

Calorimetric Determination of H^+ / M^+ ($M = Na, K$) Ion Exchange in γ -Titanium Phosphate

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Abstract. H^+ / M^+ ($M = Na, K$) ion exchange on γ -titanium phosphate (γ -TiP) at 25°C and under static conditions has been studied. Titration and hydrolysis curves and the exchange isotherms were determined. The substitution was followed by X-ray diffraction. Direct calorimetric measurements were carried out at different degrees of conversion and the variation of the exchange enthalpy and the hydrolysis enthalpy of γ -TiP were obtained. The results are compared to the values of ΔH° obtained in previous works from titration data.

Key words: Ion exchange, lamellar phosphates, intercalation.

1. Introduction

During the past 20 years, several studies on the ion exchange properties of lamellar inorganic materials have been performed [1, 2]. Information on γ -type layered Group IV phosphates is presently important since these materials, owing to their large interlayer distance, seem to have some potential applications for the exchange of large cations. Thus, γ -Ti(HPO₄)₂ · 2H₂O (γ -TiP) [3, 4] has a basal spacing of 11.6 Å, much greater than those of α -Ti(HPO₄)₂ · H₂O (α -TiP) and α -Zr(HPO₄)₂ · H₂O (α -ZrP) (7.6 Å) [5, 6].

Thermodynamic data are usually obtained by determining the exchange isotherm at different temperatures. In compounds of the α -ZrP type, the variation of the enthalpy in the ion exchange reaction is small [7–12]. In these cases, the data obtained are only reliable when the exchange isotherms are determined very accurately. Therefore, it is advisable to make direct determinations of the ion-exchange heats in order to confirm the results obtained by determination of ΔH by temperature variation of the ion exchange reaction [13–18].

The H^+ / M^+ ($M = Na, K$) ion exchange process in γ -TiP shows the thermodynamic characteristics described above [19, 20]. In this paper, the enthalpy variations of ion exchange for both systems have been determined by direct calorimetric measurements.

In the following discussion, 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 given in parentheses. Thus, for example, Ti(HPO₄)₂ · 2H₂O and TiH_{1.5}Na_{0.5}(PO₄)₂ · H₂O are written as $\overline{H}H \cdot 2H_2O(11.6 \text{ \AA})$ and $\overline{H}_{1.5}\overline{Na}_{0.5} \cdot H_2O(11.0 \text{ \AA})$.

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2. Experimental

2.1. REAGENTS

All chemicals used were of reagent grade. The MOH (M = Na, K) solutions were standardized against HCl which was previously standardized against Na₂CO₃. γ -TiP was obtained by using 16 · 5M H₃PO₄ and reflux times of 10 days, as previously described [4].

2.2. ANALYTICAL PROCEDURES

The pH measurements were made with a Crison Model 501 pH-meter, equipped with glass and saturated calomel electrodes. The released phosphate groups were measured spectrophotometrically [21] using a Perkin-Elmer Model 200 spectrophotometer. The sodium and potassium ions in solution were determined by atomic absorption spectroscopy, using a Perkin-Elmer Model 372. The diffractometer used was a Philips Model PV 1050/23 with Ni filtered CuK α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.3. CALORIMETRIC MEASUREMENTS

A Setaram Calvet Standard, Model 1201 isothermic differential calorimeter, was used. The processes occur at 25°C and under static conditions (without shaking). Equal amounts of γ -TiP were introduced in the laboratory and reference cells. The solutions used were distilled water in the reference cell and 0.025–0.200M NaCl or 4×10^{-3} – 0.025M KCl or (0.04M MCl + *c*M MOH) ($4 \times 10^{-3} \leq c \leq 0.045$) (M = Na, K) in the laboratory cell. The greater affinity of γ -TiP for K⁺ as compared to Na⁺ in MCl solutions, makes it necessary to use a higher concentration of NaCl in order for the process to take place in adequate times for obtaining great accuracy in the calorimetric measurements.

The system was calibrated by special cells based on the Joule effect and also by measuring the neutralization enthalpies:



The values of ΔH obtained were 13.34 kcal/mol (M = Na) and 13.32 kcal/mol (M = K) in good agreement with previously reported values [22, 23].

2.4. ION EXCHANGE STUDIES

After each calorimetric measurement, the solid and solution phases were separated by filtration. The pH of the solution was measured and the concentrations of P and M (M = Na, K) were determined. The reaction times varied between 1 and 3 h. The solid was present in the solution in a ratio of 250 mL : 1g.

3. Results and Discussion

The amount of Na⁺ retained by the solid, the degree of decomposition of the solid and the pH at the end point of each calorimetric measurement were determined. These values are plotted, against the amount of Na⁺ added, in Figure 1. When NaOH was not added, the end pH decreased (2.60–2.16) as the NaCl concentration in the initial solution increased. Simultaneously, the conversion increased until values close to 25% were obtained. When

NaOH was added, the end pH increased slightly with the amount of NaOH added until a point where it suddenly increased. The inflection point of the pH curve concurred with the 50% conversion point. For additions of NaOH higher than 5.0 meq/g γ -TiP the conversion increased, but 85% uptake of Na⁺ was never exceeded.

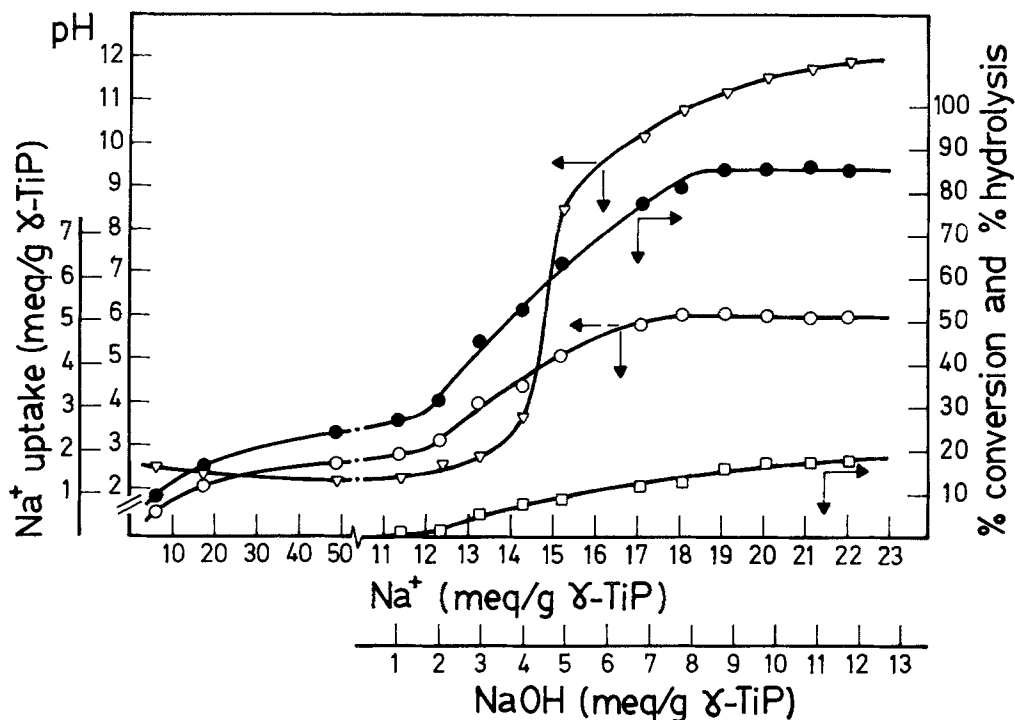


Fig. 1. H⁺/Na⁺ system: titration (∇) and hydrolysis (□) curves, exchange isotherm (○) and exchange isotherm corrected by the hydrolysis effect (●).

In the H⁺/K⁺ system, γ -TiP behaved in the same way (Figure 2). The value of the pH in the first zone of the curve of end pH varied from 2.95 to 2.05. For additions of 4.0–5.0 meq KOH/g γ -TiP, it suddenly increased, the conversion in this zone being 50%. The limit of conversion was also 85%.

As a consequence of our working conditions, the results reported above were obtained without shaking and with short reaction times (1–3 h). Thus, the end situation reached may or may not be close to that of the thermodynamic equilibrium. In previous studies [19,20,24,25] the equilibrium conditions in which the systems were studied involved a dynamic situation (shaking) and reaction times of 48 h. The plotting of the end pH against the molar fraction of exchange allows the behavior of γ -TiP in both working conditions to be compared (Figure 3). In dynamic conditions, the conversion ranges of $0.00 < \bar{X}_{Na} \leq 0.25$ and $0.00 < \bar{X}_K \leq 0.50$ were studied by using (MCl + HCl) solutions, a constant equilibrium pH being reached. In static conditions, when the solutions used were only of MCl the end pH depended on the conversion degree reached by the solid. When \bar{X}_{Na} increased, the end pH decreased coinciding with the equilibrium one when $\bar{X}_{Na} = 0.25$. In the H⁺/K⁺ system, by addition of KCl solutions in the concentrations and times used, the equilibrium pH was not reached. Higher conversions were reached by using (MCl + MOH) solutions. Under

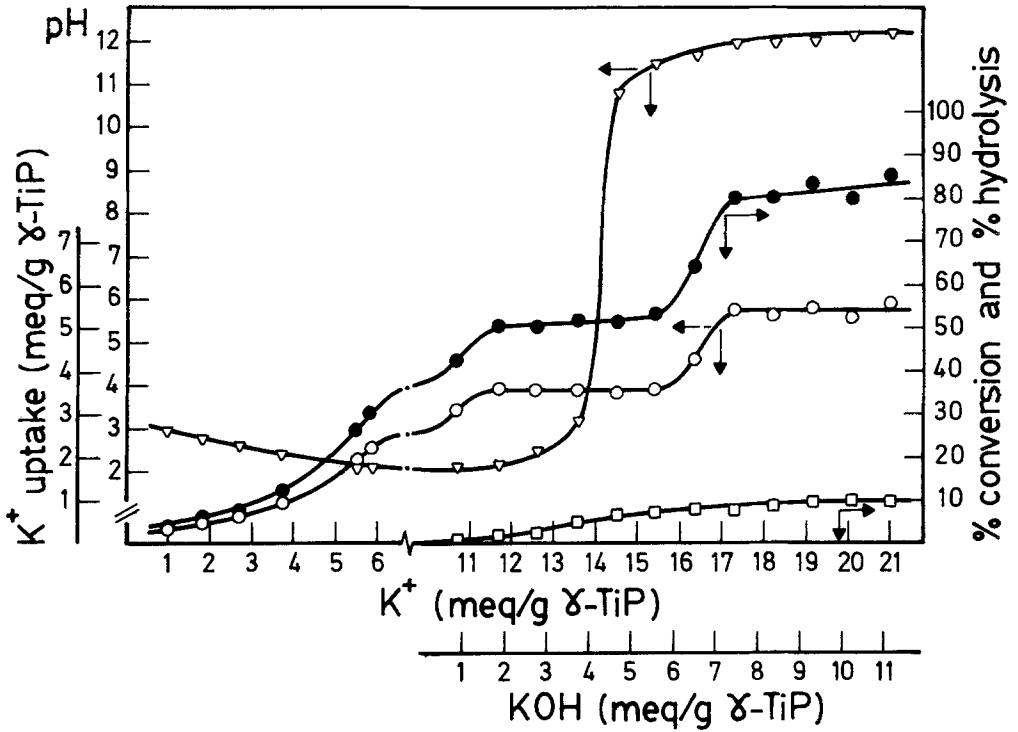


Fig. 2. H^+/K^+ system: titration (∇) and hydrolysis (\square) curves, exchange isotherm (\circ) and exchange isotherm corrected by the hydrolysis effect (\bullet).

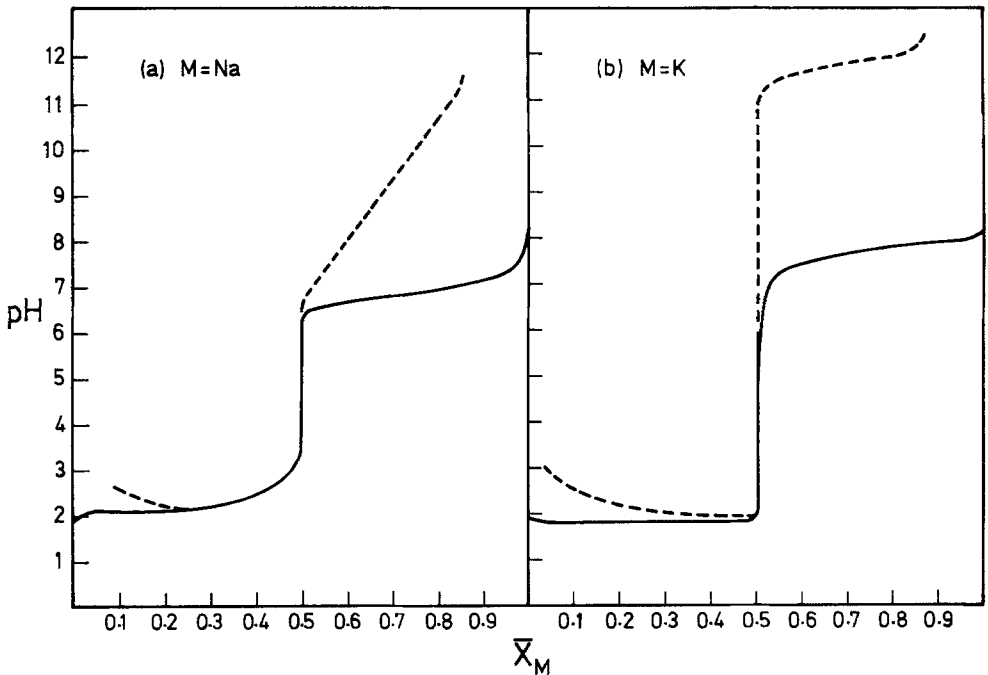


Fig. 3. Titration curves in dynamic conditions [24,25]. The dashed lines represent the titration curve reproduced from Figure 1 and 2.

working conditions, the equilibrium pH is reached in the range $0.25 < \bar{X}_{Na} < 0.50$ and $\bar{X}_K = 0.50$. When $\bar{X}_M > 0.50$, the end situation is rather far from the equilibrium one.

By X-ray diffraction of the samples stabilized in air, the following crystalline phases were detected: $\overline{HH} \cdot 2H_2O$ (11.6 Å), $\overline{H}_{1.5}Na_{0.5} \cdot H_2O$ (11.0 Å), $\overline{HNa} \cdot 3H_2O$ (13.2 Å), $\overline{HNa} \cdot 2H_2O$ (12.6 Å), $\overline{HNa} \cdot H_2O$ (11.1 Å), $\overline{NaNa} \cdot 2H_2O$ (12.8 Å), $\overline{NaNa} \cdot H_2O$ (11.5 Å), $\overline{H}_{1.5}K_{0.5} \cdot H_2O$ (11.0 Å), \overline{HK} (10.8 Å) and $\overline{KK} \cdot (2-3)H_2O$ (14.2 Å) [24–28]. In a recent paper [26], the best dried conditions to determine the relative concentration of each phase with different ionic content as a function of the degree of the solid conversion, were found to be: 200 °C in samples $0.00 \leq \bar{X}_M \leq 0.50$, the \overline{HH} (9.1 Å), \overline{HNa} (10.1 Å) and \overline{HK} (10.8 Å) phases being detected; 80 °C in samples $0.50 \leq \bar{X}_{Na} \leq 1.00$ with the \overline{HNa} (10.1 Å) and $\overline{NaNa} \cdot H_2O$ (11.5 Å) phases and dried in air for samples $0.50 \leq \bar{X}_K \leq 1.00$ with the presence of the \overline{HK} (10.8 Å) and $\overline{KK} \cdot (2-3)H_2O$ (14.2 Å) phases. In Figures 4 and 5, X-ray patterns of some exchanged solids treated in the stated conditions, can be seen. In the exchange solids, only two crystalline phases with different ionic content coexisted. It should be noted that the ratio of the crystalline phases for a defined fraction of exchange concurred with the ratio found in dynamic systems [26].

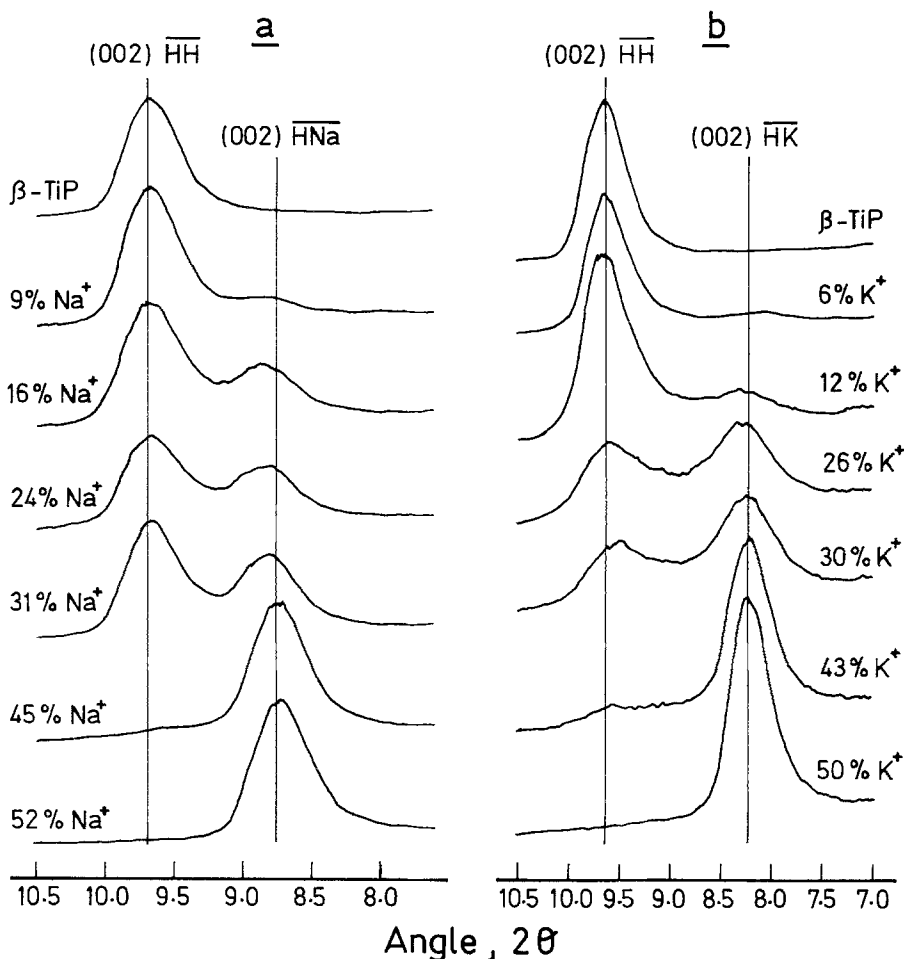


Fig. 4. X-ray patterns of samples with $0.00 \leq \bar{X}_M \leq 0.50$ conversion treated at 200 °C: (a) M = Na, (b) M = K.

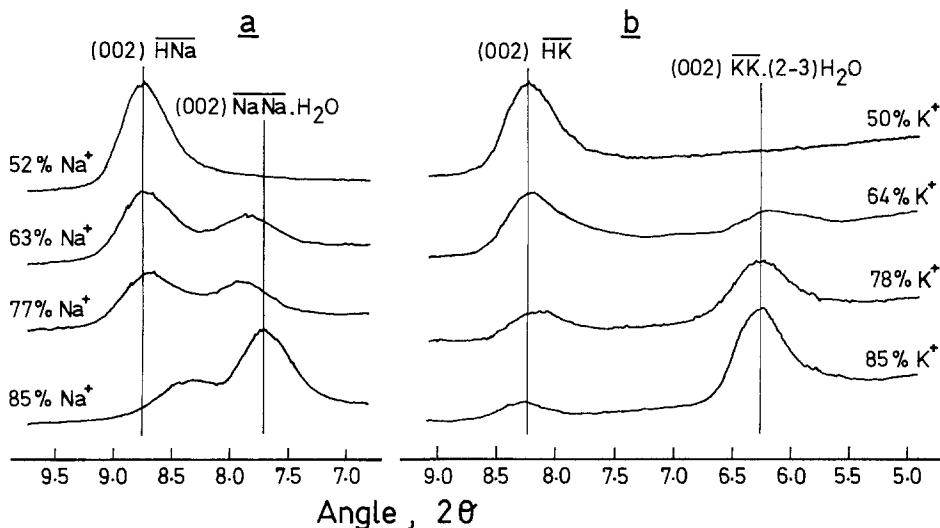
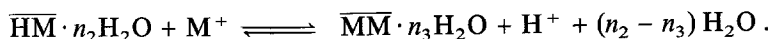
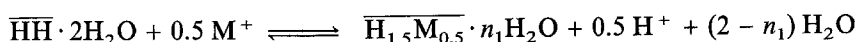


Fig. 5. X-ray patterns of samples with $0.50 \leq \bar{X}_M \leq 1.00$ conversion: (a) $M = \text{Na}$ heated at 80°C , (b) $M = \text{K}$ stabilized in air.

From the data reported, the existence of three steps in the H^+/M^+ ($M = \text{Na}, \text{K}$) ion exchange in $\gamma\text{-TiP}$ (static or dynamic conditions), can be inferred:



Never did two of these processes take place in appreciable amounts together. This fact made it possible to use the entire conversion range of the $\gamma\text{-TiP}$ to determine the thermodynamic data either by temperature variation of the ion exchange reaction or by direct calorimetric measurements. The possibility of some light reciprocal solubility of the two coexisting phases has been neglected.

The calorimetric curves always show the same shape: an unique and fast peak, the intensity of which quickly decreased. When $(\text{MCl} + \text{MOH})$ solutions were used and for $\bar{X}_M > 0.50$, the base line was not reached in the measurement time. When the conversion increased, the diffusion capacity of the counterions in the solid became more difficult and the ion exchange process became slower. Several contact hours were needed in order for the conversion to exceed 85% and the calorimetric curve moved close to the base line during a long time. If the calorimetric measurements were made under these conditions, the error in the enthalpy variation measured would be very high because small changes in the base line would significantly vary the experimental values obtained. A similar effect was observed in the H^+/Na^+ ion exchange in $\gamma\text{-TiP}$, with maximum conversions close to 70% in the measurement times used [18]. The calorimetric behavior of this latter system is similar to that studied in this paper so that the results are treated in the same way. Assuming that the ion exchange process takes place without secondary reactions, the enthalpy variation (ΔH) can mainly be attributed to: (a) the ion exchange reaction (ΔH_x°) and (b) the neutralization reaction when $(\text{MCl} + \text{MOH})$ solutions were used (ΔH_N). When the initial solution contains MOH , the exact knowledge of the neutralization enthalpy makes the calculation of (a) possible

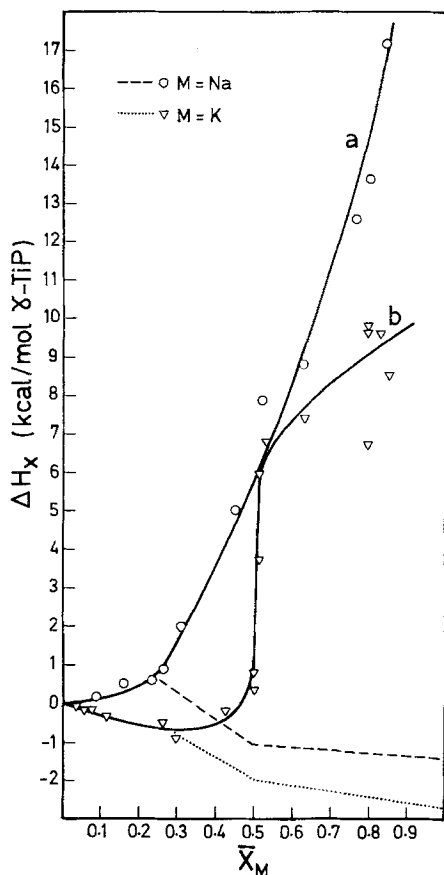
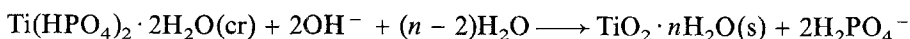
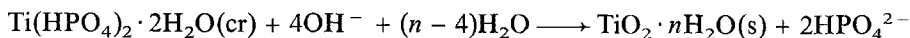


Fig. 6. Variation of the reaction heat against the substitution extent: (a) M = Na, (b) M = K. The dashed lines show the results obtained from titration data [19,20].

($\Delta H_x^\circ = \Delta H - \Delta H_N$). Figure 6 shows the variation of ΔH_x as a function of the extent of the exchange in both studied systems. In the zone in which alkaline solutions were not used, a good agreement between the values of ΔH_x° found by calorimetric and temperature variation of the ion exchange reaction methods [19,20] was observed. For conversions higher than 25–30% there were discrepancies which increased with the conversion. When alkaline solutions were used, the heat of ion exchange coexisted with the hydrolysis reaction of the exchanger (Figures 1 and 2). This hydrolysis reaction usually involves endothermic enthalpy variations. In order to obtain good agreement between the value of the enthalpy variation obtained by temperature variation of the ion exchange reaction and calorimetric methods, it is necessary to attribute to the hydrolysis process of the γ -TiP, an enthalpy of 120 ± 10 kcal/mol. This value could be related to the ‘hydrolysis’ reactions originating from the break-up of the crystalline lattice of the exchanger:



When the enthalpy variations of the neutralization and hydrolysis processes are deducted from the experimental values, in every step of both systems, a good agreement between the

values of ΔH_x° derived from both methods was found (Figure 7). Therefore, the difference found between the two methods allows an estimate of the enthalpy of the hydrolysis reactions. The uncertainty in the ΔH_x° values obtained by calorimetric measurements increased with the degree of hydrolysis undergone by the material.

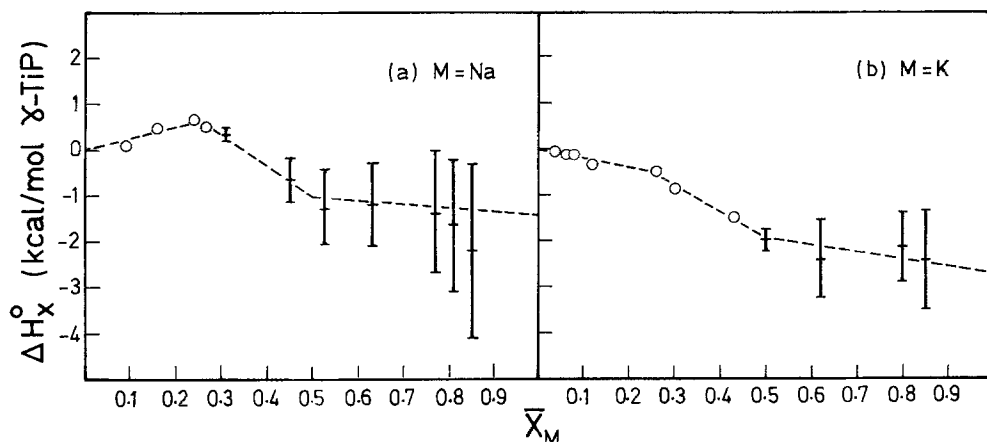


Fig. 7. Variation of the heat in the H^+/M^+ exchange in γ -TiP against the substitution extent: (a) $M = Na$, (b) $M = K$. The dashed lines show the results obtained from titration data [19,20].

The enthalpy variation of the hydrolysis process can give information about the relative stability of the exchanger. Thus the value of the enthalpy change in the hydrolysis process of α -TiP (170 ± 15 kcal/mol) [18] is bigger than the one found for γ -TiP. Therefore, the α -structure of the titanium bis(monohydrogen orthophosphate) is thermodynamically more stable than the γ -structure. This fact justifies the transformation of the γ -form into the α -form when the first one remains in contact for a long time with aqueous solutions of H_3PO_4 [29].

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