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Studies of Inorganic Ion Exchangers. IV.[1] Ion Exchange Equilibrium between Titanium(IV) Bis(hydrogenphosphate) and NaCl–KCl Aqueous Solution

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In order to develop an inorganic ion exchanger, ion exchange equilibriums between titanium(IV) bis(hydrogenphosphate) and NaCl–KCl aqueous solution have been investigated together with the possibility of separation of Na and K ions. A suitable quantity of $Ti(HPO_4)_2\cdot H_2O$ (monohydrate), or $Ti(HPO_4)_2$ (anhydrate) was added to a fixed volume of the mixed solution of 0.1 M NaCl with 0.1 M KCl at various ratios. The Na and K ions in the equilibrium solution were determined, and the mole fractions of the ions distributed in the liquid and solid phases estimated. When 0.1 or 0.5 g of the monohydrate were added to 10 ml of each initial solution, the sum of the ion exchange capacities for Na and K ions was approx. 0.1—0.3 meq/g. When 0.1 g of the anhydrate were added to 10 ml of each of the initial solutions, the pH of the final solutions showed values in the range of 1.6—1.9. With the mole fractions of KCl/(NaCl+KCl) above 0.5 in the initial solution, only 2.5—3.5 meq/g of the K ion adsorbed. With an excess (0.5 g exchanger to 10 ml soln) of the anhydrate, all K ions and a part of Na ions were removed together from the solution with the mole fractions of KCl/(NaCl+KCl) being in a range of 0—0.8. The K ion could be effectively separated, when a suitable amount of the anhydrate was added to a solution containing approx. an equimole of NaCl and KCl; however, the elution of K ion with HCl could not be eased by this static method.

Titanium phosphate has been of recent interest as an inorganic ion exchanger similar to zirconium phosphate.[2] In order to develop an ion exchanger for industrial use, titanium(IV) bis(hydrogenphosphate) hemihydrate ($Ti(HPO_4)_2\cdot 1/2H_2O$) has been synthesized by refluxing amorphous titanium(IV) phosphate with concentrated phosphoric acid.[3] The X-ray diffraction pattern of the hemihydrate differs from that of the titanium(IV) bis(hydrogenphosphate) monohydrate ($Ti(HPO_4)_2\cdot H_2O$), known already.[4] It has been observed that the hemihydrate has an ion exchangeability toward ions of large size, such as the potassium ion. Further more, $Ti(HPO_4)_2\cdot 0$—$1/2H_2O$ was prepared[5] by refluxing concentrated phosphoric acid with a sulfuric acid solution of $TiOSO_4$, the intermediate in the production process of titanium(IV) oxide. In a previous work,[1] the ion exchange properties of the hemihydrate towards alkali metals and ammonium ions have been reported where it was found that the equilibrium ion exchange capacities (Q^A) of the hemihydrate towards Na and K ions were larger than those of the monohydrate, and that the selectivity quotient (K^M_H) and distribution coefficient (K_D) increased in the order $Cs^+ < Li^+ < NH_4^+ < Na^+ < K^+$. This result will aid in the separation of the Na and K ions. In the present work, the ion exchange equilibria between titanium(IV) bis(hydrogenphosphate) and NaCl–KCl aqueous solutions have been examined under various conditions. It has been confirmed that the K ion can be selectively separated from an aqueous solution containing approx. equivalent moles of Na and K ions. In this paper, the experimental data derived will be presented.

Experimental

Preparation of Ion Exchangers. Titanium(IV) bis(hydrogenphosphate) were prepared by the refluxing methods described in previous reports.[3,5] The composition of the monohydrate and hemihydrate, were found as follows: TiO_2, 31.1%; P_2O_5, 54.6%; H_2O, 14.4%; giving an empirical formula of $Ti(HPO_4)_2\cdot H_2O$. For the hemihydrate: TiO_2, 33.1%; P_2O_5, 58.8%; H_2O, 7.7%; giving the formula as the anhydrous salt, $Ti(HPO_4)_2$.

Ion Exchange Equilibrium and Analysis of Na and K Ions. The ion exchanger (0.100 g) was placed in a 20 ml stoppered test tube, and the initial solution (10 ml), varying in volume ratio of 0.1 M NaCl and 0.1 M KCl added. The contents were shaken periodically and the pH of the supernatant liquid measured after 48 h. A portion of the supernatant liquid (5.00 ml) was taken, and diluted with distilled water to 1000 ml and the Na and K ions determined using a flame photometer at 589 and 768 nm, respectively.

Separation of K Ion from NaCl–KCl Aqueous Solution. The solution mixed in the proper ratio of 0.1 M NaCl and 0.1 M KCl (100 ml) was placed in a 300 ml stoppered Erlenmeyer flask, and to this $Ti(HPO_4)_2$ (2.00 g) was added. The contents of the flask were periodically shaken and the pH of the supernatant liquid and the concentration of Na and K ions determined after 48 h. The ion exchanger was separated from the mother liquor using a centrifugal separator. The adsorbed Na and K ions in the solid phase were eluted with 0.1, 0.5, 1, and 5 M HCl (100 ml) respectively. The K ion in the effluent was determined by flame photometry.

Results and Discussion

Ion Exchange Equilibrium between Titanium(IV) Bis(hydrogenphosphate) and NaCl–KCl Aqueous Solution. When the powder of titanium(IV) bis(hydrogenphosphate) was added to the initial solution varying ratio in volume of 0.1 M NaCl with 0.1 M KCl, the mole fractions of Na and K ions, estimated from the analytical data, are shown in Figs. 1—4.

In No. 1 (Fig. 1), the monohydrate (0.1 g) as ion exchanger was added to the initial solution (10 ml). Consequently, the mole fraction ratios of the Na and K ions in the final solutions were approx. the same as those of the mole fraction of 0.1 M NaCl and 0.1 M KCl in the initial solution at all times and this is indicated by the straight line dividing the L–Na^+ and L–K^+ areas, as seen in Fig. 1. The sum of the mole fractions of the Na and K ions in the solid phase was

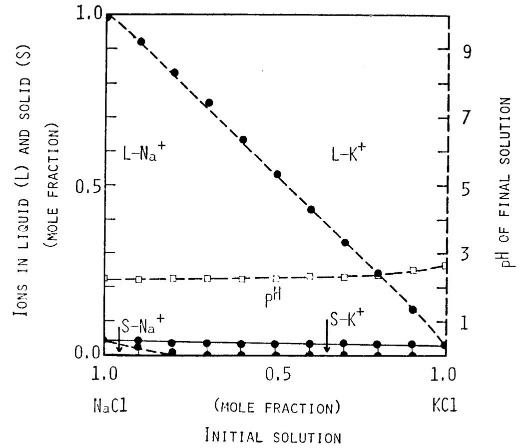

Fig. 1. Distribution of ions in liquid and solid phases on the equilibrium between 0.1 g of $Ti(HPO_4)_2 \cdot H_2O$ and 10 ml of M/10 MCl.

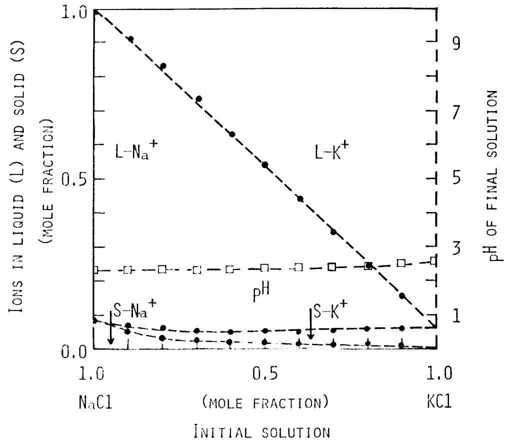

Fig. 2. Distribution of ions in liquid and solid phases on the equilibrium between 0.5 g of $Ti(HPO_4)_2 \cdot H_2O$ and 10 ml of M/10 MCl.

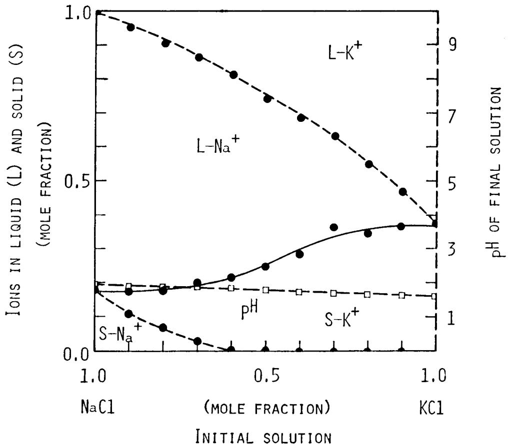

Fig. 3. Distribution of ions in liquid and solid phases on the equilubrium between 0.1 g of $Ti(HPO_4)_2$ and 10 ml of M/10 MCl.

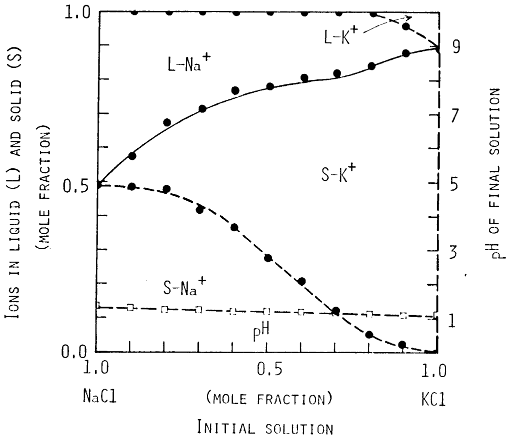

Fig. 4. Distribution of ions in liquid and solid phases on the equilibrium between 0.5 g of $Ti(HPO_4)_2$ and 10 ml of M/10 MCl.

0.03—0.04, a value equivalent to the mole fraction of the H^+ in the final solution, corresponding to an ion exchange capacity of 0.3—0.4 meq/g, *i.e.* the ion exchange capacity of the monohydrate was considerably smaller in weakly acid solution (pH 2.2—2.7). In the mole ratio range 1.0—0.8 (NaCl to NaCl+KCl), the Na ion was absorbed together with the K ion in the solid phase. In the mole ratio 0.8—0.0 (NaCl to NaCl+KCl), only the K ion was adsorbed. However, the ion exchange capacity was small as mentioned above.

In No. 2 (Fig. 2), the monohydrate (0.5 g) was added to the initial solution (10 ml). In this case, the sum of the mole fractions of Na and K ions adsorbed in the solid phase was 0.05—0.08. The ion exchange capacity however was 0.10—0.16 meq/g, and decreased more than No. 1. Both Na and K ions were adsorbed in the solid phase regardless of the mole ratio of NaCl with KCl in the initial solution, *i.e.* neither ion could be separated.

In No. 3 (Fig. 3), the anhydrate (0.1 g) as ion exchanger was added to the initial solution (10 ml). The pH of the final solution showed values in the range 1.6—1.9, and this value decreased gradually with increasing mole fraction of potassium chloride in the final solution. The sum of the mole fractions of Na and K ions adsorbed in the solid phase was 0.18—0.38 corresponding to an ion exchange capacity of 1.8—3.8 meq/g, *i.e.* the ion exchange capacity of the anhydrate was 3.6—4.7 times higher than that of the monohydrate. With a mole ratio of NaCl to NaCl+KCl in the initial solution in the range 0.0—0.5, the ion exchange capacities were 2.5—3.8 meq/g and only the K ion was adsorbed. The above results show that the Na and K ions remained considerably in the final solution, although the anhydrate exhibited selective adsorptive behaviour towards the K ion. Consequently, five times the anhydrate in No.4 (Fig. 4) was used compared to No.3. The sum of the mole fractions of Na and K ions in the solid phase was 0.49—0.89, 2.5 times greater than the sum in No. 3. but the ion exchange capacities derived from the mole fractions were 0.98—1.78 meq/g. When the mole ratio of NaCl to NaCl+KCl was 1.0—0.2, all K ions contained in the solution were adsorbed completely. However, at all points of the mole ratio of NaCl to NaCl+KCl, both the Na and K ions were adsorbed into the solid phase,

Table 1. The distribution of ions in the solid and liquid phases

Ion exchanger No.	$Ti(HPO_4)_2$ (g)	Initial solution M/10 NaCl (ml)	M/10 NaOH (ml)	M/10 KCl (ml)	M/10 KOH (ml)	Final Solid Na^+	Solid K^+	Liquid Na^+	Liquid K^+	pH
						(mole fraction)				
5	0.1	6.0	4.0	—	—	0.34	0.00	0.66	0.00	5.50
	0.1	5.4	3.6	0.6	0.4	0.25	0.10	0.64	0.01	5.50
	0.1	4.8	3.2	1.2	0.8	0.17	0.18	0.62	0.03	5.60
	0.1	4.2	2.8	1.8	1.2	0.11	0.25	0.58	0.06	5.86
	0.1	3.6	2.4	2.4	1.6	0.07	0.30	0.52	0.11	5.72
	0.1	3.0	2.0	3.0	2.0	0.05	0.32	0.46	0.19	5.86
	0.1	2.4	1.6	3.6	2.4	0.03	0.34	0.38	0.25	5.28
	0.1	1.8	1.2	4.2	2.8	0.01	0.39	0.25	0.35	5.25
	0.1	1.2	0.8	4.8	3.2	0.00	0.40	0.19	0.41	5.22
	0.1	0.6	0.4	5.4	3.6	0.00	0.41	0.09	0.50	5.14
	0.1	—	—	6.0	4.0	0.00	0.42	0.00	0.58	4.00
6	0.1	2.0	8.0	—	—	0.64	0.00	0.36	0.00	7.60
	0.1	1.8	7.2	0.2	0.8	0.56	0.08	0.35	0.01	7.64
	0.1	1.6	6.4	0.4	1.6	0.47	0.17	0.33	0.03	7.82
	0.1	1.4	5.6	0.6	2.4	0.38	0.26	0.29	0.07	7.82
	0.1	1.2	4.8	0.8	3.2	0.33	0.31	0.25	0.11	8.02
	0.1	1.0	4.0	1.0	4.0	0.31	0.35	0.19	0.15	8.10
	0.1	0.8	3.2	1.2	4.8	0.27	0.39	0.13	0.21	8.08
	0.1	0.6	2.4	1.4	5.6	0.23	0.43	0.03	0.31	7.70
	0.1	0.4	1.6	1.6	6.4	0.18	0.46	0.03	0.33	7.66
	0.1	0.2	0.8	1.8	7.2	0.12	0.50	0.02	0.36	7.60
	0.1	—	—	2.0	8.0	0.00	0.58	0.00	0.42	7.36

i.e. it was impossible to separate them. This is the manner in which an excess of ion exchanger is employed toward both ions in the initial solution. Thus, it may be expected from experiments Nos. 3 and 4 that the selective adsorption of the anhydrate towards the K ion is achieved.

Effects of pH *on Ion Exchange Equilibrium.* Generally, the ion exchange capacity of an acid salt as an ion exchanger increased with a rise in pH of the aqueous solution. In a previous work,[1)] the equilibrium ion exchange capacities of titanium(IV) bis(hydrogenphosphate) with the alkali metal and ammonium chlorides, and the saturation ion exchange capacities have been estimated. As a direct consequence of this the values of the latter at pH 4.5 were larger than those of the former measured in the acid liberated from the ion exchange. In the present study, the ion exchange equilibrium between $Ti(HPO_4)_2$ and a weak acid-neutral aqueous solution containing the Na and K ions has been examined, the results of which are given in Table 1.

In No. 5 (Table 1), the mole ratio of the sodium and potassium chlorides with the sodium and potassium hydroxides in the initial solution was adjusted to 6 : 4 and consequently the pH values of the initial solutions were about 12.7. On adding the anhydrate to the alkaline aqueous solutions, an ion exchange reaction took place and consequently the pH of the solution dropped to betweeen 4.0 and 5.5. The ion exchange capacities of the anhydrate toward the Na and K ions were 3.4 and 4.2 meq/g at pH 5.5 and 4.0, respectively. The ion exchange capacity toward the K ion did not greatly increase in comparison with that estimated in the acid aqueous solutions of No. 3 (3.8 meq/g).

In No. 6 (Table 1), the mole ratio of the chloride and hydroxide was adjusted to 2 : 8 in the initial solution. The pH values of the initial solutions were about 13.0. When anhydrate was added to the alkaline aqueous solutions, the pH of the solution changed, lying in the range 7.4—8.1. The ion exchange capacities of the anhydrate toward Na and K ions were 6.4 and 5.8 meq/g, respectively. In the presence of both Na and K ions the sum of the ion exchange capacities for both ions was about 6 meq/g in all cases. In that case neither ion could be separated despite the ratio of the Na and K ions in the initial solution.

The ion exchange isotherms for the Na and K ions in Nos. 3, 5, and 6 are shown in Fig. 5.

As reported earlier in No.3, the solutions were acidified by the ion exchange reaction. K ions were adsorbed on the ion exchanger when fractions of K ion in the final solution were in the range of 0.33—1.00 as shown by the isotherm. The ion exchange capacities increased as the pH of the final solution increased. However, it is clear from the isotherms in Nos. 5 and 6 that the separation of Na and K ions using the anhydrate may be progressively more difficult with the increase in pH of the final solution.

Separation of Na^+ *with* K^+ *and Elution of* K^+ *from Ion Exchanger.* From the above results the separation of K ion from a NaCl–KCl solution, such as sea water which contains a small quantity of KCl to NaCl, is

Table 2. The separation of Na with K ions from the NaCl-KCl mixed solution and the elution of potassium ion

Ion exchanger $Ti(HPO_4)_2$ (g)	Initial solution M/10 NaCl (ml)	M/10 KCl (ml)	$\frac{K}{Na+K}$ (wt %)	Final Solid Na^+	K^+	Liquid Na^+ (mole fraction)	K^+	pH	Ions released from solid Elute	K^+ (%)
2.00	40	60	66	0.00	0.42	0.40	0.18	1.44	0.1 M HCl	4.2
2.00	50	50	56	0.02	0.40	0.48	0.10	1.43	0.1 M HCl	4.1
2.00	50	50	56	0.03	0.41	0.47	0.09	1.43	0.5 M HCl	6.0
2.00	50	50	56	0.02	0.40	0.48	0.10	1.44	1.0 M HCl	10.5
2.00	50	50	56	0.03	0.40	0.47	0.10	1.43	5.0 M HCl	35.5
2.00	60	40	49	0.05	0.35	0.55	0.05	1.43	0.1 M HCl	4.1

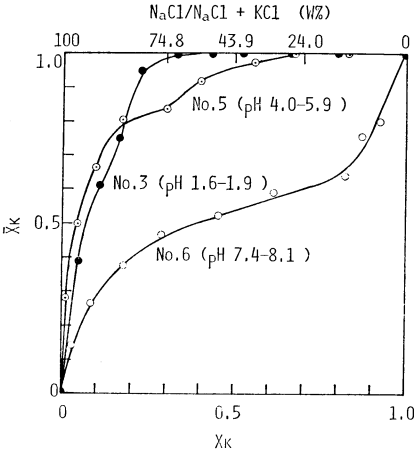

Fig. 5. Ion exchange isotherms between potassium and sodium ions on $Ti(HPO_4)_2$.
X_k: the mole fraction of K^+ in the solution.
$\bar{X}_k$: the mole fraction of K^+ in the exchanger.

difficult. However, K ions can be separated in high yield from an aqueous solution containing approx. an equivalent mole of NaCl and KCl, using an appropriate amount of ion exchanger. The separation of both ions using $Ti(HPO_4)_2$ and the elution of K ion are summarized in Table 2.

These experiments confirm that the K ion can be adsorbed in the solid pahse and that most of the Na ions remain in the liquid phase. With hydrochloric acid as the eluate in the static method, the adsorbed K ions were not released completely from the ion exchanger since the selectivity quotient (K^{M}_{H}) of $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$ toward K ion is larger than that of the hemihydrate toward other ions as reported in a previous paper.[1] When $Ti(HPO_4)_2$ was used as the ion exchanger for the separation of K ion, the release of K ion was not smooth. The granulation of $Ti(HPO_4)_2$ and the recovery of K ion by the column method need further study.

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