

Synthesis of New *n*-Alkylamines Intercalation Compounds with α -Titanium Phosphate. Process Selectivity and Structural and Morphological Characterization

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The simultaneous intercalation of two or more *n*-alkylamines into α -titanium phosphate, $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, has been investigated. The intercalation of large *n*-alkylamine molecules has been observed to be faster if there is a shorter alkyl chain amine, acting as a catalyst, yielding at completion single amine intercalates. New individual intercalation phases containing two different amines are obtained. In the case of a vapor mixture of several amines ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$, $n = 2-8$), the compound obtained depends on the reaction time, providing selectivity. The morphology and crystallinity of the prepared materials are very sensitive to the preparation route. All synthesized phases showed monoclinic symmetry.

Introduction

In addition to their possible use as molecular sieves, the metal(IV) phosphate/*n*-alkylamine intercalation materials seem to be useful as precursors in pillaring reactions owing to their stability in aqueous medium, suitable interlayer distance, and moderate affinity of the intercalated species toward the active centers¹⁻³ of the host. For this reason, both the structure and the morphology of these materials should be considered.

The intercalation of *n*-alkylamines in the vapor phase into α -titanium phosphate (α -TiP) is a spontaneous process where each amino group of the organic compound interacts with one hydrogen of the phosphate group, giving a stable bonding.⁴ The final reaction product is a saturated phase; the intercalation occupies all solid active centers, meaning that 2 mol of amine are intercalated per 1 mol of α -TiP.⁵ The process rate decreases when the length of the amine alkyl chain increases. In this way, the methylamine-saturated intercalate can be prepared in 6 h; on the other hand, the *n*-hexylamine intercalate needs 1 month of reaction time to be fully saturated. Thus, the intercalation of long-chain amines is a very time demanding process. However, the study of more complicate systems provides the synthesis of new mixed intercalation phases. The literature describes a catalytic effect in the ion-exchange

of large cations over α -TiP when low concentrations of small cations (e.g. Na^+) are present in the reaction media.⁶ Moreover, α and γ -titanium phosphates show the possibility of selective uptake in ion-exchange processes.⁷⁻¹¹ The coexistence of a short-chain amine with a larger one should favor the intercalation kinetics (a small amine can reduce the activation energy for the intercalation of a large one by opening the phosphate layers). The initial main aim of this work was to decrease the saturation time by the simultaneous intercalation of two differently sized molecules. In the same way, the selectivity of amines intercalation over α -TiP crystals is also described in this paper.

Experimental Section

Materials. All chemicals were of reagent grade (Aldrich) and used without further purification. α -TiP was prepared as previously reported.¹² The crystalline solid obtained was washed with water until all chloride was eliminated (AgNO_3 test), dried at 50 °C, and ground to a particle size of less than 0.03 mm.¹³

Intercalation Procedure. Intercalation compounds were obtained by placing α -TiP in an atmosphere saturated with amine vapors at room temperature. The time necessary to

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Table 1. Contact Time, Interlayer Distance, Microanalytical Data (C and N), Weight Loss (TG data), and Proposed Composition of the Intercalation Compounds Obtained by Solid–Vapor Contact

intercalated amines	contact time	$d_{002}/\text{\AA}$	% C	% N	% weight loss	composition
ethylamine/propylamine	2 h	15.1	14.59	6.87	39.31	Ti(HPO ₄) ₂ ·EtA·PropA·H ₂ O
	18 h	16.1	18.19	8.05	40.15	Ti(HPO ₄) ₂ ·0.7EtA·1.3PropA·H ₂ O
ethylamine/ <i>n</i> -butylamine	8 h	18.8	22.42	7.01	27.25	Ti(HPO ₄) ₂ ·2ButA·H ₂ O
ethylamine/ <i>n</i> -pentylamine	6 h	20.3	24.13	7.73	43.12	Ti(HPO ₄) ₂ ·EtA·PentA·H ₂ O
propylamine/ <i>n</i> -hexylamine	5 days	20.6	25.61	6.27	47.91	Ti(HPO ₄) ₂ ·PropA·HexA·H ₂ O
	8 days	23.1	30.36	5.98	52.12	Ti(HPO ₄) ₂ ·2HexA·H ₂ O
<i>n</i> -butylamine/ <i>n</i> -octylamine	18 days	24.3	30.50	6.19	56.59	Ti(HPO ₄) ₂ ·ButA·OctA·H ₂ O

reach saturation is a function of the amines alkyl chain length (as well as the particle size, degree of crystallinity, vapor pressure, and temperature). The solids obtained were dried at 50 °C and stored in a desiccator over a solution of 50% H₂-SO₄.

Analytical Procedures. The diffractometer used was a Philips model PW 1729/1720 with Cu K α radiation. Thermal analysis was performed with a Mettler TA model 4000 (TG 50, DSC 30, under nitrogen, heating rate 5 °C min⁻¹). The phosphorus and titanium content in the solids was determined by using a SpectraSpec spectrometer DCP-AEC after dissolving a weighted amount of sample in HF(aq). Microanalytical data (C, N) were obtained with a Perkin-Elmer model 240B elemental analyzer. Electron micrographs were recorded with a JEOL JSM-6100 scanning electron microscope operating at 20 kV.

Results and Discussion

Ethylamine/*n*-Propylamine System. When α -TiP is submitted to react with an atmosphere saturated with ethyl- and *n*-propylamine vapors from 2 to 48 h, simultaneous intercalation of both guests takes place. The interlayer distance of the intercalates is in the range of the single-phase intercalates (intercalation phases of 14.3 Å for ethylamine and 16.9 Å for *n*-propylamine). First, a phase having a 15.1 Å interlayer distance, containing an equivalent amount of ethyl- and *n*-propylamine (elemental and thermogravimetric analyses, Table 1) is observed. Then, after 48 h of contact time, an intercalation compound showing a *d* spacing of 16.1 Å is obtained and the ratio of intercalated *n*-propylamine increases (Table 1). Figure 1b,c shows XRD patterns of the evolution as a function of the contact time.

Ethylamine/*n*-Butylamine System. The *n*-butylamine intercalation into α -TiP layers gives rise to saturated material after 10 days of solid–vapor contact time.⁵ Nevertheless, if α -TiP is placed in contact with both ethyl- and *n*-butylamine vapors, the *n*-butylamine-saturated phase is achieved in only 8 h (Figure 1d, Table 1). Longer contact time (e.g. 2 days) is not desirable, because the lamellar nature of the solid is lost, due to the acid–base reaction yielding an amorphous gel.

Ethylamine/*n*-Pentylamine System. After 6 h the intercalation process provides a solid having an interlayer distance of 20.3 Å (Figure 1e), which is slightly lower than that observed for the α -TiP/*n*-pentylamine intercalation compound (21.1 Å). Chemical analyses (Table 1) indicates that both guests are present in the solid in a molar ratio 1:1. As for the above case, if the contact time is increased to 1 day, the material recovered is an amorphous gel.

Ethylamine/*n*-Hexylamine System. When α -TiP reacts simultaneously with ethyl- and *n*-hexylamine vapors for 2 days, a novel intercalate, *d* = 18.5 Å, is obtained (Figure 1f). The basal spacing of this material

is the average between the α -TiP/ethylamine (14.3 Å) and α -TiP/*n*-hexylamine (23.1 Å) values. The XRD pattern of the intercalate also shows the 14.3 Å reflection, corresponding to the pure ethylamine intercalation compound. The arrangement of the amines within the interlayer region seems to be a mixed bilayer of ethylamine/*n*-hexylamine extended molecules. When the intercalation time increases to 5 days, the XRD pattern of the solid obtained is quite different. In this case, three reflections at 23.1, 14.3, and 10.6 Å can be seen from Figure 1g. The first two peaks correspond respectively with α -TiP/*n*-hexylamine and α -TiP/ethylamine intercalation compounds. The third reflection can be associated with an arrangement of the amine molecules parallel to the phosphate layer.¹⁴ If the reaction is allowed to proceed, amorphous gels are readily obtained.

Ethylamine/*n*-Heptylamine System. The XRD pattern of the intercalation compound obtained after 18 h shows, as in the previous case, three signals (Figure 1h): 25.6 Å (α -TiP/*n*-heptylamine), 14.3 Å (α -TiP/ethylamine), and the last one at 10.6 Å, as for the above system. Within 5 days of interaction, the signal at 25.6 Å disappears and the reflection at 14.3 Å lost intensity. Simultaneously, the intensity of the reflection at 10.1 Å increases (Figure 1i). Due to the high molecular size difference of the guests, it is probably difficult to arrange the molecules in a bilayered position. Moreover, this kind of position should imply low space occupancy. Hence, the process can take place by forming either simple guest intercalation compounds or solid solutions of both amines, in a parallel arrangement to the inorganic layer. For longer reaction times, the α -TiP/*n*-heptylamine intercalate tended to disappear as ethylamine molecules began to diffuse in the interlayer region. In the same way, *n*-heptylamine molecules also diffuse into the α -TiP/ethylamine intercalation compound, but at a lower rate. The tendency to distribute statistically provides higher intensity of the signal of the 10.6 Å phase.

Ethylamine/*n*-Octylamine and Ethylamine/*n*-Decylamine Systems. Ethylamine intercalation into α -TiP layers takes place in a short time (less than 12 h). However, when the process occurs in the presence of *n*-octyl- or *n*-decylamine, the reaction time takes 2 days. This behavior can be explained by assuming that the amines having a long alkyl chain can block the cavity entrances, preventing the diffusion of the short-chain amines. Even so, a few number of entrances remain available for slow ethylamine diffusion, increasing the saturation time. XRD patterns of solids obtained with these systems present sharper and narrower peaks than those obtained for systems with smaller

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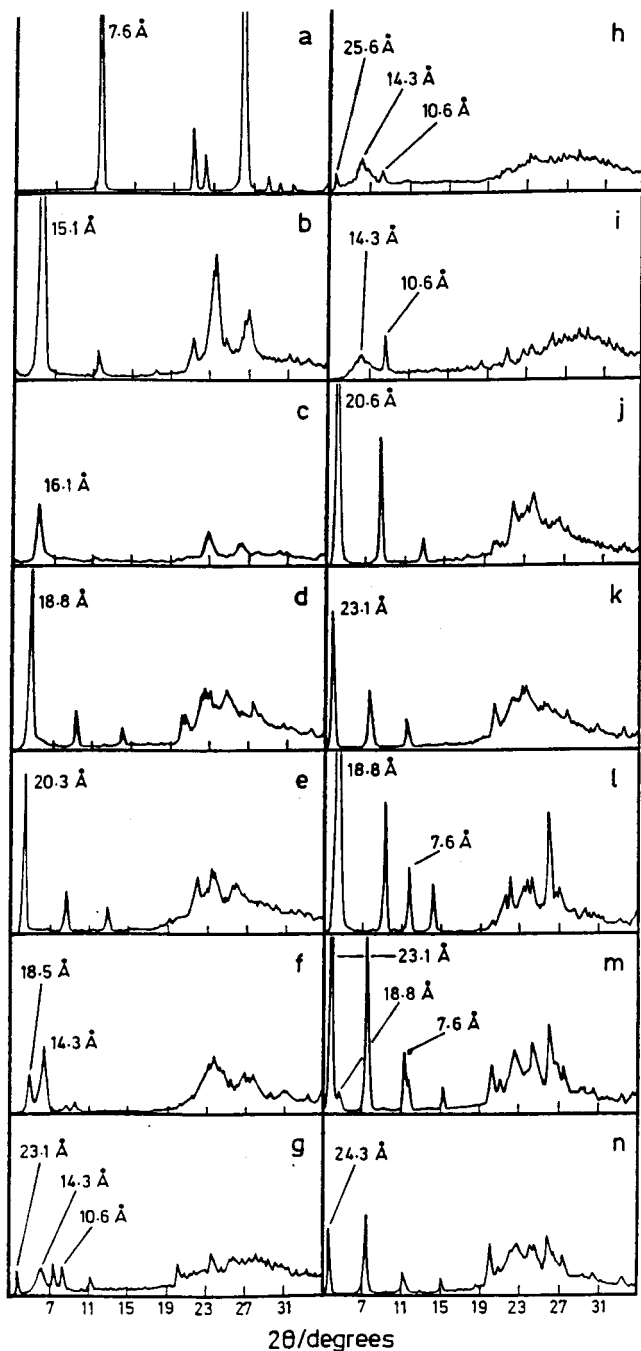


Figure 1. Powder XRD patterns of the samples obtained by contact of α -TiP (a) with ethylamine/propylamine for 2 h (b), ethylamine/propylamine for 18 h (c), ethylamine/*n*-butylamine for 8 h (d), ethylamine/*n*-pentylamine for 6 h (e), ethylamine/*n*-hexylamine for 2 days (f), ethylamine/*n*-hexylamine for 5 days (g), ethylamine/*n*-heptylamine for 18 h (h), ethylamine/*n*-heptylamine for 5 days (i), propylamine/*n*-hexylamine for 5 days (j), propylamine/*n*-hexylamine for 8 days (k), *n*-butylamine/*n*-octylamine for 2 days (l), *n*-butylamine/*n*-octylamine for 6 days (m), and *n*-butylamine/*n*-octylamine for 18 days (n).

difference between the alkyl chain of the amines. The higher crystallinity can be due to the slower opening of the layers, because the access of ethylamine molecule is slower and the molecules can be arranged more orderly.

***n*-Propylamine/*n*-Hexylamine System.** The intercalation compounds obtained when α -TiP reacts with *n*-propyl- and *n*-hexylamine vapor had a great dependence on the reaction time. For less than 5 days, a

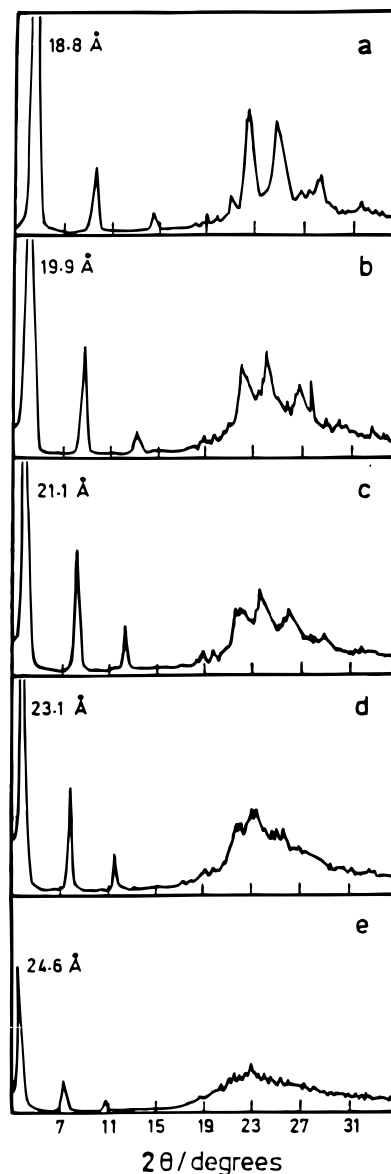


Figure 2. Powder XRD patterns of the samples obtained by contact of α -TiP with a mixture of different amines ($C_nH_{2n+1}NH_2$, $n = 2-8$) for 6 h (a), 1 day (b), 5 days (c), 12 days (d), and 30 days (e).

phase having an interlayer distance of 20.6 Å (Figure 1j), which is the approximate average value of each single guest intercalation compound into α -TiP that has been obtained. In this case the intercalation process affects all host acid centers (2 mol of amine/mol of Ti). Elemental and TG analyses determine that the molar ratio of amines in the solid is 1:1 (Table 1). For longer contact time (8 days), the longer chain amine is exclusively intercalated (Figure 1k, Table 1). It is significant to point out that *n*-hexylamine intercalation into α -TiP takes place in 20 days;⁵ nevertheless, when the process is carried out in the presence of *n*-propylamine, the reaction time is reduced to 8 days.

***n*-Butylamine/*n*-Octylamine System.** When the reaction time is 2 days, the exclusive intercalation of *n*-butylamine molecules is observed. The XRD pattern also shows some host layers that were not intercalated (Figure 1l, Table 1). After 6 days the process provides an intercalate of higher interlayer distance (23.1 Å), coexisting with a small amount of both α -TiP (7.6 Å)

Table 2. Contact Time, Interlayer Distance, Microanalytical Data (C and N), Weight Loss (TG data), and Proposed Composition of the Intercalation Compounds Obtained by Solid–Vapor Contact between α -TiP and a Mixture of *n*-alkylamine Vapors ($C_nH_{2n+1}NH_2$, $n = 2-8$)

contact time	$d_{002}/\text{\AA}$	% C	% N	% weight loss	composition
6 h	18.8	23.12	6.48	45.33	Ti(HPO ₄) ₂ ·2ButA·H ₂ O
1 day	19.9	25.62	6.93	47.78	Ti(HPO ₄) ₂ ·ButA·PentA·H ₂ O
5 days	21.1	27.78	6.02	49.59	Ti(HPO ₄) ₂ ·2PentA·H ₂ O
12 days	23.1	30.35	5.92	51.96	Ti(HPO ₄) ₂ ·2HexA·H ₂ O
24 days	23.1	31.02	6.03	52.75	Ti(HPO ₄) ₂ ·2HexA·H ₂ O
30 days	24.6	32.78	6.12	53.42	Ti(HPO ₄) ₂ ·HexA·HepA·H ₂ O

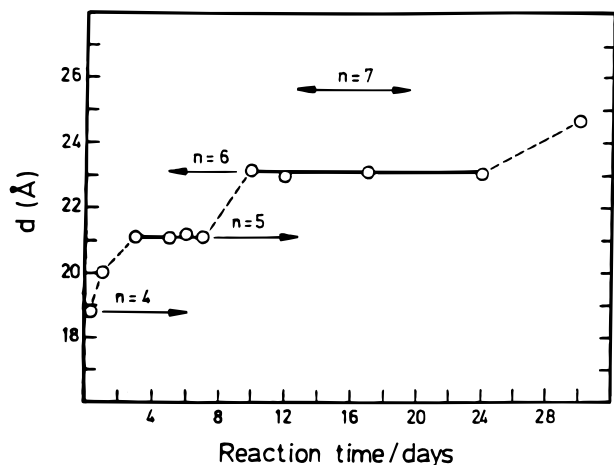


Figure 3. Interlayer distance of α -TiP/*n*-alkylamines ($C_nH_{2n+1}NH_2$, $n = 2-8$) intercalation compounds as a function of the reaction time.

and α -TiP/*n*-butylamine (18.8 Å) compounds (Figure 1m). Later on, the XRD pattern of the solid obtained after 18 days shows a sole phase of 24.3 Å (Figure 1n). This value is exactly the arithmetical average of single amine intercalates.⁵ Hence, the amines are arranged in a bimolecular mixed position (Table 1).

System $C_nH_{2n+1}NH_2$ ($n = 2-8$). When α -TiP is placed in contact with a mixture of vapors of ethyl-, propyl-, *n*-butyl-, *n*-pentyl-, *n*-hexyl-, *n*-heptyl- and *n*-octylamine, the composition of the intercalation compounds obtained is greatly dependent on the reaction time. After 6 h the process provides the sole intercalation of *n*-butylamine (Figure 2a); after 1 day, an intercalate containing both *n*-butyl- and *n*-pentylamine is obtained (Table 2, Figure 2b), showing a *d* spacing which is the average value of the single amine intercalation phases. Longer contact times (3–7 days) lead to pure α -TiP/*n*-pentylamine intercalation compound (Table 2, Figure 2c). In the reaction time range 8–10 days, *n*-pentylamine is really replaced by *n*-hexylamine, until the pure *n*-hexylamine intercalate is reached (Table 2, Figure 2d). Finally, after 30 days, a mixed intercalate containing *n*-hexyl- and *n*-heptylamine is ready (Table 2, Figure 2e). The intercalation of *n*-octylamine was not detected in the studied reaction time. Figure 3 shows the α -TiP basal spacing evolution as a function of the contact time. The overall process takes place in a stepwise manner, alternating relatively large periods of stable single phases with evolution stages which are longer as the alkyl chain of the involved amines increases in size.

Structural Data of Intercalation Compounds. The intercalation compounds described in this work are of poor crystallinity (Figures 1 and 2). Hence, structural information cannot be obtained from the powder XRD

Table 3. Unit Cell Parameters of α -ZrP and Some of Its Ion Exchange Phases

compound	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	β /deg
Zr(HPO ₄) ₂ ·H ₂ O ¹⁵	9.060(2)	5.297(1)	15.414(3)	101.71(2)
ZrKH(PO ₄) ₂ ¹⁷	9.2208(7)	5.3280(4)	16.6336(17)	114.351(11)
ZrNaH(PO ₄) ₂ ·H ₂ O ¹⁸	8.8264(2)	5.3494(1)	16.0275(6)	101.857(4)

patterns of these materials by using conventional methods of indexing.

Structural data of some hydrogen and ion-exchange phases of α -titanium phosphate type materials are described in the literature.^{15–18} As can be seen in Table 3, the unit cell parameters associated with the structure of the layer (*a* and *b*) are similar in the starting material and the ion-exchange phases, changing the parameters associated to the shifting of the interlayer distance and the relative position of the metal(IV) phosphate layers (*c* and β). Although the structural behavior of the intercalation compounds should be expected to be the same as that of the ion exchange phases, this assumption must be checked out.

Assuming that the intercalation compounds presumably have monoclinic symmetry, the *a* and *b* parameters of the unit cell will be the same as that of the α -TiP. Thus, if the values of the independent parameters *c* and β are known, it will be possible to index the powder XRD patterns of these compounds; however this is not so easy to perform.

As an alternative, for α -titanium phosphate type materials, an approximate method for performing the indexing in a monoclinic base through an orthorhombic cell has been described.¹⁹ The following relationships are established among the interlayer distance (d_{002}), the reticular parameters, and the *hkl* index: $a_0 = a_m$, $b_0 = b_m$, $c_0 = 6d_{002}$, $h_0 = h_m$, $k_0 = k_m$, $l_0 = 2h_m + 3l_m$. Table 4 lists the powder XRD data of the α -TiP, the results obtained from its indexing in a monoclinic base,²⁰ and the comparison with the data obtained from the “orthorhombic formalism”.¹⁹ The agreement obtained is excellent. This result encouraged us to apply this formalism to the present intercalation phases.

Table 5 compiles both the *hkl* planes of α -TiP whose relative intensity surpasses 70% and the predictable value of *d* for each of them, taking into account the above assessments. The values of d_{002} , d_{112} , and d_{20-4} increases when the basal spacing of the intercalation

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Table 4. Powder XRD Data for α -TiP

monoclinic ²⁰			orthorhombic	
<i>h k l</i>	$d_{\text{calc}}/\text{\AA}$	$d_{\text{obs}}/\text{\AA}$	<i>h k l</i>	$d_{\text{calc}}/\text{\AA}$
0 0 2	7.569	7.604	0 0 6	7.604
1 1 0	4.258	4.261	1 1 2	4.254
2 0 -2	4.231	4.232	2 0 -2	4.240
1 1 -2	4.041	4.046	1 1 -4	4.048
1 1 2	3.457	3.457	1 1 8	3.449
2 0 -4	3.422	3.422	2 0 -8	3.441
2 1 0	3.149	3.150	2 1 4	3.142
0 1 4	3.026	3.026	0 1 12	3.028
3 0 -2	2.877	2.876	3 0 0	2.877
1 1 4	2.609	2.611	1 1 14	2.604
2 0 -6	2.586	2.585	2 0 -14	2.601
0 0 6	2.532	2.533	0 0 18	2.535
0 2 0	2.503	2.503	0 2 0	2.503
3 1 -2	2.494	2.494	3 1 0	2.494
2 0 4	2.389	2.390	2 0 16	2.379
1 1 -6	2.374	2.374	1 1 -16	2.382
0 2 3	2.244	2.244	0 2 9	2.244
3 1 1	2.246	2.244	3 1 9	2.243
2 1 4	2.156	2.157	2 1 16	2.149
1 1 6	2.021	2.022	1 1 20	2.018
2 2 -4	2.020	2.022	2 2 -8	2.021
4 0 0	2.025	2.022	4 0 8	2.021

phase increases. However, the values of d_{020} and d_{31-2} remain constant (index $hk0$ in the orthorhombic cell). An acceptable accordance with the experimental data is observed. Therefore, it can be concluded that the intercalation of *n*-alkylamines in α -TiP leads to phases of monoclinic symmetry in which the inorganic portion of the structure does not alter significantly in relation with the starting material.

Reaction Mechanism. The final intercalation compound obtained from vapor mixtures of a couple of amines into α -TiP depends on two factors concerning the alkyl chain of the amine: its relative length and whether there is an odd or even number of carbon atoms. The alkyl chain length has influence on both the reaction kinetics and thermodynamics. The shorter the chain, the faster the diffusion, and intercalation takes place quickly. Nevertheless, thermodynamically, the compounds obtained having longer alkyl chain are more stable (assuming that the energy of the interaction of P-OH and R-NH₂ groups is alike); thus, stability is mostly related to the hydrophobic interaction between the alkyl chains. Ethylamine intercalation together with similarly sized amines, e.g. propylamine, gives rise to mixed intercalates, but time favors intercalation of longer chain amines. This tendency is even stronger for the system ethylamine/*n*-butylamine, because only the longer chain amine remains intercalated. Therefore, ethylamine acts as a catalyst, opening the layers to assist the intercalation of the longer amine. This

situation changes radically when ethylamine is submitted to react with the host together with longer chain amines. The diffusion capacity of long-chain amines is comparatively lower than short ones; thus, only external solid acid centers are reached. Long chain amines are anchored to the host interlamellar, most external acid centers blocking the ethylamine molecules entrance. The catalytic activity of the short molecule is not observed in this case, because the expansion of the host interlamellar space is not high enough to allow the bigger amine to diffuse. The process provides an ethylamine intercalate, but at longer time than for ethylamine vapor alone. On the other hand, the presence of the long-chain amine vapor prevents disordered intercalation, resulting in highly crystalline intercalates, impossible to prepare directly. When ethylamine reacts with the layered phosphate in the presence of medium-sized amines (*n*-pentyl-, *n*-hexyl-, and *n*-heptylamine) the situation is intermediate to the earlier described ones. These amines have good diffusivity into the α -TiP layers not blocking the plate entrances; however, they show lower mobility. The ethylamine effect over the phosphate fails in low crystallinity materials. Such effect takes place faster the shorter the alkyl chain of the competitive amine (*n*-pentylamine, 1 day; *n*-hexylamine, 7 days) is, or as in the *n*-heptylamine case, mixed amine intercalates having both amines arranged in parallel to the phosphate layer are formed. This catalytic behavior is also observed in the propylamine/*n*-hexylamine and *n*-butylamine/*n*-octylamine systems. In the first case, the final product of the reaction is the *n*-hexylamine intercalate (which is the thermodynamic, stable compound). Intermediate mixed intercalates are obtained with shorter contact time, as a consequence of the propylamine's higher diffusivity. In the *n*-butylamine/*n*-octylamine case, the kinetic phase, *n*-butylamine intercalate, is first obtained. Then, although increasing the contact time favors synthesis of the mixed materials, *n*-butylamine shows a catalytic effect over *n*-octylamine and single *n*-octylamine intercalation compound is obtained.

Mixed intercalates showing an amine molar ratio of 1:1 are synthesized when the difference in chain length is not too great (2-5, 2-6, 3-6, and 4-8). The interlayer distance of these materials is half of the basal spacing of the single amine intercalates (in some cases exactly the middle value). The interlayer distance of these mixed intercalates depends on, besides the length of the alkyl chains, the tail to tail interaction of the molecules arranged in a bilayered disposition. In this way, if both amines have an even-even or odd-odd

Table 5. Powder XRD Data (in \AA) for the Ti(HPO₄)₂·Amine(s)·H₂O Compounds

amine(s)	0 0 2		1 1 2		2 0 -4		0 2 0		3 1 -2	
	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}
EtA·PropA	15.1	15.1	4.04	4.07	4.03	3.99	2.50	2.54	2.49	2.51
0.7EtA·1.3PropA	16.1	16.1	4.08	4.03	4.06	4.00	2.50	2.55	2.49	2.50
2ButA	18.8	18.8	4.14	4.11	4.13	4.11	2.50	2.56	2.49	2.51
ButA·PentA	19.9	19.9	4.16	4.11	4.15	4.11	2.50	2.55	2.49	2.48
EtA·PentA	20.3	20.3	4.17	4.13	4.15	4.16	2.50	2.54	2.49	2.48
PropA·HexA	20.6	20.6	4.17	4.17	4.16	4.18	2.50	2.56	2.49	2.49
2PentA	21.1	21.1	4.18	4.14	4.16	4.11	2.50	2.55	2.49	2.48
2HexA	23.1	23.1	4.20	4.21	4.19	4.18	2.50	2.56	2.49	2.49
ButA·OctA	24.3	24.3	4.21	4.25	4.20	4.27	2.50	2.57	2.49	2.50
HexA·HepA	24.6	24.6	4.22	4.25	4.20	4.14	2.50	2.57	2.49	2.50

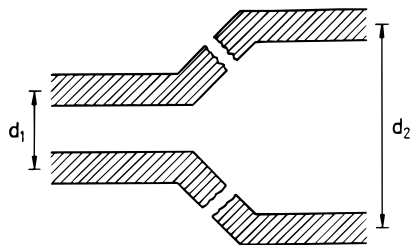


Figure 4. Schematic representation of the "inorganic layer" fracture by intercalation of *n*-alkylamines into α -TiP.

number of carbon atoms, the tail to tail interaction should be similar to that of single amine intercalation compounds. Nevertheless, for mixed systems having an odd-even composition, the arrangement of the ending CH_3 groups is different, and the interlaminar distance must depend on additional factors (such as the packing parameter).²¹

When α -TiP is placed in an atmosphere saturated with vapors of all the studied amines, the behavior is similar to the above cases. After a short time (6 h), the *n*-butylamine intercalation compound is formed, the *n*-pentylamine intercalate is ready if the contact time is longer. The substitution of the four-carbon amine by the five-carbon atoms seems to be easy through a mixed intercalation compound, giving a low interlayer spacing enlargement (2.3 Å). The α -TiP/*n*-pentylamine phase is metastable in the reaction media. In the next stage, the substitution of *n*-pentylamine molecules by *n*-hexylamine takes place, providing the saturated α -TiP/*n*-hexylamine intercalation compound. The latest material is also metastable and evolves into the α -TiP/*n*-heptylamine intercalate. As can be seen from Figure 3, the metastability "lifetime" of these phases increases when the guest size is increased; a very peculiar effect is also observed: a stepwise growing of the basal spacing following a controlled sequence of reaction.

Morphological Data of the Intercalation Compounds. The combination of powder XRD and SEM shows that the α -TiP is constituted by pseudo-hexagonal plates of average dimensions $5000 \times 5000 \times 1850 \text{ \AA}^3$.²² In this study, these techniques were applied to the intercalation compounds of composition $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_n\text{H}_{2n+1}\text{NH}_2 \cdot \text{H}_2\text{O}$ ($n = 2-6$), which have been previously synthesized. Although the morphology is similar in every case, measurable differences have been observed. In relation to the starting material, the plates width remains quite constant, whereas the average area of the face of the plate decreases.

Given that the intercalation of *n*-alkylamines into α -TiP does not result in delamination, the low quality of the powder XRD patterns recorded (Figures 1 and 2) must be related to the high disorder of the amine molecules placed in the interlaminar region. On the other hand, that the plates fracture in a direction perpendicular to the material's 002 direction, implying lower particle size, must be related to the fact that the advance of the intercalation reaction provides the coexistence of two basal spacings in the same interlaminar region (Figure 4). It should be expected that the

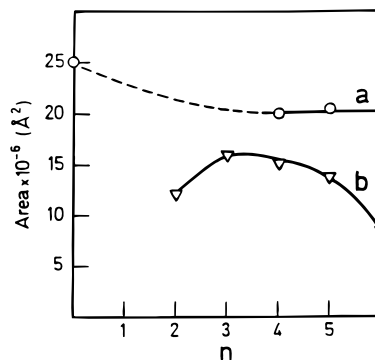
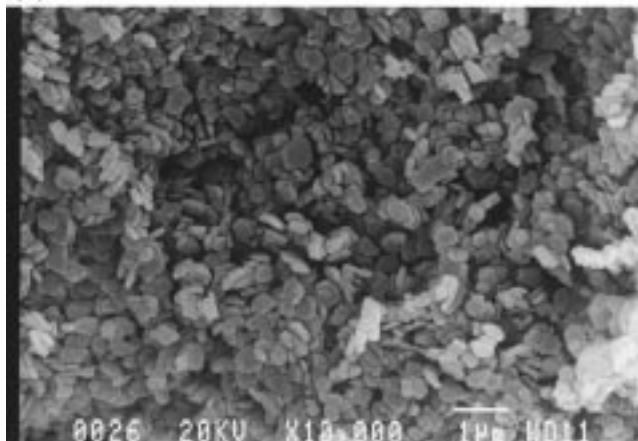


Figure 5. Average area of the plate basal face in the $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{C}_n\text{H}_{2n+1}\text{NH}_2 \cdot \text{H}_2\text{O}$ ($n = 2-6$) compounds obtained by interaction of α -TiP with the vapor of *n*-alkylamines mixture (a) and a single *n*-alkylamine (b).

(a)



(b)

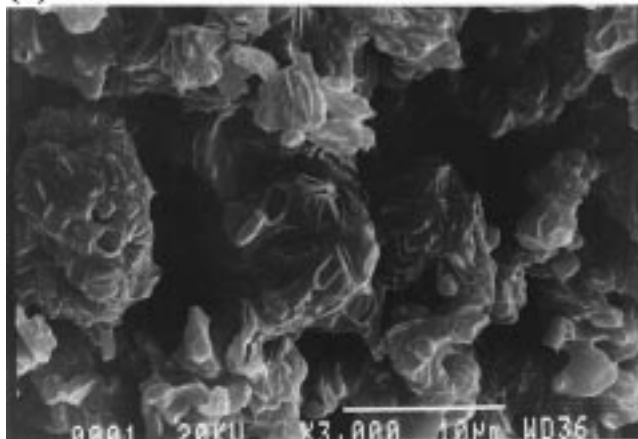


Figure 6. SEM images of the samples obtained by α -TiP contacting with ethylamine 4 h (a) and 2 days (b). (The white line in each photograph denotes the scale, 1 μm for a, and 10 μm for b.)

stability of the "mixed" layer will be lower the higher the $d_2 - d_1$ value. The experimental data support this statement.

When the intercalation process takes place under the conditions shown in Figure 3, the average area of the plates is independent of the composition of the intercalation compound, being ca. 80% of the α -TiP value (Figure 5a). Under this condition, the process develops by steps, with slight increases of the interlayer distance at each stage. The material stress

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through the reaction is minimal and breaking of the plates is unusual.

However, when the reaction is performed in the presence of a single amine vapor, the particles size of the compounds obtained is lower; moreover, it is a function of the size of the intercalated amine (Figure 5b). In agreement with that, the vapors of $C_nH_{2n+1}NH_2$ ($n > 2$) lead to a higher breaking of the plates as the amine alkyl chain length increases (Figure 5b). The low particle size of the compound $Ti(HPO_4)_2 \cdot 2C_2H_5NH_2 \cdot H_2O$ may be related to the kinetics of the intercalation process. Increasing the reaction rate will provide higher structural disorder in the interlayer region, with the possibility of accumulation of a higher amount of residual stress.

The special behavior of the ethylamine is not just related to the particle size of its stoichiometric intercalation compounds. Either ethyl- or methylamine provide layered intercalation compounds of well-defined composition after a few hours of contact time with the solid phosphate. If these intercalates stay in the corresponding amine vapor atmosphere, they transform into amorphous gels and the amine percentage in the solid phase increases.⁵ However, the intercalation compounds obtained from the remainder of the n -alkylamines remain crystalline, independent of the contact time. Figure 6a shows the SEM photograph of $Ti(HPO_4)_2 \cdot 2C_2H_5NH_2 \cdot H_2O$ obtained after 4 h of solid-

vapor contact. The shown morphology is similar to the intercalation compound with the largest alkyl chain amine. Nevertheless, if the reaction time is extended for 2 days, ethylamine leads to the formation of interparticle aggregates (Figure 6b).

In conclusion, the final reaction product of the interaction between α -titanium phosphate and n -alkylamine mixed vapors is a function of the contact time. The thermodynamic stability of the reaction product increases with the length of the alkyl chain of the amine intercalate. Therefore, the long reaction time is necessary to reach equilibrium conditions and is very sensitive to the amine mixture. When the reaction rate is low, individual mixed phases, not previously described, can be isolated. The synthetic route used for the preparation of a particular compound establishes its morphology and crystallinity. In all cases, the intercalation process implies the partial fracture of the layer's plates and, consequently, the lessening of the material's particle size. This effect is even stronger the higher the basal spacing is.

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