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THERMODYNAMIC TREATMENT OF H^+/K^+ ION-EXCHANGE ON γ-TITANIUM PHOSPHATE

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ABSTRACT

The H^+/K^+ ion-exchange process in γ-$Ti(HPO_4)_2 \cdot 2H_2O$ was studied, titration and hydrolysis curves and exchange isotherms being obtained at 278.15, 298.15, 313.15 and 328.15 (±0.1) K. Three differentiated processes of substitution and crystalline phases of 25, 50 and 100% of conversion were reached. The equilibrium constants, the standard molar Gibbs free energies, enthalpies and entropies of the exchange reaction were determined.

INTRODUCTION

γ-$Ti(HPO_4)_2 \cdot 2H_2O$ is a lamellar solid with monoclinic symmetry [1]. Its interlayer distance (1.16 nm) [1–3] is close to that of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ (1.22 nm) [4] and both are much greater than that of α-$M(HPO_4)_2 \cdot H_2O$ (0.76 nm) ($M = Zr, Ti$) [5,6].

Ion-exchange properties of the crystalline α-variety of insoluble acid salts of tetravalent metals have been widely studied [7–10] and several thermodynamic determinations were carried out [11–14]. However, relatively little attention has been paid to the γ-variety. Ion-exchange studies have shown for γ-TiP good properties in the retention of several alkaline [2,15,16] and alkaline earth [17] ions.

In this paper, the H^+/K^+ system in γ-TiP is studied, the values of the thermodynamic functions of exchange being reported.

EXPERIMENTAL

All chemicals used were of reagent grade. γ-Titanium phosphate was obtained as previously described [3]. KOH solutions were standardized by titration against HCl(aq) which had been previously standardized against Na_2CO_3. The exchanger was equilibrated with (KCl + HCl) or (KCl + KOH) solutions at 278.15, 298.15, 313.15 and 328.15 (±0.1) K following the dynamic procedure described by Clearfield et al. [18]. The solid was present in the solution at approximately 2 $g\ l^{-1}$ mass concentration.

The concentration of phosphorus and titanium in the solids was gravimetrically determined [19]. Measurements of pH were made with a Crison pH meter, Model 501, equipped with glass and saturated-calomel electrodes. The released phosphate groups were measured spectrophotometrically [20] using a Perkin-Elmer Model 200. The potassium ions in solution were determined by atomic absorption spectroscopy with a Perkin-Elmer Model 372.

RESULTS AND DISCUSSION

Titration and hydrolysis curves, exchange isotherms and exchange isotherms corrected by hydrolysis at 298.15, 313.15 and 328.15 K are plotted in Fig. 1 against the amount, $n(K^+)$, of K ions added divided by the mass, $m\{\gamma\text{-TiP}\}$ of γ-titanium phosphate. When solutions of (KCl + HCl) are added, the results are similar at the three working temperatures, the 50% substitution being reached in the absence of acid. When solutions of (KCl + KOH) are added, the influence of temperature is important and saturation is only reached at 298.15 K. This fact makes necessary an additional determination at 278.15 K with (KCl + KOH) solutions (Fig. 2).

The H^+/K^+ substitution process in γ-TiP occurs in three stages, crystalline phases of 25, 50 and 100% of conversion being formed. Over the entire composition range, only two different crystalline phases coexist [16]. The first two steps of exchange were reached by the addition of (KCl + HCl) solutions in the form

$$\mathrm{Ti(HPO_4)_2\cdot 2H_2O(cr)} + \tfrac{1}{2}\mathrm{K^+(aq)} + (n_1-2)\mathrm{H_2O(l)} \rightleftharpoons \mathrm{TiH_{1.5}K_{0.5}(PO_4)_2}\cdot n_1\mathrm{H_2O(cr)} + \tfrac{1}{2}\mathrm{H^+(aq)} \quad (1)$$

$$\mathrm{TiH_{1.5}K_{0.5}(PO_4)_2}\cdot n_1\mathrm{H_2O(cr)} + \tfrac{1}{2}\mathrm{K^+(aq)} + (n_2-n_1)\mathrm{H_2O(l)} \rightleftharpoons \mathrm{TiHK(PO_4)_2}\cdot n_2\mathrm{H_2O(cr)} + \tfrac{1}{2}\mathrm{H^+(aq)} \quad (2)$$

The third step is only reached when the half exchanged phase is in contact with (KCl + KOH) solutions, the fully exchanged phase being obtained

$$\mathrm{TiHK(PO_4)_2}\cdot n_2\mathrm{H_2O(cr)} + \mathrm{K^+(aq)} + \mathrm{OH^-(aq)} + (n_3-n_2-1)\mathrm{H_2O(l)} \rightarrow \mathrm{Ti(KPO_4)_2}\cdot n_3\mathrm{H_2O(cr)} \quad (3)$$

Eliminating the neutralization reaction and only considering the exchange reaction one obtains

$$\mathrm{TiHK(PO_4)_2}\cdot n_2\mathrm{H_2O(cr)} + \mathrm{K^+(aq)} + (n_3-n_2)\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Ti(KPO_4)_2}\cdot n_3\mathrm{H_2O(cr)} + \mathrm{H^+(aq)} \quad (4)$$

Following a similar procedure to that described by Suárez et al. [12], the

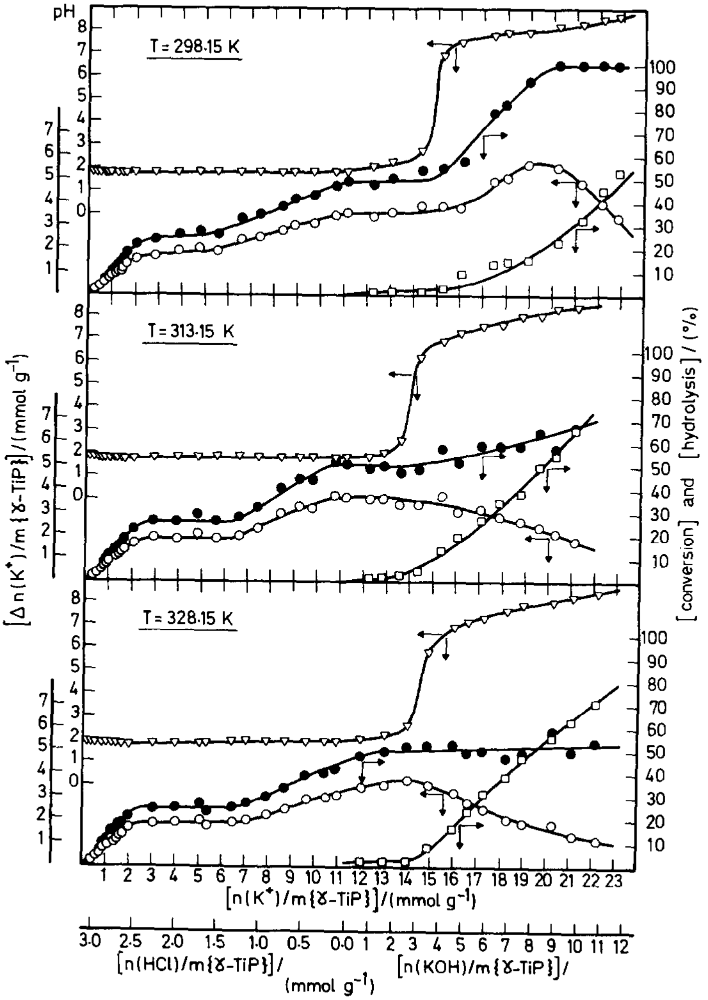

Fig. 1. Titration curve (▽), exchange isotherm (○), percentage hydrolysis of the exchanger (□) and exchange isotherm corrected to take hydrolysis into account (●).

following expressions for the equilibrium quotients in each stage are obtained

$$K_1' = \{x(\mathrm{K}^+, 1, \mathrm{s})/x(\mathrm{H}^+, 1, \mathrm{s})\}\{m(\mathrm{H}^+, 1)/m(\mathrm{K}^+, 1)\}^{1/2} \times \{f(\mathrm{H}^+, 1)/f(\mathrm{K}^+, 1)\}^{1/2} \quad (5)$$

$$K_2' = \{x(\mathrm{K}^+, 2, \mathrm{s})/x(\mathrm{H}^+, 2, \mathrm{s})\}\{m(\mathrm{H}^+, 2)/m(\mathrm{K}^+, 2)\}^{1/2} \times \{f(\mathrm{H}^+, 2)/f(\mathrm{K}^+, 2)\}^{1/2} \quad (6)$$

$$K_3' = \{x(\mathrm{K}^+, 3, \mathrm{s})/x(\mathrm{H}^+, 3, \mathrm{s})\}\{m(\mathrm{H}^+, 3)/m(\mathrm{K}^+, 3)\} \times \{f(\mathrm{H}^+, 3)/f(\mathrm{K}^+, 3)\} \quad (7)$$

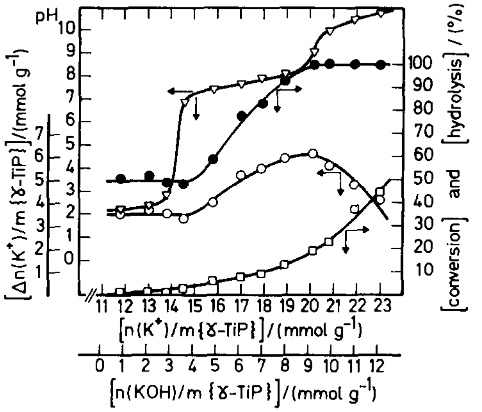

Fig. 2. At $T = 298.15$ K: titration curve (▽), exchange isotherm (○), percentage hydrolysis of the exchanger (□) and exchange isotherm corrected to take hydrolysis into account (●).

where x is the molar fraction in the solid exchanger, m is the molality and f is the activity coefficient of the ions in solution [21]. The equilibrium quotients (K_i') are calculated for each experimental point.

The equilibrium constants are obtained by application of the Gaines and Thomas thermodynamic treatment [22]. For the first exchange stage

$$\log_{10} K_1 = \int_0^1 (\log_{10} K_1') d\{x(\mathrm{K}^+, 1, \mathrm{s})\} - (n_1 - 2) \log_{10} a_\mathrm{w} \tag{8}$$

where a_w is the activity of water in the solution, its contribution to $\log_{10} K_1$ being considered negligible. The integral is calculated by plotting $\log_{10} K_1'$ against $x(\mathrm{K}^+, 1, \mathrm{s})$ and determining the area under the curve. K_2 and K_3 are obtained by application of a similar treatment.

Plotting the equilibrium constants against $1/T$ one obtains the value of ΔH_m^0 for each exchange stage. ΔG_m^0 is obtained from the K values and ΔS_m^0 from ΔH_m^0 and ΔG_m^0. Table 1 shows the values obtained for the thermodynamic constants in the $\mathrm{H}^+/\mathrm{K}^+$ ion-exchange in γ-TiP. Thermodynamics of the third step are determined only from two working temperatures, thus, increasing the uncertainty of the values obtained.

TABLE I

Thermodynamic values for the $\mathrm{H}^+/\mathrm{K}^+$ exchange in γ-$\mathrm{Ti(HPO_4)_2 \cdot 2H_2O}$

Stage	$-\log_{10} K$				ΔH_m^0 (kJ mol^{-1})	ΔG_m^0 (kJ mol^{-1})	ΔS_m^0 (J K^{-1} mol^{-1})
	278.15 K	298.15 K	313.15 K	328.15 K			
$\overline{\mathrm{HH}} \rightleftharpoons \overline{\mathrm{H_{1.5}K_{0.5}}}$	-	−0.57	−0.54	−0.53	−2.19	−3.23	3
$\overline{\mathrm{H_{1.5}K_{0.5}}} \rightleftharpoons \overline{\mathrm{HK}}$	-	0.06	0.09	0.16	−5.98	0.35	−21
$\overline{\mathrm{HK}} \rightleftharpoons \overline{\mathrm{KK}}$	6.19	6.23	-	-	−3.16	35.42	−129

The enthalpy variation in the three processes of exchange is negative. In alkaline medium, the increase in temperature facilitates the endothermic processes of hydrolysis [23] against the exothermic processes of ion-exchange. The variation of entropy is close to zero in the first step and negative in the second and third ones. This suggests, in agreement with Kullberg and Clearfield [11], that half and full exchanged phases formed in situ have a hydration greater than that of γ-TiP. At room temperature, the 25% substitution process of H ions by K ions in γ-TiP is spontaneous. γ-Titanium phosphate is a suitable material for retaining K ions in diluted solutions of this ion.

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