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Thermodynamic treatment of H^+/Sr^{2+} ion-exchange in γ-titanium phosphate

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Abstract

The H^+/Sr^{2+} ion-exchange in γ-$Ti(HPO_4)_2 \cdot 2H_2O$ was studied. Exchange isotherms and pH curves were obtained at 298.15, 313.15 and 328.15($\pm$0.1) K. The half-exchanged phase $TiHSr_{0.5}(PO_4)_2 \cdot 3H_2O$ (interlayer distance 1.34 nm) was detected. The equilibrium constants and the standard molar Gibbs free energy, enthalpy and entropy of the exchange reaction were determined.

INTRODUCTION

The phosphate γ-$Ti(HPO_4)_2 \cdot 2H_2O$ (γ-TiP) is a lamellar solid with a basal spacing of 1.16 nm. Its structure is not so far known, but it has monoclinic symmetry. The dimensions of the unit cell are $a = 0.529$ nm, $b = 0.644$ nm, $c = 2.394$ nm, and $\beta = 103.9°$ [1].

The phosphates of tetravalent metals are interesting mainly because of their ion-exchange properties. The behaviour of γ-TiP with respect to the retention of alkali metals [2], alkaline-earth metals [3–5], NH_4^+ [6] and Cu^{2+} [7] ions has been studied.

When the strontium ions enter into the exchanger equilibrated with $SrCl_2$ solution, a crystalline phase in which the half of the hydrogen ions have been substituted by strontium ions is obtained without hydrolysis of the exchanger. Conversions higher than 50% can be obtained by using $SrCl_2 + Sr(OH)_2$ solutions but, at the same time, hydrolysis becomes important, so that a conversion degree higher than 80% is not obtained [3].

When we try to systematize the ion-exchange properties of a solid we have to know the thermodynamic magnitudes of the ionic substitution processes. These data have been determined in γ-TiP for the H^+/M^+ (M = alkali metal) [8], H^+/Cu^{2+} [7] and H^+/Ca^{2+} [5] processes. In this paper, the H^+/Sr^{2+} system in γ-TiP is studied, and the values of the thermodynamic functions of exchange are reported.

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EXPERIMENTAL

All chemicals used were of reagent grade. γ-Titanium phosphate was obtained as previously described [9]. The exchanger was equilibrated with ($SrCl_2$ + HCl) solutions at 298.15, 313.15 and 328.15(±0.1) K following the dynamic procedure described by Clearfield et al. [10]. The solid was present in the solution at approximately 4 g l^{-1} mass concentration.

The concentrations of phosphorus and titanium in the solids were gravimetrically determined. The released phosphate groups were measured spectrophotometrically [11] using a Perkin–Elmer Model 200. Measurements of pH were made with a Orion pH meter Model SA-720. The strontium ions in solution were determined by atomic absorption spectroscopy with a Varian Model SpectrAA-300. The diffractometer used was a Philips Model PV 1050/23 ($\lambda = 0.15418$ nm). Thermal analyses were performed with a Mettler Model TA4000 (TG50, DSC30; rate of heating, 8 K min^{-1}).

RESULTS AND DISCUSSION

Exchange isotherms and pH curves are shown in Fig. 1. The substitution progresses as Sr^{2+} is added. The theoretical exchange capacity of γ-TiP, derived from its formula, is 7.25 mequiv. g^{-1}. Conversions of 50% are

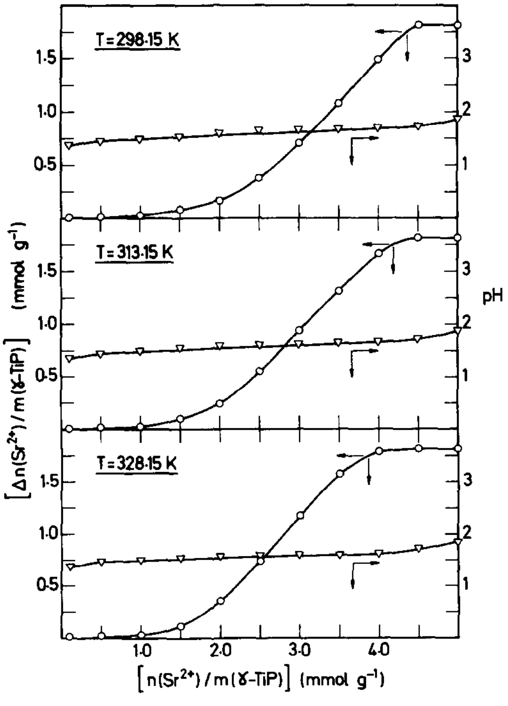

Fig. 1. Exchange isotherms (○) and pH curves (▽).

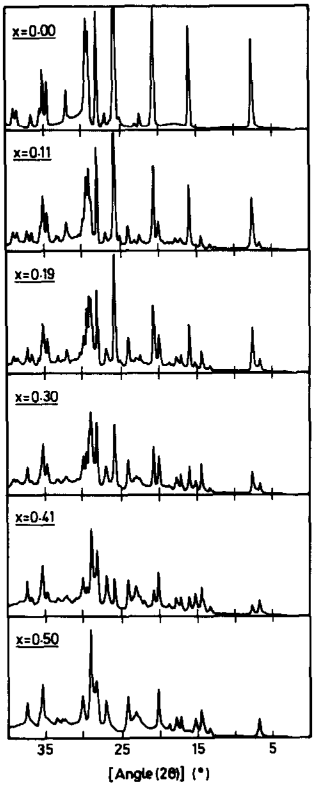

Fig. 2. X-ray patterns of some exchanged solids obtained at 298.15 K, stabilized in air.

reached more easily as the temperature becomes higher. The equilibrium pH slightly increases with the degree of conversion. The extent of hydrolysis of the exchanger was $\leqslant 1\%$, as determined from the analysis of phosphorus in the equilibrium solutions. Treatment of the exchanged solids with hydrochloric acid solutions and subsequent analysis of phosphorus in solution indicated that there is no precipitation of strontium phosphate.

X-ray diffraction data of the half-exchanged phase stabilized in air concur with those reported by Allulli et al. [3], giving an interlayer distance of 1.34 nm. Thermal analysis indicates the existence of three molecules of crystallization water, in agreement with the findings of La Ginestra and Massucci [12]. The crystalline phase obtained has the composition $TiHSr_{0.5}(PO_4)_2 \cdot 3H_2O$ (briefly represented by $\overline{HSr_{0.5}} \cdot 3H_2O$ (1.34 nm)).

In Fig. 2, X-ray patterns of samples stabilized in air with $0.00 \leqslant x \leqslant 0.50$ composition are shown, where x is the molar fraction of exchange defined as the fraction of hydrogen atoms substituted in γ-TiP; its value is the equivalent fraction of strontium in the solid when all the interchangeable hydrogen atoms of the exchanger are involved in the substitution process. Two reflections in the zone of interlayer distance corresponding to the $\overline{HH} \cdot 2H_2O$ (1.16 nm) and $\overline{HSr_{0.5}} \cdot 3H_2O$ (1.34 nm) phases can be observed over the entire compositional range. X-ray patterns of samples of intermediate composition may be reproduced by combining those corresponding to the pure phases ($\overline{\mathrm{HH}} \cdot 2H_2O$ and $\overline{\mathrm{HSr}}_{0.5} \cdot 3H_2O$). This indicates the formation during ion exchange of an individual crystalline phase of composition $TiHSr_{0.5}(PO_4)_2 \cdot 3H_2O$ coexisting with the initial one until $x = 0.50$.

The exchange reaction can be expressed in its ionic form as in eqn. (1). Following a similar procedure to that described previously [8], the equilibrium constant takes the form of eqn. (2), where the concentrations of the species in the solid phase are expressed in terms of their respective equivalent fractions (E), taking into account that the γ-TiP in this process has only 1 mol of interchangeable hydrogen ions per mole of exchanger, so that its "real" exchange capacity is 3.62 mequiv. g^{-1}, corrected for the activity coefficient in the solid phase (f_{cr}). The concentrations of the species in the solution phase are expressed in terms of molalities (m), corrected for the activity coefficient in solution (f_{aq}) [13].

$$2H^+(cr) + Sr^{2+}(aq) \rightleftharpoons Sr^{2+}(cr) + 2H^+(aq) \tag{1}$$

$$K = \left[E(Sr^{2+})/E(H^+)^2\right]\left[m(H^+)^2/m(Sr^{2+})\right] \times \left[f_{cr}(Sr^{2+})/f_{cr}(H^+)^2\right]\left[f_{aq}(H^+)^2/f_{aq}(Sr^{2+})\right] \tag{2}$$

The equilibrium quotient expressed in eqn. (3) is calculated for each experimental point. The equilibrium constant is obtained from eqn. (4) by application of the Gaines and Thomas thermodynamic treatment [14], where a and b are the water activities of solutions in equilibrium with pure forms of the exchanger, Z is the valence of the ion, and n_w refers to the number of water molecules of one "exchange equivalent" of the solid. The second and fourth terms of eqn. (4) can be omitted without significant error [15], yielding eqn. (5):

$$K' = \left[E(Sr^{2+})/E(H^+)^2\right]\left[m(H^+)^2/m(Sr^{2+})\right]\left[f_{aq}(H^+)^2/f_{aq}(Sr^{2+})\right] \tag{3}$$

$$\log_{10}K = (Z_H - Z_{Sr}) + \log_{10}\left[f_{cr}(Sr^{2+})/f_{cr}(H^+)^2\right] + \int_0^1 (\log_{10}K')\, d\left[E(Sr^{2+})\right] - Z_H Z_{Sr}\int_a^b n_w\, d(\log_{10}a_w) \tag{4}$$

$$\log_{10}K = (Z_H - Z_{Sr}) + \int_0^1 (\log_{10}K')\, d\left[E(Sr^{2+})\right] \tag{5}$$

In order to describe the ion-exchange process more clearly, the equilibrium reaction can be expressed in terms of the solid phases involved, as in reaction (6). This has the advantage of indicating the composition of the crystalline solid phases involved, and thus the "real" exchange capacity of the exchanger in the substitution step considered. From eqn. (6), we can define an equilibrium quotient in the form of eqn. (7), which is related to K'

as in eqn. (8). Equation (5) can be expressed, per mole of exchanger, in the form of eqn. (9), where $K_1 = K^{1/2}$:

$$\mathrm{Ti(HPO_4)_2\cdot 2H_2O(cr)} + 1/2\mathrm{Sr^{2+}(aq)} + \mathrm{H_2O} \rightleftharpoons \mathrm{TiHSr_{0.5}(PO_4)_2\cdot 3H_2O(cr)} + \mathrm{H^+(aq)} \tag{6}$$

$$K_1' = \left[E(\mathrm{Sr^{2+}})/E(\mathrm{H^+})\right]\left[m(\mathrm{H^+})/m(\mathrm{Sr^{2+}})^{1/2}\right]\left[f_{\mathrm{aq}}(\mathrm{H^+})/f_{\mathrm{aq}}(\mathrm{Sr^{2+}})^{1/2}\right] \tag{7}$$

$$(K')^{1/2} = \left[E(\mathrm{Sr^{2+}})\right]^{-1/2} K_1' \tag{8}$$

$$\begin{aligned}\log_{10} K_1 &= -1/2 - 1/2\int_0^1 \left[E(\mathrm{Sr^{2+}})\right] \mathrm{d}\left[E(\mathrm{Sr^{2+}})\right] \\ &\quad + \int_0^1 (\log_{10} K_1')\, \mathrm{d}\left[E(\mathrm{Sr^{2+}})\right] \\ &= \int_0^1 (\log_{10} K_1')\, \mathrm{d}\left[E(\mathrm{Sr^{2+}})\right]\end{aligned} \tag{9}$$

The use of phase molar fractions is usual in studies of materials similar to γ-TiP, because it gives information about the system composition when several crystalline phases coexist [16]. For this reason, we replace the equivalent fractions of the ions in the solid phase E by the corresponding phase molar fractions, x. Since $E(\mathrm{Sr^{2+}}) = x(\overline{\mathrm{HSr}}_{0.5})$ and $E(\mathrm{H^+}) = x(\overline{\mathrm{HH}})$ over the entire substitution range, the equilibrium quotient can be expressed as in eqn. (10), and thus the equilibrium constant can be calculated from expression (11). The integral is calculated by plotting $\log_{10} K_1'$ against $x(\overline{\mathrm{HSr}}_{0.5})$ and determining the area under the curve.

$$K_1' = \left[x(\overline{\mathrm{HSr}}_{0.5})/x(\overline{\mathrm{HH}})\right]\left[m(\mathrm{H^+})/m(\mathrm{Sr^{2+}})^{1/2}\right]\left[f_{\mathrm{aq}}(H^+)/f_{\mathrm{aq}}(\mathrm{Sr^{2+}})^{1/2}\right] \tag{10}$$

$$\log_{10} K_1 = \int_0^1 (\log_{10} K_1')\, \mathrm{d}\left[x(\overline{\mathrm{HSr}}_{0.5})\right] \tag{11}$$

Plotting the equilibrium constants against $1/T$ one obtains the value of $\Delta H_{\mathrm{m}}^\circ$. $\Delta G_{\mathrm{m}}^\circ$ is obtained from the K values and $\Delta S_{\mathrm{m}}^\circ$ from $\Delta H_{\mathrm{m}}^\circ$ and $\Delta G_{\mathrm{m}}^\circ$. Table 1 shows the values obtained from the thermodynamic constants in the $\mathrm{H^+/Sr^{2+}}$ ion-exchange in γ-TiP.

TABLE 1

Thermodynamic values for the $\mathrm{H^+/Sr^{2+}}$ exchange in γ-TiP

Stage	$-\log_{10}K$			$\Delta H_{\mathrm{m}}^\circ$ (kJ mol^{-1})	$\Delta G_{\mathrm{m}}^\circ$ (kJ mol^{-1})	$\Delta S_{\mathrm{m}}^\circ$ (kJ mol^{-1})
	298.15 K	313.15 K	328.15 K			
$\overline{\mathrm{HH}} \rightleftharpoons \overline{HSr}_{0.5}$	0.66	0.58	0.51	9.31	3.75	19

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