Studies of Inorganic Ion Exchangers. V.[1] The Preparation of the Granulated Product from Titanium(IV) Bis(hydrogenphosphate) and Carbonaceous Materials, and Its Ion-exchange Properties

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In order to develop an inorganic ion exchanger for industrial use, a mixture of titanium(IV) bis(hydrogenphosphate), a carbonaceous material (sugar, flour, or sodium ligninsulfonate), and an additive (H_2SO_4 or H_3PO_4) was sintered, and the resultant sintered product was crushed to obtain a granulated product, the ion-exchange property of which was then investigated. The mixing ratio of the titanium phosphate to the carbonaceous material has an influence on the ion-exchange capacity and the durability of the granulated product. In consideration of this influence, the weight ratio of the titanium phosphate to carbon included in the carbonaceous material was expediently chosen as 1 : 0.5. The acid additives promoted the carbonization of the carbonaceous material, whereby the sintered product of porosity was obtained. The weight ratio of the carbonaceous part to the titanium phosphate in the product decreased with an increase in the temperature within the range from 185 to 350 °C. In a batch method, a granulated product including $Ti(HPO_4)_2 \cdot H_2O$ adsorbed Na^+, but not K^+. A granulated product including $Ti(HPO_4)_2 \cdot 1/2H_2O$, however, adsorbed these ions, the equilibrium ion-exchange capacities toward Na^+ and K^+ being 1.28—1.78 and 1.56—2.34 meq/g respectively, and the selectivity quotient and the distribution coefficient toward K^+ showed larger values than those toward Na^+. In a column method, when a NaCl (26.66 g/l)-KCl (0.67 g/l) aqueous solution flowed into a column which had been packed with the granulated product (5 g) including the hemihydrate, the ion-exchange capacities of this granulated product toward Na^+ and K^+ were 1.1—1.2 and 0.38—0.58 meq/g, respectively, showing the separation factor (α^{K}_{Na}) of 18—25. When artificial brackish water also flowed into the column, very small quantities of the Mg^{2+} and Ca^{2+} were adsorbed; consequently, a selective ion-exchange property of the granulated product toward K^+ was recognized. Also, the carbonaceous part in the granulated product adsorbed such coloring matter as Methylene Blue.

Some phosphates of multivalent metals are known as inorganic ion-exchangers; among them, zirconium phosphate is used as a typical inorganic ion-exchanger in the field of analytical chemistry. With a view to developing inorganic ion-exchangers for industrial use, our attention was paid to titanium phosphate, which is almost equivalent in stability to zirconium phosphate and which is rather cheap as a raw material. Our studies revealed that titanium(IV) bis(hydrogenphosphate) 0—1/2 hydrate [$Ti(HPO_4)_2 \cdot 0—1/2H_2O$],[2] with an X-ray diffraction pattern quite different from that of the known titanium(IV) bis(hydrogenphosphate) monohydrate [$Ti(HPO_4)_2 \cdot H_2O$],[3] could be prepared by refluxing various titanium compounds with concentrated phosphoric acid and that titanium(IV) bis(hydrogenphosphate) 0—1/2 hydrate had a unique ion-exchange property.[4] In order to establish an industrial method of producing $Ti(HPO_4)_2 \cdot 0—1/2H_2O$, this compound was synthesized by refluxing a sulfuric acid solution of $TiOSO_4$, as an intermediate in the production of titanium(IV) oxide, with concentrated phosphoric acid.[5] In the previous report,[1] the ion-exchange equilibria between titanium(IV) bis(hydrogenphosphate) and an aqueous solution of NaCl–KCl under various conditions were investigated. As a result of the investigation, it was found that K^+ was separated more effectively than Na^+ when the anhydride was added to a solution containing equivalents of NaCl and KCl, but trouble occurred in the separation of the solid phase from the liquid phase because the crystals of the titanium(IV) bis(hydrogenphosphate) were too small. In the batch method, on the other hand, it was not easy to effect the elution of K^+ adsorbed on the microcrystals. These difficulties constituted a great obstacle for the practical use of the compound. Generally, inorganic ion-exchangers of a hydrated oxide or hydroxide formed as a gel have been used for analytical use after a dry solid of the gel has been crushed into particles of an adequate size, but an ideal strength can not be expected for them. In case a column is packed with an inorganic ion-exchanger obtained by further pulverizing the dry solid or supplied in microcrystalline form, water can not pass through the column smoothly. Reported in this paper is a result of our investigations with an eye to granulating the inorganic ion-exchanger. A mixture of microcrystalline titanium(IV) bis(hydrogenphosphate), a viscous carbonaceous material, such as sugar or wheat flour, and some of an additive such as an inorganic acid was sintered at a given temperature, the sintered product was then so crushed as to have a granule size proper for an ion-exchanger. The ion-exchange capacities of the resultant granulated product toward K^+ and Na^+ were examined according to the batch method and compared with those when titanium(IV) bis(hydrogenphosphate) was used as the raw material. A result of the test made to separate K^+ from Na^+ by the column method is also reported in this paper.

Experimental

Preparation and Analysis of Ion-exchangers. Titanium(IV) bis(hydrogenphosphate) as an ion-exchanger was synthesized in accordance with the refluxing method described in previous report.[2,5] The synthetic conditions and the composition of the products are shown in Table 1.

Preparation of Granulated Products. In a 50-ml porcelain crucible was placed given amounts of titanium (IV) bis(hydro-

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

No.	Reaction conditions							Reaction products				
	Raw material		Mother liquid			Temp	Time					
	ATiP[a] (g)	$TiOSO_4$[b] (ml)	H_3PO_4 (mol/l)	H_2SO_4 (mol/l)	Volume (ml)	(°C)	(h)	TiO_2 (%)	P_2O_5 (%)	H_2O (%)	$TiO_2 : P_2O_5 : H_2O$ (mole ratio)	Empirical formula
1	—	30.0	6.76	3.08	900	135	50	32.1	54.4	14.5	1.05 : 1.00 : 2.10	$Ti(HPO_4)_2 \cdot H_2O$
2	25.0	—	8.08	3.39	900	160	50	12.1	25.8	62.1	(1.00 : 1.17 : 51.3)	
					(dry product)			31.9	57.4	10.8	0.99 : 1.00 : 1.48	$Ti(HPO_4)_2 \cdot 1/2H_2O$
3	—	30.0	8.03	3.40	900	160	50	32.6	57.7	9.0	1.01 : 1.00 : 1.23	$Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$
4	75.0	—			2850	160	50	34.2	57.9	7.9	1.04 : 1.00 : 1.07	$Ti(HPO_4)_2$

a) Amorphous titanium phosphate containing TiO_2 42.4%, P_2O_5 33.8%, H_2O 23.3%. b) Solution containing TiO_2 250 and H_2SO_4 1044 g/l.

genphosphate) or a hydrate thereof (a product not as yet rinsed in the production of titanium(IV) bis(hydrogenphosphate), and a carbonaceous material (a reagent-grade saccharoseas sugar, commercially available wheat flour, or a reagent-grade sodium ligninsulfonate). When anhydrous titanium(IV) bis(hydrogenphosphate) was used, 9 M H_2SO_4, 7 M H_3PO_4, and an adequate amount of water were added; the mixture was stirred homogeneously and then dried at 105 °C for about 3 h until it became a dark brown solid. Next, a lid cap was put on the crucible, which was then placed in an electric furnace kept at a given temperature in order to sinter the content of the crucible. After allowing the content to stand and cool, the sintered brown-black product was weighed, crushed so as to have an adequate granule size, sived, throughly washed with water until the acids in the granulated product could no longer be detected, and then dried at 50—60 °C for 24 h. The size distribution of the typical granulated product was found to be as follows; 16—32 mesh 16 w%, 32—42 mesh 52 w%, 42—65 mesh 29 w%, 65—100 meash 3 w%. The strength of the granulated product was determined to be 87—94% with the testing method (JIS-K 1474) used for granular activated carbon.

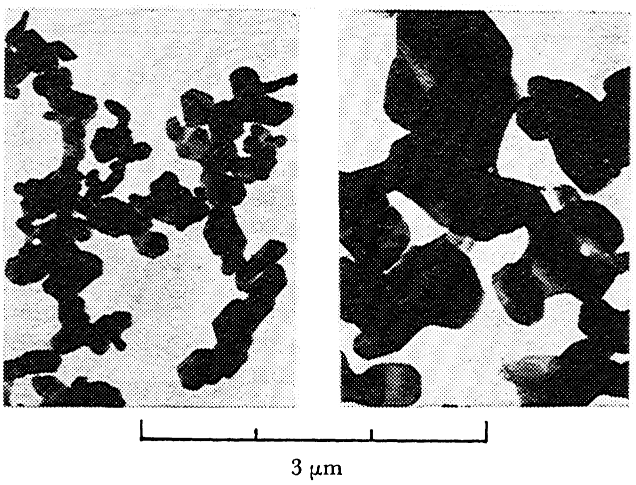
Measurement of Ion-exchange Capacities by the Batch Method. The equilibrium ion-exchange capacity (Q^A, meq/g) between the granulated product and an aqueous solution of the chloride (NaCl, KCl), and the saturated ion-exchange capacity (Q°, meq/g) at pH 4.5 were both measured in accordance with the method previously reported,[4] such ion-exchange characteristics as a selectivity quotient (K_H^M) and a distribution coefficient (K_D) were derived from the above ion-exchange capacities.

Adsorption of Na^+ and K^+ by the Column Method. A column of Pyrex glass (9 mm in inner diameter and 200 mm in height) was packed with 5.0 g of the dried granulated product (60—100 mesh) previously moistened with water. A given volume (500 ml, 1000 ml, or 1500 ml) of a sample solution (the aqueous solution of NaCl-KCl or artificial brackish water; the compositions and concentrations of these solutions are shown in Table 4) was permitted to flow through the column at a flow rate of 0.4—0.5 ml/min. Every 10-ml portion of the effluent from the column was collected in a fraction-collector. The pH value of each fraction was measured, and the Na^+ and K^+ contained therein were determined by flame photometry, while the Mg^{2+} and Ca^{2+} were determined by atomic absorptiometry, thereby estimating the quantity of each ion adsorbed on the granulated product. The cations adsorbed on the granulated product were subjected to complete elution with 30 ml of 6 M hydrochloric acid and an adequate amount of water; each ion in the eluate was determined, whereby the ion-exchange capacity of the granulated product, the distribution coefficient (K_D^M), and the separation factor (α_{Na}^K) were also then calculated.

Adsorption Test of Coloring Matter. To 100 ml of a solution of methylene blue with a concentration of 1 ppm were added 1 g of the granulated product (0.33 g in carbon content) or 0.33 g of active carbon (Pittsburg Co.). The mixture was stirred occasionally, and the coloring matter in the supernatant liquid was determined at a given time interval, using a spectrophotometer at the wave length of 660 nm in order to examine the change in the concentration of methylene blue in the solution with the lapse of time.

Results and Discussion

Titanium(IV) Bis(hydrogenphosphate) as Microcrystals. The titanium(IV) bis(hydrogenphosphate) monohydrate and 0—1/2 hydrate, formed by refluxing various titanium compounds with phosphoric acid, were all microcrystalline. Electron microscope photographs of both hydrates are shown in Fig. 1.



$Ti(HPO_4)_2 \cdot H_2O$ $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$

Fig. 1. Electron microscope photographs of titanium (IV) bis(hydrogenphosphate).

As has already been reported,5) the crystals of these hydrates were quite different in their X-ray diffraction patterns. Besides, they were different in their appearances in the electron-microscope photographs; the monohydrate, showing a good crystallinity, had a crystal structure of hexagonal plates, with a particle size of 0.3—0.6 μ, while the 0—1/2 hydrate has a particle size of 1—2 μ. Since it was very difficult to flow water through a column packed with such microcrystalline hydrates, therefore, the granulation of these microcrystalline hydrates was contemplated.

Granulation of Titanium(IV) Bis(hydrogenphosphate) with The Aid of a Carbonaceous Material. The use of a binder, such as silicic acid gel, poly(vinyl alcohol), or gelatin, came into question for the production of a granulated product of titanium(IV) bis(hydrogenphosphate). Although a composite material of titanium(IV) bis(hydrogenphosphate) and silicic acid gel was expected to have a good stability to heat, it was impossible to produce the composite material possessing satisfactory strength in water according to our present techniques. The granulated product obtained by using poly(vinyl alcohol) or gelation as a binder had good strength, but was devoid of the stability required for inorganic ion-exchangers capable of withstanding use at a high temperature. Hence, an attempt has been made the granulation of titanium(IV) bis(hydrogenphosphate) with the aid of a carbonaceous material as a binder. The conditions for preparing the product and composition thereof are summarized in Table 2.

The carbonaceous material was selected from among saccharose, wheat flour, and sodium ligninsulfonate. A mixture containing saccharose was melted by heating, and the viscous melt was carbonized while bubbling. A mixture containing wheat flour gave a relatively hard sintered product containing nitrogen of proteins. These materials are carbohydrates with a definite carbon content. Sodium ligninsulfonate was chosen from the view point of utilizing pulp-waste liquor. In addition to these materials, a pitch is also regarded as a promising carbonaceous material.

Regarding the proportion of titanium(IV) bis(hydrogenphosphate) to the carbonaceous material in the preparation of the ion-exchanger, the use of a larger amount of the latter increases the strength of the granulated product, but naturally results in decrease in the ion-exchange capacity.

Taking the balance of these effects into consideration, the raw materials were so mixed that the ratio by weight of titanium(IV) bis(hydrogenphosphate) to C was 1 : 0.5. Sulfuric acid or phosphoric acid as an additive served to accelerate the carbonization of the carbonaceous materials by virtue of its dehydration effect and gave a relatively porous sintered product. In Table 2, Nos. 1—5 show the results obtained by using Titanium(IV) bis(hydrogenphosphate) monohydrate and sugar as carbonaceous material, and by sintering the mixture at 185—300 °C. As the carbonization proceeded rapidly at 300 °C, the heating time in this case was shortened. Nevertheless, a decrease in the weight of the granulated product was observed. The ratio by weight of Carb. (carbonaceous part formed by heating) to titanium(IV) bis(hydrogenphosphate) decreased as the temperature was elevated. Accordingly, the product sintered at a relatively lower temperature was not carbonized completely. The same tendency was observed in the cases of Nos. 6—10, wherein titanium(IV) bis(hydrogenphosphate) 0—1/2 hydrate was used.

TABLE 2. PREPARATION OF GRANULATED PRODUCTS FROM TITANIUM PHOSPHATE WITH CARBONACEOUS MATERIAL AND THEIR ANALYSIS

No.	Preparation conditions										Products		
	TiP Ti(HPO$_4$)$_2$·H$_2$O (△) Ti(HPO$_4$)$_2$ 0—1/2 H$_2$O (▲) (g)$^{c)}$		Carbonaceous material Sugar(○), Flour(⊙), Sodium ligninsulfonate (●) (g)		TiP : C$^{a)}$	Addition agents 7 M H$_3$PO$_4$ (g)	9 M H$_2$SO$_4$ (g)	H$_2$O (g)	Temp (°C)	Time (min)	Yield (g)	TiP (%)	Carb.$^{b)}$ (%)
1	3.20	△	4.00	○	1.00:0.50	0.90	0.10	1.00	185	120	5.59	61.9	38.1
2	3.20	△	4.00	○	1.00:0.50	0.90	0.10	1.00	200	90	5.48	63.4	36.6
3	3.20	△	4.00	○	1.00:0.50	0.90	0.10	1.00	220	60	5.43	64.1	37.9
4	3.20	△	4.00	○	1.00:0.50	0.90	0.10	1.00	250	60	5.20	67.1	32.9
5	3.20	△	4.00	○	1.00:0.50	0.90	0.10	1.00	300	30	5.03	69.5	30.5
6	9.00(3.20)	▲	4.00	○	1.00:0.50	—	—	—	185	90	5.98	53.5	46.5
7	9.00(3.20)	▲	4.00	○	1.00:0.50	—	—	—	200	60	5.83	54.9	45.1
8	9.00(3.20)	▲	4.00	○	1.00:0.50	—	—	—	250	60	5.46	58.6	41.4
9	9.00(3.20)	▲	4.00	○	1.00:0.50	—	—	—	300	30	5.33	60.0	40.0
10	9.00(3.20)	▲	4.00	○	1.00:0.50	—	—	—	350	30	5.26	60.8	39.2
11	3.20	▲	4.00	○	1.00:0.50			1.50	220	90	5.64	56.7	43.3
12	3.20	▲	4.00	○	1.00:0.50	0.90	0.10	1.00	220	90	5.61	61.7	38.3
13	3.20	▲	4.00	⊙	1.00:0.50	0.90	0.10	15.0	220	90	5.50	65.0	35.0
14	3.20	▲	3.60	●	1.00:0.50	0.90	0.10	15.0	220	90	5.85	57.8	42.2
15	64.00	△	80.00	○	1.00:0.50	18.00	2.00	42.0	220	300	95.6	62.4	37.6
16	64.00	▲	80.00	○	1.00:0.50	18.00	2.00	26.0	220	300	108	64.4	35.6

a) C: Carbon contained in the used carbonaceous material. b) Carb.: Carbonaceous part formed by heating.
c) The values in parentheses indicate the TiP content in the wet sample.

In these cases, a solid centrifuged from the mother liquor in the course of synthesis was directly used as titanium(IV) bis(hydrogenphosphate), so that it contained some phosphoric acid and sulfuric acid, which also functioned as additives. Nos. 11 and 12 show the influence of the additives on the sintered product. As is evident from the above discussion, the carbonization was remarkably promoted by the addition of phosphoric acid and sulfuric acid; the Carb./titanium(IV) bis(hydrogenphosphate) ratio (by weight) was decreased from 0.76 (No. 11 in the case of adding no additive) to 0.62 (No. 12 in the case of adding the additive). In Nos. 12, 13, and 14, the sintering experiments were performed using different kinds of the carbonaceous material. The use of wheat flour or sodium ligninsulfonate as carbonaceous material required a relatively greater amount of water than the case of using saccharose for the kneading of the raw material. No remarkable difference was found in the weights of the sintered products, but the Carb./titanium(IV) bis(hydrogenphosphate) ratio (by weight) was 0.54 in the case of wheat flour, 0.62 in the case of saccharose, and 0.73 in the case of sodium ligninsulfonate. (In the case of the sintered product using sodium ligninsulfonate, the sodium contained therein was extracted with hydrochloric acid, and the product was then dried to obtain the yield. Thus, "Carb." was free from sodium.). For reference's sake, Nos. 15 and 16 show the conditions for the preparation of the granulated products used in the column method and their compositions.

Ion-exchange Capacities of The Granulated Products. The ion-exchange titration curves of the granulated products containing the monohydrate and the 0—1/2 hydrate toward Na^+ and K^+, obtained according to

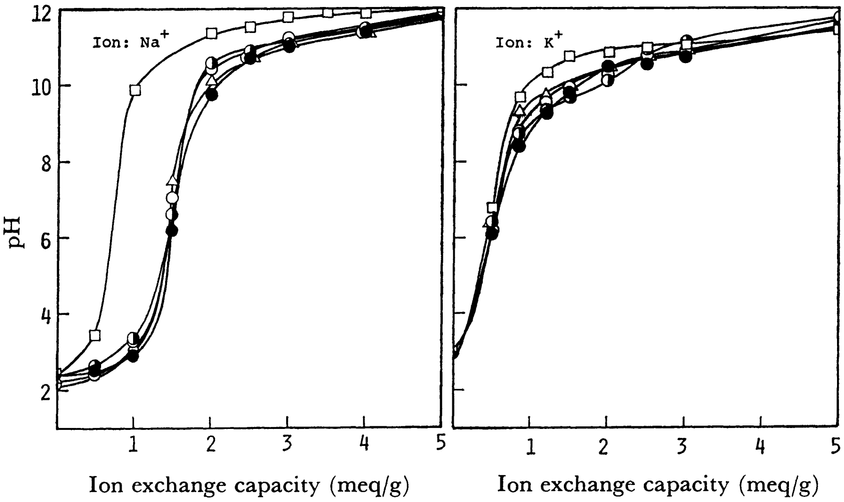


Fig. 2. Ion-exchange titration curves of the product granulated from Ti$(HPO_4)_2\cdot H_2O$ with carbonaceous material.
Carbonaceous material: Sugar.
Heating temperature: △; 185, ○; 200, ◑; 220, ●; 250, □; 300.

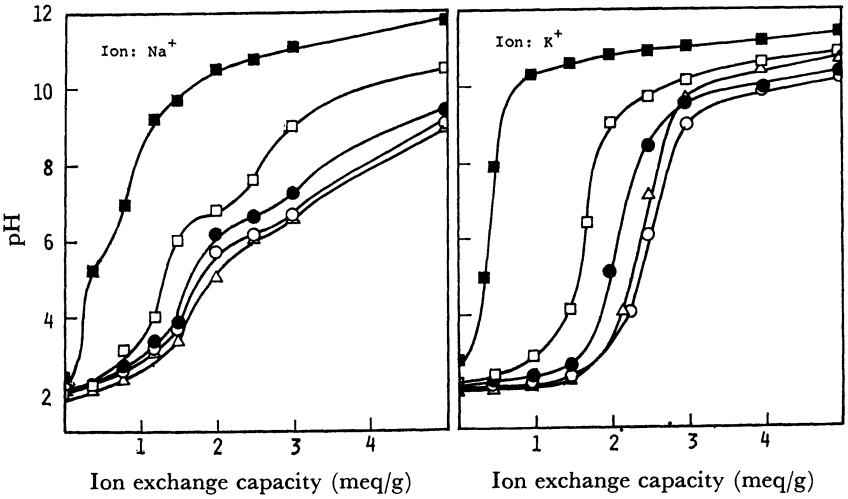


Fig. 3. Ion-exchange titration curves of the product granulated from Ti$(HPO_4)_2\cdot$0—1/2 H_2O with carbonaceous material.
Carbonaceous material: Sugar.
Heating temperature: △; 185, ○; 200, ●; 250, □; 300, ■; 350.

the method of the previous report,[4] are shown in Figs. 2 and 3 respectively.

In Fig. 2, the ion-exchange capacities toward Na^+ of the granulated products containing the monohydrate were 1.22—1.35 and 1.45—1.55 meq/g at the pH values of 4.5 and 7.0 respectively, except for the case wherein the product was sintered at 300 °C. These values were quite small as compared with those of the ion-exchange capacities of the monohydrate itself given in the previous reports[3,4] (3.6 and 7.5 meq/g at pH values of 4.5 and 7.0 respectively). The noticeable decrease in the ion-exchange capacity of the sintered product at pH 7.0 is considered to be a response to the change in the crystal structure of the monohydrate contained in the granulated product in the course of heating. It may also be considered that the surface of the crystals of titanium(IV) bis(hydrogenphosphate) was coated with the formed Carb. to slow down the speed of ion-exchange; thereafter Na^+ was hydrated in a neutral to alkaline solution to form a hydrated ion which was not adsorbed into the cavities of the ion-exchanger. This resulted, as is shown in Fig. 2, in a rapid rise in the titration curves at the point where the quantities of ion-exchange were small.

The ion-exchange capacities toward K^+ of the granulated product containing the monohydrate were 0.18—0.26 and 0.6 meq/g at pH values of 4.5 and 7.0 respectively. These values were half the values of the ion-exchange capacity of the monohydrate itself.

In Fig. 3, the ion-exchange capacities toward Na^+ of the granulated products containing the 0—1/2 hydrate, were 0.30—1.78 and 0.75—3.25 meq/g at pH of 4.5 and 7.0 respectively. The ion-exchange capacities of the granulated product varied remarkably according to the sintering temperature; these values decreased in the range of 185—350 °C with the elevation of the sintering temperature. This is probably ascribable to the same reason as in the case discussed above wherein the granulated product containing the monohydrate was used.

The ion-exchange capacities toward K^+ of the granulated products containing the 0—1/2 hydrate were 0.40—2.34 and 1.7—2.6 meq/g at pH 4.5 and 7.0 respectively. These values were extremely small as

TABLE 3. ION-EXCHANGE PROPERTIES OF GRANULATED PRODUCTS TOWARD Na AND K IONS

Iox-exchanger				Ion-exchange properties					
Sample No.	Row material	Heating temp (°C)	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°)	Adsorption quantity (A, %)	Distribution coefficent (K_D, ml/g)
1	△ + ○	185	Na	0.73	1.25	0.58	0.584	29.2	20.6
2	△ + ○	200	Na	0.90	1.30	1.27	0.692	36.0	28.1
3	△ + ○	220	Na	0.92	1.22	1.81	0.754	36.8	29.1
4	△ + ○	250	Na	0.95	1.35	1.45	0.704	38.0	30.6
5	△ + ○	300	Na	0.43	0.68	0.37	0.632	17.2	10.4
1	△ + ○	185	K	0.24	0.26	1.28	0.923	9.6	5.30
2	△ + ○	200	K	0.19	0.20	1.57	0.950	7.6	4.11
3	△ + ○	220	K	0.22	0.24	1.06	0.917	8.8	4.82
4	△ + ○	250	K	0.24	0.26	1.28	0.923	9.6	5.30
5	△ + ○	300	K	0.14	0.18	0.21	0.778	5.6	2.96
6	▲ + ○	185	Na	1.08	1.77	1.19	0.610	43.2	38.1
7	▲ + ○	200	Na	1.10	1.78	1.27	0.618	44.0	39.3
8	▲ + ○	250	Na	1.05	1.70	1.17	0.618	42.0	36.2
9	▲ + ○	300	Na	0.86	1.28	1.07	0.672	34.4	26.3
10	▲ + ○	350	Na	0.28	0.30	1.96	0.933	11.2	6.31
6	▲ + ○	185	K	1.90	2.28	15.8	0.833	76.0	158.3
7	▲ + ○	200	K	1.98	2.34	20.6	0.846	79.2	190.4
8	▲ + ○	250	K	1.72	1.93	18.5	0.891	68.8	110.1
9	▲ + ○	300	K	1.46	1.56	20.5	0.936	58.4	70.4
10	▲ + ○	350	K	0.35	0.40	1.12	0.875	14.0	8.14
11	▲ + ○	220	K	2.07	2.50	23.1	0.828	82.8	240.7
12	▲ + ○	220	K	2.12	2.72	19.7	0.779	84.8	278.9
13	▲ + ⊙	220	K	1.90	2.31	14.7	0.823	76.0	158.3
14	▲ + ●	220	K	1.24	1.60	3.42	0.775	49.6	163.2

△: $Ti(HPO_4)_2 \cdot H_2O$, ▲: $Ti(HPO_4)_2 \cdot 1/2\, H_2O$, ○: sugar, ⊙: flour, ●: sodium ligninsulfonate. Equilibrium capacity: ion-exchange capacity at pH 4.5 in Fig. 4. Saturation capacity: ion-exchange capacity at pH 4.5 in Figs. 2 and 3.

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

Adsorption quantity: $Q^A/C \times 100 = A$

Distribution coefficient: $K_D = A/I \cdot (100 - A)$

C: Initial quantity of MCl (2.5 meq)

S: MCl solution (25 ml)

I: Ion-exchanger (0.5 g)

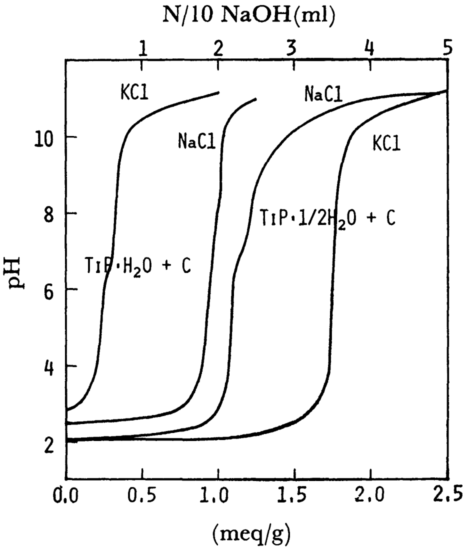


Fig. 4. Titration curves for equilibrium solution of granulated product with sodium and potassium chlorides.

compared with those of the 1/2 hydrate itself, determined to be 4.1 and 6.7 meq/g at pH 4.5 and 7.0 respectively. However, the ion-exchange capacities within such ranges are almost equal to those of commercially available cation-exchange resins; thus they can be utilized satisfactorily as ion-exchangers.

Ion-exchange Characters of The Granulated Products. The titration curves drawn for the estimation of the quilibrium ion-exchange capacity are shown in Fig. 4. The ion-exchange characters of the granulated product toward Na^+ and K^+ are summarized in Table 3.

The equilibrium ion-exchange capacities (Q^A) toward K^+ and Na^+ of the granulated products containing the monohydrate (Nos. 1—5) were 0.43—0.95 and 0.14—0.24 meq/g respectively.

Although the saturation ion-exchange capacities (Q°) toward Na^+ show significantly large values at pH 4.5, as has been described above, the satisfactory results expected for the separation between Na^+ and K^+ were not obtained in connection with the selectivity quotient (K_H^M) and the distribution coefficient (K_D). On the other hand, the values of Q^A toward Na^+ and K^+ of the granulated product containing the 0—1/2 hydrate were 0.86—1.10 and 1.46—1.98 meq/g respectively, except for those obtained for the product sintered at 350 °C. The values of Q° toward Na^+ and K^+ of the same product were 1.28—1.78 and 1.56—2.34 meq/g respectively, except for those obtained for the product sintered at 350 °C. The values of Q^A and Q° were at their maximum for the granulated product sintered at 200 °C, and these values decreased with the elevation in the sintering temperature. Especially, the values of the ion-exchange capacity for the product sintered at 350 °C decreased to 1/6 of the values for the product sintered at 200 °C. It is considered that, at high temperatures, some changes occurred in the structure of the 1/2 hydrate contained in the sintered product. The values of K_H^M and K_D toward K^+ were extremely large as compared with those toward Na^+, thus proving that the granulated products containing the 1/2 hydrate had an excellent adsorption selectivity toward the K^+ ion. As is evident from the previous paper,[4] the value of K_D toward K^+ was 15.7 for the 1/2 hydrate itself, a value almost equal to that of the granulated product. The value of K_D toward K^+ for the 1/2 hydrate itself was 607.0 ml/g, while the values of K_D for the granulated products decreased to about 1/3—1/5 of the above value, probably becouse the products contained the Carb. These results indicate that the sintering temperature for the granulated products influencing the ion-exchange capacity is most suitably within the range of 200—250 °C. Accordingly, the granulated products sintered at 220 °C were used in the subsequent samples of Nos. 11—14. In Nos. 11 and 12, the influence on the ion-exchange character of the additive at the time of sintering was observed. In the case of the sample of No. 12, wherein the additive was added, a slight increase was observed in the ion-exchange capacity. This phenomenon was probably caused by the fact that the carbonization of the carbonaceous material was promoted by the addition of the inorganic acids; then, the value of the titanium(IV) bis(hydrogenphosphate)/Carb. increased, as is shown in Table 2.

The influence of the carbonaceous material on the ion-exchange properties was examined in Nos. 12, 13, and 14. In these results, the Q^A and Q° values decreased in the order of sugar, wheat flour, and sodium ligninsulfonate. A similar tendency also appeared in other ion-exchange properties, such as K_H^M and K_D. Among the carbonaceous materials used, sugar showed the best result.

Selective Adsorption toward K^+ as Determined by The Column Method. As has already been reported,[1,4] the values of K_H^M toward Na^+ and K^+ of $Ti(HPO_4)_2 \cdot$ 0—1/2H_2O showed a sufficient value for the separation of the two ions. As the value of K_H^M toward K^+ was large, the elution of adsorbed K^+ on the batch method using hydrochloric acid was not easy. Since titanium(IV) bis(hydrogenphosphate) was microcrystalline, as has been described above, this compound was quite inappropriate for the column method. Accordingly, the selective adsorption toward K^+ in an aqueous solution of NaCl–KCl and in artificial brackish water was investigated according to the column method, using the granulated product prepared in this study. The results obtained are shown in Table 4.

In the table, the distribution coefficients, K_D^{Na} and K_D^K, are obtained as the values of $\overline{m}$Na/mNa and $\overline{m}$K/mK respectively, wherein $\overline{m}$Na and $\overline{m}$K stand for the amounts (meq) of Na^+ and K^+ respectively adsorbed on 1 g of the ion exchanger, and mNa and mK, for the amount (meq) of Na^+ and K^+ respectively existing in 1 ml of the solution under the equilibrium adsorption conditions. The separation factor, α_M^K, between K^+ and $M^{1+ \text{ or } 2+}$ (M=Na, Mg, or Ca) is indicated by the following formula:[6)]

$$\alpha_M^K = (\overline{m}\mathrm{K} \cdot \mathrm{mM})/(\overline{m}\mathrm{M} \cdot \mathrm{mK}) = k_D^K/k_D^M.$$

In Nos. 1 and 2, the concentration of KCl–NaCl in water was about twice as much as that of natural sea water, and the atomic ratio of Na/K was 50.8. As the

TABLE 4. SELECTIVE ADSORPTION OF POTASSIUM ION BY A COLUMN METHOD FROM A NaCl–KCl MIXED SOLUTION AND ARTIFICIAL BRACKISH WATER

Granulated product No.	Kind	(g)	NaCl–KCl solution (Artificial brackish water) NaCl (g/l) KCl (g/l)	(ml)	Ion-exchange Na (meq/g)	Ion-exchange K (meq/g)	Ion-exchange properties Na/K (atomic ratio)	Distribution coefficient K_D^{Na}	Distribution coefficient K_D^K	Separation factor α_{Na}^K
1	$Ti(HPO_4)_2 \cdot H_2O+C$	5	53.32 1.34	1000	0.483	0.068	7.11	0.530	3.78	7.13
2	$Ti(HPO_4)_2 \cdot 1/2H_2O+C$	5	53.32 1.34	1000	1.05	0.577	1.83	1.15	32.1	27.9
3	$Ti(HPO_4)_2 \cdot 1/2H_2O+C$	5	26.66 0.67	500	1.05	0.337	2.79	2.30	41.9	18.2
4	$Ti(HPO_4)_2 \cdot 1/2H_2O+C$	5	26.66 0.67	1000	1.12	0.526	2.13	2.45	58.5	23.9
5	$Ti(HPO_4)_2 \cdot 1/2H_2O+C$	5	26.66 0.67	1500	1.15	0.575	2.00	2.52	64.0	25.4
6	$Ti(HPO_4)_2 \cdot 1/2H_2O+C$	5	41.26 13.40	1000	0.856	1.05	0.814	1.18	5.84	4.95
7	$Ti(HPO_4)_2 \cdot 1/2H_2O+C$	5	(26.66) (0.67) ($MgCl_2 \cdot 6H_2O$ 7.19) ($MgSO_4 \cdot 7H_2O$ 4.24) ($CaSO_4$ 1.55)	1000	0.938 (Mg; 0.0423 M mol/g) (Ca; 0.00343 M mol/g)	0.440	2.13 (Mg/K; 0.0961) (Ca/K; 0.0078)	2.06	45.5 (K_D^{Mg} 0.809) (K_D^{Ca} 0.394)	22.1 (α_{Mg}^K 56.2) (α_{Ca}^K 115)

granulated product containing the monohydrate (No. 1) which was packed into a column adsorbed only a little K^+, the product was not suitable as an ion-exchanger for K^+. On the other hand, the granulated product containing the 0—1/2 hydrate (No. 2) showed an ion-exchange capacity of 0.557 meq/g toward K^+, an atomic ratio of the adsorbed Na^+ to the adsorbed K^+ of 1.83, and a separation factor, α_{Na}^K, of 27.9. In Nos. 3, 4, and 5, an aqueous solution of NaCl–KCl was used in which the concentrations of NaCl and KCl were almost equal to those in sea water. When this solution was permitted to flow through the column, the amounts of Na^+ and K^+, and the α_{Na}^K value were increased according to the increase in the flow. In No. 6, the sum of the concentrations of NaCl and KCl was equal to that in No. 2 (54.66 g), but the concentration of KCl in No. 6 was increased ten times as much as that of No. 2, decreasing the concentration of NaCl accordingly. As a result, the ion-exchange capacity toward Na^+ was decreased from 1.05 to 0.856 meq/g, while the ion-exchange capacity toward K^+ was increased from 0.577 meq/g to 1.05 meq/g. As the concentration of K^+ in the sample solution was comparatively high in this case, the α_{Na}^K value was about 5. Artificial brackish water was used as the sample solution in No. 7. As a result, the ion-exchange capacities toward Na^+ and K^+ were both somewhat decreased as compared with the case of No. 4, wherein an aqueous solution of NaCl–KCl with the same concentrations of NaCl and KCl was used. However, the atomic ratio of Na to K in No. 7 was equal to 2.13 in the case of No. 4. Although considerable amounts of Mg^{2+} and Ca^{2+} were contained in the artificial brackish water, those ions were adsorbed very little on the granulated product containing the 0—1/2 hydrate, and both the α_{Mg}^K and α_{Ca}^K values showed a large number. The pH values of the effluents and the changes in the concentration of the individual ions were examined in order to check the behavior of the individual ions adsorbed on the granulated product in the column. The result obtained are shown in Fig. 5.

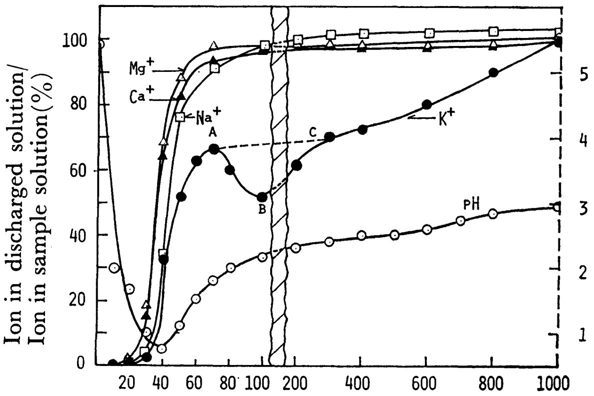


Fig. 5. The concentration of each ion containing in the discharged solution from the column.
Ion-exchanger: glanulated product of $Ti(HPO_4)_2 \cdot 1/2\ H_2O+C$ (5 g), sample solution: artificial brackish water (see Table 4).

As soon as the aqueous solution of NaCl–KCl or the artificial brackish water, each having a pH value of 5—6, was passed through the column as a sample solution, an ion-exchange reaction took place whereby the pH value of the effluent decreased so rapidly that the pH value dropped to the minimum value of 0.75 when the volume of the effluent reached 30—40 ml. Thereafter, the pH value gradually increased as the volume of the effluent became larger, shown about 2, 2.5, and 3 at the stages where the volumes of the effluent reached 100, 500, and 1000 ml respectively. As a large amount of

Na^+ was contained in the sample solution, the concentration of Na^+ in the effluent rapidly increased to the same level as that of the sample solution when 30 ml of the effluent discharged from the column. The concentration of Na^+ in the effluent eventually reached 102—103% of that in the sample solution supplied. This phenomenon was considered to show that the Na^+ initially adsorbed on granulated product was gradually replaced by K^+ in the following sample solution. Although K^+ was also contained together with Na^+ in the effluent, the concentration of K^+ showed a peak at Point, A, in Fig. 4 where the volume of the effluent reached about 70 ml. With the increase in the volume of the effluent, the concentration of K^+ was decreased to a valley, B, and then again increased to Point C. This phenomenon was also observed in Nos. 3—5, wherein the concentration of K^+ in the sample solution was low, but it not observed in Nos. 1, 2, and 6, wherein the concentration of K^+ was comparatively high. In the latter case, the concentration of K^+ increased, as is shown by the dotted line connecting Points A and C in Fig. 4. Before Na^+ began to appear in the effluent, Mg^{2+} and Ca^{2+} were contained therein, and their concentrations were increased rapidly. In view of the facts that the α^{K}_{Na} value reached 22.1 by passing the artificial brackish all at once through a column in which the granulated products containing the 0—1/2 hydrate had been placed, and that K^+ could be separated effectively from Mg^{2+} and Ca^{2+}, the effective separation of K^+ from sea water can be expected by further improvement in the technical problems.

Adsorption of Coloring Matter by The Granulated Products. In the preparation of the granulated products, the carbonaceous material used as a binder was converted by heating it into substances composed predominantly of carbon. If this carbonaceous part had an adsorbing effect like active carbon, the granulated products would have the functions of both ion-exchange and adsorption. Using methylene blue as the material to be adsorbed, the granulated product was added to an aqueous solution of methylene blue and the change in the color density with the lapse of time was examined, the resulting being shown in Fig. 6.

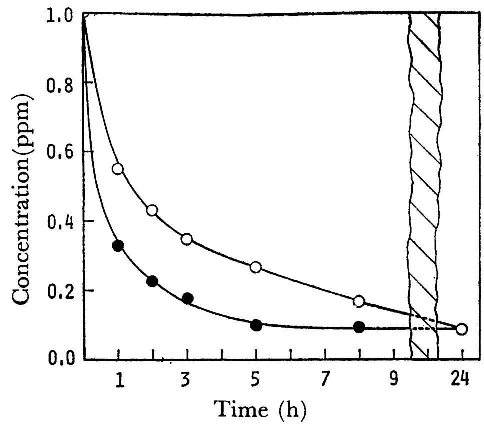


Fig. 6. Adsorption of methylene blue by granulated product and active carbon. 1 g (C; 0.33 g) of granulated product or 0.33 g of active carbon were added to 100 ml of methylene blue aqueous solution (1 ppm), respectively.

○: Granulated product, ●: active carbon.

Since the sintering temperature for preparing the granulated products was as low as 200—250 °C, we were unable to obtain a product with an adsorbing capacity equivalent to active carbon, but the product could adsorb coloring matter to some extent.

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