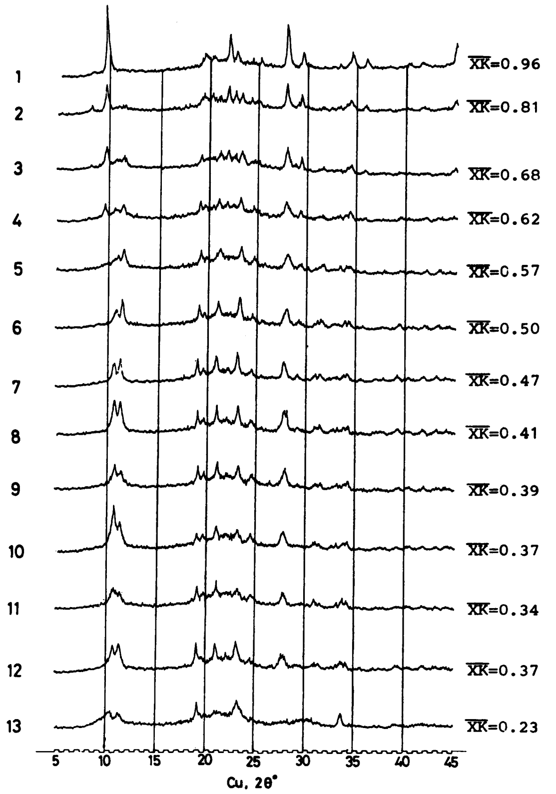

Fig. 5. The X-ray powder patterns of wet exchanged forms of hafnium potassium phosphate at several stages of backward exchange. The numbers 1 to 13 indicate the corresponding points in Fig. 2.

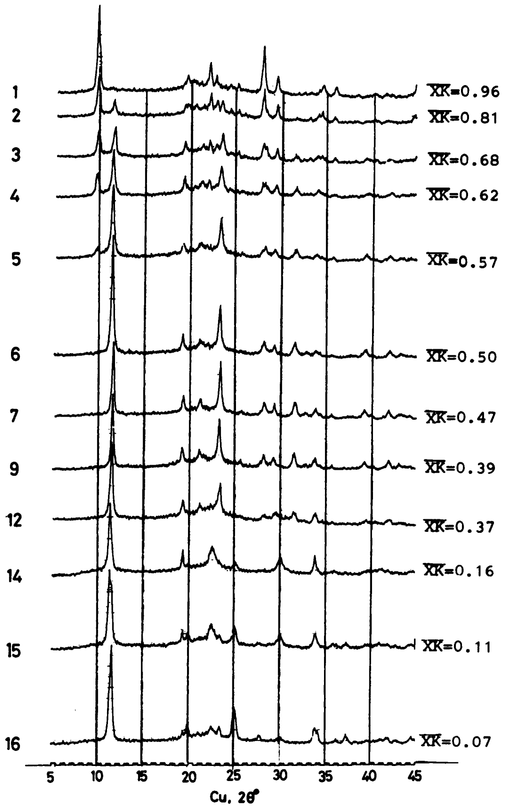

Fig. 6. The X-ray powder patterns of dry exchanged forms of hafnium potassium phosphate at several stages of backward exchange. The numbers 1 to 16 indicate the corresponding points in Fig. 2.

sium salt was converted into the dihydrogen form. This fact correlates with the deviation of the forward and the backward curves from each other; it can be considered that, in the backward process, the solid-solution formation takes place, that is H^+ ions are incorporated with the monopotassium form without any esssential change in the crystal structure. In α-zirconium phosphate, it is known that a wider range of the solid-solution formation is observed as the degree of crystallinity becomes poorer. The same trend may be thought to be found in α-hafnium phosphate. The complete desorption of K^+ ions was not possible under the experimental conditions used, but it was confirmed that some portion of the exchanger was converted into α-hafnium phosphate. In this case, the diffraction line around $2\theta=25°$ (d=3.5 Å) is useful in identifying α-hafnium phosphate, because the line at $2\theta=11.6°$ (d=7.6 Å) overlapped with that of the anhydride of monopotassium salt. In the same way, the monopotassium-salt phase can be differentiated from α-hafnium phosphate for the forward process (Fig. 3). The backward exchange can be shown as follows:

$$\begin{tikzcd}
\begin{array}{c}\mathrm{Hf(KPO_4)_2\cdot 3H_2O}\\ (10.8\,\text{Å})\end{array} \arrow[r] \arrow[d] & \begin{array}{c}\mathrm{Hf(KPO_4)(HPO_4)\cdot H_2O}\\ (8.1\,\text{Å})\end{array} \arrow[r] \arrow[d] & \left\{\begin{array}{c}\mathrm{Hf(HPO_4)_2\cdot xH_2O}\\ (8.1\,\text{Å})\\ \\ \mathrm{Hf(HPO_4)_2\cdot H_2O}\\ (7.6\,\text{Å})\end{array}\right. \\
\begin{array}{c}\mathrm{Hf(KPO_4)_2\cdot H_2O}\\ (9.2\,\text{Å})\end{array} & \begin{array}{c}\mathrm{Hf(KPO_4)(HPO_4)}\\ (7.6\,\text{Å})\end{array} &
\end{tikzcd}$$

Ternary H^+-Li^+-K^+ Ion Exchange. Figure 7 shows the titration curve for Li^+-H^+ and K^+-H^+ binary ion exchange on α-hafnium phosphate in the forward direction obtained by the present authors. From the selectivity point of view, it is clear that the exchanger prefers K^+ ions to Li^+ ions up to an ion-exchange capacity of around 2 meq $M^+\cdot g^{-1}$ α-hafnium phosphate, where M^+ denotes the Li^+ or K^+ ion. Above this capacity, the selectivity is reversed until the completion of the exchange. However, this argument has to be examined experimentally, because, in the ternary H^+-Li^+-K^+ system, some new solid phases including Li^+ and K^+ ions might be formed, and this might affect the selectivity of two ions. On the other hand, if no such new solid phases are formed, the selectivity should follow those obtained in the binary systems. Figure 8 gives the variation in the alkali-metal-ion uptake with the pH. Thus, up to an ion-exchange capacity of about 2 meq$\cdot g^{-1}$ exchanger, K^+ ions were preferably taken up, whereas Li^+ ion remained in the equilibrating

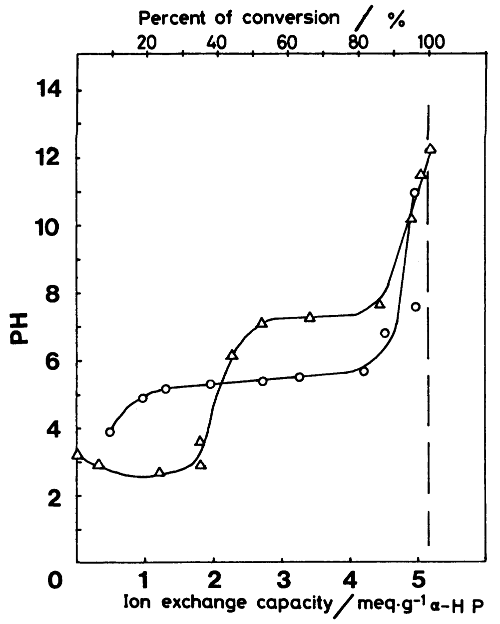

Fig. 7. The pH titration curves for binary H^+–Li^+ and H^+–K^+ forward exchange on α-hafnium phosphate. △: K^+, ○: Li^+.
α-HP stands for α-hafnium phosphate.

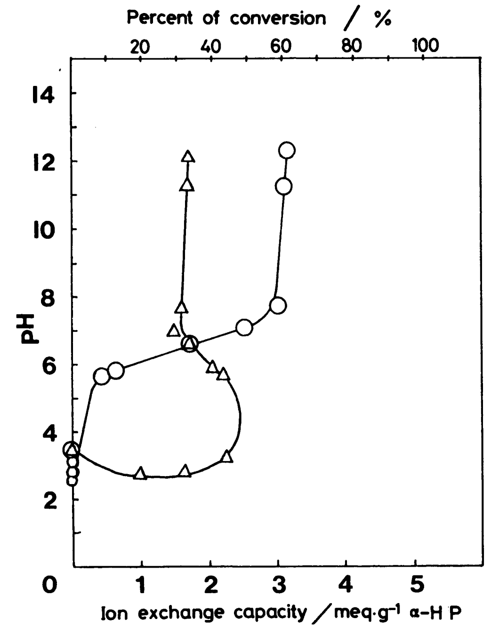

Fig. 8. K^+ and Li^+ uptake curves for ternary H^+–Li^+–K^+ exchange on α-hafnium phosphate.

△: K^+, ○: Li^+.
α-HP stands for α-hafnium phosphate.

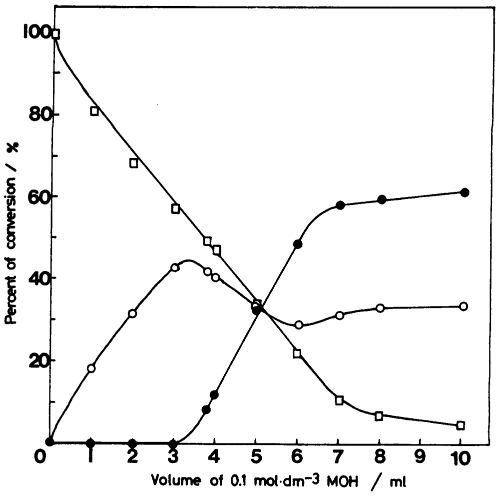

Fig. 9. Distribution of H^+, Li^+, and K^+ ions on α-hafnium phosphate at different hydroxide concentrations.
□: H^+, ●: Li^+, ○: K^+.

solution. Above this point, *i.e*, above $\overline{X_K}=0.43$, the Li^+-ion uptake started and the pH value of the solution rose steeply. The lithium-ion uptake proceeded as not only H^+ ions but also K^+ ions were replaced by Li^+ ions. The pH-titration curve thus behaved differently from that for the binary system after the half exchange, but the selectivity sequence of the K^+ and Li^+ ions is almost exactly the one expected from the binary systems. Figure 9 represents the distribution of H^+, Li^+, and K^+ ions on α-hafnium phosphate at varying hydroxide concentrations. Thermogravimetry showed that the final product of the titration was dehydrated over the range of 120—400 °C. Its chemical composition was $Hf(K_{0.67}Li_{1.23}H_{0.10})(PO_4)_2\cdot 1.17H_2O$. However, the X-ray patterns showed that the reflections were rather broad and that the crystallinity had deteriorated. The sample in the wet state had one broad line at $2\theta=11°$ ($d=8$ Å), whereas that in the dry state had two lines, at about 11° and 10.3° ($d=8.6$ Å). The formation of a phase having a larger interlayer distance than that in the wet state can not be the consequence of dehydration. There is some possibility that an amorphous form was converted into the crystalline form during storage and drying, but no definite assignment to the known phase is possible at present.

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