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ION-EXCHANGE PROPERTIES OF γ -TITANIUM PHOSPHATE AND ITS MONOSODIUM FORMS TOWARDS Mg^{2+} AND Ca^{2+} IONS

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SUMMARY

The ion-exchange properties of γ -Ti (HPO₄)₂·2H₂O, a new layered inorganic ion exchanger with a γ -structure, towards Mg^{2+} and Ca^{2+} ions have been investigated by determining the uptake curves as a function of the pH of equilibrating solutions. Despite the large inter-layer distance of the exchanger (11.6 Å), the H^+/Mg^{2+} exchange is so slow at room temperature that only 15% Mg^{2+} conversion was reached even after 3 months of equilibration. Full Mg^{2+} conversion was obtained, however, at 60°C. The uptake curve shows two steps of exchange (0–50%, 50–100%). The first occurs at low pH (*ca.* 1.6) with a phase transition and leads to γ -TiMg_{0.5}H(PO₄)₂·3.5H₂O (13.0 Å), and the second, at pH *ca.* 7, without drastic changes in the X-ray powder patterns. The H^+/Ca^{2+} ion-exchange process occurs with a similar mechanism at room temperature but the first step takes place in the range 0–35% Ca^{2+} conversion.

The ion-exchange properties of γ -TiHNa(PO₄)₂·3H₂O (inter-layer distance 13.4 Å) have also been examined. It was found that, in neutral medium, only Na^+/Ca^{2+} or Na^+/Mg^{2+} exchanges occur, while the proton is exchanged only in alkaline medium. The ion exchange occurs in two steps, the first with a phase transition to γ -TiM^{II}_{0.3}Na_{0.4}H(PO₄)₂·3H₂O and the second without further appreciable change in the X-ray diffraction patterns. The Na^+/Mg^{2+} exchange is very low but it may be completed at 60°C. The ion-exchange mechanism has been interpreted by assuming the formation of a monolayer of hydrated cations within the layer of the exchanger.

The potential use of γ -Ti(HPO₄)₂·2H₂O as water-softening agent is limited by the slow exchange rates of Mg^{2+} cations.

INTRODUCTION

Inorganic ion exchangers belonging to the class of layered insoluble acid salts of tetravalent metals may be obtained with two different structures, usually known as α or γ structures. The ion-exchange properties of the α -layered compounds [*i.e.*, α -Zr(HPO₄)₂·H₂O and similar compounds] have been extensively investigated^{1,2}, but little is known about γ -materials. After γ -Zr(HPO₄)₂·2H₂O, first obtained by Clearfield *et al.*³, γ -Ti(HPO₄)₂·2H₂O has been recently prepared in different laboratories^{4–6}. The structure of γ -compounds is unknown but much experimental evidence suggests

that the texture of the γ -layers is more compact than that of the α -layers^{4,7,8}. In addition, the mutual disposition of the γ -layers seems to be different to that of α -layers. In the α -compounds the water molecule is hydrogen bonded to $\equiv\text{POH}$ groups belonging to the same layer, the layers being held by Van der Waals forces and staggered in such a way as to create a close-packed structure¹. The much larger inter-layer spacing of γ -titanium and -zirconium phosphates (11.6 and 12.2 Å, respectively) compared with that of the corresponding α -layered compounds (7.6 Å) could thus arise from the presence of inter-layer hydrogen bonds, involving both $\equiv\text{POH}$ groups of adjacent layers and water molecules^{3,9}.

Few papers have dealt with the ion-exchange properties of γ -compounds. Dollimore and co-workers^{10,11} studied the thermal decomposition of $\gamma\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its alkali metal half-exchanged forms, and Dyer and Ocon¹² prepared the calcium form of γ -zirconium phosphate to evaluate the Ca^{2+} self-diffusion constant; details of the ion-exchange processes were not reported. More recently, Clearfield and co-workers have investigated the uptake of alkali metal ions⁹ and some transition metal ions¹³.

Little work has been reported on $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, and only the uptakes of Na^+ , Sr^{2+} , K^+ and NH_4^+ have been studied^{5,8}.

From these studies it can be inferred that γ -compounds possess some peculiar properties (low steric hindrance to diffusion of counter ions, fast exchange rates, etc.) that make them attractive materials for ion-exchange investigations and practical uses. It was therefore of interest to collect further information on the ion-exchange properties of γ -materials. In this paper the ion-exchange behaviour of $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its monosodium forms towards Mg^{2+} and Ca^{2+} cations is reported.

EXPERIMENTAL

Chemicals and ion-exchange materials

Carlo Erba (Milan, Italy) R.P.E. products were used without further purification. $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared by refluxing amorphous titanium phosphate¹⁴ in 15.5 M H_3PO_4 (refluxing temperature *ca.* 175°C) for 10 days. The exchanger was washed first with 0.2 M H_3PO_4 solution and then with water until the pH was 3.5–4 and stored in a vacuum desiccator containing saturated sodium chloride solution ($P/P_0 \approx 0.7$). The monosodium forms, $\gamma\text{-TiHNa}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\gamma\text{-TiHNa}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, were obtained by titrating at 25°C and 5°C, respectively, (see later) $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ suspended in 0.2 M sodium chloride solution, with 0.1 M sodium hydroxide solution. The material was brought to constant weight in a vacuum desiccator containing saturated barium chloride solution ($P/P_0 \approx 0.9$ at room temperature).

Ion-exchange procedures

The Ca^{2+} and Mg^{2+} uptake curves of $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ as a function of pH were obtained by equilibrating several samples of the exchanger (1 g) with 200 ml of 0.050 M calcium chloride or magnesium chloride solution acidified with hydrochloric acid (low uptake values) or containing increasing amounts of calcium hydroxide or magnesium oxide (high uptake values).

The $\text{Na}^+/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}$ ion-exchange isotherms were measured by equilibrating several samples of the monosodium form of the exchanger (1 g) with increasing volumes of 0.050 M calcium chloride or magnesium chloride solution.

The exchange of Ca^{2+} and Mg^{2+} as a function of time was followed with the procedures described earlier¹⁵.

Analytical procedures

Titanium(IV) and phosphates were determined as described previously¹⁴. The metal ions were analysed with a Perkin-Elmer Model 305 atomic-absorption spectrometer. The water contents of the various salt forms were obtained from the percentage weight losses, at different temperatures, of the samples, previously conditioned at $P/P_0 \approx 0.7$. The X-ray powder diffraction patterns were taken with a General Electric diffractometer using Ni-filtered Cu K α radiation.

RESULTS

Mg²⁺ and Ca²⁺ uptake on $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$

Preliminary experiments on $\text{H}^+/\text{Mg}^{2+}$ and $\text{H}^+/\text{Ca}^{2+}$ exchanges were performed by equilibrating 1 g of $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ with 200 ml of 0.050 M MgCl_2 or CaCl_2 solution. Fig. 1 reports the change in the pH of the solutions as a function of time for both cases. It can be seen that after a first sharp decrease, probably due to the exchange of the surface protons, the pH of the solution slowly tends towards constant values which are very different for the two ions (2.60 and 1.55 for $\text{H}^+/\text{Mg}^{2+}$ and $\text{H}^+/\text{Ca}^{2+}$, respectively). The rates of exchange slow down, probably because of the accumulation of the exchanged protons in the solutions, but after *ca.* 100 h, Ca^{2+} cations replace about 50% of the total exchangeable protons (7.25 mmol/g) and Mg^{2+} only *ca.* 7%. Thus the exchanger shows a considerably higher affinity for Ca^{2+} .

In order to acquire information on the ion-exchange processes the metal ion uptakes as a function of pH (Fig. 2) were determined from the titration curves for the exchanger, performed by the batch procedure; the X-ray diffractograms of samples at various level of exchange were also taken. Ca^{2+} ions are exchanged in two steps (0–50 and 50–100% of conversion, see Fig. 2, curve a), the first occurring at very low pH values and the second at *ca.* pH 5. The determination of phosphate groups in equilibrating solutions showed that the degree of hydrolysis was less than 5%.

In the first stages of ion exchange, up to *ca.* 35% of Ca^{2+} loading, two phases were observed, the original $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ and an exchanged phase with an inter-layer distance of 13.4 Å. At higher loading (> 35%) up to complete conversion a single phase with a similar inter-layer distance was present as if Ca^{2+} ions were exchanged via solid solution. It is as if 0.35 mole of Ca^{2+} per mole of exchanger was able to enlarge the inter-layer spacing from 11.6 to 13.4 Å and the 13.4 Å phase has room enough to accommodate the remaining 0.65 mole of Ca^{2+} without further increase in the inter-layer distance. In contrast, at high Ca^{2+} conversion the inter-layer distance slowly decreases, probably because of the increased electrostatic attraction between the positive counter ions placed between the layers and the negative charges of the $\gamma\text{-Ti}_n(\text{PO}_4)_{2n}^{2n-}$ macro-anions constituting the layers themselves, and the fully Ca^{2+} exchanged form, conditioned at $P/P_0 \approx 0.7$, has an inter-layer distance of

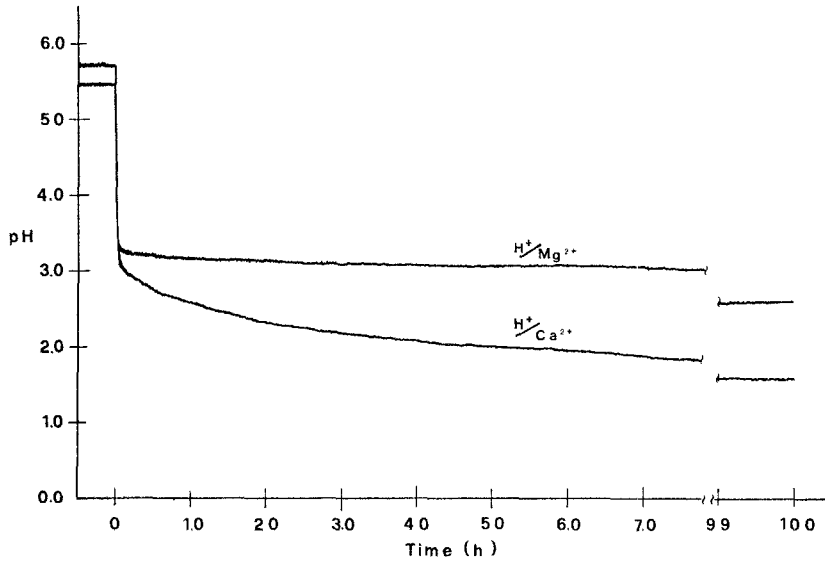
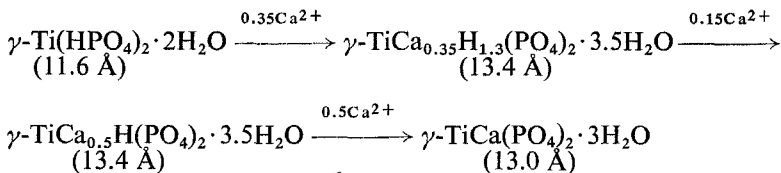


Fig. 1. Variation of pH, as a function of time, due to H⁺/Mg²⁺ and H⁺/Ca²⁺ exchange on γ -Ti(HPO₄)₂·2H₂O. Conditions: 1 g of exchanger in 200 ml of 0.05 M MgCl₂ or CaCl₂ solution at 20°C.

13.0 Å. Similar behaviour has been found for the H⁺/Cu²⁺ exchange¹³ on γ -Zr-(HPO₄)₂·2H₂O, where the dihydrogen phase is first completely converted into a partially Cu-exchanged phase at a degree of exchange of 38% and then no other phase transition occurs up to full Cu conversion. Furthermore, a similar trend has been also found for the H⁺/Sr²⁺ exchange on γ -Ti(HPO₄)₂·2H₂O (ref. 5).

Thus, the first end-point in the H⁺/Ca²⁺ uptake curves is related to the replacement of the first 50% of exchangeable protons by Ca²⁺ counter ions. The exchange of the remaining 50% requires higher energy, probably owing to the electrostatic repulsion arising from the insertion of the incoming Ca²⁺ ions within a monolayer of Ca²⁺ counter ions already present between the sheet of the exchanger.

This process occurs without further increase in the inter-layer distance and requires more and more energy, as is evidenced by the continuous rise in the pH of the uptake curve. The water contents of the phases having 35, 50 and 100% of Ca²⁺ conversion were determined and the ion-exchange process can be represented schematically by the reaction



The dehydration behaviour of half and fully exchanged Ca²⁺ phases has been investigated. These phases retain 1 mole of water when dried over P₄O₁₀ and are completely anhydrous at 200°C. Table I reports the X-ray powder diffraction patterns of hydrated and anhydrous Ca²⁺ exchanged phases.

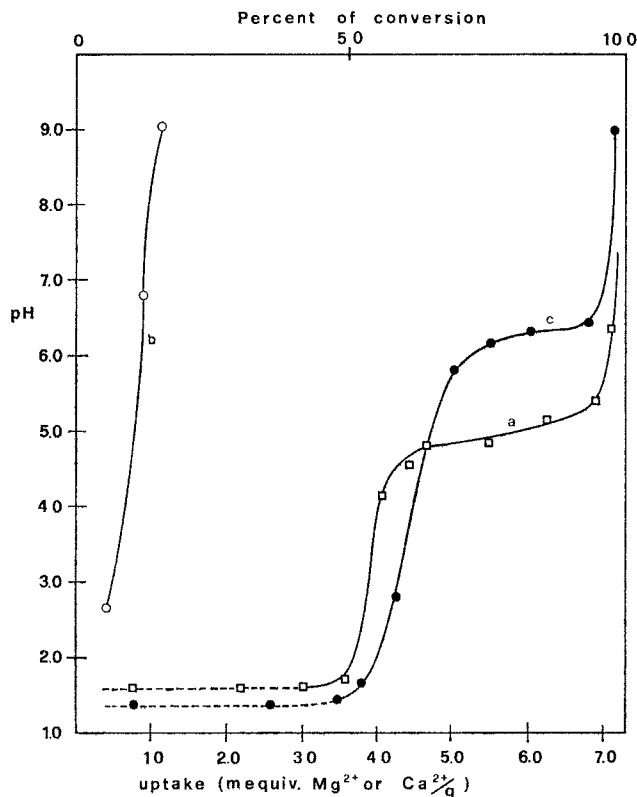


Fig. 2. Uptake curves of γ -Ti(HPO₄)₂·2H₂O titrated with: (a) 0.05 M CaCl₂ solutions containing known amounts of HCl (dashed line) or of Ca(OH)₂ (full line), equilibration time 10 days, temperature 20°C; (b) 0.05 M MgCl₂ solutions containing known amounts of solid MgO, equilibration time 10 days, temperature 20°C; (c) 0.05 M MgCl₂ solutions containing known amounts of HCl (dashed line) or of solid MgO (full line), equilibration time 10 days, temperature 60°C.

The behaviour of the H⁺/Mg²⁺ ion exchange was found to be more complicated. As can be seen from Fig. 2, curve b, after 10 days of equilibration the Mg²⁺ uptake curve does not show any definitive plateau of exchange, and when the pH is that of a saturated MgO solution, the maximum uptake of 15% was reached. The Mg²⁺ conversion does not increase with further addition of solid MgO. On the other hand, the X-ray diffractogram of a sample having 15% of Mg²⁺ loading shows the presence of a new exchanged phase at $d = 13.0 \text{ \AA}$ and of the original γ -Ti(HPO₄)₂·2H₂O in the ratio 1:3. Thus, two immiscible phases, co-existing in the same crystallites, are present and the ion-exchange process, once started, should proceed to the pure exchanged phase. The lack of further exchange may be ascribed to a kinetic effect; for this reason the samples were left to equilibrate for times as long as 3 months. The pH of equilibrating solutions did decrease but the percentage Mg²⁺ conversion increased very little.

The H⁺/Mg²⁺ ion exchange was then carried out at 60°C and after 10 days of equilibration Fig. 2, curve c, was obtained. The shape of the uptake curve is now very similar to that obtained for the H⁺/Ca²⁺ exchange performed at 20°C and

TABLE I

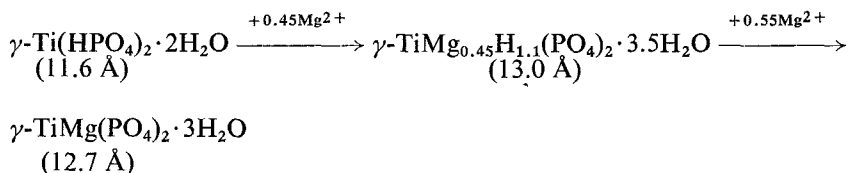
X-RAY POWDER DIFFRACTION PATTERNS, d (Å), OF HYDRATED AND ANHYDROUS PHASES OF γ -TITANIUM PHOSPHATE CONVERTED INTO CALCIUM FORM

The composition is simply indicated by the counter ions and water content. Drying conditions are given in parentheses. S = strong; M = medium; W = weak; V = very.

$H\text{Ca}_{0.5} \cdot 3.5\text{H}_2\text{O}$ ($P/P_0 \approx 0.7$)		$H\text{Ca}_{0.5} \cdot \text{H}_2\text{O}$ ($P_4\text{O}_{10}$ at r.t.)*		$H\text{Ca}_{0.5}$ (200°C)		$\text{Ca} \cdot 3\text{H}_2\text{O}$ ($P/P_0 \approx 0.7$)		$\text{Ca} \cdot \text{H}_2\text{O}$ ($P_4\text{O}_{10}$ at r.t.)*		Ca (200°C)	
13.4	VS	10.9	S	10.1	S	13.0	VS	11.1	S	10.3	S
6.70	W	7.62	W	7.49	M	6.60	W	7.82	VW	7.33	VW
6.27	W	6.06	W	5.21	W	6.18	W	6.08	VW	5.46	VW
5.21	W	5.50	VW	4.52	W	5.15	W	5.53	W	5.33	VW
4.45	W	5.18	VW	3.89	VW	4.42	W	4.87	W	4.54	W
3.70	M	4.76	W	3.60	M	3.67	M	4.57	VW	3.64	M
3.26	VW	4.54	VW	3.55	M	3.18	VW	3.79	M	3.6	M
3.20	VW	3.75	M	3.43	W	3.09	W	3.68	M	3.45	VW
3.11	VW	3.67	S	3.41	W	3.03	W	3.45	VW	3.15	W
3.03	W	3.46	W	3.16	M	2.95	W	3.15	W		
2.96	W	3.42	W								
2.65	VW	3.15	M								

* r.t. = room temperature.

similar considerations apply. In the first stages of $\text{H}^+/\text{Mg}^{2+}$ exchange two immiscible phases with inter-layer distances 11.6 and 13.0 Å were present, requiring the pH of exchange to be constant. Conversion to this exchanged phase is complete at 45% of Mg^{2+} loading. Above this value, the pH of the solution first rises sharply, to an even higher pH than the second region of the $\text{Ca}^{2+}/\text{H}^+$ exchange, while the remaining 50% of exchangeable protons are replaced by Mg^{2+} without further substantial modification of the X-ray diffraction patterns. The second step of the exchange occurs with only a slight increase in the pH of the solution. Also with Mg^{2+} exchange the fully exchanged phase has an inter-layer distance slightly lower than that of the half-exchanged phase. The $\text{Mg}^{2+}/\text{H}^+$ ion-exchange process at 60°C can therefore be summarized by the reaction



Both the half-exchanged and fully exchanged Mg^{2+} phases retain 2 mole of water when dried over P_4O_{10} and are completely anhydrous at 200°C . Table II lists the X-ray diffraction patterns of hydrated and anhydrous Mg^{2+} phases. It is interesting that we experienced difficulties in obtaining a constant weight of the Ca^{2+} and Mg^{2+} exchanged phases maintained over saturated sodium chloride or barium chloride solutions, as the water content can vary from 0.5 to 1 mole (without any appreciable change in the inter-layer spacing) with small changes in the relative humidity.

Mg²⁺ and Ca²⁺ uptake of the γ -monosodium forms

It is known that α -Zr(HPO₄)₂·H₂O at room temperature does not exchange strongly hydrated cations such as Mg²⁺; however, when α -phases with a larger inter-layer distance such as α -ZrHNa(PO₄)₂·5H₂O or α -Zr(HPO₄)₂·5H₂O are used, these cations are readily taken up². It was therefore of interest to examine the uptake of Ca²⁺ and Mg²⁺ ions on γ -phases having inter-layer distances larger than that of γ -Ti(HPO₄)₂·2H₂O.

Allulli *et al.*⁵ found that when one proton of γ -Ti(HPO₄)₂·2H₂O is replaced by Na⁺, the inter-layer distance increases by 1.6 Å and the phase γ -TiHNa(PO₄)₂·3H₂O is obtained. Thus, this monosodium form seems to be a very suitable exchanger for the uptake of large cations. However, when we tried to prepare this material, a monosodium form with an inter-layer distance even shorter than that of the original dihydrogen form was obtained. Chemical analyses showed that the composition of our monosodium form was TiHNa(PO₄)₂·2H₂O. Owing to its small inter-layer distance (11.3 Å), this phase was expected to be a very poor exchanger towards Ca²⁺ and Mg²⁺ ions, and preliminary experiments confirmed this expectation.

Efforts were thus devoted to obtaining the monosodium form with a large inter-layer distance. As a working hypothesis it was assumed that the temperature of 25°C was too high to obtain the trihydrated form; therefore, the titration of Ti(HPO₄)₂·2H₂O with sodium hydroxide was performed at a lower temperature. It was found that at 5–10°C the phase TiHNa(PO₄)₂·3H₂O with an inter-layer distance of 13.4 Å was easily formed. It is interesting that, once formed, this phase is stable at temperatures considerably higher than 10°C. It was found that by heating the material suspended in 0.1 M sodium chloride solution, its large inter-layer distance starts to decrease to 11.3 Å only at temperatures above 80°C.

The Mg²⁺ and Ca²⁺ uptake on γ -TiHNa(PO₄)₂·3H₂O (13.4 Å) prepared at low temperature was therefore investigated at room temperature. As expected from the equilibrium pH of the second step of the H⁺/Ca²⁺ exchange, the proton of γ -TiHNa(PO₄)₂·3H₂O is difficult to exchange in neutral or acidic medium and the

TABLE II

X-RAY POWDER DIFFRACTION PATTERNS, d (Å), OF HYDRATED AND ANHYDROUS PHASES OF γ -TITANIUM PHOSPHATE CONVERTED INTO MAGNESIUM FORM

The composition is simply indicated by the counter ions and water content. Drying conditions are given in parentheses. Symbols as in Table I.

<i>HMg_{0.5}·3.5H₂O</i> (<i>P/P₀</i> ≈ 0.7)		<i>HMg_{0.5}·2H₂O</i> (<i>P₄O₁₀</i> at r.t.)*		<i>HMg_{0.5}</i> (200°C)		<i>Mg·3H₂O</i> (<i>P/P₀</i> ≈ 0.7)		<i>Mg·2H₂O</i> (<i>P₄O₁₀</i> at r.t.)*		<i>Mg</i> (200°C)	
13.0	VS	12.5	VS	9.75	VS	12.7	VS	11.9	VS	9.75	VS
6.36	W	6.18	VW	5.33	M	6.50	W	8.79	W	6.60	W
6.18	W	5.63	W	4.50	W	6.32	W	5.60	W	5.33	M
4.39	W	5.03	VW	4.00	VW	6.14	W	4.07	W	4.48	W
3.95	W	4.03	W	3.55	M	5.09	VW	3.85	W	3.98	W
3.76	M	3.60	W	3.47	M	4.89	VW	3.58	W	3.55	M
3.39	W	3.58	VW	3.17	M	4.37	VW	3.16	W	3.47	M
3.33	W	3.45	VW			3.58	M			3.17	M
		3.15	W			3.16	W				

* r.t. = room temperature.

monosodium form behaves as a monofunctional exchanger in so far as only $\text{Na}^+/\text{Ca}^{2+}$ or $\text{Na}^+/\text{Mg}^{2+}$ exchange occurs when the compound is equilibrated with 0.050 *M* calcium chloride or magnesium chloride solution.

Fig. 3 shows the $\text{Na}^+/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}$ ion-exchange isotherms obtained at 20°C (curves a and c, respectively), obtained after equilibration for 10 days. After longer times (1 month) the $\text{Na}^+/\text{Ca}^{2+}$ ion-exchange isotherm shifted to a different pathway, represented by curve b, while the $\text{Na}^+/\text{Mg}^{2+}$ isotherm remains unchanged. The $\text{Na}^+/\text{Ca}^{2+}$ ion-exchange process therefore seems to occur in two steps, the first being faster than the second.

Considering the ion-exchange isotherms obtained after 1 months of equilibration, it can be observed that the greatest $\text{Na}^+/\text{Ca}^{2+}$ exchange occurs at very low ionic fractions of Ca^{2+} in solution. The composition of the solution is nearly constant, as if two immiscible phases, the monosodium and monocalcium forms, were co-existing with the one being transformed into the other. In fact, the X-ray diffraction patterns of samples having an increasing Ca^{2+} loading show that two immiscible phases, the original monosodium form and a phase containing Na^+ , Ca^{2+} and H^+ counter ions, were co-existing up to $\bar{X}_{\text{Ca}} \approx 0.6$. Above this conversion the remaining sodium ions are replaced by Ca^{2+} without further changes in the X-ray diffraction patterns. Thus the $\text{Na}^+/\text{Ca}^{2+}$ ion-exchange process can be represented by the reactions

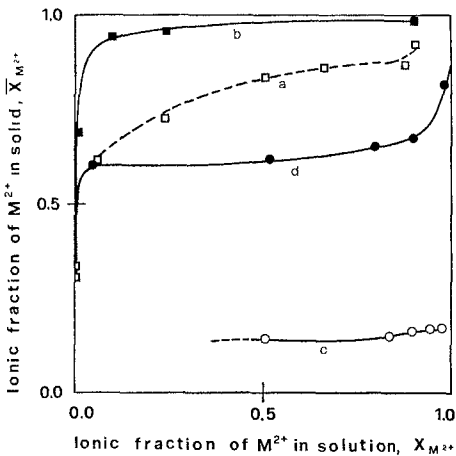
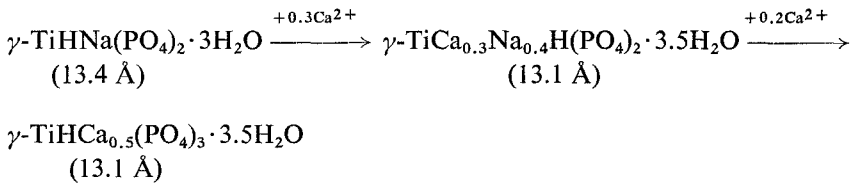
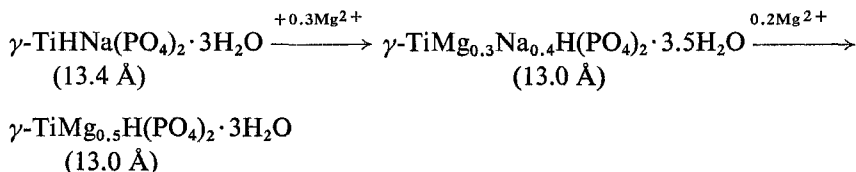


Fig. 3. $\text{Na}^+/\text{Mg}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$ ion-exchange isotherms on $\gamma\text{-TiHNa}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$: (a) Ca^{2+} replaces Na^+ in the exchanger, concentration 0.05 *M*, temperature 20°C, equilibration time 10 days; (b) as (a) but equilibration time 1 month; (c) Mg^{2+} replaces Na^+ in the exchanger, concentration 0.05 *M*, temperature 20°C, equilibration time 10 days; (d) as (c) but temperature 60°C.

It is noteworthy that the inter-layer distance of the monocalcium phase obtained from the monosodium form is slightly lower than that of the similar phase obtained from the $\text{Ca}^{2+}/\text{H}^+$ exchange. Moreover, the X-ray powder patterns are also different, as if the Ca^{2+} ion could find two different exchange sites between the layers of the exchanger. As happens for the $\text{H}^+/\text{Mg}^{2+}$ exchange, Mg^{2+} uptake on $\gamma\text{-TiHNa}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ occurs to a limited extent at room temperature (see Fig. 3, curve c). A maximum conversion of 15% was obtained at a high Mg^{2+} ionic fraction in solution, also after 1 month of equilibration time, without changes in the inter-layer distance. The $\text{Na}^+/\text{Mg}^{2+}$ ion exchange was then performed at 60°C (equilibration time 10 days) and curve d in Fig. 3 was obtained. The exchange process now occurs in two steps, the first at a constant and very low Mg^{2+} ionic fraction in solution, and the second, not complete, at $X_{\text{Mg}} \approx 0.96$, in the sloping region of the curve. X-ray diffractograms showed that in the first step two immiscible phases were co-existing, the original monosodium form and an exchanged Mg^{2+} phase having an inter-layer distance of 13.0 Å. At $\bar{X}_{\text{Mg}} = 0.6$ the latter phase is the only one present and further Mg^{2+} uptake occurs without changes in the X-ray diffraction patterns. The $\text{Na}^+/\text{Mg}^{2+}$ exchange, at 60°C , can thus be summarized by the reactions



DISCUSSION

Although the lack of knowledge of the crystalline structure of layered insoluble acid salts of the γ -type prevents a sound discussion of the observed ion-exchange processes, some considerations based on the results of this and previous work, and on the comparison with the known ion exchange behaviour of α -zirconium phosphate towards alkaline earth metal ions may be made.

It is interesting, for example, to compare the inter-layer distances of anhydrous divalent forms of α -zirconium and γ -titanium phosphates. It is already known that in α -zirconium phosphate, owing to the relatively large distance between the $\equiv\text{P-OH}$ group of the same layer and the mutual arrangement of adjacent layers, there are present large cavities (one for each zirconium atom) where even large divalent counter ions, such as Ba^{2+} , may be accommodated without any appreciable increase in the original inter-layer distance¹. For this reason, all $\alpha\text{-ZrM(II)}(\text{PO}_4)_2$ compounds have an inter-layer distance similar to that of $\text{Zr}(\text{HPO}_4)_2$ (ref. 2). In contrast, the inter-layer distance of $\gamma\text{-Ti}(\text{HPO}_4)_2$ (and probably of other γ -layered acid salts) increases appreciably when divalent counter ions are accommodated between the layers. This fact seems to indicate that large cavities do not exist between adjacent layers of γ -materials. Thus, even a small cation such as Mg^{2+} cannot be accommodated without an appreciable increase in the inter-layer distance (9.7 against 9.2 Å). The lack of large cavities in the inter-layer space of γ -compounds may be related to the very compact structure of γ -layers and/or to a packing of the layers different to that in α -compounds.

In a previous paper⁸ it was shown that the structure of γ -layers does not change appreciably during ion-exchange or dehydration processes and that each square centimetre of layer contains $9.9 \cdot 10^{-10}$ formula weight of exchanger or $9.9 \cdot 10^{-10} \cdot 6.02 \cdot 10^{23} \cdot 2$ fixed charges.

Let us now suppose that the divalent cations are intercalated in the inter-layer spacing as a monolayer of spherical cations. The maximum number of such cations must be $6.10^{14}/\text{cm}^2$ in order to neutralize the negative fixed charges present on the surface of two adjacent layers. It can be calculated that the limiting diameter for the formation of a compact hexagonal monolayer, containing $6 \cdot 10^{14}$ divalent cations per square centimetre, is 4.4 Å. Thus even large cations, such as Ba^{2+} , could be easily arranged as a monolayer in the inter-layer space of γ -compounds. It is interesting that for Mg^{2+} the increase in the inter-layer distance from 9.2 to 9.7 Å is less than the value expected from its crystalline diameter (1.3 Å). This means that the small counter ions can partially dip between adjacent $\equiv \text{P}-\text{O}^-$ groups of the same γ -layer. The extent of the dip should decrease with increasing diameter of the counter ions so that, for large counter ions, the increase in the inter-layer distance should be almost equal to the diameter of the counter ions. For $\gamma\text{-TiCa}(\text{PO}_4)_2$ the increase is 1.1 Å, and this seems to confirm that the divalent counter ions are indeed arranged as a monolayer in the inter-layer space of γ -compounds.

Let us examine the hydrated γ -phases. It is interesting that all of the known fully exchanged γ -forms of divalent cations are trihydrated and have about the same inter-layer distance (12.7–13.4 Å) as if the diameters of the hydrated counter ions were about the same irrespective of the nature of the divalent cations involved. This fact may be understood if it is assumed that a monolayer of hydrated cations is formed in this instance also. In the fully exchanged forms, the diameter of the hydrated counter ions, as discussed before, will not exceed 4.0–4.4 Å (according to the structure of the monolayer) independently of the nature of the counter ions. Thus the inter-layer distance of $\gamma\text{-Ti}(\text{HPO}_4)_2$ is expected to increase from 9.2 to 13.2–13.6 Å when hydrated forms of divalent cations are formed, in agreement with the experimental values.

It may be observed that the differences in the chemical composition of the half $\gamma\text{-TiM}_{0.5}\text{H}(\text{PO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ forms and of the full $\gamma\text{-TiM}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ forms can be thought of as the replacement of $0.5\text{H}_2\text{O}$ and one proton with 0.5M^{2+} . The inter-layer distance of the half-exchanged forms is therefore similar to that of the fully exchanged forms (it is only slightly higher, 13.0–13.4 Å, probably owing to the smaller electrostatic attraction between the monolayer of cations and the surface fixed charges). However, in the half-exchanged forms the divalent cation–divalent cation distance is, on average, much higher than in the fully exchanged forms and the insertion of divalent cations in place of the protons, which are covalently held to the phosphate groups, causes a sudden increase in the electrostatic repulsions. This effect is manifested in the uptake curves by the sharp increase in the pH of the equilibrating solution at about 50% conversion.

When $\gamma\text{-TiHNa}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ (13.4 Å) is employed as exchanger, the uptake of divalent cation occurs in two steps, the first being much faster than the second. Initially the phase $\gamma\text{-TiM}^{11}_{0.3}\text{Na}_{0.4}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ with an inter-layer distance slightly shorter (13.1 Å) than that of the monosodium compound is formed. In the second step the incoming cations replace the sodium ions present in a phase with a shorter

inter-layer distance and the internal diffusion of the counter ions may be a slow process. The internal diffusion of Mg^{2+} cations seems very slow also at $60^{\circ}C$ and the points in the second step of the Na^{+}/Mg^{2+} isotherms (see Fig. 3, curve d) might not be equilibrium points. From the practical point of view the exchange properties of γ -titanium phosphate compare favourably with those of α - $Zr(HPO_4)_2 \cdot H_2O$. Calcium cations are exchanged at lower pH values and the H^{+}/Mg^{2+} exchange requires lower temperatures¹⁶. The exchange rates are also faster. In contrast, α - $ZrHNa(PO_4)_2 \cdot 5H_2O$ seems to be a better exchanger¹⁵ towards Ca^{2+} and Mg^{2+} than γ - $TiHNa(PO_4)_2 \cdot 3H_2O$. The use of the latter phase as water-softening agent is limited by the slow diffusional process of Mg^{2+} . Work is in progress to see whether the rates of uptake of this ion could be increased by the presence of another cation that acts as a catalyst.

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