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The Synthesis and Ion-exchange Properties of $TiH_2(PO_4)_2 \cdot 1/2H_2O$

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In order to develop an ion-exchanger for industrial use, a new compound, titanium dihydrogen bis (phosphate) hemihydrate, was prepared by means of a reflux between titanium phosphate and concentrated phosphoric acid; then the conditions of synthesis and the ion-exchange properties of the products were investigated. The amorphous titanium phosphate used as the starting material was formed by the reaction of titanium tetrachloride with phosphoric acid in diluted hydrochloric acid. The phase equilibrium of the TiO_2–P_2O_5–H_2O system has been studied at the refluxing temperatures of the mother liquors. The solid phase in equilibrium with the mother liquor containing 13—64% P_2O_5 had the components of TiO_2 (29—32%), P_2O_5 (53—54%), and H_2O (15—16%); its composition was $TiH_2(PO_4)_2 \cdot H_2O$, which had already been known, but the solid phase in equilibrium with the mother liquor containing more than 64% P_2O_5 had as components TiO_2 (31—32%), P_2O_5 (57—58%), and H_2O (10—11%); therefore, its composition corresponded to $TiH_2(PO_4)_2 \cdot 1/2H_2O$. The X-ray diffraction pattern of this compound was entirely different from that of monohydrate, and some large *d*-values were recognized. From the DTA and TGA, the processes of the dehydration of monohydrate and hemihydrate were also different from each other; however, both compounds were converted to titanium pyrophosphate (TiP_2O_7) at 800 °C. $TiH_2(PO_4)_2 \cdot H_2O$ can adsorb sodium ions, but the ions of a large radius, such as potassium and cecium, are not adsorbed. In contrast to this, $TiH_2(PO_4)_2 \cdot 1/2H_2O$ had an excellent ion-exchange property; its ion-exchange capacities were 4.0 meq/g to K^+ and 2.0 meq/g to Cs^+ at pH 4. These capacities were about eight times those of monohydrate. The solubilities of the phosphate used as an ion-exchanger were remarkably low. Therefore, the titanium dihydrogen bis (phosphate) hemihydrate thus obtained may be utilized as a useful inorganic ion-exchanger for potassium and cesium ions.

The phosphates of poly-valence metals such as chromium,[2] zirconium,[3] and tin,[4] have hitherto been known as inorganic ion-exchangers. In order to develop an inorganic ion-exchanger capable of recovering potassium from sea water, we have previously investigated the ion-exchange characters of magnesium, calcium, aluminium, and iron phosphate,[5] further synthesized iron trihydrogen bis (phosphate), which was fairly stable to phosphoric acid as a regenerant of the exchanger, and examined its ion-exchange character.[6] The phosphates of bivalent and trivalent metals, however, generally do not have enough stability to be good inorganic ion-exchangers.

In the present work, titanium phosphate, which is an economical raw material, has been examined. Titanium phosphates with the composition of $3TiO_2 \cdot P_2O_5 \cdot xH_2O$ ($x=1, 3, 6$) are already known.[7] Also, crystalline titanium hydrogen phosphate with the composition of $TiH_2(PO_4)_2 \cdot H_2O$ was prepared by the reflux of amorphous titanium phosphate with phosphoric acid at the boiling point, and its ion-exchange property was examined.[8] This compound showed a higher resistance to hydrolysis than the amorphous titanium phosphate; it adsorbed Li^+ and Na^+, but not the ions of a large radius, such as K^+ and Cs^+. Therefore, this crystalline titanium hydrogen phosphate is not suitable as an industrial ion-exchanger. Recently, titanium phosphate with the composition of $(TiO)_{0.535}(HPO_4)_{0.639}(OH)_{0.17} \cdot aq.$ was synthesized, and it could recover cesium in radioactive waste materials.[9] The molar ratio of Ti to P in this non-stoichiometric compound is larger than that in the above crystalline titanium phosphate, so it may be supposed that this compound is lacking in chemical resistance to an acidic eluent. Titanium phosphate-silicate for the separation of radioactive materials was also synthesized.[10] In the study of the TiO_2–P_2O_5–H_2O system at 20 °C, $Ti(OH)PO_4 \cdot 2H_2O$ and $TiH_2(PO_4)_2$ existed as solids in the system.[11] However, in the general method of preparing inorganic ion-exchanger by the reflux of amorphous phosphate with phosphoric acid, the data of the above equilibrium system cannot be applied to the preparation because of the difference between the refluxing temperature and room temperature.

When the phase equilibrium of the Fe_2O_3–P_2O_5–H_2O system was examined,[6] the existence of several kinds of iron hydrogen phosphate was known. In the present work, it is supposed that titanium hydrogen phosphate, as the solid phase of the equilibrium to concentrated phosphoric acid, also exists in the TiO_2–P_2O_5–H_2O system. From the results of the phase equilibrium on the reflux of amorphous titanium phosphate with phosphoric acids of various concentrations, it is known that $TiH_2(PO_4)_2 \cdot 1/2H_2O$, which differs in its molar ratio of the water of crystallization, is present. The X-ray diffraction pattern of this compound was entirely different from that of $TiH_2(PO_4)_2 \cdot H_2O$, and large *d*-values were noticed in it. The investigation of its ion-exchange properties showed this salt to have an adsorption capacity to ions of a larger ionic radius, such as K^+ and Cs^+. In this paper, an experimental study of the preparation of titanium dihydrogen bis (phosphate) hemihydrate and its ion-exchange properties will be described.

Experimental

Synthesis. Amorphous titanium phosphate, used as the raw material, was initially prepared in the following way: 800 ml of 2 M HCl placed in a beaker and mixed with 50 g of $TiCl_4$ solution. To this was slowly added 800 ml of 1.45 mol/l H_3PO_4, while simultaneously the mixture in the beaker was vigorously stirred at room temperature. Thus, amorphous titanium phosphate was precipitated. This was allowed to stand overnight and then separated from the mother liquor by the use of a centrifugal separator. The product was washed with distilled water, centrifugally separated from the wash liquid, and finally vacuum-dried over phosphorus pentoxide for 24 h.

Crystalline titanium phosphate was prepared in the following way: 10 g of amorphous titanium phosphate, prepared previously, was placed in a Kjeldahl flask and mixed with 150—180 ml of phosphoric acid of an appropriate concentration. The mixture was kept at a proper temperature by the evaporation of a little water, and then heated at its boiling point for 12—36 h after the reflux condenser had been connected to the flask. Immediately the resulting precipitate was separated centrifugally from the mother liquor. To the precipitate alcohol or acetone was added, and the mixture was vigorously shaken up; then the precipitate was separated from the wash liquid by using the centrifugal separator. The product thus obtained as the precipitate was washed enough by repeating this procedure several times, and finally it was vacuum-dried over phosphorus pentoxide for 24 h.

Analysis. P_2O_5: A 0.5 g portion of the product was weighed exactly and then refluxed with 50 ml of 1 M NaOH in a stainless steel flask for 60 min. The amorphous precipitate obtained by this treatment was separated from the mother liquor by filtration and washed sufficiently with hot water. The mother liquor and wash liquid were put together, and the volume of the solution was adjusted to 250 ml. The phosphorus content was determined gravimetrically as magnesium pyrophosphate.

TiO_2: A 0.1 g portion of the product was weighed exactly and then refluxed with 10 ml of 18 M H_2SO_4 and 5 g of $(NH_4)_2SO_4$ in a Kjeldahl flask until it had dissolved completely. The volume of the sample solution was then adjusted to 250 ml with distilled water. 10 ml of 9 M H_2SO_4 and 10 ml of 3% H_2O_2 were added to a 25 ml portion of the diluted solution; the meta-titanic acid peroxide thus turned yellow. The titanium content was determined colorimetrically at 420 nm. The content of TiO_2 in titanium phosphate was also derived as follows:

$$100\% - (P_2O_2)\% - (H_2O)\% = (TiO_2)\%$$

H_2O: A 0.2 g portion of the product was weighed exactly and then heated in an electric furnace regulated to 800 °C for about 2 h until it had reached a constant weight. In this case, the weight loss corresponds to the water content of the product. The water content was also given by thermal gravimetric analysis.

The Components in the Liquid Phases: Exactly a 10 ml portion of the mother liquor was taken, and the specific gravity was measured. The volume of the sample solution was adjusted to 250 ml. A 100 ml portion of the diluted solution was neutralized with a sodium hydroxide solution. The white precipitate thus obtained was separated from the mother liquor and washed with hot water. The TiO_2 content was determined gravimetrically by the calcination of the precipitate. On the other hand, the mother liquor and wash liquid were put together, and the volume of the solution was adjusted to 250 ml. The P_2O_5 content was determined gravimetrically as magnesium pyrophosphate by using a portion of the solution.

X-Ray Diffraction Pattern: The X-ray diffraction pattern was obtained by using a Rigaku-Denki model 2001 diffractometer with Ni-filtered Cu$K\alpha$ radiation, with 20 KVP and 15 mA.

DTA and TGA: The differential thermal analysis (DTA) and thermogravimetric measurements (TGA) were performed simultaneously at a heating rate of 5 °C/min with a Rigaku-Denki model DC-C1-S thermal analyzer.

Ion-exchange Titration Curve: A 0.200 g portion of a product was placed in a 50 ml stoppered Erlemeyer flask, and 25 ml of the solution, mixed in the proper ratio of 0.1 M MCl to 0.1 M MOH (M=Na, K, Cs), was added to it. The contents in the flask were shaken up at times, and the pH of the solution was measured after 24 h. Then, the ion-exchange titration curve was drawn from the relations between the pH and the ion-exchange capacity, which was estimated from the mixed ratio of 0.1 M HCl to 0.1 M MOH.

Results and Discussion

Preparation of $TiH_2(PO_4)_2 \cdot H_2O$ and $TiH_2(PO_4)_2 \cdot 1/2H_2O$. The conditions of synthesizing crystalline titanium hydrogen phosphates and the results of the analysis of the products are summarized in Table 1.

Composition by Chemical Analysis: Amorphous titanium phosphate, with the composition of $1.9TiO_2$, P_2O_5, $3.7H_2O$, was used as the raw material. The reaction product No. 1, which was obtained by refluxing amorphous titanium phosphate with a suitable amount of 10%

TABLE 1. SYNTHESIS AND ANALYSIS OF HYDROGEN TITANIUM PHOSPHATES

No.	Reaction condition a)									Reaction product	
	Temp. (°C)	Time (h)	Mother liquor			Washing liquid	TiO_2 (%)	P_2O_5 (%)	H_2O (%)	TiO_2:P_2O_5:H_2O (Mole ratio)	Estimated formura
			(s.g)	P_2O_5%	TiO_2%						
1	104	36	1.043	6.9	0.0	Acetone	35.9	41.2	22.9	1.55:1.00:4.39	(Non-crystal)
2	107	24	1.141	13.2	0.1	Acetone	32.3	55.2	14.9	1.04:1.00:2.13	$TiH_2(PO_4)_2 \cdot H_2O$
3	110	12	1.244	30.3	0.2	Acetone	28.8	54.6	16.6	0.94:1.00:2.38	$TiH_2(PO_4)_2 \cdot H_2O$
4	120	12	1.429	45.7	0.3	Ethanol	31.1	53.7	15.2	1.03:1.00:2.23	$TiH_2(PO_4)_2 \cdot H_2O$
5	144	12	1.652	56.1	0.4	Acetone	31.7	55.0	14.9	1.02:1.00:2.14	$TiH_2(PO_4)_2 \cdot H_2O$
6	160	12	1.648	58.8	0.4	Acetone	29.9	54.5	15.6	0.97:1.00:2.26	$TiH_2(PO_4)_2 \cdot H_2O$
7	165	12	1.670	62.0	0.3	Ethanol	31.9	52.6	15.5	1.08:1.00:2.34	$TiH_2(PO_4)_2 \cdot H_2O$
8	176	24	1.687	65.5	0.4	Ethanol	32.2	57.8	10.0	0.99:1.00:1.36	$TiH_2(PO_4)_2 \cdot 1/2H_2O$
9	176	36	1.712	66.1	0.3	Acetone	32.2	57.3	10.5	1.00:1.00:1.44	$TiH_2(PO_4)_2 \cdot 1/2H_2O$
10	170	30	1.687	64.5	0.4	Ethanol	30.9	58.0	11.1	0.95:1.00:1.51	$TiH_2(PO_4)_2 \cdot 1/2H_2O$
	Raw material					Water–ethanol	42.9	40.2	18.9	1.90:1.00:3.71	

a) The mixture of amorphous titanium phosphate (raw material, 10) and phosphoric acid (150—160 ml) was refluxed under a certain condition.

phosphoric acid (P_2O_5, 7.3%) for 36 h, was still the non-crystalline powder. It could be expected that when phosphoric acid of a comparatively lower concentration was used, the reaction could not reach the equilibrium state even by means of a reaction at a refluxing temperature for a fairly long time. In the No. 2—7 products, which were equilibrium-solid phases with a 13—62% P_2O_5 content in the mother liquor, their compositions were found to be 29—32% TiO_2, 53—54% P_2O_5, and 15—16% H_2O, and its components corresponded to those of $TiH_2(PO_4)_2 \cdot H_2O$ known already. In the No. 8—10 products, which were equilibrium-solid phases with a P_2O_5 content of more than 64% in the mother liquor and at a refluxing temperature 170—180 °C, the compositions were found to be 31—32% TiO_2, 57—58% P_2O_5, and 15—16% H_2O. From these results, the expected composition was given as $TiH_2(PO_4)_2 \cdot 1/2H_2O$.

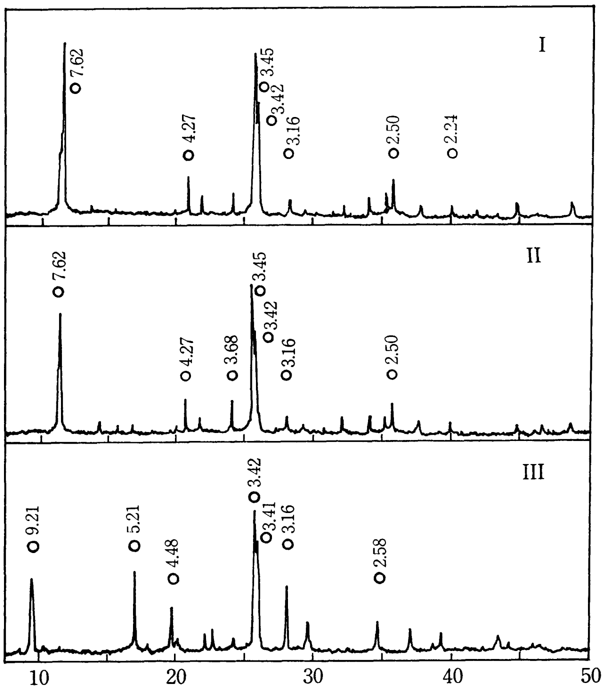

Fig. 1. X-Ray diffraction patterns of titanium hydrogen phosphates.
I: Product obtained by reflux in phosphoric acid of P_2O_5 13.2% at 107 °C for 24 h (No. 2). II: Product obtained by reflux in phosphoric acid of P_2O_5 58.8% at 160 °C for 12 h (No. 6). III: Product obtained by reflux in phosphoric acid of P_2O_5 66.1% at 176 °C for 36 h (No. 9).
Numerals near peaks indicate distance (Å) between planes in crystals.

X-Ray Diffraction Patterns: The X-ray diffraction patterns of the products, which are prepared in different concentrations of phosphoric acid in the mother liquor, are shown in Fig. 1. I and II are the X-ray diffraction patterns for monohydrate, known already. These diffraction data agreed almost entirely with those of the ASTM X-ray data cards and also with those of $TiH_2(PO_4)_2 \cdot H_2O$, prepared by Alberti *et al.*[8] III is the pattern for hemihydrate obtained by the reflux of amorphous titanium phosphate with concentrated phosphoric acid. In this diagram, diffraction lines newly appeared at the positions of 9.21, 5.21, 4.38 Å, *etc.* The X-ray diffraction values of hemihydrate were clearly different from those of monohydrate, as is shown in Table 2. For the formation of two crystalline titanium phosphates having a Ti/P atomic ratio of exactly 1.0, a fairly long time was needed, even at the reflux temperature. The course of the formation of hemihydrate by the reaction between amorphous titanium phosphate and concentrated phosphoric acid is shown in Fig. 2 by the X-ray diffraction patterns changing successively.

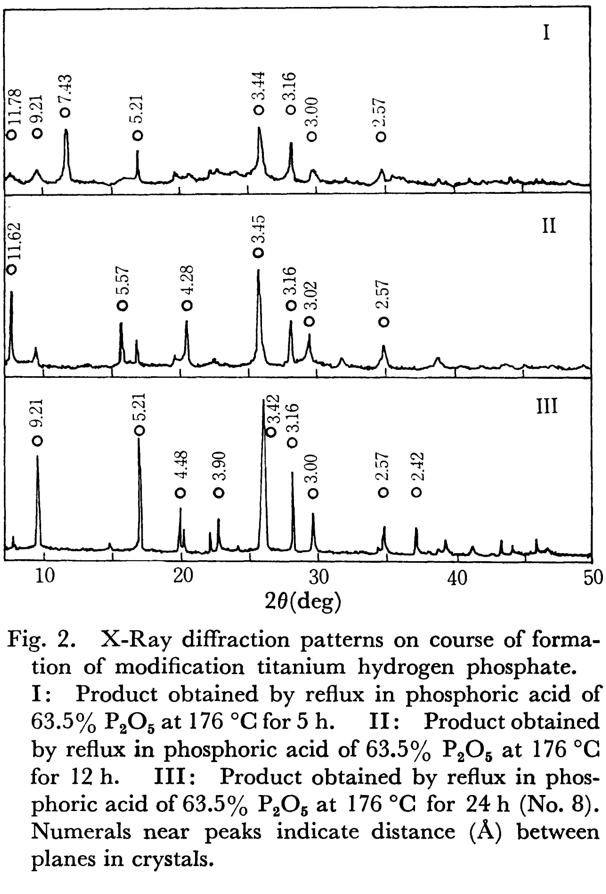

Fig. 2. X-Ray diffraction patterns on course of formation of modification titanium hydrogen phosphate.
I: Product obtained by reflux in phosphoric acid of 63.5% P_2O_5 at 176 °C for 5 h. II: Product obtained by reflux in phosphoric acid of 63.5% P_2O_5 at 176 °C for 12 h. III: Product obtained by reflux in phosphoric acid of 63.5% P_2O_5 at 176 °C for 24 h (No. 8). Numerals near peaks indicate distance (Å) between planes in crystals.

When the concentration of phosphoric acid in the mother liquor was low, as has been mentioned above, the reaction product did not crystallize easily, so a slight crystallization of the product occurred upon refluxing for several hours, as is shown in I. It was observed from the X-ray patterns that a metastable crystalline product was produced by refluxing for 12 h at 176 °C and also by refluxing for a fairly long time at 170 °C. The X-ray diffraction pattern for this product is shown in II; in the diagram peculier diffraction lines appeared at 11.6 and 5.57 Å. The object, hemihydrate as a stable form, was obtained by refluxing for more than about 20 h at above 170 °C. The X-ray diffraction pattern of hemihydrate is shown in III.

Effect on the Concentration of Phosphoric Acid in the Mother Liquor: From the TiO_2–P_2O_5–H_2O system at the refluxing temperatures of the mother liquors, we ascertained the existences of $TiH_2(PO_4)_2 \cdot H_2O$ and $TiH_2(PO_4)_2 \cdot 1/2H_2O$ as the solid phase in the equilibrium state to the mother liquor. If pyrophosphoric acid is contained in the liquid phase, it may be supposed, as a matter of course, that another solid phase appears. However, the pure phosphoric acid of P_2O_5 66% theoretically does not contain pyrophosphoric acid.[12] In fact, the existence of condensed phosphoric acids in this liquid phase was not observed by paper or ion-exchange chromatography. The amount of TiO_2 dissolved in the liquid phase was nearly zero when the concentration of phosphoric acid was low; it slightly increased with the increase in the concentration of phosphoric acid.

Change in Titanium Hydrogen Phosphate upon Heating. The DTA and TGA curves for two crystalline titanium phosphates are shown in Fig. 3. The X-ray diffraction values for some titanium phosphates previously registered on ASTM X-ray data cards, the products obtained in this work, and their heated products are summarized in Table 2. In the DTA curve for monohydrate (I), the broad endothermic peak at 70—100 °C seemed to be due to the elimination of water adhering to the crystal powder. It was confirmed from the X-ray diffraction, which characterized pyrophosphate in the heated product at 185 °C, that the endothermic peak at 210 °C was a result of the dehydration of the water of crystallization and the condensation. The endothermic peaks at 260 and 510 °C were also due to the condensation. However, the reason why these condensations take place progressively upon heating is not yet known. The behavior of the DTA and TGA curves for hemihydrate (II) differed from those of I, a dehydration gradually occurred from 100 °C to about 300 °C, and a weight loss corresponding to the weight of the water of crystallization of this salt was observed in this temperature range. Then a large endothermic peak, which was due to the condensation, appeared at 415 °C.

Table 2. X-ray diffraction data for titanium hydrogen phosphate, reaction product and its heating product

$TiH_2P_2O_8\cdot H_2O$[a)]	$H_2(Ti(PO_4))\cdot H_2O$[b)]	Product No. 4	Product No. 8	Heating product of No. 4 or No. 8 (800 °C)	TiP_2O_7[c)]
			11.47W		
			9.21M		
7.62 S	7.55 S	7.62 S			
			5.21 S		
4.62W			4.48M	4.57W	
4.27M	4.23W	4.27W	4.39W		4.20M
	4.02W	4.02W			
3.80M			3.90W	3.95 S	3.82 S
			3.71W		
		3.68W	3.66W		
3.44 S	3.44 S	3.45 S		3.53 S	3.45 S
	3.41M	3.42 S	3.42 S		
3.51W	3.15W	3.13W	3.16M	3.22M	3.15 S
	3.03W	3.05W	3.00W		
2.77M		2.76W		2.79W	
	2.61W	2.61W			
	2.53W	2.53W	2.57W		
2.59 S	2.49W	2.49W			
			2.42W		
2.38W	2.38W	2.38W		2.38W	
			2.29W		2.34M
2.24M	2.24M	2.24W			
2.16W	2.16W			2.18W	2.15W
			2.08W		
2.02W	2.02W	2.02W	2.04W		
1.96M	1.96W	1.96W	1.97W		
	1.94W	1.94W			
				1.91W	1.89M
1.87M	1.86W	1.87W		1.76W	1.74M
				1.61W	1.60M
				1.52W	1.50 S
				1.39W	1.38M

a) According to data on Deutsche Akad. der Wissensch., Berlin, Inst. f. Anorg. Chem. (1968). b) According to Michel and Weiss (1967). c) According to Levi and Peyronel (1935). These data were registered in ASTM X-ray data cards.

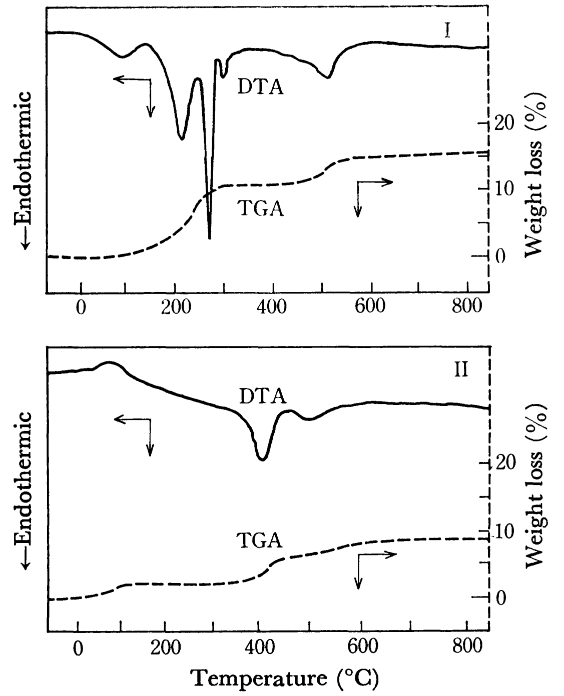

Fig. 3. DTA and TGA curves for titanium hydrogen phosphates.
I: Titanium hydrogen phosphate (No. 3). II: Modification titanium hydrogen phosphate (No. 8). Sample: 200 mg, heating rate: 5 °C/min.

Hemihydrate and the product obtained by heating it at 185 °C for 2 h gave almost the same X-ray diffraction pattern. Therefore, at this heating temperature, pyrophosphate was not yet formed. However, the X-ray diffraction values of the heated products of monohydrate and hemihydrate at 800 °C were all the same, and these values agreed with the diffraction data of TiP_2O_7 registered on an ASTM X-ray data. It was also confirmed by means of chemical analysis that the two heated products both had the composition of $TiO_2\cdot P_2O_5$.

Ion-exchange Properties of Titanium Hydrogen Phosphates. It has already been reported that the ion-exchange capacity of $TiH_2(PO_4)_2\cdot H_2O$ showed values as high as

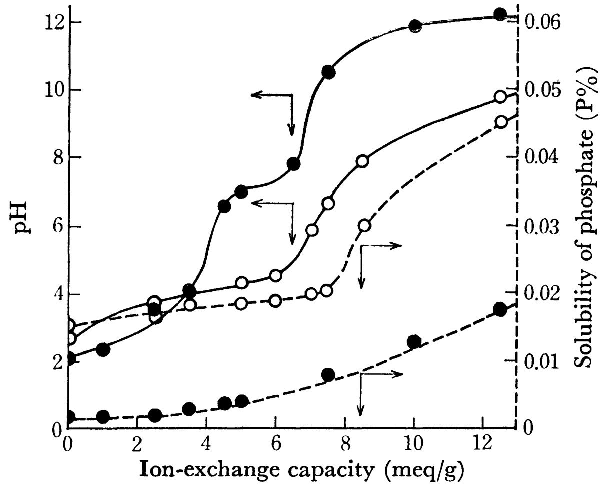

Fig. 4. Na ion-exchange titration curve and solubility of titanium hydrogen phosphates.
○: Titanium hydrogen phosphate, $TiH_2(PO_4)_2 \cdot H_2O$ (No. 3). ●: Modification titanium hydrogen phosphate, $TiH_2(PO_4)_2 \cdot 1/2H_2O$ (No. 8).
Ion-exchanger: 0.200 g, mixed solution of 0.1 mol/l NaOH and 0.1 mol/l NaCl: 25.0 ml.

~7 meq/g for Li^+ and Na^+, but ions with a large radius, such as K^+ and Cs^+, were scarcely adsorbed.[8] The $TiH_2(PO_4)_2 \cdot 1/2H_2O$ prepared in this work gave large *d*-values in the X-ray diffraction data. Therefore, it was supposed that there was a layer structure in the crystal and that, among the layers, various cations could be adsorbed.

Ion-exchange Capacities of Phosphates to Na^+: The sodium ion-exchange titration curves of monohydrate and hemihydrate and their solubilities are shown in Fig. 4. The ion-exchange capacities of monohydrate at pH 4 and 7 were 3.6 and 7.5 meq/g respectively; these capacities were the same as those previously reported.[8] On the other hand, the ion-exchange capacities of hemihydrate at pH 4 and 7 were 3.3 and 5.1 meq/g respectively. In an acid solution the solubility of the ion-exchanger was reduced by about one seventh as compared with that of monohydrate.

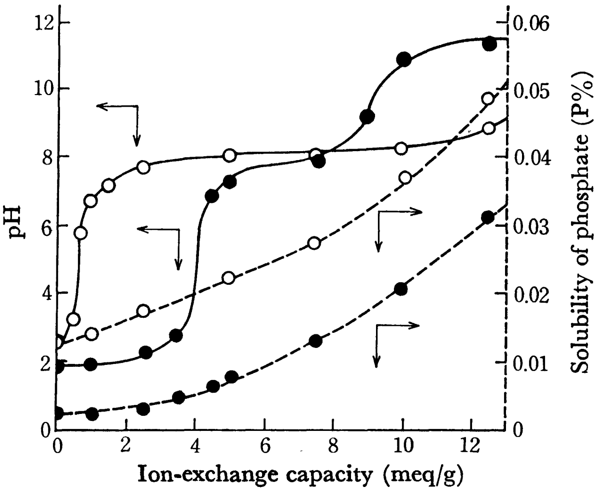

Fig. 5. K ion-exchange titration curve and solubility of titanium hydrogen phosphates.
○: Titanium hydrogen phosphate, $TiH_2(PO_4)_2 \cdot H_2O$ (No. 3). ●: Modification titanium hydrogen phosphate, $TiH_2(PO_4)_2 \cdot 1/2H_2O$ (No. 8).
Ion-exchanger: 0.200 g, mixed solution of 0.1 mol/l KOH and 0.1 mol/l KCl: 25.0 ml.

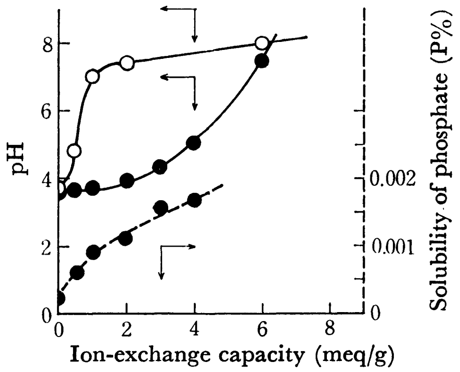

Fig. 6. Cs ion-exchange titration curve and solubility of titanium hydrogen phosphates.
○: Titanium hydrogen phosphate, $TiH_2(PO_4)_2 \cdot H_2O$ (No. 3). ●: Modification titanium hydrogen phosphate, $TiH_2(PO_4)_2 \cdot 1/2H_2O$ (No. 8).
Ion-exchanger: 0.200 g, mixed solution of 0.1 mol/l CsOH and 0.1 mol/l CsCl: 25.0 ml.

Ion-exchange Capacities of Phosphates to K^+: The potassium ion-exchange titration curves of monohydrate and hemihydrate and their solubilities are shown in Fig. 5. The ion-exchange capacities of monohydrate at pH 4 and 7 were 0.5 and 7.5 meq/g respectively. On the other hand, the ion-exchange capacities of hemihydrate at pH 4 and 7 were 4.0 and 4.7 meq/g respectively, and in an acid solution with the same conditions as above the adsorption of the potassium ion was about 8 times that of monohydrate. Besides, the solubility of the ion-exchanger was consideably less than that of monohydrate.

Ion-exchange Capacities of Phosphates to Cs^+: The cesium ion-exchange titration curves of monohydrate and hemihydrate and the solubilities of the latter are shown in Fig. 6. It has previously been reported that the Cs^+ with a large ionic radius was scarcely adsorbed in monohydrate.[8] In the present study, however, a little adsorption was observed, as is shown in the diagram. The ion-exchange capacities of hemihydrate at pH 4 and 7 were 2.0 and 5.5 meq/g respectively, and the solubility of the ion-exchanger was extremely small. The solubility of the monohydrate used as an ion-exchanger could not be estimated, because a colloidal solution was formed by the dissolution of the salt as the pH rose.

As has been mentioned above, the crystalline titanium hydrogen bis(phosphate) hemihydrate could also adsorb such large ions as K^+ and Cs^+; therefore, it may be expected to be an inorganic ion-exchanger.

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