compared with the same type of bond in six-coordinate species with all three possible spin states. The previously determined values[10,11] are 2.310 Å for intermediate-spin, 2.316 Å for high-spin, and 2.043 Å for low-spin bond lengths. The value in this five-coordinate complex thus maintains a trend that was first noted[30] in five-coordinate high-spin iron(III) complexes with axial anionic ligands. In these complexes, the axial bond is much shorter than expected. However, unlike the case for the high-spin species with an anionic ligand, the observed distance in [Fe(OEP)(3-Cl-py)]ClO_4 is not quite as short as that appropriate for a low-spin species. This has also been observed in high-spin [Fe(OEP)(2-MeHIm)]ClO_4;[4] the axial bond distance in this complex is substantially shorter than the analogous bond distance in the high-spin six-coordinate species but is still longer than the expected low-spin distance. The axial bond length in [Fe(OEP)(3-Cl-py)]ClO_4 is longer than the 2.068 (4) Å value found in [Fe(OEP)(2-MeHIm)]ClO_4. This parallels the usual pattern that has been observed in metalloporphyrin species; namely, axial imidiazole bonds are always shorter than axial pyridine bonds. The reason for the phenomenon is not clear; we have discussed the matter briefly elsewhere.[31]

The perchlorate ion in both complexes is located close to an axial pyridine ligand. In [Fe(OEP)(3-Cl-py)]ClO_4, the interaction is reasonably tight with the closest approach of a perchlorate oxygen atom to a pyridine carbon atom of O···C = 3.2 Å. The separations in [Fe(OEP)$(3\text{-Cl-py})_2$]ClO_4 are about 0.1 Å larger.

Summary. Reaction of equimolar quantities of 3-chloropyridine and [Fe(OEP)($OClO_3$)] has been found to lead to the simultaneous preparation of crystalline five-coordinate [Fe(OEP)(3-Cl-py)]ClO_4 and to a new phase of the previously characterized bis(3-chloropyridine) complex. The mono(pyridine) complex can apparently be prepared because of the formation of π–π dimers. These dimers, observed in the solid state, are also thought to persist in solution. The magnetic susceptibilities and Mössbauer spectra of this admixed intermediate-spin compound are modulated by exchange interactions between magnetic centers in the dimer.

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Supplementary Material Available: Tables IS and IIS, listing anisotropic temperature factors and fixed hydrogen atom positions, respectively, for [Fe(OEP)(3-Cl-py)]ClO_4, and Tables IIIS and IVS, listing anisotropic temperature factors and fixed hydrogen atom positions, respectively, for [Fe(OEP)$(3\text{-Cl-py})_2$]ClO_4 (6 pages); tables of calculated and observed structure factors (×10) (32 pages). Ordering information is given on any current masthead page.

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Lamellar Inorganic Ion Exchangers. H^+/Ca^{2+} Ion Exchange in γ-Titanium Phosphate

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The H^+/Ca^{2+} ion-exchange process was studied. Exchange isotherms and titration and hydrolysis curves were obtained at 5.0, 25.0, 40.0, and 55.0 (±0.1) °C. The $TiH_{1.25}Ca_{0.37}(PO_4)_2\cdot 3.5H_2O$ (13.1 Å) phase was formed by using $CaCl_2$ + HCl solutions. Equilibrium constants, free energy, enthalpy, and entropy of the exchange reaction were determined. The ion-exchange process and the thermal behavior of the exchanged solids were followed by X-ray diffraction. When the temperature was increased, the $TiH_{1.25}Ca_{0.37}(PO_4)_2\cdot 3.5H_2O$ (13.1 Å) phase was transformed into the $TiH_{1.25}Ca_{0.37}(PO_4)_2\cdot H_2O$ (10.9 Å) phase and subsequently into the $TiH_{1.25}Ca_{0.37}(PO_4)_2$ (10.2 Å) phase originating at $T > 200$ °C mixtures of $Ti(HPO_4)_2$ (9.1 Å) and $TiHCa_{0.5}(PO_4)_2$ (10.2 Å) phases. Conversions higher than 37.5% with partial decomposition of γ-TiP and precipitation of calcium phosphate were obtained by using $CaCl_2$ + $Ca(OH)_2$ solutions. The hydrolysis increased with temperature.

Introduction

The phosphates of polyvalent metals are very interesting due to their ion-exchange properties. Several studies on their amorphous[1] and crystalline[2,3] forms have been performed. Among the latter, the α- and γ-varieties of zirconium and titanium phosphates are the most widely studied.[4-7] The structure of α-ZrP is known.[8,9] α-ZrP and α-TiP are lamellar solids with monoclinic symmetry and a basal spacing of 7.6 Å. The structure of the γ-variety is not solved, but its symmetry is also monoclinic[10,11] and the structural arrangement is layered with basal spacings of 12.2 Å (γ-ZrP) and 11.6 Å (γ-TiP).

Lamellar phosphates have many potential applications in renal dialysis, water softening, chromatography, catalysis, membranes, and solid electrolytes fields.[3]

The exchange of alkaline-earth-metal cations in lamellar phosphates has received considerable attention.[12-15] Alberti et

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al.[15] found that γ-titanium phosphate is able to retain Ca ions from acidic solutions at room temperature. Due to this fact, to the special interest of γ-TiP as an ion exchanger, and to the importance of the recuperation of Ca^{2+} from wash waters in the detergent industry,[3] we have made the present study in which a structural and thermodynamic study of the H^+/Ca^{2+} ion-exchange process in γ-TiP is reported.

For the sake of brevity the various ionic forms are simply indicated by their counterions (under a bar) and water content while their interlayer distances are reported in parentheses.

Experimental Section

Reagents. All chemicals used were of reagent grade. The $Ca(OH)_2$ solutions were standardized with HCl which had previously been standardized against Na_2CO_3. The γ-TiP was obtained by using 16.5 M H_3PO_4 and reflux times of 10 days as previously described.[16]

Analytical Procedures. Analysis of phosphorus and titanium in the solids was carried out gravimetrically.[17] The phosphate groups released during exchange were measured spectrophotometrically[18] on a Perkin-Elmer Model 200 instrument. The calcium ions were determined by atomic absorption spectroscopy in a Perkin-Elmer Model 372 instrument and complexometrically by addition of EDTA.[17] The pH measurements were made with a Crison Model 501 pH meter, equipped with glass and saturated calomel electrodes. Thermogravimetric analyses (TG) were made in a Setaram Model MTB 10-8 instrument. Differential thermal analysis (DTA) was carried out in a Setaram Model MTB M4 instrument. The diffractometer used was a Philips Model PV 1050/23 with Cu Kα radiation (λ = 1.5418 Å).

Ion-Exchange Studies. The exchanger was equilibrated with $CaCl_2$ + HCl or $CaCl_2$ + $Ca(OH)_2$ solutions at 5.0, 25.0, 40.0 and 55.0 (±0.1) °C by following the procedure described by Clearfield et al.[19] The concentration of the $CaCl_2$ + HCl solutions was 2.5×10^{-2} N (ionic strength at equilibrium 3×10^{-2}). The $CaCl_2$ + $Ca(OH)_2$ solutions were prepared with constant amounts of 2.5×10^{-2} N $CaCl_2$ and increasing amounts of $Ca(OH)_2$ in such a manner that the ionic strength in the equilibrium is constant if the exchange process behaves ideally. Complementary experiments in order to determine the hydrolysis were carried out by the addition of NaCl + NaOH solutions to the γ-TiP at 25.0 °C. The equilibration time was 48 h. The solid was present in the solution in an approximate ratio of 400 mL:1 g.

Results and Discussion

Titration curves and exchange isotherms at 5.0, 25.0, 40.0 and 55.0 °C against the initial concentration of calcium added are plotted in Figure 1. In the exchange isotherms the amount of calcium ions that passes from the liquid phase into the solid phase during the ion-exchange reaction is expressed in mequiv/g of γ-TiP.

When $CaCl_2$ + $Ca(OH)_2$ solutions are added to the γ-TiP it might be expected that partial decomposition of the exchanger would occur due to the presence of the hydroxyl groups in solution. It can be expressed as[20]

$$Ti(HPO_4)_2{\cdot}2H_2O(c) + 4OH^- + (n-4)H_2O \rightarrow TiO_2{\cdot}nH_2O(s) + 2HPO_4^{2-} \quad (1)$$

$$Ti(HPO_4)_2{\cdot}2H_2O(c) + 2OH^- + (n-2)H_2O \rightarrow TiO_2{\cdot}nH_2O(s) + 2H_2PO_4^- \quad (2)$$

When the counterion is stable in solution in the presence of phosphate ions, the hydrolysis degree can be obtained by measuring the phosphorus concentration in the equilibrium solutions. This is not the case with calcium ion present because it reacts with the phosphate groups released by the exchanger to form insoluble calcium phosphate at pH > 4.[21] The hydrolysis degree could only be known by measuring the concentration of phosphorus in solution when all the precipitated calcium phosphate is dissolved.

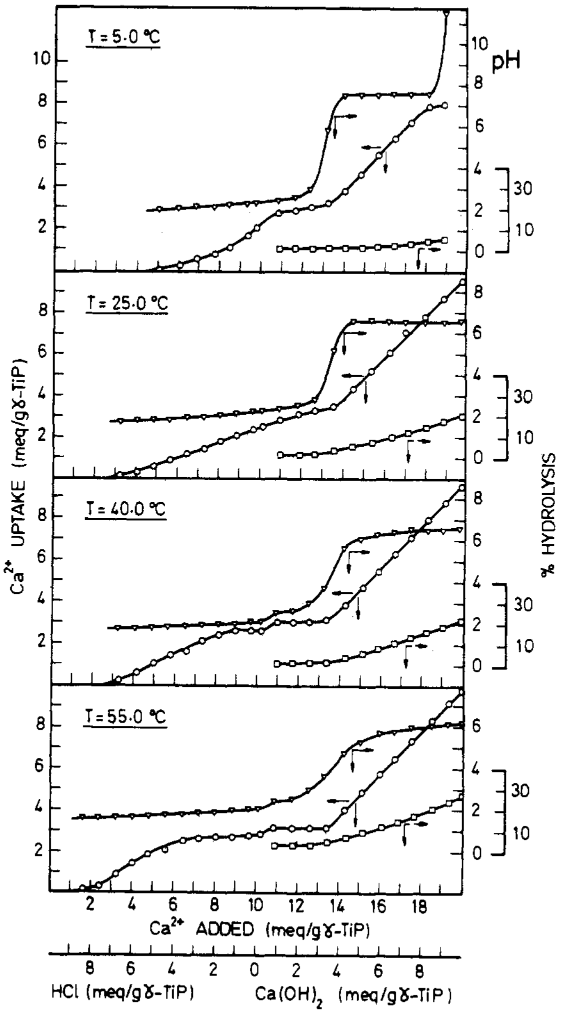

Figure 1. Titration (▽) and hydrolysis (□) curves and exchange isotherms (○).

Samples similar to those used in the ion-exchange experiments have been prepared, and after the equilibration time, constant amounts of HCl solutions (150 mL/g of γ-TiP) were added. Thus, when the dissolution of the precipitated calcium phosphate and the possible reverse reaction of the ion-exchange process are finished, the final pH of the solution is 1. The solid phase and the solution remained in contact at 25.0 °C for 24 h. After this time, the concentration of phosphorus in the solution is measured. This concentration will be called the "apparent" content of phosphorus.

At least two more factors should be noted: (a) the presence of $TiO_2{\cdot}nH_2O$ resulting from the decomposition of γ-TiP, which at pH 1 can retain phosphate anions, and (b) the expected increase in the decomposition of the exchange material as a consequence of the lasting contact time with the liquid phase and the increase in the liquid:solid ratio.

In order to find a ratio between the apparent content in phosphorus and the hydrolysis degree of the exchanger, γ-TiP is equilibrated with NaCl + NaOH solutions at 25.0 °C under the conditions stated in the Experimental Section. The content of phosphorus is determined in the equilibrium solution ("real" content). Since the equilibrium pH is higher than 6,[20,22] $TiO_2{\cdot}nH_2O$ does not retain phosphate anions and the γ-TiP hydrolysis can be determined. HCl solutions are added to similar samples under the earlier conditions. After 24 h at 25.0 °C, the apparent concentration of phosphorus in solution is determined.

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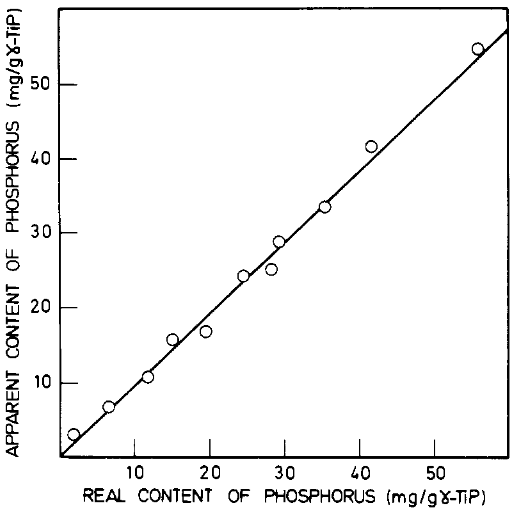

Figure 2. Variation of the phosphorus content in the solutions as a function of the adsorption of phosphate anions by $TiO_2 \cdot nH_2O$ at pH 1.

The plotting of the apparent phosphorus content against the real one results in a straight line with a slope slightly lower than unity (Figure 2).

The concentration of phosphorus is determined from the equilibrium solutions remaining constant or lightly increasing with the addition of $Ca(OH)_2$ (equilibrium pH <4) and quickly decreasing as the pH increases. The real phosphorus content related to the γ-TiP decomposition is determined by following the method earlier described. Both phosphorus concentrations (real and in the equilibrium) concur for moderate additions of $Ca(OH)_2$. When the amount of $Ca(OH)_2$ added is higher than 3.0 mequiv/g of γ-TiP, the calcium phosphate precipitation begins. In Figure 1 is plotted the percentage of γ-TiP hydrolyzed.

Exchange isotherms (Figure 1) show that the retention exceeds the theoretical exchange capacity of the γ-TiP (7.25 mequiv/g of γ-TiP) at every studied temperature so that the precipitated calcium phosphate must have a molar ratio P:Ca lower than 2.

The solids, after separation from the equilibrium solutions, were dried in air at room temperature. X-ray diffraction behavior is shown in Figure 3a. In the samples with retention higher than 3.6 mequiv of Ca/g of γ-TiP, obtained from $CaCl_2 + Ca(OH)_2$ and affected by the γ-TiP decomposition, a similarity among the X-ray patterns can be observed although the retention increases as the same time that a low-intensity diffraction line appears near to a value of $2\theta = 32°$. This line can be assigned either to a new exchange phase of the γ-TiP or to the precipitated calcium phosphate.

When the γ-TiP is refluxed with a saturated solution of $Ca(OH)_2$ and the resulting solid is washed with distilled water, its chemical analysis shows a P:Ca molar ratio of 0.70. Its X-ray pattern has a maximum diffraction peak at 2.80 Å ($2\theta = 32.0°$). Under our working conditions, the precipitation of $Ca_3(PO_4)_2 \cdot nH_2O$ is produced.

When $CaCl_2 + HCl$ solutions are used, the effect of temperature on the γ-TiP behavior is quite strong. The substitution progresses at the same time that the working temperature increases (Figure 1). At 55.0 °C and for additions of 8.0–10.0 mequiv of $CaCl_2$/g of γ-TiP, the retention is constant and equal to 37.5% of the exchange capacity of the γ-TiP. At 40.0 °C, the 37.5% conversion is not reached until the addition of 8.8 mequiv of $CaCl_2$/g of γ-TiP is made. At 25.0 and 5.0 °C and by addition of 10 mequiv of $CaCl_2$/g of γ-TiP, conversions of 34.5 and 26.9% are respectively reached. The process occurs at equilibrium pH from 1.7 to 2.2 (Figure 1) and practically without hydrolysis (≤1%). By additions of $CaCl_2 + Ca(OH)_2$, conversions higher than 37.5% are obtained. A composition close to 45% of substitution seems to be especially stable, reaching 50% by the addition of 4.0–5.0 mequiv of $Ca(OH)_2$/g of γ-TiP. The hydrolysis is not excessive, increasing with the temperature from values lower than 1% at 5.0 °C to 8% at 55.0 °C. At 5.0 °C the saturation is reached with hydrolysis lower than 5% and equilibrium pHs close to 7.5. In the remaining working temperatures, the hydrolysis increases faster and, thus, the $Ca_3(PO_4)_2 \cdot nH_2O$ precipitation allows the conversions to decrease for the same amount of $Ca(OH)_2$ added. Equilibrium pHs decrease when the temperature increases with values between 5.5 and 6.6.

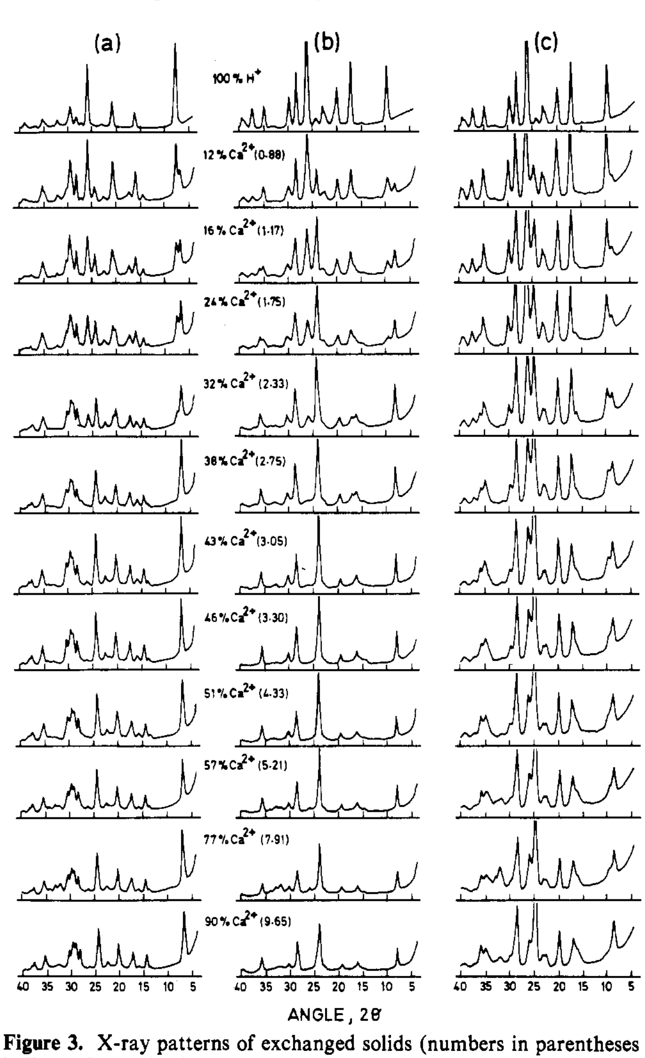

Figure 3. X-ray patterns of exchanged solids (numbers in parentheses indicate the retained calcium amount expressed in mequiv/g of γ-TiP): (a) stabilized in air at room temperature, (b) heated at 80 °C; (c) heated at 200 °C.

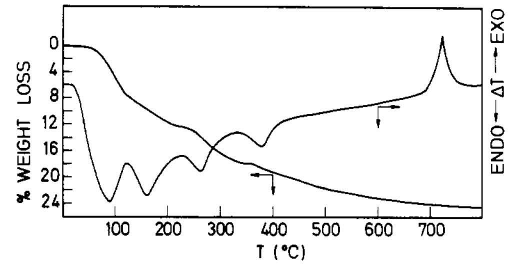

Figure 4. DTA and TG curves of the $\overline{H_{1.25}Ca_{0.37} \cdot 3.5H_2O}$ phase.

X-ray patterns of the exchanged solids stabilized in air are shown in Figure 3a. In the $0.000 < \bar{X}_{Ca} < 0.375$ conversion range, the presence of two reflections in the region of the interlayer distance is observed, one of which (corresponding to the 002 plane of γ-TiP) appears at 11.6 Å and the other at 13.1 Å. The latter reflection increases at the same time that the conversion increases. The characteristic reflection of γ-TiP is not observed when $\bar{X}_{Ca} = 0.375$. X-ray patterns of intermediate samples can be reproduced by combination of the patterns corresponding to the limit samples, showing the coexistence of two phases in this composition range.

Thermal analysis of a 37.5% substitution sample stabilized in

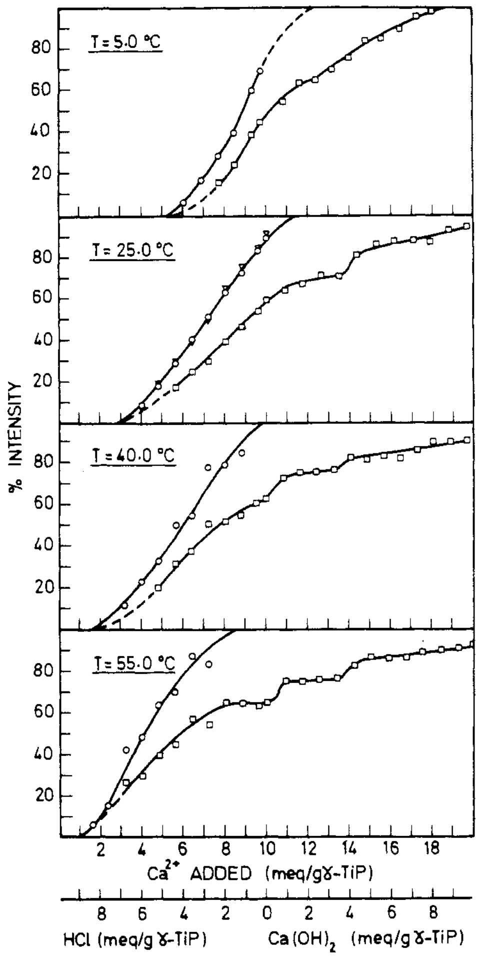

Figure 5. Relative intensity of the exchanged phases coexisting with the dihydrogen phase when the samples are stabilized in air (○) or treated at 80 °C (▽) or 220 °C (□).

air (Figure 4) enables the composition $\overline{H_{1.25}Ca_{0.37}}\cdot 3.5H_2O$ (13.1 Å) to be assigned. This is very similar to the $\overline{H_{1.30}Ca_{0.35}}\cdot 3.5H_2O$ (13.4 Å) composition described by Alberti et al.[15]

The X-ray patterns of samples $\bar{X}_{Ca} > 0.375$ stabilized in air (Figure 3a) are very similar over the entire composition range. As stated before, only the appearance of a new reflection of low intensity at $d = 2.78$ Å corresponding to $Ca(PO_4)_2\cdot nH_2O$ is observed. The retention of calcium ions occurs without appreciable variation of the $\overline{H_{1.25}Ca_{0.37}}\cdot 3.5H_2O$ (13.1 Å) phase structure.

When the solids are treated at 80 °C, X-ray patterns of $\bar{X}_{Ca} < 0.375$ samples (Figure 3b), show the coexistence of two reflections in the interlayer distance zone over the entire conversion range, one of which at 9.1 Å corresponds to β-TiP and the other at 10.9 Å is due to the $\overline{H_{1.25}Ca_{0.37}}\cdot H_2O$ phase. The rest of the pattern notably varies, new lines of diffraction appearing at $d =$ 7.8, 5.47, 4.56, 3.71, 3.12, 2.96, and 2.52 Å. When the exchange solids are obtained from $CaCl_2 + Ca(OH)_2$ solutions, their X-ray patterns (Figure 3b) are very similar to that of the $\overline{H_{1.25}Ca_{0.37}}\cdot H_2O$ (10.9 Å) phase, except for the appearance of bands with low intensity corresponding to precipitated calcium phosphate.

When the treatment temperature increases, the 37.5% substitution phase is transformed into $\overline{H_{1.25}Ca_{0.37}}$ (10.2 Å) (very unstable). At 200–220 °C, a reflection at 9.1 Å and some reflections characteristic of the β-TiP ($Ti(HPO_4)_2$) are superimposed on the original pattern.

Figure 3c shows the X-ray patterns of the $\bar{X}_{Ca} \leq 0.375$ exchanged solids treated at 220 °C. Over the entire composition range, the coexistence of two reflections at 9.1 and 10.2 Å can be observed. In $\bar{X}_{Ca} > 0.375$ solids (Figure 3c) the situation is qualitatively the same since the reflection at $d = 9.1$ Å only disappears when the working temperature is 5.0 °C and the additions of $Ca(OH)_2$ are 8.0 mequiv/g of γ-TiP concurring with the saturation of the γ-TiP.

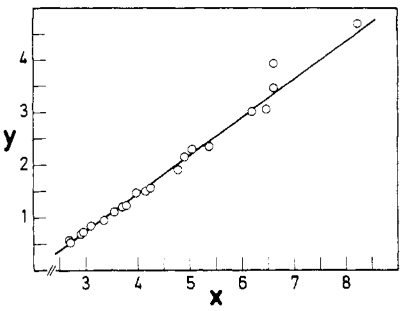

Figure 6. Plot of eq 6.

When the exchange materials are stabilized in air or treated at 80 °C, the interlayer distances of the present phases are, for $0.000 < \bar{X}_{Ca} < 0.375$ conversions, separated enough to allow us to make quantitative studies. When the solids are treated at 220 °C, these studies can be made over the whole substitution range. A detailed study of the zone of low angles allow us to evaluate (but cutting out the peak areas and weighing them) the relative intensity of the reflection corresponding to the interlayer distance of each phase (Figure 5).

In lamellar materials such as γ-zirconium phosphate, the molar concentration (C_j) of a crystalline phase j in a mixture is a linear function of the relative intensity (I_j) of the diffraction line chosen for the qualitative analysis[23,24]

$$C_j = f_j I_j \qquad (3)$$

where f_j is a constant of proportionality characteristic for each crystalline phase.[25]

When $CaCl_2 + HCl$ solutions are used, the relative intensity of the major reflection of the exchanged phase for samples stabilized in air or treated at 80 °C (Figure 5) increases with the conversion (Figure 1) until at $\bar{X}_{Ca} = 0.375$ it is the only reflection present. The curves obtained at 25.0 °C are very similar in both conditions. This fact means that the ratios of the proportionality constants of the present phases either in air or at 80 °C may be very similar. The behavior of the 37.5% conversion phase when it is heated at 220 °C can only be explained from the existence of thermal splittings such as those already detected in the Na and K phases of γ-TiP.[26-28] The process can be summarized:

$$z\overline{H_{1.25}Ca_{0.37}}\ (10.2\ \text{Å}) \xrightarrow{220\ °C} \begin{cases} (z-y)\overline{HH}\ (9.1\ \text{Å}) \\ y\overline{H_{2(1-x)}Ca_x}\ (10.2\ \text{Å}) \end{cases} \qquad (4)$$

The $\overline{H_{2(1-x)}Ca_x}$ composition phase can be known by relating the exchange isotherms (Figure 1) to the curves of the relative intensity at 220 °C (Figure 5). The molar fraction of exchange will be given by

$$\bar{X}_{Ca} = x\,\frac{f_{\overline{H_{2(1-x)}Ca_x}}\, I_{\overline{H_{2(1-x)}Ca_x}}}{f_{\overline{H_{2(1-x)}Ca_x}}\, I_{\overline{H_{2(1-x)}Ca_x}} + f_{\overline{\beta\text{-HH}}}\, I_{\overline{\beta\text{-HH}}}} \qquad (5)$$

and thus

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$$\underbrace{\frac{I_{\beta\text{-}\overline{HH}}}{I_{\overline{H_{2(1-x)}Ca_x}}}}_{y} = \underbrace{\frac{1}{\overline{X}_{Ca}}}_{x} \times \underbrace{\frac{f_{\overline{H_{2(1-x)}Ca_x}}}{f_{\beta\text{-}\overline{HH}}}}_{m} - \underbrace{\frac{f_{\overline{H_{2(1-x)}Ca_x}}}{f_{\beta\text{-}\overline{HH}}}}_{n} \quad (6)$$

which has the **y** = **mx** + **n** form. Plotting **y** against **x** (Figure 6) the values of **m** = 0.72 and **n** = –1.43 are obtained. From these data, $x = 0.50$ is obtained.

The thermal behavior of the 37.5% substitution phase can be summarized as

$$4\overline{H_{1.25}Ca_{0.37}}\cdot 3.5H_2O\ (13.1\ \text{Å}) \xrightarrow{80\ ^\circ C} 4\overline{H_{1.25}Ca_{0.37}}\cdot H_2O\ (10.9\ \text{Å}) \xrightarrow{200\ ^\circ C} 4\overline{H_{1.25}Ca_{0.37}}\ (10.2\ \text{Å}) \xrightarrow{220\ ^\circ C} \begin{cases} \overline{HH}\ (9.1\ \text{Å}) \\ 3\overline{HCa_{0.5}}\ (10.2\ \text{Å}) \end{cases} \quad (7)$$

When $CaCl_2 + Ca(OH)_2$ solutions are used and the samples are heated at 220 °C, the relative intensities of the reflections corresponding to the exchange phase (Figure 5) increase at the same time that the conversion occurs (Figure 1).

Alberti et al.[15] proposed the formation of half-exchanged and fully exchanged phases in the reaction with $CaCl_2 + Ca(OH)_2$. When the solutions in contact with the γ-TiP have high pHs, the processes

$$\overline{H_{1.25}Ca_{0.37}}\cdot 3.5H_2O \xrightarrow{0.13\,Ca^{2+}} \overline{HCa_{0.5}}\cdot 3.5H_2O \xrightarrow{0.5\,Ca^{2+}} \overline{Ca}\cdot 3H_2O \quad (8)$$

may simultaneously take place, their extent depending on the solution pH and the temperature.

When $CaCl_2 + HCl$ solutions are used, the exchange process happens without secondary reactions:

$$Ti(HPO_4)_2{\cdot}2H_2O(c) + {}^3/_8Ca^{2+}(aq) + {}^3/_2H_2O(l) \rightleftharpoons TiH_{1.25}Ca_{0.37}(PO_4)_2{\cdot}3.5H_2O(c) + {}^3/_4H^+(aq) \quad (9)$$

Assuming the considerations stated in earlier papers,[20] the equilibrium constant of the direct exchange reaction, takes the form

$$K = \left(\frac{\bar{a}_{Ca}}{\bar{a}_H}\right)\left(\frac{a_H{}^2}{a_{Ca}}\right)^{3/8}(a_w)^{-3/2} \quad (10)$$

where the quantities with bars represent the species in the solid phase and those without bars represent the species in solution.

Along a plateau, one solid of constant composition is converted into another of constant composition.[29] If we choose as the standard reference state an activity of 1 for the pure solids, we arrive at

$$K = \left(\frac{a_H{}^2}{a_{Ca}}\right)^{3/8}(a_w)^{-3/2} \quad (11)$$

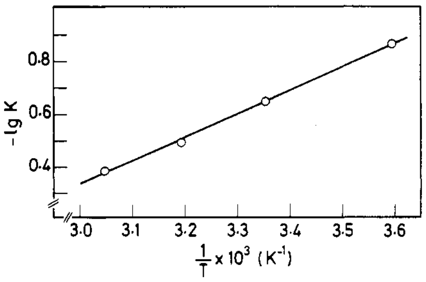

Figure 7. Plot of –log K against $1/T$.

The water activity, a_w, of the solutions is close to one. Thus, from the pH of the plateaus and the metal ion activities of the solutions, values of K were calculated.

From a plot of the equilibrium constant against $1/T$ (Figure 7), the value of $\Delta H° = 4.03$ kcal/mol is obtained. $\Delta G° = 0.87$ kcal/mol is obtained from K values, and $\Delta S° = 11$ eu is obtained from the values of $\Delta H°$ and $\Delta G°$.

The temperature has an influence on the substitution process. The endothermicity of the reaction makes γ-TiP an adequate material for retaining calcium ions in aqueous solution in acidic media and at high temperature.

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(29) Kulberg, L.; Clearfield, A. *J. Phys. Chem.* **1981**, *85*, 1585.