Studies of Inorganic Ion Exchangers. III.[1] Ion Exchange Properties of $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ to Alkali Metal and Ammonium Ions

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In order to develop an inorganic ion exchanger for industrial use, the ion exchange behaviour of $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ with alkali metal and ammonium ions has been investigated. The ion exchange capacities of $Ti(HPO_4)_2 \cdot 1/2H_2O$ (hemihydrate) have been determined by forward and backward titration. The saturation ion exchange capacities (Q^A) of the hemihydrate to Li, Na, K, Cs, and NH_4 (M) ions by the forward titration method were 1.9, 3.2, 4.1, 2.5, and 3.7 meq/g at pH 4.5, respectively. The ion exchange capacities (Q°) of the hemihydrate from 0.1 M MCl were 0.31, 1.84, 2.31, 0.21, and 1.01 meq/g to each of the ions. The selectivity quotients ($K_{\rm H}^{\rm M}$) estimated from the Q^A and Q° were 0.028, 3.77, 15.7 0.008, and 0.255 to each of the ions, and the selectivities of the hemihydrate increased in the order $Cs^+ < Li^+ < NH_4^+ < Na^+ < K^+$. The empirical formula of the 50% ion exchange products derived from the hemihydrate may be represented by $TiMH(PO_4)_2 \cdot 0—1/2H_2O$, (where, M=Na, K, and NH_4). The ion exchange of Li and Cs ions did not take place completely however to give a 50% ion exchanger, and the hemihydrate was then converted into a non-stoichiometric compound.

Certain metal oxides, hydroxides, acid salts, heteropolyacids, insoluble hexacyanoferrate (II), and zeolite have been known as inorganic ion exchangers.[2] Zirconium phosphate, as an acid salt of a multivalent metal is useful as an ion exchanger in analytical chemistry.[3] In order to develop an ion exchanger for industrial use, the ion exchange behavior of various phosphates has been investigated.[4,5] Titanium phosphate as an ion exchanger appears promising because of the stability and low price of the raw material. The titanium(IV) bis(hydrogenphosphate) hemihydrate ($Ti(HPO_4)_2 \cdot 1/2H_2O$) has been synthesized by refluxing amorphous titanium(IV) phosphate (ATP) with concentrated phosphoric acid.[6] The X-ray diffraction pattern of the hemihydrate was entirely different from that of the titanium(IV) bis(hydrogenphosphate) monohydrate ($Ti(HPO_4)_2 \cdot H_2O$), known already.[7] It has been reported[6] that the hemihydrate has an ion exchangeability with ions of relatively large ionic radius, such as potassium and cesium. Further, $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ has also been prepared by refluxing a phosphoric acid and a sulfuric acid solution of $TiOSO_4$, which is the intermediate in the industrial process of titanium(IV) dioxide.[1] In the present work, the ion exchange properties of the hemihydrate toward Li, Na, K, Cs, and NH_4 ions have been investigated. Alberti *et al.*[7] examined the ion exchange properties of $Ti(HPO_4)_2 \cdot H_2O$ with Li, Na, and K ions, and Takaguchi and Tomita[8,9] reported the ion exchange behaviour of the monohydrate with Li and Na ions by forward and backward titration. However, no data of the ion exchange reactions of the hemihydrate exist except for the Na, K, and Cs ions as determined previously by the forward titration.[6] Ion exchange characteristics, such as selectivity quotient, degree of absorption and distribution coefficient for the hemihydrate do not exist. The ion exchange behaviour of the hemihydrate towards Li, Na, K, Cs, and NH_4 ions has been observed by forward and backward titration, and the saturation and equilibrium capacities determined. Ion exchange characteristics have been introduced from the relationship between the capacities. The ion exchange characteristics of the monohydrate have also been estimated and contrasted with the hemihydrate. Moreover, the apparently 50%, 100%, and the 50% →H ion exchange products have been examined by X-ray diffraction and chemical analysis.

Experimental

Preparation of Ion Exchanger. Titanium(IV) bis(hydrogenphosphate) were prepared by the methods described previously,[1,6] the conditions for the monohydrate and hemihydrate and the analytical results being summarized in Table 1.

Analysis. Product components, such as P_2O_5, TiO_2, and H_2O were determined by methods previously reported.[6] The M_2O (M=Li, Na, K, Cs) content was derived from the following equation.

$$100\% - (P_2O_5\% + TiO\% + H_2O\%) = M_2O\%$$

The NH_3 content was determined by Kjeldahl's method. The X-ray diffraction patterns were obtained under the conditions reported previously.[6]

pH *Titration Curves.* *Forward Reaction*: The product (Nos. 1 and 2) (0.100 g)portion was placed in a 20 ml stoppered test tube, and the solutions in the proper ratio of 0.1 M MCl to 0.1 M MOH added (10 ml). The contents in the test tube were shaken periodically and the pH of the supernatant liquid measured after 48 h. The forward titration curve was drawn from the relation between the pH and the ion exchange capacity estimated from the mixed ratio of 0.1 M MCl to 0.1 M MOH.

Backward Reaction: 0.5 M MOH solution (40 ml) was gradually added to the product (0.01 mol)(Nos. 1, 2, and 3); the neutralized product was separated from the mother liquor after 48 h, washed with water, and vacuum-dried over phosphorus pentoxide for 24 h. A portion (0.100 g) of the apparently 100% ion exchange product thus obtained was placed in a (10 ml) stoppered test tube, and the solution 10 ml, mixed in the proper ratio of 0.1 M MCl to 0.1 M HCl added. The contents in the test tube were shaken periodically and the pH of the supernatant liquid measured after 48 h. The backward pH titration curve was then drawn from the relation between the pH and the ion exchange capacity.

Dissolution of Ion Exchanger. A portion of the above supernatant liquid (5.00 ml) was taken, and the phosphorus dissolved determined colorimetrically as phosphomolybdenum blue.

Saturation Capacity at pH 4.5 *(Q°, meq/g).* Titanium(IV) bis(hydrogenphosphate) as an ion exchanger is stable

Table 1. Synthesis and analysis of titanium(IV) bis(hydrogenphosphate)

No.	Reaction conditions							
	Raw material		Mother liquor					
	ATP[a] (g)	$TiOSO_4$[b] (ml)	H_3PO_4 (mol/l)	H_2SO_4 (mol/l)	Volume (ml)	Temp (°C)	Time (h)	Method[c]
1		30.0	8.03	3.40	900	150	50	PPT
2	25.0		13.0	1.80	880	160	50	REF
3		20.0	8.60	2.82	600	163	50	REF
4		30.0	10.9	3.06	900	165	50	REF

No.	Reaction products				
	TiO_2 (%)	P_2O_5 (%)	H_2O (%)	$TiO_2 : P_2O_2 : H_2O$ (mole ratio)	Estimated formura
1	31.2	54.6	14.2	1.01 : 1.00 : 2.05	$Ti(HPO_4)_2 \cdot H_2O$
2	32.0	56.4	10.1	1.01 : 1.00 : 1.43	$Ti(HPO_4)_2 \cdot 1/2H_2O$
3	32.4	57.5	8.85	1.01 : 1.00 : 1.22	$Ti(HPO_4)_2 \cdot 0—1/2H_2O$
4	32.4	60.7	7.6	0.95 : 1.00 : 0.99	$Ti(HPO_4)_2 \cdot$

a) Amorphous titanium phosphate containing TiO_2 42.7%, P_2O_5 33.8%, H_2O 23.3%. b) Solution containing TiO_2 250 and H_2SO_4 1044 g/l. c) PPT : Precipitation method, REF : Refluxing method.

in an acidic aqueous solution up to a pH of 4.5. Therefore, the ion exchange capacity at pH 4.5 on the forward titration curve was determined as the saturation ion exchange capacity.

The Equilibrium Capacity at pH *4.5 (Q^A, meq/g).* The ion exchanger (0.500 g) was mixed with 0.1 M MCl (25 ml) solution in a 50 ml stoppered Erlenmeyer flask and the contents in the flask periodically shaken. After equilibration, a portion of the supernatant liquid(10.00 ml) was titrated potentiometrically with 0.1 M NaOH using a recording auto titrator (Hiranuma Sangyo Co.). The relation between the pH and the volume of 0.1 M NaOH was drawn as the titration curve. In the titration curve, the ion exchange capacity, corresponding to a volume of 0.1 M NaOH consumed at pH 4.5, was determined as the equilibrium ion exchange capacity.

Selectivity Quotient (K_H^M). This was derived as follows.

$$K_H^M = \frac{(M^+)i}{(H^+)i} \cdot \frac{(H^+)s}{(M^+)s} = \frac{Q^A}{Q^\circ - Q^A} \cdot \frac{Q^A}{C - Q^A},$$

where C is the initial amount (2.5 meq) of 0.1 M MCl used for the determination of the equilibrium ion exchange capacity.

Absorption Quantity (A). This was obtained as follows.

$$Q^A/C \cdot 100 = A(\%).$$

Distribution Coefficient (K_D, ml/g). This was obtained from the expression,

$$\{A/(100-A)\} \cdot S/I = K_D,$$

where S is the volume (25 ml) of 0.1 M MCl used for the determination of the equilibrium ion exchange capacity, and I, the weight (0.500 g) of ion exchanger used.

Results and Discussion

The Ion Exchange Behavior of Titanium(IV) Bis(hydrogenphosphate) Dissolution. The ion exchange titration curves of the hemihydrate to alkali metal (Li, Na, K, Cs) and ammonium ions and solubility curves are shown in Figs. 1, 3, 4, 5, and 6.

Lithium Ion: As shown by the forward titration curve in Fig. 1, the ion exchange capacities of the hemihydrate with Li^+ were 1.9 and 3.9 meq/g at pH 4.5 and 7.0, respectively, and these increased linearly in the pH range 2.6—7. The P dissolved in the aqueous solution from the ion exchanger was 0.001—0.005% at pH 1—5. The forward and backward titration curves showed a hysteresis loop, and it is thought that the apparently 100% Li product used for the backward titration did not sufficiently absorb the Li^+. In the backward titration, the dissolved P was smaller than in the forward titration.

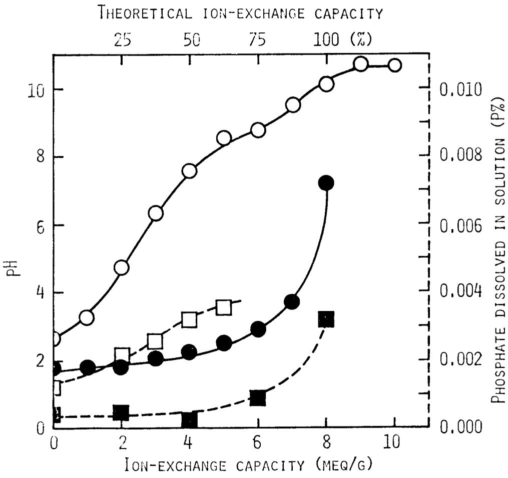

Fig. 1. Li ion-exchange titration curve of and dissolution curve of $Ti(HPO_4)_2 \cdot 1/2H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

The ion exchange titration curve and the solubility curve of the monohydrate with Li^+ have been reported.[7,8] In contrast to the hemihydrate, the results of re-examination with regard to the monohydrate are shown in Fig. 2. The ion exchange behavior in the forward titration agrees with the previous reports.[7,8] The capacities of the monohydrate were 1.9 and 7.0 meq/g at pH 4.5 and 7.0, respectively. In the range of ion exchange capacities 1—6 meq/g, the pH of the

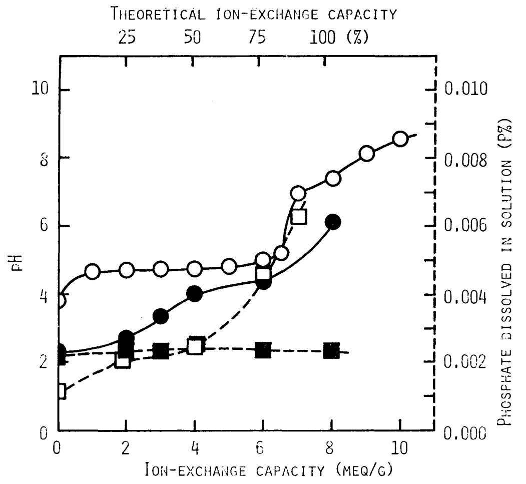

Fig. 2. Li ion-exchange titration curve and dissolution curve of $Ti(HPO_4)_2 \cdot H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

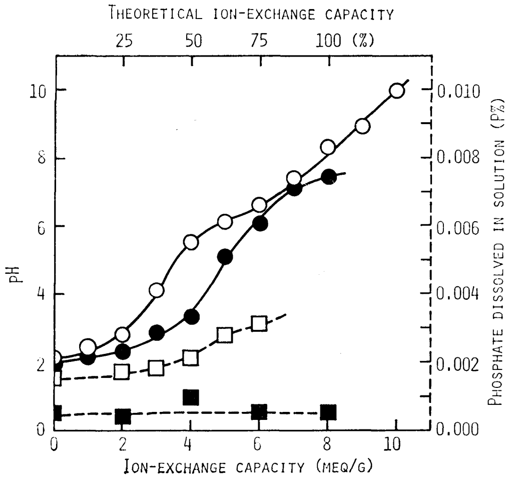

Fig. 3. Na ion-exchange titration curve and dissolution curve of $Ti(HPO_4)_2 \cdot 1/2H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

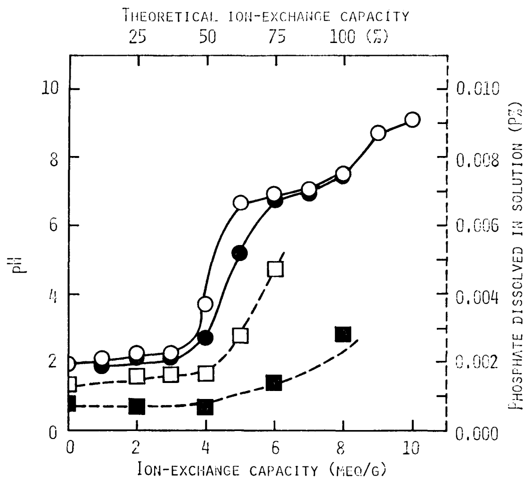

Fig. 4. K ion-exchange titration curve and dissolution curve of $Ti(HPO_4)_2 \cdot 1/2H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

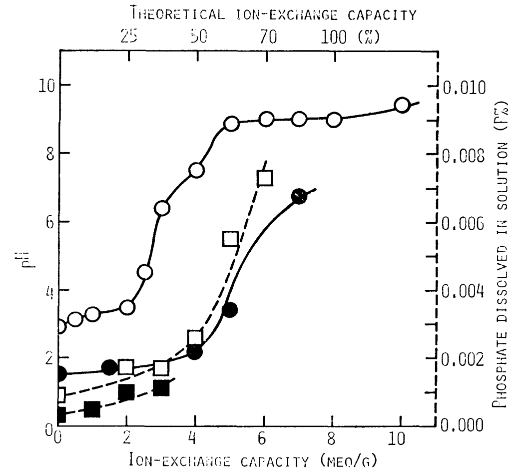

Fig. 5. Cs ion-exchange titration curve and dissolution curve of $Ti(HPO_4)_2 \cdot 1/2H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

solution was 4.5—5.0, and then the change of pH slacked up entirely. The P dissolved in the solution at pH 3.8—7.0 was from 0.001—0.006% and the backward titration curve did not agree with the forward titration curve, the P dissolved in the backward titration being about 0.0025%. As reported above, the pH of the solution equilibrated with the hemihydrate for the forward titration increased with an increase in the ion exchange capacity. The pH in the case of the monohydrate did not change as much in the range of ion exchange capacities 0—6 meq/g. The ion exchange capacities of the hemihydrate and monohydrate at pH 5 were 3.5 and 6.0 meq/g, respectively. It is unreasonable that the ion exchange capacity of the hemihydrate, which provides the large spacings recognized by the X-ray diffraction pattern, should be less than that of the monohydrate which provides the small spacings. The explanation may be that an inorganic ion exchanger can absorb the metal ion, excluding part of the water molecules from the hydrated ion at the cavities and then the ion exchange reaction takes place. When the monohydrate is used as the ion exchanger for Li^+, this explanation is reasonable. Approximately 84% of H^+ in the monohydrate exchanged with Li^+. It is well documented that the size of the alkali metal ions is in the order of $Li^+ < Na^+ < K^+ < Cs^+$, though the degree of hydration is the order of $Cs^+ < K^+ < Na^+ < Li^+$, and the Li^+ is hydrated particularly in neutral and alkaline solutions. It is the hemihydrate which provides the cavities through which large ion particles can pass and when it is used

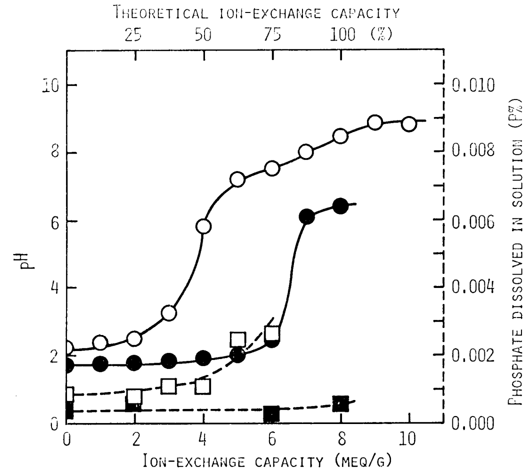

Fig. 6. NH_4 ion-exchange titration curve and dissolution curve of $Ti(HPO_4)_2 \cdot 1/2H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

as the ion exchanger for Li^+, the fully hydrated Li^+ is adsorbed. Consequently the H^+ in the exchanger largely remains further ion exchange is restricted.

Sodium Ion: The forward titration curve in Fig. 3, indicates the ion exchange capacities of the hemihydrate with Na^+ as 3.2 and 6.6 meq/g at pH 4.5 and 7.0, respectively. The P dissolved in the solution was 0.0015—0.003% in the pH range 2.0—6.5. The behavior of the backward titration curve did not agree with that of the forward titration curve. Therefore, it is assumed that the apparently 100% Na product used as the starting material for the backward titration is in reality an 85% ion exchange product. The P dissolved in the backward titration solution was about 0.0005%, the same as with Li^+ and the ion exchange capacities of the hemihydrate with Na^+ were less than those of the monohydrate (5.8, 7.6 meq/g from Fig. 4 in a previous report[6]) at pH 4.5 and 7.0. This may be explained in terms of the adsorption of hydrated ions as mentioned above.

Potassium Ion: In the forward titration curve in Fig. 4 the ion exchange capacities of the hemihydrate to K^+ were 4.1 and 6.7 meq/g at pH 4.5 and 7.0, respectively. The P dissolved in the solution was about 0.0015% in a pH range 2.0—3.7, and then was increased rapidly at higher pH. A 50% K product corresponding to a composition of $TiKH(PO_4)_2 \cdot 1/2H_2O$ was formed from the aqueous solution at pH 4.5, and was stable in weakly acidic solution. The backward titration curve was similar to that of the forward titration curve. The P dissolved in the solution of backward titration was about 0.0007% below pH 4.5.

Cesium Ion: In the forward titration curve in Fig. 5, the ion exchange capacities of the hemihydrate with Cs^+ were 2.5 and 3.3 meq/g at pH 4.5 and 7.0, respectively. The P dissolved in the solution was 0.001—0.002% in the pH range 2.7—3.5, and the dissolubility of the ion exchanger markedly increased above pH 3.5. The backward titration curve was at a considerable distance from the forward titration curve, the explanation being that an apparently 87% Cs product adsorbs Cs^+ to 35% of the theoretical ion exchange capacity of $Ti(HPO_4)_2 \cdot 1/2H_2O$. Also damage is caused to the exchanger by the alkaline aqueous solution.

Ammonium Ion: In the forward titration curve in Fig. 6, the ion exchange capacities of the hemihydrate to NH_4^+ were 3.7 and 4.8 meq/g at pH 4.5 and 7.0, respectively. The P dissolved in the solution was about 0.001%. An apparently 100% NH_4 product was in reality about 50% ion exchanger. Consequently, the backward titration curve, drawn using this product, was at a considerable distance from the forward titration curve. As seen in the X-ray diffraction pattern of Fig. 9, the apparently 100% NH_4 product changed to an amorphous product by the ammoniacal solution. The hemihydrate however provides wide spacings which can adsorb ions of large ionic radii, such as NH_4^+. Therefore, it may be anticipated that the hemihydrate with prove useful for the exclusion of NH_4^+ in a solution below pH 4.5.

The ion exchange properties of the monohydrate with NH_4^+ have not been investigated, since, the behaviors of ion exchange are examined, and shown in Fig. 7. The radius of the NH_4^+ is larger than that of the Li^+ and Na^+. Therefore, the monohydrate, which provides narrow spacings, does not show ion exchangeability with NH_4^+. Part of the ion exchanger dissolved in the ammoniacal solution, and a considerable change in the structure was observed.

Ion Exchange Characters. The titration curves drawn for the estimation of the equilibrium ion exchange capacity are shown in Fig. 8. The various ion exchange characters of titanium(IV) bis(hydrogenphosphate) to the alkali metals and ammonium ions are summarized in Table 2.

The equilibrium ion exchange capacities (Q^A) of

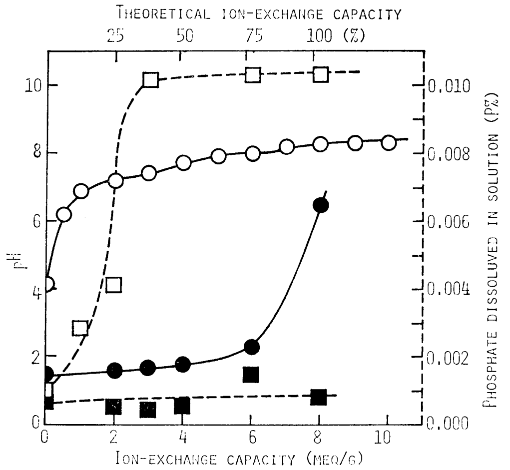

Fig. 7. NH_4 ion-exchange titration curve and dissolution curve of $Ti(HPO_4)_2 \cdot H_2O$.
○: Forward titration, ●: backward titration, □: P released to the external solution on the forward titration, ■: P released to the external solution on the backward titration.

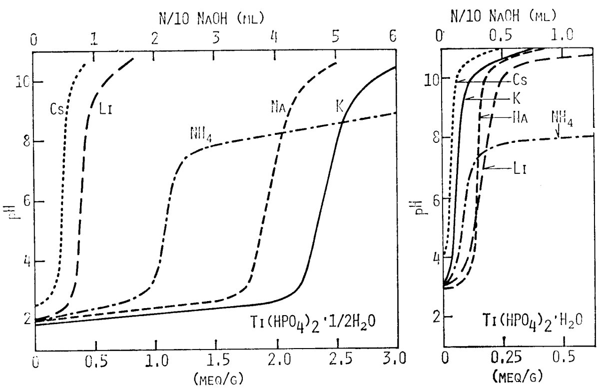

Fig. 8. Titration curves for equilibrium solution of titanium hydrogen phosphate with alkali metal and ammonium chlorides.

the monohydrate with Li^+, Na^+, K^+, Cs^+, and NH_4^+ were 0.025—0.12 meq/g, *i.e.*, the monohydrate hardly adsorbed the above ions in acidic solution at equilibrium. The Q^A of the hemihydrate to NH_4^+, Na^+, and K^+, except for Li^+ and Cs^+, were 1.0, 1.8, and 2.3 meq/g, respectively.

Generally, titanium(IV) bis(hydrogenphosphate) is stable in acid solution below pH 4.5. The saturation ion exchange capacity (Q°) of the monohydrate with Na^+ was 5.8 meq/g at pH 4.5. With other ions however, the Q° of the monohydrate was less than 0.6 meq/g. The Q° of the hemihydrate with Li^+, Na^+, K^+, Cs^+, and NH_4^+ was between 1.9—4.1 meq/g.

The selectivity quotients (K_H^M) of the hemihydrate, estimated from the values of Q^A and Q°, were 3.77 for Na^+ and 15.7 for K^+. It is thought that the values of K_H^M are significant for the separation of sodium and potassium ions.

The adsorption quantities (A) of the monohydrate for the alkali metal and ammonium ions were less than 5%. However, the A of the hemihydrate increased in the order of $Cs^+<Li^+<NH_4^+<Na^+<K^+$, and exhibited a remarkably high value of 92.4% for K^+.

The distribution coefficients (K_D) of the hemihydrate with Na^+ and K^+ showed remarkably large values. The K_D of K^+ was about 4 times that of K_D for Na^+. Therefore, $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ may be considered as an ion exchanger for the recovery of potassium in sea water and brine.

X-Ray Diffraction Patterns. *Li^+ Exchangers*: A diffraction line of 11.6 Å, which characterized the hemihydrate, disappeared in the pattern of a 50% Li product. Where some lines appeared split in the pattern of the hemihydrate, this disappeared from the pattern of the 50% Li product; *i.e.*, half the diffraction lines decreased. In a previous report,[1] $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ was thought to consist of at least two species and not just one crystallite. The X-ray diffraction pattern of a 50%→H product returned to that of the initial H form. The X-ray diffraction data of an apparently 100% Li product was approximately the same as the 50% Li product, a fact subsequently proved by analysis.

Na^+ Exchanger: The diffraction lines of the hemihydrate at 11.6 and 9.21 Å diasppeared in the 50% Na product. A single diffraction line at 10.2 Å appeared in the 50% Na product. Several lines appeared (in pairs) in the X-ray diffraction pattern of the hemihydrate, but disappeared from the 50% Na product. Therefore, it is assumed that the 50% Na product is a single crystallite. In the 50% Na→H product, the diffraction line at 11.2 Å appeared, and the number of diffraction lines that decreased was greater than in the case of the hemihydrate. The X-ray diffraction data of an apparently 100% Na product was very similar to that of the 50% Na product. The 85% ion exchanger was attacked by the alkaline solution and the intensities of the X-ray diffraction

TABLE 2. ION EXCHANGE PROPERITIES OF TITANIUM HYDROGEN PHOSPHATE TO ALKAI METAL AND AMMONIUM IONS

Exchanger	Ion	Equilibrium capacity (Q^A, meq/g)	Saturation capacity at pH 4.5 (Q°, meq/g)	Selectivity quotient (K_H^M)	Mole fraction (Q^A/Q°)	Absortion quantity (A, %)	Distribution coefficient (K_D, ml/g)
$Ti(HPO_4)_2 \cdot H_2O$	Li	0.12	0.6	0.0126	0.20	2.4	1.23
	Na	0.11	5.8	0.0009	0.02	4.4	2.30
	K	0.05	0.6	0.0019	0.01	2.0	1.02
	Cs	0.025	0.4	0.0006	0.07	1.0	0.51
	NH_4	0.035	0.1	0.077	0.35	1.4	0.71
$Ti(HPO_4)_2 \cdot 1/2H_2O$	Li	0.31	1.9	0.028	0.163	12.4	7.08
	Na	1.84	3.2	3.77	0.575	73.6	139.4
	K	2.31	4.1	15.7	0.564	92.4	607.9
	Cs	0.21	2.5	0.008	0.084	8.4	4.59
	NH_4	1.01	3.7	0.255	0.27	40.4	33.9

Equilibrium capacity: Ion exchange capacity at pH 4.5 in Fig 8.

Saturation capacity: Ion exchange capacity at pH 4.5 in Figs. 1, 7, and 4—6.[6]

Selectivity quotient: $K_H^M = \frac{(M^+)I}{(H^+)I} \cdot \frac{(H^+)S}{(M^+)S} = \frac{Q^A}{Q^\circ - Q^A} \cdot \frac{Q^A}{C - Q^A}$.

Absorption quantity: $Q^A/C \times 100 = A$. Distribution coefficient: $K_D = A/I \cdot S/(100-A)$.

C: Initial quantity of MCl (2.5 meq). S: MCl solution (25 ml). I: Ion exchanger (0.5 g).

TABLE 3. X-RAY DIFFRACTION DATA OF TITANIUM HYDROGEN PHOSPHATE AND ION EXCHANGE PRODUCTS

$Ti(HPO_4)_2\cdot 1/2H_2O$	Exchangers of Li ion			Exchangers of Na ion			Exchangers of K ion			Exchangers of Cs ion			Exchangers of NH_4 ion		
(No. 2) (Å)	50% (Å)	50%→H (Å)	100% (Å)	50% (Å)	50%→H (Å)	100% (Å)	50% (Å)	50%→H (Å)	100% (Å)	50% (Å)	50%→H (Å)	87% (Å)	50% (Å)	50%→H (Å)	100% (Å)
11.6M		11.6M			11.2W	11.6M			12.3 S				11.3 S	11.3 S	11.3W
				10.16 S		10.8W	11.0 S	10.8 S							
9.21M	9.50M	9.21W	9.82M								9.21W			9.21W	
		6.10W			5.98W										
5.60W		5.57W		5.34 S		5.37M	5.47 S	5.50W	5.47W				5.47 S	5.79W	5.53W
5.21 S	5.24 S	5.21 S	5.24 S								5.21M			5.21M	
					4.69W					4.72W					
4.48M	4.41W	4.48M	4.44W	4.57W		4.57W					4.50W			4.41W	
4.31W		4.31W					4.37W	4.35W		4.27W			4.35M		
4.00W	3.97W	3.98W	3.97W	3.97W									4.00 S	4.00M	4.00W
3.90W		3.90W			3.80 S	3.81W	3.93W	3.95W	3.93W	3.93W	3.90W				
3.65M				3.62 S	3.74 S	3.62 S									
	3.53 S		3.56 S	3.54 S			3.59W	3.59W		3.56W	3.56W		3.57W	3.56M	
3.44 S	3.41 S	3.42 S	3.42 S				3.50M	3.46M			3.44M		3.49M	3.42M	
									3.18W				3.19W		
3.16 S	3.14 S	3.16 S	3.16 S	3.15 S	3.16 S	3.16 S	3.16 S	3.15 S	3.14M	3.15M	3.16 S	3.16W	3.14M	3.15M	
3.01W	3.00W	3.00W	3.02W	3.01W	3.02W		3.04W	3.04W		2.96W	3.01W	2.97W	3.04W	2.99W	
							2.79W	2.77W	2.85W	2.86W			2.85W		
							2.71W						2.78W	2.57W	
2.58W	2.53W	2.57W	2.55W	2.54M	2.56W	2.55W	2.52W	2.52W	2.52W	2.55W	2.58W	2.56W	2.52W	2.53W	
2.41W	2.45W	2.41W	2.45W				2.38W						2.40W		

50%: Product of forward titration. 50%→H: Product of backward titration. 100%: Product of forward titration.
Abbreviations: S=strong, M=medium, W=weak.

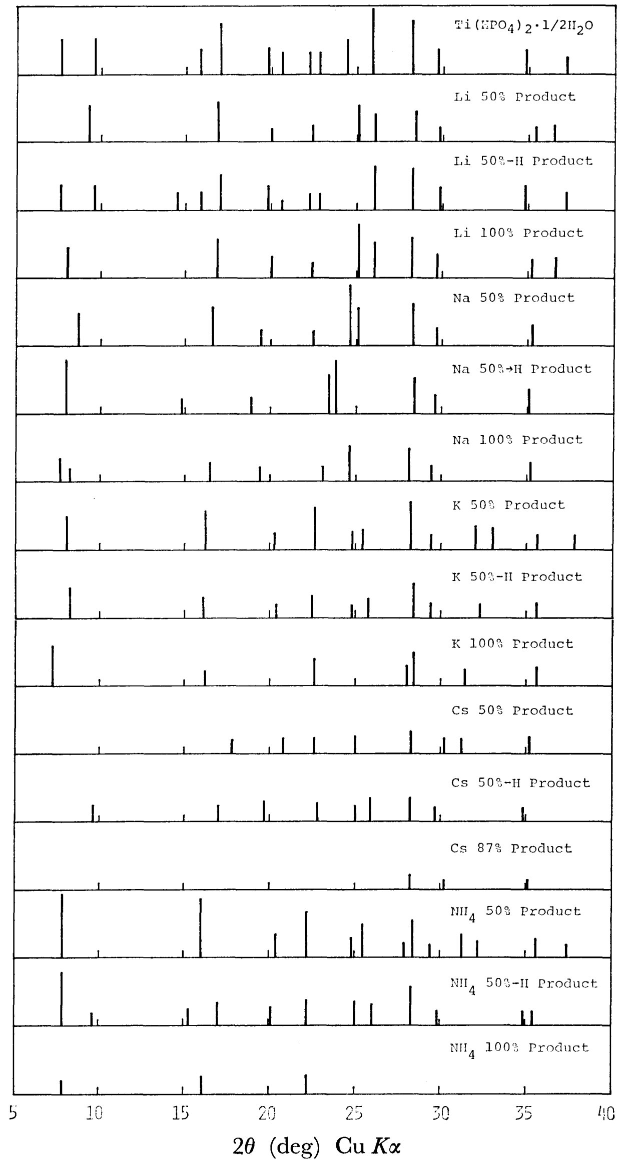

Fig. 9. X-Ray diffraction patterns of titanium hydrogen phosphate and its ion exchange products.

pattern decreased.

K^+ Exchanger: The X-ray diffraction lines at 11.6 and 9.21 Å, which characterized the hemihydrate, disappeared in the X-ray diffraction pattern of the 50% K product. The number of diffraction lines was reduced by a half in contrast with that in the case of the hemihydrate. The diffraction intensities however were increased considirably. As seen in Fig. 4, the 50% K product was in a state of equilibrium with the aqueous solution at pH 4.5. Thus, it is assumed that the composition of this product agrees with that of $TiKH(PO_4)_2 \cdot 0—1/2H_2O$. The X-ray diffraction pattern of a 50% K→H product did not change so much with that of the 50% K product. In an apparently 100% K product, the diffraction line at 12.3 Å reappeared and the intensity of all the diffraction lines increased. As seen in Fig. 4, the apparently 100% K product was in a state of equilibrium with the aqueous solution at pH 7.5. Therefore, it is assumed that the composition of the product agrees with that of $TiK_2(PO_4)_2 \cdot 0—1/2H_2O$.

Cs^+ Exchanger: The 50% Cs product was attacked by the CsOH aqueous solution, and the intensity of the X-ray diffraction pattern decreased. With an apparently 87% Cs product, the ion exchange reaction was not completed, being converted into an amorphous substance.

NH_4^+ Exchanger: In the 50% NH_4 product, the diffraction line at 11.3 Å appeared, and the intensity of all diffraction lines was relatively high. It is assumed from the forward titration curve in Fig. 6 that the product $TiNH_4H(PO_4)_2 \cdot 0—1/2H_2O$, is formed. The diffraction lines at 9.21, 5.21, and 3.42 Å, which characterize the hemihydrate, reappeared in the diffraction pattern of the 50% NH_4→H product. There is the possibility that the product was reconverted to the hemihydrate. The apparently 100% NH_4 product was attacked by the ammoniacal solution, and converted into an amorphous substance.

Composition of the Apparently 50% Ion Exchangers. From the view point of stability, $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ possibly underwent ion exchange to become $TiMH(PO_4)_2 \cdot 0—1/2H_2O$. The conditions for preparation of the 50% products and their analytical results are summarized in Table 4.

From these results, the compositions of the 50% products were estimated as follows; $TiLi_{0.6}H_{1.4}(PO_4)_2 \cdot 1/2H_2O$, $TiNaH(PO_4)_2 \cdot 0.17H_2O$, $TiKH(PO_4)_2 \cdot 0.31H_2O$, $TiNH_4H(PO_4)_2 \cdot 1/2H_2O$, and $Ti_{0.8}Cs_{0.6}H_{2.3}(PO_4)_2 \cdot 0.11H_2O$. As described above, the products of $TiMH(PO_4)_2 \cdot 0—1/2H_2O$ readily obtained by the ion exchange of $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ with Na, K, and NH_4 ions respectively. Ion exchange of the hemihydrate with Li or Cs ions, however, brought about conversion of $Ti(HPO_4)_2 \cdot 0—1/2H_2O$ to a non-stoichio-

Table 4. Preparation of apparently 50% ion exchange products and analysis

Salt	Reaction conditions $Ti(HPO_4)_2$ (g)	0.1M-MOH[a] (ml)	Temp (°C)	Time (h)	Reaction products Yield (g)	TiO_2 (%)	P_2O_5 (%)	H_2O (%)	M_2O[b] (%)	$TiO_2 : P_2O_5 : H_2O : M_2O$ (mole ratio)
Li salt	2.40	100	20	48	1.98	30.7	53.1	9.1	7.1	1.03 : 1.00 : 1.45 : 0.63
Na salt	4.80	200	20	48	4.76	30.1	53.4	4.4	12.1	1.00 : 1.00 : 0.65 : 0.52
K salt	4.80	200	20	48	4.73	28.9	49.6	5.1	16.4	1.05 : 1.00 : 0.81 : 0.50
Cs salt	2.40	87	20	48	1.37	20.1	46.0	6.3	27.6	0.78 : 1.00 : 1.25 : 0.30
NH_4 salt	4.86	200	20	48	4.63	31.1	55.1	7.3	6.5[c]	1.00 : 1.00 : 1.04 : 0.99[d]

a) MOH: LiOH, NaOH, KOH, CsOH. b) M_2O: Li_2O, Na_2O, K_2O, Cs_2O. c) % as NH_3. d) Mole ratio as NH_3.

metric compound.

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