Intercalation of n-Alkylamines into α-Titanium Phosphate from Aqueous Solutions

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Abstract. The intercalation reactions between n-alkylamines and α-titanium phosphate in aqueous media have been investigated. The compounds with the maximum intercalation have the formula α-Ti(HOPO$_3$)$_2 \cdot 2$ C$_n$H$_{2n+1}$NH$_2 \cdot$ H$_2$O $(n = 1 - 10)$. Defined crystalline phases with lower amine content are described, the general formula being α-Ti(HOPO$_3$)$_2 \cdot m$C$_n$H$_{2n+1}$NH$_2 \cdot p$H$_2$O $(m = 1.0, 1.3, 1.5, 1.7)$. When $m = 1.0$ the n-alkylamines form a monomolecular layer. When $m > 1.0$ the layer is bimolecular. The inclination angle and the packing density of the n-alkylamines in the interlayer space is determined.

1. Introduction

α-Titanium phosphate, Ti(HOPO$_3$)$_2 \cdot$ H$_2$O (α-TiP), is a lamellar solid with a basal spacing of 7.6 Å, which presents chemical and structural properties adequate for use as an ionic exchanger [1].

Recently [2] the intercalation of n-alkylamine into α-titanium phosphate has been described as a spontaneous process where every amine group of the organic compound reacts with a hydrogen of the solid forming a stable bond. The reaction was carried out by exposing the solid to the vapour of the n-alkylamines, fully saturated materials with formula α-Ti(HOPO$_3$)$_2 \cdot 2$ C$_n$H$_{2n+1}$NH$_2 \cdot$ H$_2$O $(n = 1 - 9)$ being obtained. From the α-TiP behaviour in ion exchange processes [3], the existence of intermediate phases of intercalation before saturation may be expected. Thus, the superficial acid groups would react in the first place. The hydrogens accessible at the surface are very rare since the specific surface area of α-TiP is low ($\approx$ 10m^{2}g^{-1}). Most of the active centers are placed in the interlayer space of the solid. The way of reacting these internal hydrogens will depend on the access of the reactive molecules into the layer. This reaction will give rise to the separation of the phosphate layer followed by the diffusion of the amine molecules.

Several reaction routes may be expected, depending on the ease with which the basal spacing of the lamellar material increases and the diffusion capacity of the amine molecules. If the process of increasing the interlayer distance needs

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low energy, the amine molecules should diffuse into the solid until a homogeneous arrangement is obtained, the interlayer distance being the same for all the materials, hence, the intercalation process will take place with formation of solid solutions. If the separation of the layers is a difficult process, the amine will tend to stabilize the deformed layer before interacting with a new layer and thus different crystalline phases with interlayer distances which are usually different will coexist. Moreover, the small layers of the initial solid will break as a consequence of the intercalation process, giving materials with greater specific surface and a lower degree of crystallinity.

The intercalation of n-alkylamines in α-zirconium phosphate has been studied previously [4, 5]. The titration curves of α-ZrP with short chain (up to C_6) alkylamines have been reported [5]. The process is considered to be a topotactic acid base reaction between a layered acid host and basic guests. The intercalation reactions occur stepwise with the formation of intermediate intercalation compounds before reaching full intercalation. In many cases the first intercalate obtained has an interlayer distance of *ca.* 10.4 Å, consistent with the arrangement of amine having its alkyl chain oriented mainly parallel to the layer.

α-TiP and α-ZrP are isostructural [6, 7]. The a and b parameters of the α-TiP unit cell, which determine the dimensions of the layer, are slightly smaller than those of the α-ZrP. These differences do not affect the composition of the saturated intercalation compounds with the formulae α-M(HOPO$_3$)$_2 \cdot 2\,C_nH_{2n+1}NH_2 \cdot H_2O$ (M = Ti, Zr) since the free area surrounding each phosphate group (24.04 Å^2, α-ZrP; 21.6 Å^2, α-TiP) permits the accommodation of one molecule of amine per phosphate (the cross sectional area of a *trans-trans* alkyl chain has been evaluated to be 18.6 Å^2 [8]). It would be interesting to study the influence of these differences on the composition of the intermediate unsaturated phases.

This work presents a systematic study of the α-titanium phosphate evolution during the intercalation of linear monoamines in aqueous solution.

2. Experimental

2.1. MATERIALS

All chemicals used were of reagent grade. The α-TiP was prepared following the method of Alberti *et al.* [9], using 10M H$_3$PO$_4$ and a reflux time of 50 h. The titanium phosphate gel was prepared by precipitation of a solution of TiCl$_4$ in aqueous HCl with dilute H$_3$PO$_4$ [10]. The crystalline solid was washed with deionized water until free from chloride (test with AgNO$_3$), dried at 50 °C, and was ground to a particle size of less than 0.03 mm.

2.2. INTERCALATION PROCEDURE

The α-TiP was equilibrated during 48 h with aqueous solutions of $C_nH_{2n+1}NH_2$ ($n = 1 - 10, 0.5 - 10.0$ meq n-alkylamine/g α-TiP) at 25.0 $\pm$ 0.1 °C following

the batch method. The solid was present in the solution in an approximate ratio of 1 g : 100 mL. The solids were separated by centrifugation and dried in air at 50 °C.

2.3. ANALYTICAL PROCEDURES

The analysis for phosphorus and titanium in the solids was carried out gravimetrically. The released phosphate groups were measured spectrophotometrically as molybdovanadophosphoric acid using a Perkin–Elmer model 200 instrument. The pH measurements were made with a Orion SA-720 pH meter. Microanalytical data (C, H, N) were obtained with a Perkin–Elmer model 240B elemental analyser. Thermal analysis was performed by a Mettler TA 4000 (TG 50, DSC 30, atmosphere of nitrogen, heating rate 5 °C/min). The diffractometer used was a Philips model PW 1050/23 ($\lambda = 1.5418$Å).

3. Results

3.1. THE α-TiP/METHYLAMINE (MeA) SYSTEM

Figure 1 shows the pH of the equilibrium solutions against the amount of intercalated amine. In the titration curve, it can be observed that the equilibrium pH increases with increasing amount of methylamine in the solid phase. This increase is noticeable until an intercalation of 0.25 mol of amine per mol of titanium (12.5% of the α-TiP intercalation capacity). From this point, the increase is low, being always close to neutrality. X-ray diffraction (XRD) indicates that the methylamine intercalation in α-TiP takes place with formation of materials with low crystallinity. The band of the interlayer distance is broad and it is placed at 13.1 Å (d_{002} of the α-Ti(HOPO$_3$)$_2$·2MeA·H$_2$O phase synthesized by reaction between α-TiP and methylamine in the vapour phase [2]).

3.2. THE α-TiP/ETHYLAMINE (EtA) SYSTEM

The titration curve (Figure 2a) shows two well defined zones. When the intercalation is higher than 0.2 moles EtA/mol Ti, the pH remains constant until the exchanger is saturated. XRD indicates the coexistence of two well differentiated crystalline phases with interlayer distances of 7.6 and 14.3 Å. The intensity of the first reflection must be a direct function of the dihydrogen phase concentration in the solid. The reflection at 14.3 Å corresponds to the phase α-Ti(HOPO$_3$)$_2$·2 EtA·H$_2$O saturated in ethylamine, consistent with the results obtained when the intercalation takes place in the vapour phase. The relative intensity of this reflection with respect to the characteristic interlayer distance of the α-TiP increases in a continuous way with increasing degree of intercalation (Figure 2b).
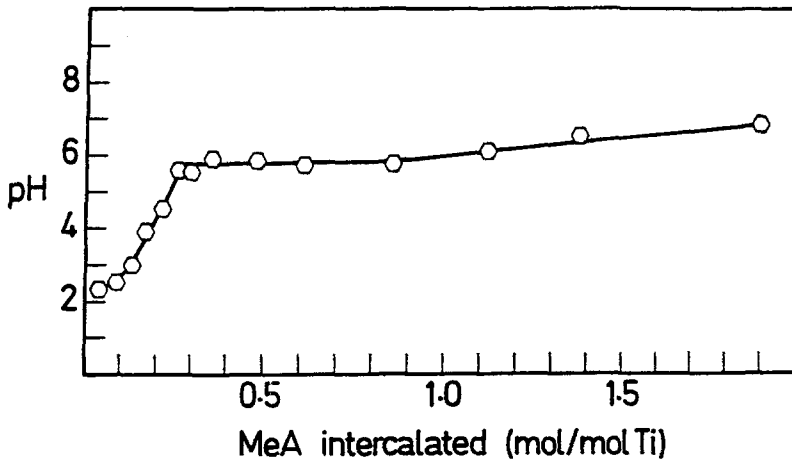
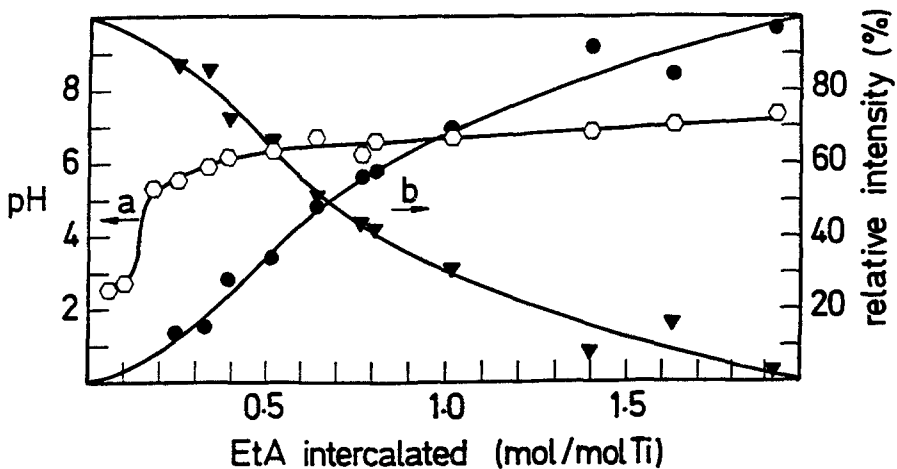Fig. 1. Titration curve of α-TiP with methylamine solution.

Fig. 2. (a) Titration curve of α-TiP with ethylamine solution (◇). (b) Relative intensity of the XRD bands at 7.6 Å (O) and 14.3 Å (●).

3.3 THE α-TiP/n-PROPYLAMINE (PrA) SYSTEM

In the titration curve (Figure 3a) two zones can be distinguished at pH 2–3 and 6–7. Over the entire composition range XRD indicates the simultaneous presence of two interlayer distances (different to the characteristic of the α-TiP) at 15.2 Å and 16.9 Å whose intensity cannot be distinguished because the angles are very close. Figure 3b shows the relative intensity of these reflections with respect to that of α-TiP.

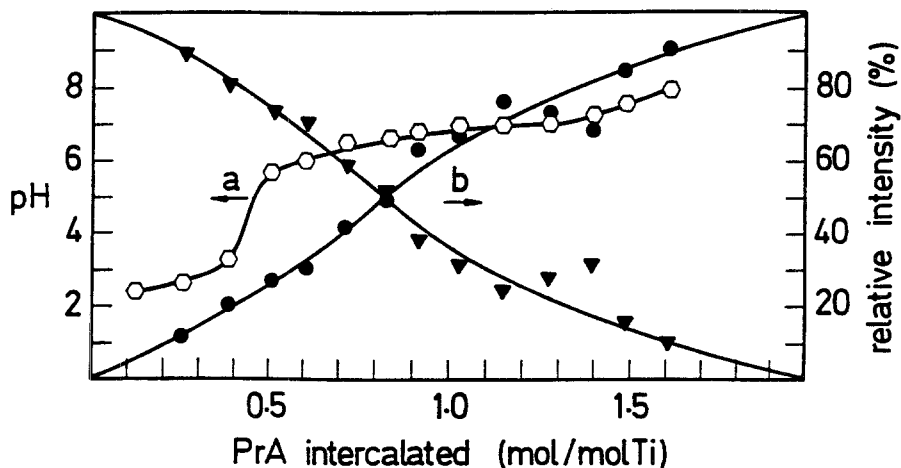When the amount of propylamine intercalated is lower than 0.4 mol PrA/mol

Fig. 3. (a) Titration curve of α-TiP with n-propylamine solution (O). (b) Relative intensity of the XRD bands at 7.6 Å (▼) and 15.2–16.9 Å (●).

Ti the intensity of the reflection at 15.2 Å is higher than that at 16.9 Å. The simultaneous presence of both crystalline phases explains the slight increase of the pH with increasing degree of intercalation. For higher intercalations the reflection at 16.9 Å is more intense than the one at 15.2 Å. The pH is higher and it increases slightly with the degree of conversion.

The intercalation of amine amounts higher than 1.3 mols PrA/mol Ti is more difficult, the equilibrium pH being over 7. The maximum intercalation reached is 1.6 mol PrA/mol Ti. At this point α-TiP is still detected, the relative intensity of its reflection being 10%. The extrapolation of this curve of relative intensity reaches zero when the amount of propylamine intercalated is 2.0 mol PrA/mol Ti, as expected from the results obtained in the vapour phase.

3.4 THE α-TiP/n-BUTYLAMINE (BuA) SYSTEM

The shape of the titration curve (Figure 4a) indicates the absence of differentiated intercalation reactions. When the amount of n-butylamine intercalated is lower than 0.4 mol BuA/mol Ti, the pH increases in a continuous way from values close to 2.0 to 6.5. XRD shows the coexistence of several intercalation phases in variable ratios. The interlayer distance of three of these phases is relatively close (16.5, 17.5 and 18.8 Å) so that its relative intensity is determined together (Figure 4b). Only one of them has been previously characterized since the phase with the highest basal spacing is the intercalation product obtained when the process takes place in the vapour phase. There is a fourth intercalation phase of low intensity ($\approx 5\%$) and with a lower basal spacing (12.4 Å). Thus, the continuous evolution of the pH must be related to the relative ratio of the crystalline solid phases in the solid material.
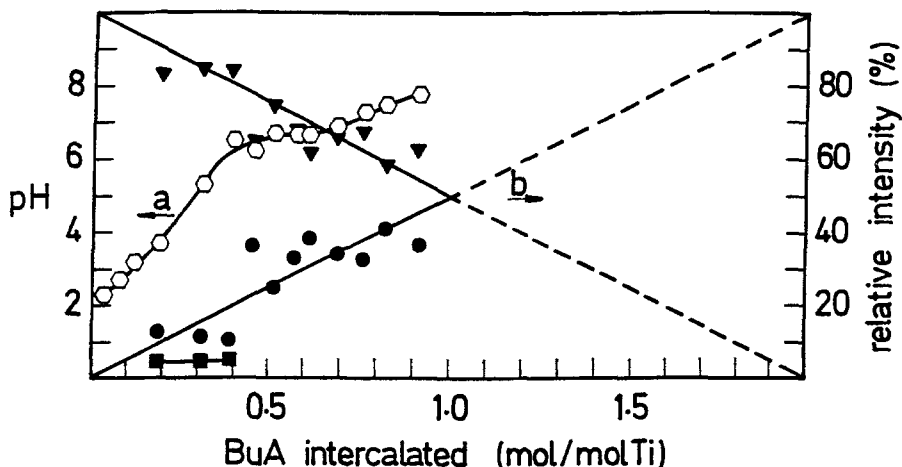
Fig. 4. (a) Titration curve of α-TiP with n-butylamine solution (O). (b) Relative intensity of the XRD bands at 7.6 Å ($\blacktriangledown$), 12.4 Å ($\blacksquare$) and 16.5–18.8 Å ($\bullet$).

3.5   THE α-TiP/n-PENTYLAMINE (PeA) SYSTEM

The shape of the titration curve (Figure 5a) is similar to the one obtained in the n-propylamine intercalation process except that the pH discontinuity from 2.5 to 5.5 is less remarkable so that a more complex intercalation process must be expected. In fact, XRD shows the simultaneous presence of three different intercalation phases with basal spacings of 18.7, 19.8 and 21.1 Å. The phase of the highest interlayer distance is the same as that obtained from the vapour phase and there are also two intermediate phases. The angular proximity of the three intercalation phases makes its quantitative individual determination impossible, hence the relative intensity of the 002 reflections was measured as a whole (Figure 5b). In the intensity of the reflection with the highest interlayer distance an increase with increasing degree of intercalation can be observed.

3.6   THE α-TiP/n-HEXYLAMINE (HeA) SYSTEM

The titration curve shows two plateaus with a pH difference lower than one. The existence of a small pH discontinuity and the slight but continuous increase in the pH value at each step suggests a complicated intercalation process. By XRD, three new crystalline phases are detected with close interlayer distances (19.7, 21.1 and 22.1 Å) in addition to the phase obtained in experiments in the vapour phase (23.1 Å). Moreover, an additional reflection at 14.5 Å is detected in some of the samples. Figure 6b shows the relative intensity of the whole of the reflections with an interlayer distance greater than 19 Å, that of the phase with a basal spacing of 14.5 Å and that of the α-TiP.
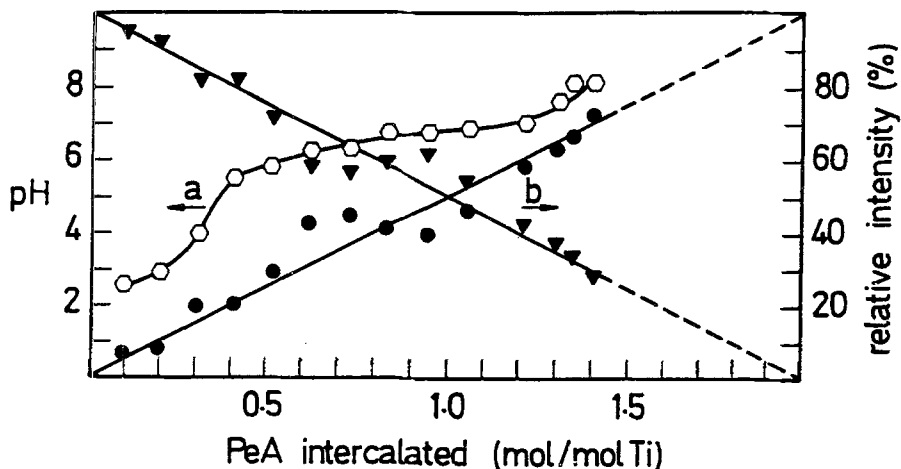
Fig. 5.   (a) Titration curve of α-TiP with n-pentylamine solution (○). (b) Relative intensity of the XRD bands at 7.6 Å (▼) and 18.7–21.1 Å (•).
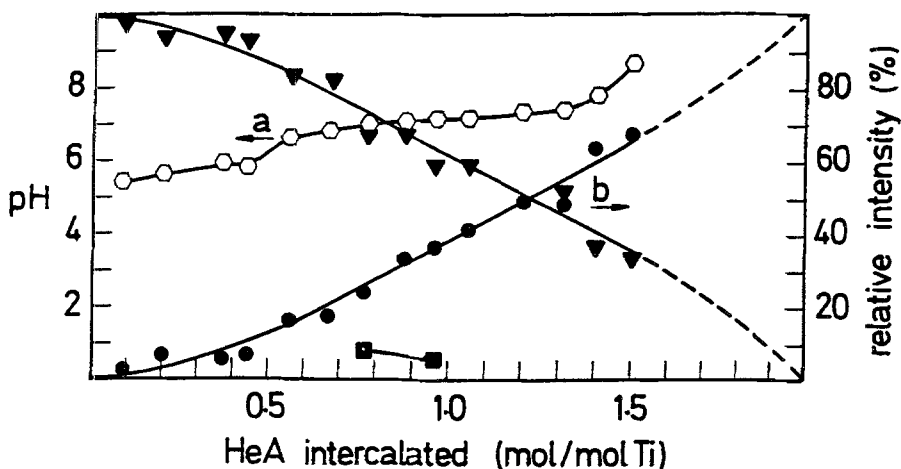

Fig. 6.   (a) Titration curve of α-TiP with n-hexylamine solution (○). (b) Relative intensity of the XRD bands at 7.6 Å (▼), 14.5 Å (■) and 19.7–23.1 Å (•).

3.7   THE α-TiP/n-HEPTYLAMINE (HpA) SYSTEM

The titration curve (Figure 7a) presents remarkable differences compared to those described earlier. The intercalation affects all the acid centers of the α-TiP, due to the existence of three plateaus in which the pH is constant. XRD indicates that the α-TiP concentration decreases in a continuous way (Figure 7b). When the pH is 3.0, the α-TiP coexists with only a crystalline intercalation phase of 21.2 Å interlayer distance. In the plateau at pH = 6.3 the coexistence of two new crystalline phases
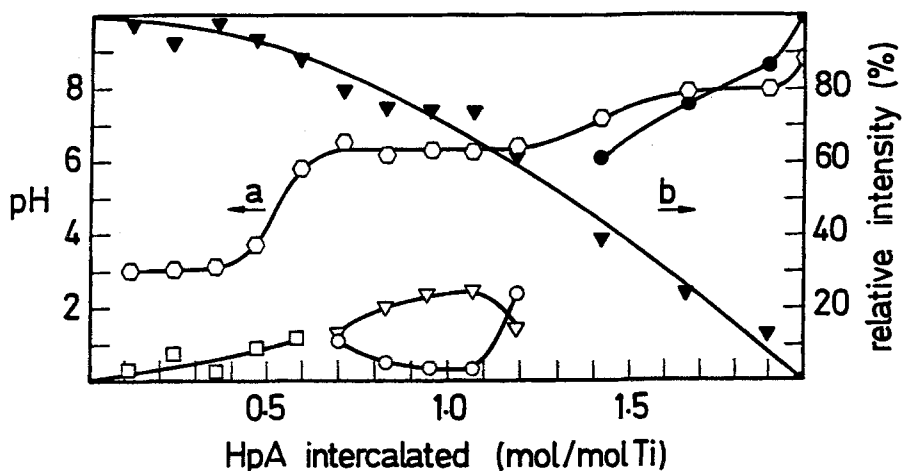
Fig. 7. (a) Titration curve of α-TiP with n-heptylamine solution ($\bigcirc$). (b) Relative intensity of the XRD bands at 7.6 Å ($\triangledown$), 21.2 Å ($\square$), 22.4 Å ($\blacktriangledown$), 23.9 Å ($\circ$) and 25.6 Å ($\bullet$).

with interlayer distances 22.4 and 23.9 Å is observed. When the pH is over 7, the only intercalation phase present has a basal spacing of 25.6 Å according to the intercalation compounds obtained in the vapour phase.

3.8   THE α-TiP/n-OCTYLAMINE (OcA) SYSTEM

The titration curve (Figure 8a) is similar to that of the α-TiP/HpA system. There are also three plateaus at pH 4.0, 5.7 and 7.5. The existence of a phase with a relatively low interlayer distance (17.1 Å) is detected over the entire composition range with a relative intensity of 5% (Figure 8b). The reflections characteristic of α-TiP remain until the material reaches saturation. The behavior is similar to that of n-heptylamine except for the phase with a basal spacing of 17.1 Å. In the plateau at pH = 5.7, the coexistence of two crystalline phases with interlayer distances of 23.1 and 24.4 Å is observed. When the pH values are greater than 7.5, the only intercalation phase present has a basal spacing of 27.8 Å coincident with the intercalation compounds obtained in the vapour phase.

3.9   THE α-TiP/n-NONYLAMINE (NoA) SYSTEM

The intercalation of n-nonylamine is difficult and the material saturation is not reached in the working conditions. The titration curve (Figure 9a) gives limited information about the characteristics of the process. The information comes from XRD. The crystalline phase obtained by intercalation in the vapour state ($d_{002} = 29.9$ Å) is detected from the beginning of the process. Its relative concentration increases with increasing degree of intercalation (Figure 9b) and it later decreases. Another different phase with an interlayer distance of 28.1 Å is also present from the
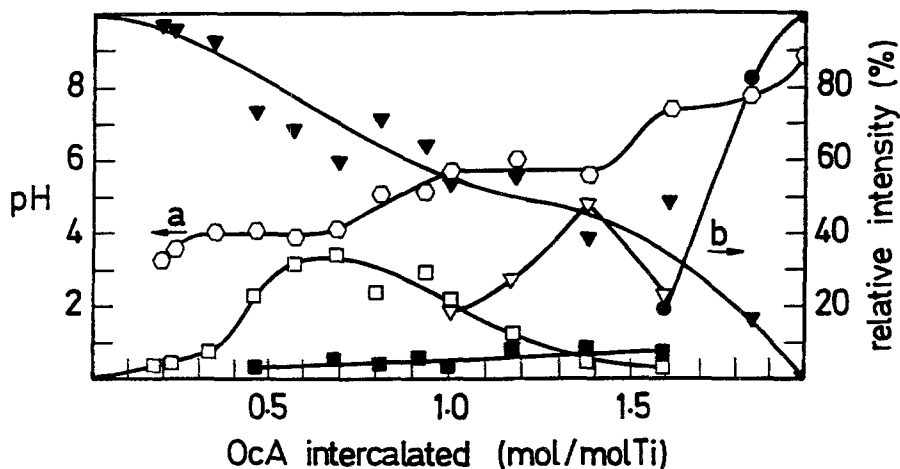
Fig. 8.   (a) Titration curve of α-TiP with *n*-octylamine solution (O). (b) Relative intensity of the XRD bands at 7.6 Å (▽), 17.1 Å (■), 23.1 Å (□), 24.4 Å (▼) and 27.8 Å (•).
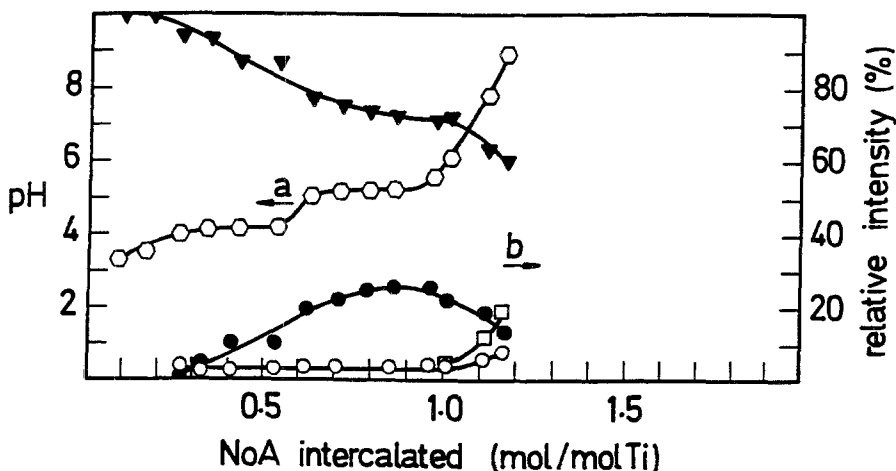

Fig. 9.   (a) Titration curve of α-TiP with *n*-nonylamine solution (O). (b) Relative intensity of the XRD bands at 7.6 Å (▼), 24.4 Å (□), 28.1 Å (o) and 29.9 Å (•).

beginning. Another phase ($d_{002} = 24.4$ Å) appears when the pH abruptly increases which means that it is difficult to reach equilibrium due to the slow diffusion of the large *n*-nonylamine molecule.

3.10   THE α-TiP/*n*-DECLYAMINE (DeA) SYSTEM

As in the previous case, the titration curve (Figure 10a) gives limited information. XRD indicates the formation of solid phases with low crystallinity, two or more
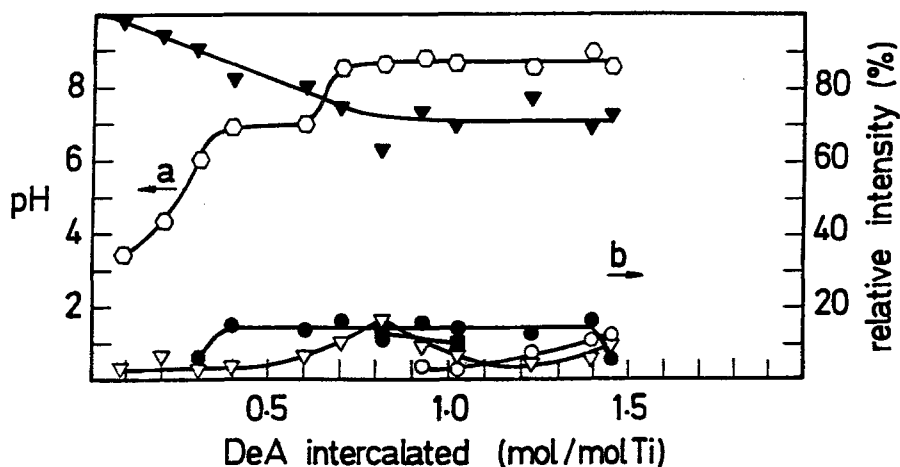
Fig. 10. (a) Titration curve of α-TiP with n-decylamine solution ($\bigcirc$). (b) Relative intensity of the XRD bands at 7.6 Å (∇), 19.5 Å ($\blacksquare$), 27.5 Å ($\blacktriangledown$), 30.3 Å (o) and 32.2 Å ($\bullet$).

phases coexisting over the entire composition range (Figure 10b). The interlayer distance of the saturated intercalation compound (32.2 Å) is only noticeable when the intercalation is higher than 0.3 mol DeA/mol Ti and its relative concentration is maintained approximately constant over the entire composition range. The appearance of a phase with a lower interlayer distance (27.5 Å) was previously observed whose relative intensity also remains constant. Only when the intercalation is higher than 0.9 moles DeA/mol Ti, a phase with $d_{002} = 30.3$ Å appears, whose relative intensity increases in a continuous way with increasing degree of intercalation. Occasionally a reflection is also detected with a low interlayer distance (19.5 Å).

3.11 HYDROLYSIS REACTION

In alkaline medium, α-TiP can lose HPO_4^{2-} groups by hydrolytic attack. Figure 11 shows the hydrolysis degree of the material as a function of the solution pH after the intercalation process (see Figures 1–10). At pH < 7 the hydrolysis is negligable and in alkaline medium increases in a marked way with the increasing pH.

4. Discussion

4.1 ARRANGEMENT OF THE AMINES IN THE SOLID PHASE

Figure 12 shows the interlayer distances of the intercalation phases of the n-alkylamines in α-TiP against the number of the carbon atoms of the intercalated n-alkylamine (A1A). The phases with a higher interlayer distance (Figure 12a) and formula $Ti(HOPO_3)_2 \cdot 2A1A \cdot H_2O$ define a straight line which satisfies Equation (1). Since the increase in the length of an alkyl chain in the *trans–trans* conformation
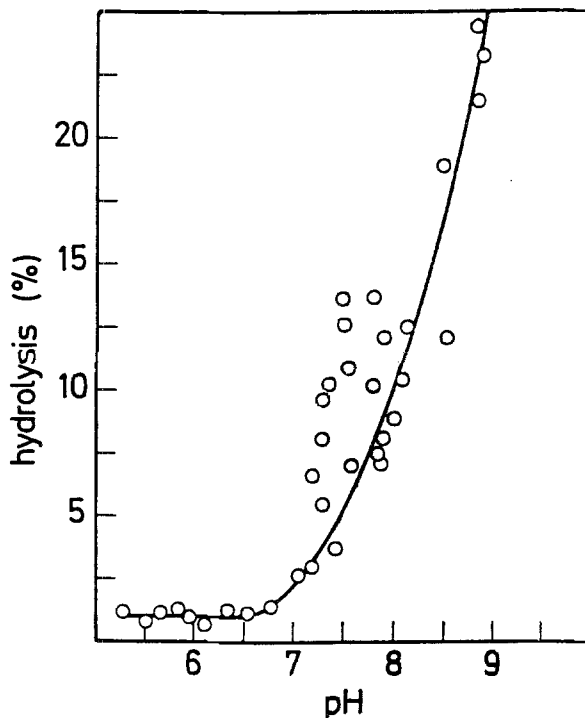
Fig. 11. Hydrolysis curve of layered host.

is 1.27 Å per atom of additional carbon, the amines are present in α-TiP as a bimolecular layer with its axial axis inclined an average of $\alpha = \sin^{-1}(2.18/2.54) = 58.7°$ with respect to the plane of the layer. The increment in the interlayer distance for each additional carbon atom is different if n_C is odd or even [2]. This alternation occurs due to the different position of the terminal -CH$_3$ groups in alkylchains, in a *trans–trans* conformation, having an odd or even number of carbon atoms [11].

$$d_{002} = 10.1 + 2.17n_C \qquad (1)$$
$$d_{002} = 7.8 + 1.05n_C \qquad (2)$$

The phases with a lower interlayer distance (Figure 12e) define the line corresponding to Equation (2). The ordinate in the origin of these lines must be related to overlap of the NH$_3^+$ groups in the surface of the phosphate layer. The difference between both straight lines is due to the different arrangement of the amine molecule, bilayered or monolayered. The value of the slope from Equation (2), 1.05, is close to the increment expected for each carbon atom if the amine molecules are monolayered and placed perpendicularly to the phosphate layer (1.27 Å). In the monolayer arrangement, the average inclination of the amines is $\alpha = \sin^{-1}(1.05/1.27) = 55.8°$, very similar to the one determined in the saturated intercalation compounds (58.7°) and close to the theoretical value assuming that the N–C bond is perpendicular to the phosphate layer (53.8°) [2, 11]. The inclination
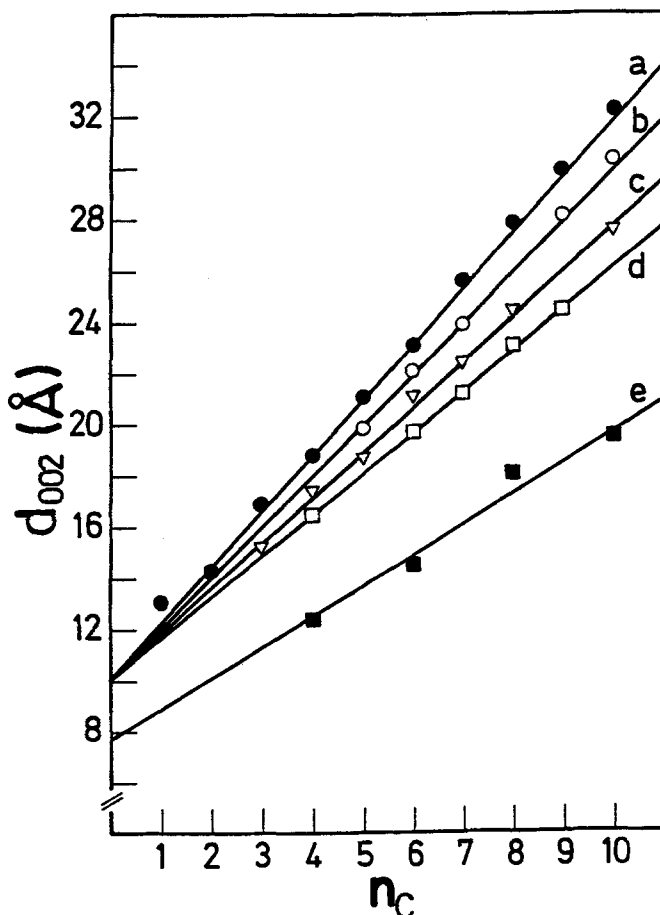
Fig. 12.   Interlayer distances of intercalation compounds of α-TiP with n-alkylamines against the number of carbon atoms in the alkyl chain:
(a) α-Ti(HOPO$_3$)$_2$ · 2 A1A·H$_2$O, (b) α-Ti(HOPO$_3$)$_2$ · z A1A·n H$_2$O,
(c) α-Ti(HOPO$_3$)$_2$ · y A1A·n H$_2$O, (d) α-Ti(HOPO$_3$)$_2$ · x A1A·n H$_2$O,
and (e) α-Ti(HOPO$_3$)$_2$ · w A1A·n H$_2$O.

angle of the amine monolayers leads to the formula α-Ti(HOPO$_3$)$_2$·A1A·nH$_2$O for these compounds. The phases with the monolayer arrangement were only detected in low concentration when the number of the carbon atoms of the n-alkylamine is even. This behaviour must be related to the steric factors which favor the compound stability as a function of the degree of interaction of the alkylamine with the phosphate layer.

The crystalline phases having a composition intermediate between α-Ti(HOPO$_3$)$_2$·2A1A·H$_2$O and α-Ti(HOPO$_3$)$_2$·A1A·nH$_2$O must necessarily present a bilayer arrangement of the amine molecules in the α-TiP interlayer spacing because the saturation of the monolayer arrangement is reached when the interca-

lation is one mole of amine per mol of titanium. Therefore, the inclination angle of the n-alkylamines in every group of the crystalline phases synthesized can be determined.

The plot of the interlayer distances of these phases against the number of carbon atoms of the alkyl chain (Figures 12b–d) gives rise to three new straight lines with an ordinate in the origin of 10.1 (bilayer arrangement) and values of 1.98, 1.77 and 1.61 for the slopes. The inclination angles of the alkyl chains are a function of the composition: α-Ti(HOPO$_3$)$_2\cdot z$A1A$\cdot n$H$_2$O (51.2°), α-Ti(HOPO$_3$)$_2\cdot y$A1A$\cdot n$H$_2$O (44.2°) and α-Ti(HOPO$_3$)$_2\cdot x$A1A$\cdot n$H$_2$O (39.3°) ($z > y > x$). Thermally induced conformation transitions have been observed in the bilayer of long chain alkylamines intercalated into α-ZrP [11]. In a similar way, conformational changes in the alkylchain are possible for the compounds described in this paper for $n_C > 8$.

4.2 PACKING OF THE AMINES IN THE SOLID PHASE

The packing fraction (V_p) of the n-alkylamines in the interlayer region of α-TiP can be determined. If we define V_p as the ratio between the volume occupied by the alkyl chains (V_c) and V_t as the volume available in the interlayer space (Equation (3)), V_t can be calculated by subtracting from the interlayer separation of each intercalation compound (d_{002}) the space occupied by the α-layers, by the molecules of the crystallization water and by the -NH$_3^+$ groups (d'). Referred to 1 cm^2 of layer, V_t is given by Expression (4) so that V_t is expressed in cm^3 if d_{002} and d' are in cm. Assuming that the interpenetration between the -NH$_3^+$ groups and the layer surface is independent of n_C, $d' = d_{002}$ for $n_C = 0$. That means, $d' = 10.1 \times 10^{-8}$ cm for a bilayer arrangement and $d' = 7.8 \times 10^{-8}$ cm for a monolayer arrangement (Equations (1) and (2)).

The volume of an alkyl chain with n_C carbon atoms can be estimated to be $n_C(1.27 \times 10^{-8})(18.6 \times 10^{-16})$ cm^3 [8]. V_c, referred to 1 cm^2 of layer, is given by expression (5) where m takes into account the degree of intercalation (m is the number of mols of intercalated n-alkylamine per mol of titanium) and 4.63×10^{14} is the number of unit formulae per cm^2 of α-TiP layer.

$$V_p = V_c/V_t \tag{3}$$

$$V_t = d_{002} - d' \tag{4}$$

$$V_c = m\, n_c(1.27 \times 10^{-8})(18.6 \times 10^{-16})(4.63 \times 10^{14})\ \text{cm}^3 \tag{5}$$

Table I compiles the packing parameters for the α-Ti(HOPO$_3$)$_2\cdot 2$A1A$\cdot$H$_2$O and α-Ti(HOPO$_3$)$_2\cdot$A1A$\cdot n$H$_2$O compounds. In every case a value very close to unity is obtained which means that the packing density is very close to that of the crystalline n-paraffins.

TABLE I

Packing parameters of the compounds with the formula
α-Ti(HOPO$_3$)$_2 \cdot m$A1A$\cdot n$H$_2$O ($m = 1, 2$).

Intercalated amine	α-Ti(HOPO$_3$)$_2 \cdot 2$A1A$\cdot$H$_2$O	α-Ti(HOPO$_3$)$_2 \cdot$A1A$\cdot n$H$_2$O
n-Ethylamine	1.04	—
n-Propylamine	0.96	—
n-Butylamine	1.01	0.95
n-Pentylamine	0.99	—
n-Hexylamine	1.01	0.98
n-Heptylamine	0.99	—
n-Octylamine	0.99	0.95
n-Nonylamine	0.99	—
n-Decylamine	0.99	0.93

TABLE II

Composition of the α-Ti(HOPO$_3$)$_2 \cdot m$A1A$\cdot n$H$_2$O ($1 < m < 2$)
phases assuming that $V_p = 0.90 - 1.00$.

Intercalation compound	Amine intercalated amount
α-Ti(HOPO$_3$)$_2 \cdot x$A1A$\cdot n$ H$_2$O	$x = 1.32 - 1.47$
α-Ti(HOPO$_3$)$_2 \cdot y$A1A$\cdot n$ H$_2$O	$y = 1.46 - 1.62$
α-Ti(HOPO$_3$)$_2 \cdot z$A1A$\cdot n$ H$_2$O	$z = 1.63 - 1.81$

4.3 COMPOSITION OF THE INTERMEDIATE PHASES

The phases with composition α-Ti(HOPO$_3$)$_2 \cdot m$A1A$\cdot n$H$_2$O ($1 < m < 2$) could
not be isolated so that the composition cannot be determined experimentally. An
estimation of the m value can be obtained if we assume that the packing parameter
(V_p) in that phase takes values from 0.90 to 1.00. This agrees with the *space filling*
postulate [12] according to which *the most probable arrangement should be that
in which the most economical use is made of the interlayer space* and with the data
obtained in this paper (Table I) for the characterized phases. Table II shows the
compositions of the intermediate phases according to the earlier discussion. Table
III lists the interlayer distances of intercalation compounds obtained in aqueous
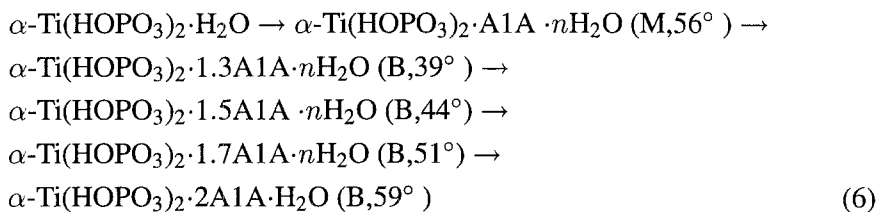solution.

TABLE III

Interlayer distances (in Å) for α-Ti(HOPO$_3$)$_2 \cdot x$A1A$\cdot y$ H$_2$O compounds.

Interlated amine	$x = 1.0$	$x = 1.3$	$x = 1.5$	$x = 1.7$	$x = 2.0$
Methylamine	—	—	—	—	13.1
Ethylamine	—	—	—	—	14.3
Propylamine	—	—	15.2	—	16.9
Butylamine	12.4	16.5	17.5	—	18.8
Pentylamine	—	—	18.7	19.8	21.1
Hexylamine	14.5	19.7	21.1	22.1	23.1
Heptylamine	—	21.2	22.4	23.9	25.6
Octylamine	17.1	23.1	24.4	—	27.8
Nonylamine	—	24.4	—	28.1	29.9
Decylamine	19.5	—	27.5	30.3	32.2

5. Conclusions

In some cases (PrA, BuA, PeA, HeA, NoA, DeA), the pure fully intercalated phases in aqueous solutions cannot be obtained and the data of compositions and interlayer distances are those obtained from gas adsorption. In the saturated compounds the amines form a bilayer in which the carbon chains incline at roughly 59° to the titanium phosphate layers. At lower amine contents the amine rearranges to yield phases with lower interlayer spacings. Scheme (6) proposes a general mechanism of intercalation indicating the arrangement of the amines (M, monolamellar; B, bilamellar) and the average inclination angle of the alkyl chains.

$$\alpha\text{-Ti(HOPO}_3)_2 \cdot \text{H}_2\text{O} \rightarrow \alpha\text{-Ti(HOPO}_3)_2 \cdot \text{A1A} \cdot n\text{H}_2\text{O (M,56}°) \rightarrow$$
$$\alpha\text{-Ti(HOPO}_3)_2 \cdot 1.3\text{A1A} \cdot n\text{H}_2\text{O (B,39}°) \rightarrow$$
$$\alpha\text{-Ti(HOPO}_3)_2 \cdot 1.5\text{A1A} \cdot n\text{H}_2\text{O (B,44}°) \rightarrow$$
$$\alpha\text{-Ti(HOPO}_3)_2 \cdot 1.7\text{A1A} \cdot n\text{H}_2\text{O (B,51}°) \rightarrow$$
$$\alpha\text{-Ti(HOPO}_3)_2 \cdot 2\text{A1A} \cdot \text{H}_2\text{O (B,59}°) \tag{6}$$

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