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Structure Features and Thermochemistry of the Intercalation of Pyridine and α-, *β*-, and *γ*-Picolines into Crystalline α-Titanium Hydrogen Phosphate

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The insertion of polar organic molecules inside the gallery space of the synthetic crystalline lamellar α-titanium hydrogen phosphate was followed by a batch method at 298 ± 1 K. The maximum amounts intercalated were 3.34, 1.54, 1.85, and 2.21 mmol g^{-1} for pyridine (py) and α-, *β*-, and *γ*-picolines (α-, *β*-, and *γ*-pic), respectively, with expansion of the original interlamellar distance of 0.76 nm, to accommodate these molecules. The interlamellar distances for α- and *β*-pic of 1.15 and 1.12 nm indicate a parallel orientation to the inorganic sheets, while *γ*-pic with 1.32 nm forms a perpendicular monolayer of the matrix. The value of 1.80 nm for py suggests that the guest molecules are interacting simultaneous and perpendicularly to adjacent layers, in a typical Brønsted base interaction. The intercalated compounds lost water of hydration, organic matter, and water of condensation of the phosphate to give pyrophosphate on heating. The intercalation processes were also calorimetrically followed at 298.15 ± 0.02 K. From thermal effect data, the variation in enthalpy for each system was calculated. Either the intercalation based on batch method or the thermal effects were fitted to a modified Langmuir equation. The exothermic enthalpic results for these intercalation gave the following sequence of values: −44.62 ± 0.15, −1.24 ± 0.03, −1.95 ± 0.08, and −2.90 ± 0.24 kJ mol^{-1} for py and α-, *β*-, and *γ*-pic, respectively. The variation in enthalpic values for pyridine derivatives can be interpreted to reduction of the steric hindrance associated with the methyl group attached to the heterocyclic ring. Thermodynamic data (ΔG and ΔS) are in agreement with a spontaneous and favorable intercalation process.

Introduction

Phosphates of tetravalent metals are normally synthesized as insoluble acidic salts in the α-crystalline form to give the general formula $\alpha\text{-M(HPO}_4)_2\cdot n\text{H}_2\text{O}$ (M = Zr, Ti, Sn, etc.). This class of salts has a lamellar structure which makes them excellent matrixes for intercalation reactions.[1,2] In this process, the guest organic molecule interacts with the host matrix, which brings about an increase of the interlamellar distance. Due to this behavior, some of these intercalated materials can be used in many pillaring applications. In this kind of operation, the previously intercalated organic molecule can be exchanged under favorable conditions to a desired pillaring agent in a subsequent step.[3] Several organic compounds have been used as guest molecules in intercalation reactions with the aim of evaluating structural changes[4,5] and electrical[6]and thermochemical[7,8] properties. Other applications involve modification of host optical and electrical properties, changing critical temperature for superconductivity, and electrode surface modification.[5,6,9−12]

The intercalation behavior depends, among other factors, directly on the size and pK_a of the guest molecule.[1,13] Correlations between the interlamellar distance with the carbon chain length were observed in intercalation studies involving aliphatic amines.[7,8,9,14] However, most of these studies explored intercalation of zirconium hydrogen phosphate, with monoamines,[12,15,16] diamines,[10,17] and aromatic[1,2,5,18,19] amines. On the other hand, the intercalation of these amines in

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α-titanium hydrogen phosphate has scarcely been studied.[7,8,12,13,20]

Most of these reports emphasize only structural features of these compounds. The thermochemical data related to these kind of compounds are limited in the literature.[7,8,21]

The aim of this publication is to report some calorimetric data involving the intercalation of pyridine (py) and α-, *β*-, and *γ*- picolines (α-, *β*-, and *γ*-pic) into α-titanium hydrogen phosphate, to further our understanding of the intercalation process.

Experimental Section

Materials. All chemicals used were reagent grade. Titanium trichloride 15% in hydrochloric acid solution (Carlo Erba), phosphoric acid 85% (Nuclear), and aromatic amines of 98% purity, such as pyridine (Merck), α-picoline (Merck), *β*-picoline (Carlo Erba), and *γ*-picoline (Aldrich) were used. The hydrogen phosphate of crystalline titanium in the α-form (TPH) was obtained through the reaction of oxidation of titanium trichloride, with some modifications of the original method.[22] This synthesis was achieved by reacting 0.126 mol of titanium trichloride with 0.50 mol of phosphoric acid over 4 days in a polyethylene flask at 333 K with periodic stirring. The solid material was separated by centrifugation and washed with doubly distilled water until the wash water reached the pH range 3.5−4.0. The final product was then dried at 313 K and characterized as previously described.[23]The aromatic amines were carefully distilled before use.

Intercalation Procedure. First, the intercalation was followed by a batch method, which consisted of suspending 100 mg of TPH in 15.0 cm^3 of an aqueous solution of each aromatic amine in several concentrations, varied in the range 1.0×10^{-3} to 0.80 mol dm^{-3}. The suspension was mechanically stirred for 12 h at 298 ± 1 K. The time required to reach equilibrium was previously established in a series of intercalations for different times.[7,8] These processes involved constant masses of the host materials, which were treated with constant concentrations of the respective aromatic amines. Although the time of 10 h appeared to be enough to reach equilibrium, 12 h was used to ensure maximum intercalation, as is illustrated in Figure 1. After this time, the solid was separated by centrifugation and dried at 313 K. The supernatant was titrated with standard hydrochloric acid and the amount of inserted amine (n_{int}) was determined by the following expression: $n_{int} = (n_i - n_s)/m$, where n_i is the initial number of moles of amine in solution, n_s is the number of moles of amine in the supernatant after the equilibrium and m the mass of TPH.[24]

Analytical Procedure. Intercalated materials were characterized by the following techniques. Thermogravimetry (TG) used a a DuPont model 1090B instrument; samples (∼5.0 mg) were heated from 298 to 1223 K with a heating rate of 0.17 K s^{-1} under argon atmosphere. X-ray diffractometry used Cu Kα radiation in a Shimadzu model XD3A diffractometric apparatus, in the range $2\theta = 3-50°$ and with a scan rate of 4° min^{-1}. Infrared spectra were recorded on a BOMEM model MB series instrument, with a resolution of 4 cm^{-1}. SEM images were obtained in a JEOL JSM T-300 microscope, using an accelerating voltage of 15 kV.

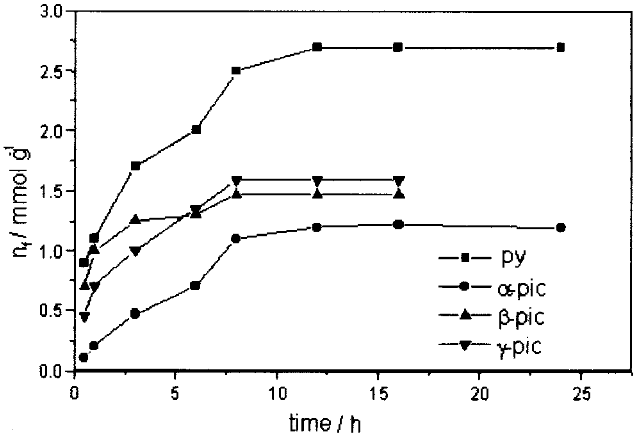

Figure 1. Isotherm of intercalation of pyridine, α-, *β*-, and *γ*-picolines as a function of the time of equilibrium.

Table 1. Number of Moles of Intercalated Aromatic Amines (n_{int}) Pyridine (py) and α-, *β*-, and *γ*-Picolines (α-, *β*-, and *γ*-pic), Interlamellar Distance (*d*), *x* Values in the Formula α-Ti(HPO_4)$_2$.*x*amine.*y*H_2O Obtained from Volumetric Titration, x_{titr}, and Thermogravimetry, x_{therm}, and the Moles of Water *Y*

guest	N_{int}/mmol g^{-1}	*d*/pm	Y	x_{titr}	x_{therm}
Py	3.31	1800	1.0	0.85	0.77
α-pic	1.54	1150	1.0	0.39	0.35
β-pic	1.85	1120	0.50	0.45	0.39
γ-pic	2.21	1320	0.43	0.54	0.41

Calorimetry. The calorimetric titration[24] was performed in a differential isothermic microcalorimetric system LKB 2277. Nearly 20.0 mg of the host was suspended in 2.0 cm^3 of double distilled water in a stainless steel ampule. The system was stirred with a gold helix and thermostated at 298.15 ± 0.02 K. After stabilization of the baseline, the apparatus was standardized and a microsyringe was coupled to the system. The microsyringe was connected to a stainless steel needle and through it increments of the amine solution were added. Each thermal effect caused by the reaction was recorded after addition. The same procedure was used to follow the thermal effect of the guest solution in water. The thermal effect of the hydration of the matrix was determined by breaking thermostated thin glass ampules containing THP (50 mg) in 0.10 dm^3 of water and the thermal effect was recorded.[8]

Results and Discussion

The number of moles of aromatic amine intercalated was obtained through a batchwise procedure and the results are shown in Table 1. These values are 3.31, 2.21, 1.85, and 1.54 mmol g^{-1} for py, *γ*-pic, *β*-pic, and α-pic, respectively. The amount of intercalated amine decreased in the sequence py > *γ*-pic > *β*-pic > α-pic. This series does not express any correlation with the basicity or the amount of amines intercalated, due to the fact that the basicity of these amines are very similar,[25,26] as evidenced by the pK_a values of 5.23, 5.97, 5.69, and 6.02 for py, and α-, *β*-, and *γ*-pic, respectively. Thus, the position of the methyl group on aromatic ring influences the amount of amine inserted into the free gallery space of matrix. As expected, a decrease in steric

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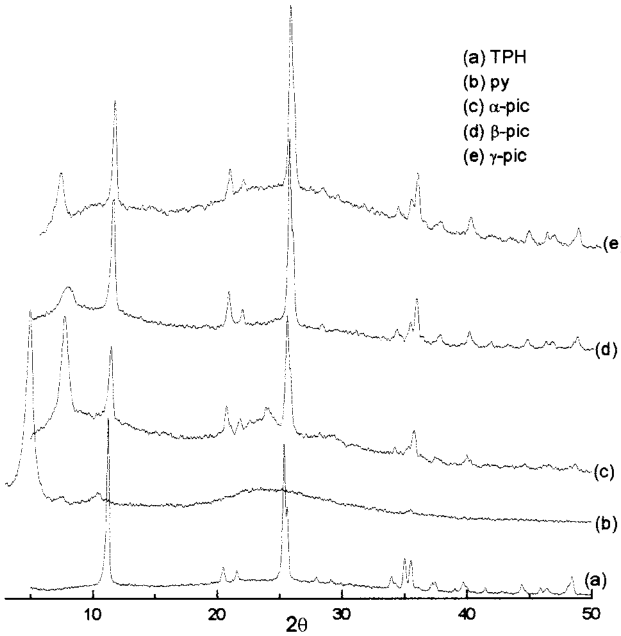

Figure 2. X-ray diffraction of $Ti(HPO_4)_2{\cdot}H_2O$ host and the intercalated compounds with pyridine (py) and α-, β-, and γ-picolines (α-, β-, and γ-pic) guests.

hindrance of the methyl group, which decreases from γ- to α-pic, induces an increase in the amount of intercalated amine. This fact is in agreement with the γ- and α- pic intercalated values of 2.21 and 1.54 mol g^{-1}, respectively. These extreme intercalated values for the pyridine derivatives are related to the furthest and the closest methyl groups attached to the nitrogen basic center, whose positions are expected to endure extreme effects due to steric hindrance, during the host−guest interaction.

The intercalation process resulted in an increase in the interlayer distance to accommodate the aromatic amines into the free space of the cavity, as followed via X-ray diffraction patterns in Figure 2. However, in all cases a relative decrease in crystallinity of the intercalated compounds could be detected. During normal intercalation the original lamellar distance of the host of 0.76 nm changed to 1.80, 1.15, 1.12, and 1.32 nm for py, and α-, β-, and γ-pic, respectively. In this process, the characteristic peak that is associated with the matrix, located at $2\theta = 11.6°$, remained in the intercalated compounds, due to incomplete intercalation, as observed for other systems.[3,4]

The lamellar distance of 1.80 nm found for intercalated pyridine molecules is in disagreement with other publications, which reported an interlamellar distance of 1.09 nm.[9,18,27] In the present case, the X-ray diffraction patterns were used to monitor the increase in the interlayer distance in each point of the isotherm of intercalation of the pyridine. The diffraction patterns for each point of the isotherm are shown in Figure 3. These values clearly demonstrated the formation of a new lamellar distance with the increase of the number of moles of py added.

With the addition of 1.20 to 2.25 mmol of pyridine, a 2θ value of 8.1°, corresponding to a interlayer distance of 1.09 nm, is observed, in agreement with other reports,[13,20] although the matrix was not saturated by the solute. The formation of a new phase occurs when 3.75 mmol of pyridine is added, as evidenced by the presence of a new diffraction peak at $2\theta = 4.9°$, corresponding to 1.80 nm for the interplanar distance, while the peak at 1.09 nm is still present. However, at saturation with 15.0 mmol of pyridine, only one peak is observed at 1.80 nm, which suggests that by addition of this amount of pyridine, the formation of the new phase is completed.

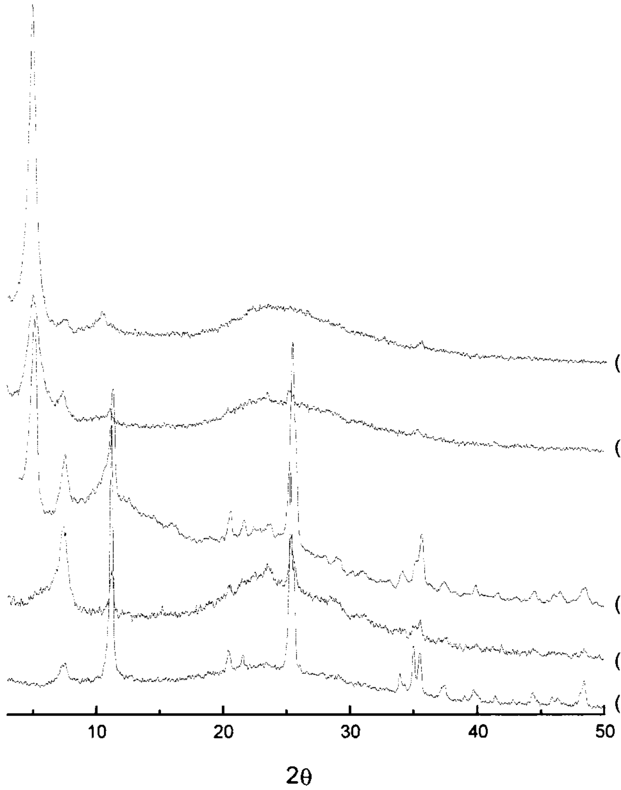

Figure 3. X-ray diffraction of the intercalated compounds with pyridine. Amount of moles of pyridine added: (a) 1.20×10^{-3}, (b) 2.25×10^{-3}, (c) 3.75×10^{-3}, (d) 6.75×10^{-3}, and (e) 15.0×10^{-3}.

The increase of the amount of the guest molecule is a remarkable feature to understand this mechanism of intercalation. Thus, these results obtained by the diffractograms are in agreement with the statement that the first pyridine molecules have the facility in inserting parallel to the planes of the matrix. To reach an interlamellar distance of 1.80 nm, however, an increase in the number of moles of guest molecules is necessary to promote a reorganization of them into the gallery space, allowing the pyridine molecules to adopt a perpendicular position in relation to the inorganic plans. The final stage is in agreement with the existence of the guest molecules interacting simultaneously with adjacent layers of the host.

The series of results obtained from diffraction patterns suggests different orientations for the inserted molecules as illustrated in Figure 4. The arrangement of amines into the interlayer can be evidenced by considering the relationship between the expansion of

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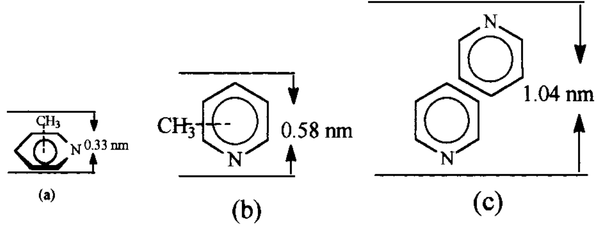

Figure 4. Pyridine or derivative molecules distributed inside the TPH layers. Length of the molecules is given in (a) parallel and (b) perpendicular positions. The net proposed expansion of pyridine (c) parallel to the inorganic layer is also shown.

interlayer distance and molecular sizes[28] of aromatic amines. In the present case, the intercalation gave a net lamellar expansion of 0.39, 0.36, 0.56, and 1.04 nm for α-, β-, and γ-pic and py, respectively. For pyridine and other aromatic amines, including picolines, it was previously proposed[29] that these kinds of molecules have lengths of 0.33 and 0.58 nm for the parallel and perpendicular distributions inside the interlamellar cavity. A general representation for any picoline assuming both orientations inserted in the lamella is shown in parts a and b of Figure 4, in which is maintained the proportionality of expansion.

The experimental values for α- and β-pic suggested that these molecules are parallelly oriented into the interlamellar cavity, which contrasted with the perpendicular position of the γ-pic. On the other hand, when pyridine molecules interact with adjacent layers into the same cavity of the matrix, a net expansion of the lamellar distance of 1.04 nm was obtained. This large net value suggest that both acidic Brønsted centers inside of each lamellae are bonded to pyridine molecules in a perpendicular orientation to the inorganic layer, in a bilayer arrangement, as shown in Figure 4c. This last orientation is compared in proportionality of the other conformations of the amines into the lamellar space as shown in parts a and b of Figure 4.

The SEM micrographs of the original matrix and of the matrix with 15.0 mmol of pyridine intercalated are shown in parts a and b of Figure 5, respectively. The morphology of the intercalated matrix is in fact changed, constituting pseudohexagonal plates. This observation about microscopic structure can be understood as a consequence of the change at the molecular level detected by X-ray diffraction patterns.

As expected, the infrared spectra of the intercalated materials presented the characteristic bands of the protonated amines. Three bands[27,30,31] of the pyridinium ion were observed at 1640, 1538, and 1480 cm^{-1}, as shown in Figure 6. The bands assigned to the ring stretch vibration modes 8a and 19a of the pyridinium ion appeared at 1640 and 1480 cm^{-1}. The weak band at 1538 cm^{-1} was attributed to the ring stretch vibration mode 19b of the same cation, which was normally related to py molecules interacting with the Brønsted acid sites of the inorganic matrix. Another band attributed to the vibration mode 9a of pyridine molecule was observed at 1213 cm^{-1}. These values suggested the existence of free pyridine in the lamellar cavity.

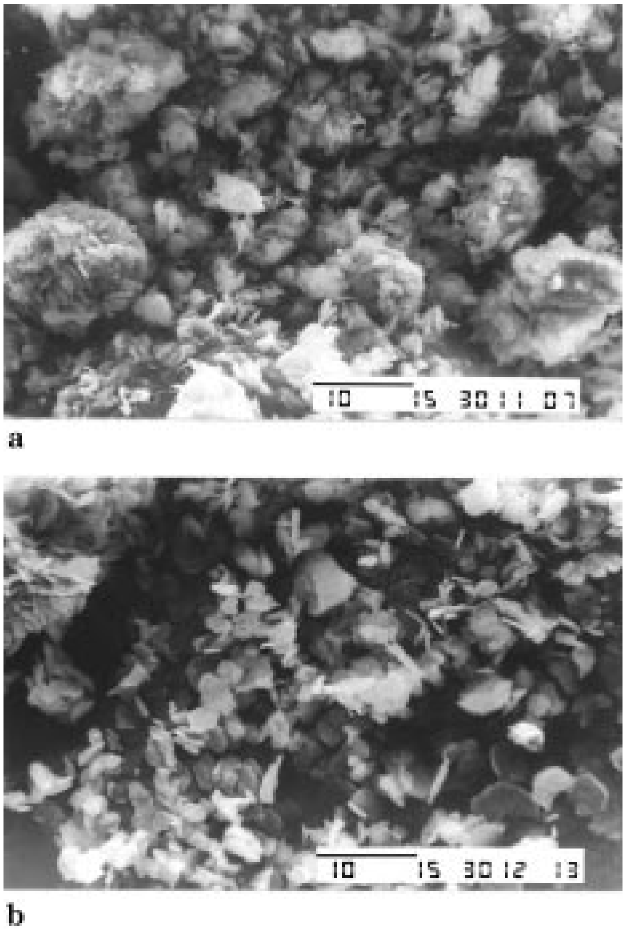

Figure 5. Scanning electon micrographs ×2000 of (a) Ti(HPO$_4$)$_2$·H$_2$O and (b) 15.0 × 10^{-3} pyridine intercalated matrix.

The bands of the P−OH group at 1250 cm^{-1} for the intercalated picolines remain in the same region in the spectra, indicating the existence of free acidic sites into the lamella. However, in this process also occurred with the protonation of nitrogen of the aromatic ring, characterized by the appearance of bands at 1538, 1550, and 1506 cm^{-1}, attributed to α-, β-, and γ-pic molecules, respectively, whose interactions correspond to Brønsted acid sites. Bands are also observed at 1634, 1635, and 1641 cm^{-1} assigned to the vibration modes 19b and 8a of α-, β-, and γ-methylpyridinium ions, respectively. Thus, the processes of intercalation of these aromatic amines into TPH can be interpreted as an acid−base reaction involving the layered acidic host[27,32] O$_3$P−OH with guest basic molecules to characterize a typical acid−base Brønsted interaction.

The amount of inserted organic molecules was determined from titration data and compared to those values obtained through thermogravimetry, as shown in Table 1. The thermogravimetric values are smaller and the difference is due to the adsorption of amines on the matrix surface. The possible excess of physisorbed amine can be removed by washing the sample and drying it before submitting to thermogravimetry. On the other hand, into the largest values collected from

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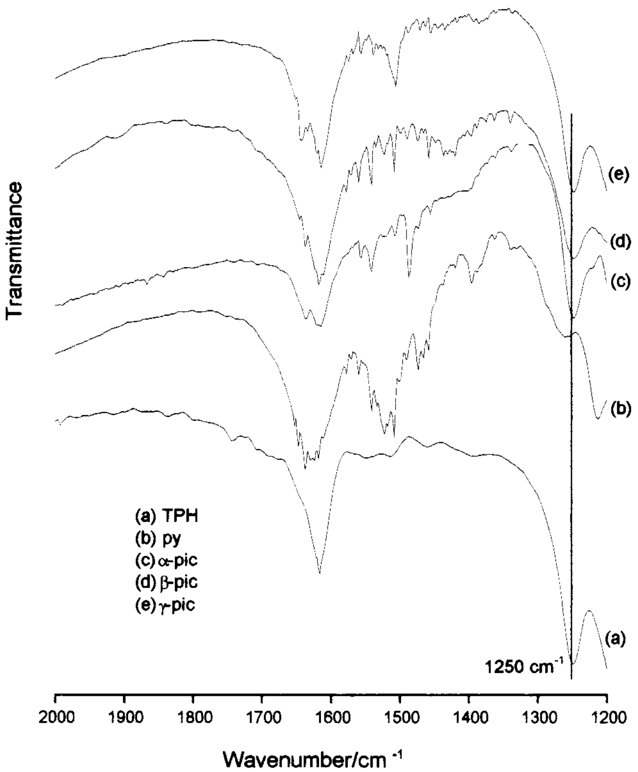

Figure 6. Infrared spectra of $Ti(HPO_4)_2{\cdot}H_2O$ host and the intercalated compounds with pyridine (py) and α-, β-, and γ-picolines (α-, β-, and γ-pic) guests.

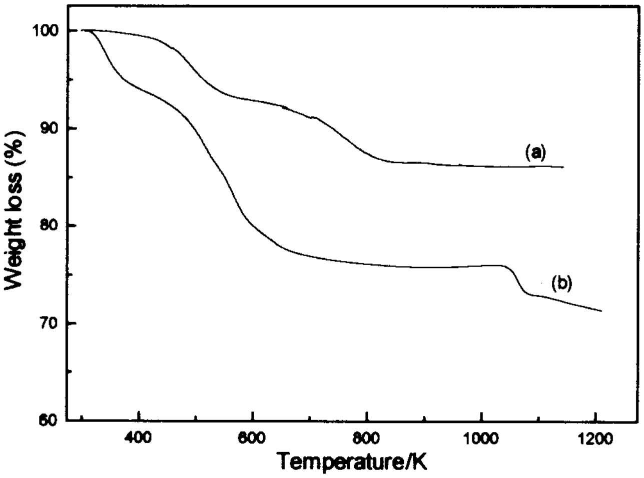

Figure 7. Thermogravimetry curves of matrix (a) TPH and (b) pyridine intercalated.

volumetric determinations should be incorporated the amount of the physically adsorbed molecules weakly bonded on surface. The thermogravimetric curves of the intercalated matrixes present a very similar behavior to that shown in Figure 7b. These intercalated matrixes showed three definite steps of mass loss, in contrast with the two steps for the host matrix. In the first stage, the mass loss occurred between 300 and 373 K, which is attributed to the loss of water of hydration. For py and α-pic intercalated compounds, losses of mass of 5.5 and 6.1%, respectively, were detected, which corresponded to the elimination of 1 mol of water of hydration. However, for β- and γ-pic intercalated matrixes, the loss of mass of 3.0 and 2.7% corresponded to 0.50 and 0.43 mol of water of hydration, respectively.

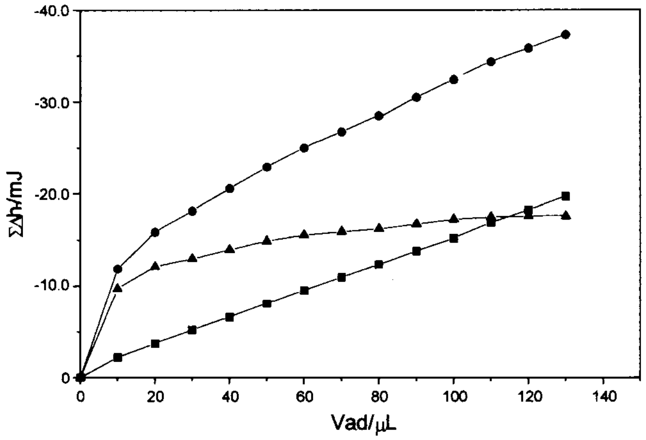

Figure 8. Experimental curves representing the sum of the thermal effects $\sum\Delta_{tit}h$ (●), $\sum\Delta_{dil}h$ (■), and $\sum\Delta_{r}h$ (▲) for calorimetric titration of intercalation of α-picoline (α-pic) into $Ti(HPO_4)_2{\cdot}H_2O$.

The second stage occurred between 373 and 700 K and corresponded to loss of mass of the organic molecule, to give 19.0, 11.3, 11.5, and 13.0% weight losses for py and α-, β-, and γ-pic, respectively. On the basis of these values, the calculated amount of intercalated amines gave 0.77, 0.35, 0.39, and 0.41 mol per each mole of the host matrix, respectively, as shown in Table 1. The third step, which occurred above 1000 K, can be attributed to the loss of mass of 1 mol of water, as a consequence of the condensation of the hydrogen phosphate group to form pyrophosphate.[7,9,33]

To obtain better information on the energetics of the intercalation processes, a series of calorimetric titrations was carried out for all systems studied, based on the general reaction below, where the aromatic amine (N=) in solution (sol) interacts with the acidic center O_3P-OH of the crystalline (c) inorganic lamellar compound to give a suspension (susp), as written:

$$O_3P{-}OH(c) + N{=}(sol) = O_3P{-}O^{-}\,{}^{+}HN{=}(susp); \quad \Delta_{int}H$$

To determine this enthalpic $\Delta_{int}H$ value a series of three independent titrations, such as (i) the hydration of the host, (ii) the dilution of the amine from the appropriate concentration (aq) to a final solution (sol), and (iii) the final interactive process, must be carried out in water to complete the following thermochemical cycle:

$$O_3P{-}OH(c) + nH_2O = O_3P{-}OH(susp); \quad \Delta_{hid}h$$

$$N{=}(aq) + nH_2O = N{=}(sol); \quad \Delta_{dil}h$$

$$O_3P{-}OH(susp) + N{=}(aq) = O_3P{-}O^{-}\,{}^{+}HN{=}(susp); \quad \Delta_{r}h$$

The data for the calorimetric titrations of α-pic are shown in Figure 8. The general thermal effects ($\sum\Delta h$) of titration and dilution and the resulting curve are represented as function of the volume added (V_{ad}). As the experimental thermal effect of the hydration of the host was null, the resultant thermal effect of the

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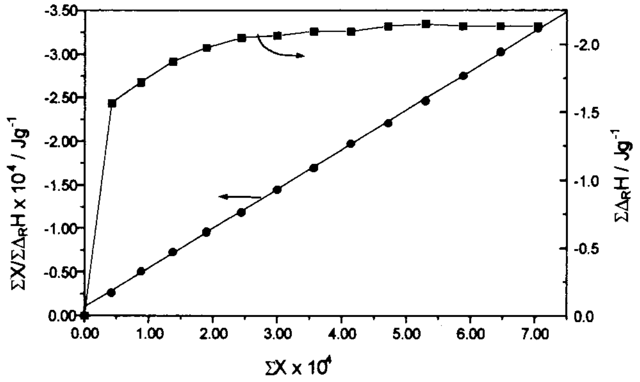

Figure 9. Isotherm of the integral enthalpy of intercalation ($\Delta_{int}H$) of γ-picoline (γ-pic) guest given by a $\Sigma\Delta_rH$ vs ΣX plot. The linearized form is given by $\Sigma X/\Sigma\Delta_r$ vs ΣX plot.

reaction ($\Sigma\Delta_rh$) can be calculated through the thermal effects of titration and dilution by means of the expression: $\Sigma\Delta_rh = \Sigma\Delta_{tit}h - \Sigma\Delta_{dil}h$. In considering those data from $\Sigma\Delta_rh$ values, the intercalation enthalpy ($\Sigma\Delta_{int}H$) can be obtained by using the previous data adjusted to the modified Langmuir equation.[34] Once the sequence of values was obtained from the calorimetric titration, the enthalpy of intercalation to form the monolayer per unit of mass of the host, $\Delta_{mono}H$, was determined by using the equation[35,36]

$$\frac{\sum X}{\sum \Delta_R H} = \frac{1}{(K-1)\Delta_{mono}H} + \frac{\sum X}{\Delta_{mono}H} \qquad (1)$$

In this equation, ΣX is the sum of the molar fraction of the amine in solution after intercalation, where X is obtained for each point of the titrand addition by using the modified Langmuir equation, which was previously shown to be a good adjustable model.[8,34,37] Δ_RH is the integral enthalpy of intercalation (J g^{-1}), obtained by dividing the resultant thermal effect of the reaction $\Sigma\Delta_rh$ by the mass of the matrix host, and K is a constant of proportionality that also includes the equilibrium constant. By using the angular and linear coefficient values from the $\Sigma X/\Delta_RH$ vs ΣX plot, it was possible to obtain the $\Delta_{mono}H$ value[8] as shown in Figure 9. Then, the enthalpy of intercalation $\Delta_{int}H$ could be calculated by means of the expression $\Delta_{int}H = \Delta_{mono}H/n_f$, where n_f is the number of fixed moles after the calorimetric equilibrium is reached.

The enthalpies of the intercalation of α-, β-, and γ-pic are exothermic in nature, with respective values −1.24 ± 0.03, −1.95 ± 0.08, and −2.90 ± 0.24 kJ mol^{-1}. However, pyridine presents a different behavior, which determined that the thermal effect could not be adjusted to eq 1. These experimental data obtained from the calorimetric titration are shown in Figure 10. On the basis of the previous results, it can be supposed that this behavior is related to the reorganization of the pyridine molecules inside the lamella. Then the enthalpy of intercalation can be calculated by means of the following equation:

$$\Delta_{int}H = \Delta_RH/n_f \qquad (2)$$

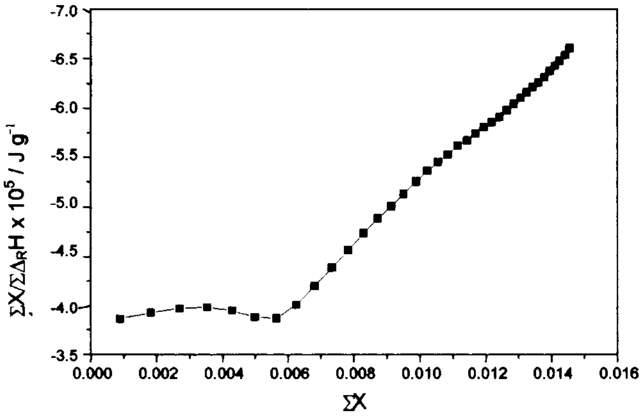

Figure 10. Experimental data obtained from calorimetric titration of $Ti(HPO_4)_2{\cdot}H_2O$ with pyridine, which were not linearized by a $\Sigma X/\Sigma\Delta_r$ vs ΣX plot.

The obtained enthalpic values were correlated with all experimental interlamellar distances. Then, taking into account the phase at 1.09 nm, an intercalated amount of 1.38 mmol g^{-1} of pyridine gave an enthalpic value of −44.62 ± 0.44 kJ mol^{-1}. Thus, following the same calculation procedure for the maximum entrance of pyridine of 3.30 mmol g^{-1}, an enthalpy of −66.76 ± 1.10 kJ mol^{-1} was acquired. This result is similar to that reported for the intercalation of pyridine in α-zirconium hydrogen phosphate, in which also an exothermic value of −59.3 kJ mol^{-1} was obtained.[21]

There is an apparent discrepancy involving the enthalpies of interaction of pyridine and those of picolines. From the point of view of the interactive effect, in any case, the ring heteroatom of these molecules can bond to the available acidic centers of the inorganic layers, to accommodate the gallery space of the lamella. However, the explanation of these distinct behaviors can be related to the following main features: (i) picoline molecules disposed in parallel or in perpendicular monolayer positions into the gallery should give the lowest enthalpic values in comparison with pyridine, which interacted directly in the perpendicular bilayer position to the acidic centers, (ii) despite the endothermic effect associated to the expansion of the layers,[21] this contribution should be more pronounced when it is associated with small distances, as occurred in the parallel arrangement of picoline molecules, and (iii) the net enthalpic value produced by pyridine intercalation in a bilayer rearrangement, giving a large interlamellar distance, can overcome easily the weak van der Waals interactive forces, maintained by the inorganic layers of the host, as manifested by the large exothermic value.

A complete series of the thermochemical data for the intercalation of pyridine and picolines are listed in Table 2. The enthalpic values for the substituted aromatic amines depend on the position of the methyl attached to the ring and becomes more exothermic as the methyl group is changed from the α- to the γ-position. The sequence observed is in agreement with a decreasing order of the steric hindrance. On the other hand, the pronounced inductive effect of the methyl group in α-pic, in comparison with β-pic, also seems to be relevant in

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Table 2. Thermochemical Data for the Guest Aromatic Amines Pyridine (py) and α-, *β*-, and *γ*-Picolines (α-, *β*-, and *γ*-pic) Intercalated into α-$Ti(HPO_4)_2\cdot YH_2O$ Host at 298.15 ± 0.02 K

guest	$\Delta_{mono}H$/ kJ mol^{-1}	$\Delta_{int}H$/ kJ mol^{-1}	ln *K*	$-\Delta G$/ kJ mol^{-1}	ΔS/kJ mol^{-1}
Py	−128.95 ± 1.29	−44.62 ± 0.44			
	−220.32 ± 2.20	−66.76 ± 1.10			
α-pic	−0.87 ± 0.01	−1.24 ± 0.03	10.94	27.11 ± 0.22	87 ± 1
β-pic	−1.44 ± 0.02	−1.95 ± 0.08	9.65	23.93 ± 0.26	74 ± 1
γ-pic	−2.21 ± 0.01	−2.90 ± 0.24	10.75	26.65 ± 0.01	80 ± 1

this kind of interaction, since a marked influence was observed in other thermochemical studies.[38,39]

Data on intercalation enthalpy are restricted to aliphatic amines[7,8] and the best understanding of this kind of system required other determinations. However, Gibbs free energies were also calculated from *K* values of eq 1, through calorimetric data, by applying the expression $\Delta G = -RT \ln K$ and are listed in Table 2. The exothermic values for all systems indicate that the reactions are spontaneous in nature. The entropic values calculated from $\Delta G = \Delta H - T\Delta S$ are also consistent with the argument that the reactions are also entropically favored. These values suggested a disruption of the molecules of the solvents upon bonding which are then formed into the interlamellar space, which were previously bonded to the inorganic matrix and also those associated with the aromatic amines. However, the increase in entropy is related to the release of these molecules to the solution after intercalation.[7,40,41]

Conclusion

The intercalation of aromatic amines into TPH provided compounds formulated as $Ti(HPO_4)_2(amines)_n\cdot xH_2O$. The amount intercalated into the free cavity of each lamella of the host does not correlate with the basicity of the amines. These guest base molecules react with the layered acidic host $O_3P{-}OH$ of the inorganic matrix by using the heteroatom of the ring, characterizing a typical acid−base Brønsted interaction. Taking into account the net expansion caused by intercalation, α- and *β*-pic are distributed in a monolayer into the free space of the lamellar crystalline compound. This orientation changed to a perpendicular position for *γ*-pic and py, being the last molecule bonded in a bilayer arrangement to both acidic centers of the same lamella. These interactive processes provide a net exothermic thermal effect, reflecting the inductive and steric hindrance of the position of the methyl group attached to picolines. However, the largest exothermic enthalpic value obtained with py should be associated with the reorganization of this base inside the lamella. These series of thermochemical data indicate that the intercalation is enthalpically and entropically favorable and thus takes place spontaneously in this system. The structural features associated to thermochemical data of this kind of system can elucidate not only the mechanism but also the energetics of guest−host interaction in an intercalation process.

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