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# Thermochemical data on intercalation of aromatic amines into crystalline α-titanium hydrogenphosphate

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## Abstract

The heterocyclic amines, 2-, 3- and 4-aminopyridine, 2-amino-4-methylpyridine and 2-aminobenzylamine, were intercalated into α-titanium hydrogenphosphate and characterized through infrared spectroscopy, X-ray diffractometry and thermogravimetry. On intercalation, these heterocyclic amines expanded the original 760 pm interlayer distance to 1338, 1177, 1262, 1577 and 1060 pm, for the same sequence of amines. The change in P–OH and amine group frequencies clearly indicated cyclic amine intercalation. From the combination of batch intercalation and calorimetric titration, the variation in enthalpy was calculated at $298.15 \pm 0.02$ K. The exothermic enthalpic results for the intercalation process gave the sequence of values: $-36.75 \pm 0.78$; $-20.42 \pm 0.28$, $-35.22 \pm 0.70$, $-14.02 \pm 0.10$ and $-29.77 \pm 0.29$ kJ mol$^{-1}$, respectively. The calculated negative Gibbs free energy and the majority of the positive entropic values are in agreement with the favorable intercalation of these guest molecules inside the cavity of the host inorganic crystalline lamellar compound.

*Keywords:* Intercalation; Thermodynamic; α-Titanium hydrogenphosphate

## 1. Introduction

Layered phosphates are of great interest as ion exchangers, precursors for molecular sieves and pillaring materials [1]. Among these phosphates, in particular α-zirconium phosphate, a large number of investigations in recent years were directed to applications in ion-exchange processes, intercalation and catalytic properties [1–4]. Some studies on titanium(IV) phosphate reactivity have been carried out on layered microcrystalline phases that present low external surface and high internal arrangement, as can be expected from the systematic correlation between surface area and crystallinity in this kind of material [5]. The main characteristics of these compounds are related to their property of intercalating a great variety of polar molecules in the cavity between the inorganic backbones formed by the phosphate layers. The host–guest interaction has been shown for a large number of alkylamines, alkanol diamines, glycols, urea, hydrazine, piperidine, pyridines, amides, amino acids and some organometallic compounds [1–4].

The intercalation behavior depends, among other factors, directly on the size and p$K_a$ of the guest molecules [6]. Correlations between the interlayer distances with the aliphatic chain sizes were observed in intercalation studies involving aliphatic amines [7–11]. The majority of these investigations deals with intercalation in zirconium hydrogenphosphate, however, amine intercalations into α-titanium hydrogenphosphate have recently been reported [6–8,11–14].

The intercalation of these species is of interest to further clarify the intercalation chemistry of layered metal phosphates and also because the process leads to the preparation and characterization of new intercalated phases. These new phases are suitable for studying the interlayer organization of the intercalated species and the host–guest interaction, as well as for their potential use in the field of storage of active species, phase-transfer catalysis and drug-release. In addition, quantitative data on guest–host interactions in typi-

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cal intercalation processes can be followed through efficient calorimetric techniques. Such a direct method enables obtaining the enthalpy of acid–base interactions on acidic solids. In spite of the great number of favorable systems that could be explored, only limited thermochemical data have been reported [5,7,8,13–16].

The aim of this investigation is to obtain calorimetric data for the intercalation of 2-, 3- and 4-aminopyridine (2, 3, 4amp), 2-amino-4-methylpyridine (ammp) and 2-aminobenzylamine (abza) into α-titanium hydrogenphosphate. Such data can contribute to better understanding of the intercalation process and to establish a relationship between the basicity center of the guest molecule and the thermochemical data.

## 2. Experimental

### 2.1. Reagents

All chemicals were reagent grade. Titanium trichloride, 15% in hydrochloric acid solution (Carlo Erba), 85% phosphoric acid (Nuclear), and cyclic amines of 99% purity (Aldrich) were used. Crystalline titanium hydrogenphosphate, in alpha form (TPH), was obtained through the oxidation reaction of titanium trichloride and the aromatic amines were distilled before use [13].

### 2.2. Intercalation

The intercalation procedure was performed by a batch method in which 100 mg of TPH compound was suspended in 15.0 $cm^3$ of an amine aqueous solution in several different concentrations, which varied from $2.0 \times 10^{-3}$ to 0.50 mol $dm^{-3}$. The solution was mechanically stirred for 12 h at 298 ± 1 K. The time required to reach equilibrium was previously established in a series of intercalations with different times. The amount of amine inserted into the lamella ($n_{int}$) was calculated by: $n_{int} = (n_i - n_s)/m$, 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 and $m$ the TPH mass [10,13].

### 2.3. Characterization

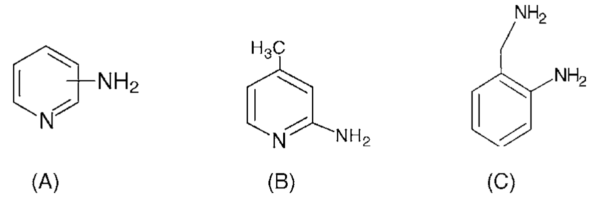
Intercalated materials were characterized by thermogravimetry (TG) with a DuPont model 1090B at a heating rate of $1.67 \times 10^{-2}$ K $s^{-1}$ in argon flow, X-ray diffractometry with Cu Kα radiation in a Shimadzu model XD3A diffractometer from 3 to 50° $2\Theta$, infrared spectrophotometry with a Bomem model MB with a resolution of 4 $cm^{-1}$.

### 2.4. Calorimetry

Calorimetric titrations were performed in an LKB 2277 differential isothermal microcalorimetry system. About 20 mg of the host material was suspended in 2.0 $cm^3$ of doubly distilled water in a stainless steel ampoule. The solid was suspended by stirring in the thermostated calorimetric cell at 298.15 ± 0.20 K. After baseline stabilization, the amine solution was incrementally added through a microsyringe coupled to a stainless steel needle. The thermal effect caused by the reaction was recorded after each addition. The same procedure was used to follow the thermal effect of the host and the guest solutions in water [10,15,16].

## 3. Results and discussion

The series of aromatic amines, 2-, 3- and 4-aminopyridine, 2-amino-4-methylpiridine and 2-aminobenzylamine, shown in Scheme 1, was intercalated into the α-$Ti(HPO_4)_2 \cdot H_2O$ matrix. With exception of 2-aminobenzylamine, all other intercalated phases have previously been structurally studied via X-ray diffraction [14], as illustrated in Fig. 1. A rela-



Scheme 1. Structural formulae for 2-, 3-, 4-aminopyridine (A), 2-amino-4-methylpyridine (B) and 2-aminobenzylamine (C).

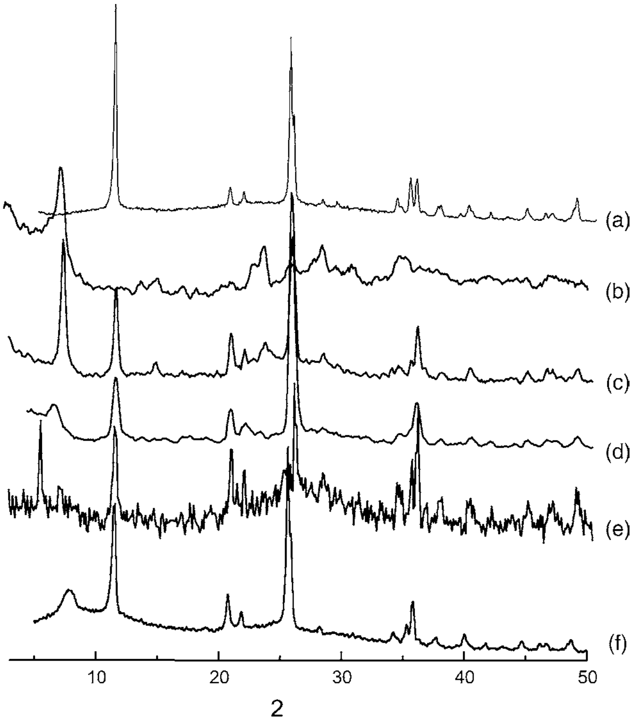


Fig. 1. X-ray diffraction patterns of $Ti(HPO_4)_2 \cdot H_2O$ host (a) and the respective intercalated compounds with guest amines: 4amp (b), 2amp (c), 3amp (d), ammp (e) and abza (f).

Table 1
Maximum intercalated amine value ($n_{\mathrm{int}}$), interlamellar distance ($d$), $x$ and $y$ values in the formula α-$\mathrm{Ti(HPO_4)_2}\cdot x\mathrm{amine}\cdot y\mathrm{H_2O}$ obtained from volumetric titration, $x_{\mathrm{titr}}$, and thermogravimetry, $x_{\mathrm{therm}}$, and the moles of water $y$

| Guest | $n_{\mathrm{int}}$ (mmol g$^{-1}$) | $d$ (pm) | $x_{\mathrm{titr}}$ | $x_{\mathrm{therm}}$ | $y$ |
|---|---|---|---|---|---|
| 2amp | 3.37 | 1338 | 0.84 | 0.79 | 0.47 |
| 3amp | 3.37 | 1177 | 0.82 | 0.76 | 0.34 |
| 4amp | 6.40 | 1262 | 1.65 | 1.47 | 1.00 |
| ammp | 4.52 | 1577 | 1.16 | | |
| abza | 1.70 | 1060 | 0.44 | 0.42 | 0.61 |

tive decrease in crystallinity of the intercalated phases was observed and the interlamellar distances are always higher than the original value of 760 pm found for TPH, as listed in Table 1. Only the guest molecule 4amp did not present the characteristic peak associated with the original matrix, located at $2\theta = 11.6°$ [14]. In this case incomplete intercalation caused matrix mixture phases [14].

Accommodation of the molecules into the free space of the cavity has been previously discussed [3,4,17]. The guest molecules 2amp and ammp are oriented in an inclined position in relation to the inorganic layers, caused by the steric hindrance of the 2-amino group attached to the ring and 3amp and 4amp assume a perpendicular position into inorganic layers [14]. An expansion of the lamella of 300 pm was observed for the 2-aminobenzylamine molecule, which suggests an arrangement in a parallel position inside the inorganic layers. The largest interlamellar distance expansion, more than 800 pm for 2-amino-4-methylpyridine is consistent with an inclined position in a double layer arrangement inside the cavity [14].

The intercalation of amines was quantitatively followed by fitting the experimental data to a modified Langmuir equation [10,14,15]. The number of intercalated amines ($n_{\mathrm{int}}$) inside the crystalline matrix was plotted against the amount of amine in the supernatant solution (Cs), the maxima values of intercalated amines are given in Table 1. The amount of amine intercalated is lower than the expected 7.76 mmol g$^{-1}$, maximum ion-exchange capacity of this inorganic matrix [1,3,15]. The isotherms presented in Fig. 2 showed that the host matrix exhibits a preference for the guest 4amp. The amount of intercalated amine decreased in the sequence: 4amp > ammp > 2amp ≈ 3amp > abza.

The mechanism of intercalation of a heterocyclic amine into the inorganic layers presumes the protonation of the basic centers by the acidic P–OH groups located in the inorganic matrix [7,8], which is supported by infrared spectrophotometry [14]. The infrared spectra in Fig. 3 indicate that the amines interacte strongly with the proton of the P–OH group. The OH band [18] at 1250 cm$^{-1}$ in all spectra except indicates partial amine saturation of the host. For the intercalated 2amp, 4amp and ammp compounds absorption bands may be associated with: (i) $-\mathrm{NH_2}$ bending vibration mode, (ii) pyridinium ion, or (iii) symmetric and asymmetric $-\mathrm{NH_3}^+$ deformation. For 2amp these bands are at 1623 and 1551 cm$^{-1}$; for 4amp at 1655 and 1581 cm$^{-1}$; and for ammp at 1631 and 1538 cm$^{-1}$. These three arylamines exhibit tautomeric equilibria [14], the canonical forms change the character of the aromatic bonds of the ring, affecting the mode of vibration of the pyridinium cation [14,19]. The presence of both bands is in agreement with formation of the organic cation, giving clear evidence of intercalation. The addition bands related to the protonation of the nitrogen pyridine ring are at 1482, 1531, and 1486 cm$^{-1}$ and are attributed to the vibration mode of the 2- and 4-aminopyridinium and 2-amino-4-methylpyridinium cations, respectively. The characteristic band for the $\mathrm{NH_3}^+$ group may also be due

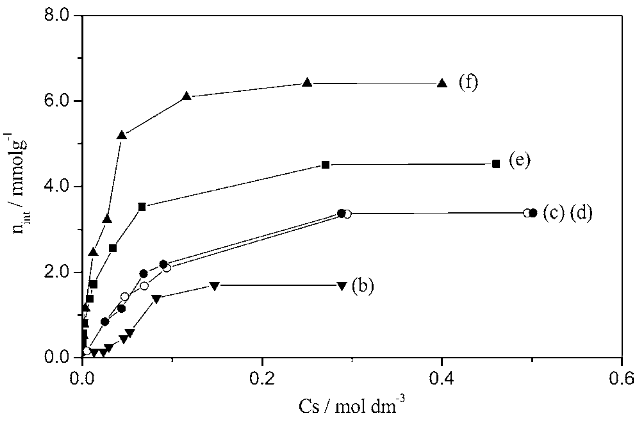


Fig. 2. Isotherm of intercalation of guest amines: abza (b), 2amp (c), 3amp (d), ammp (e) and 4amp (f) into α-titanium hydrogenphosphate at 298 ± 1 K.

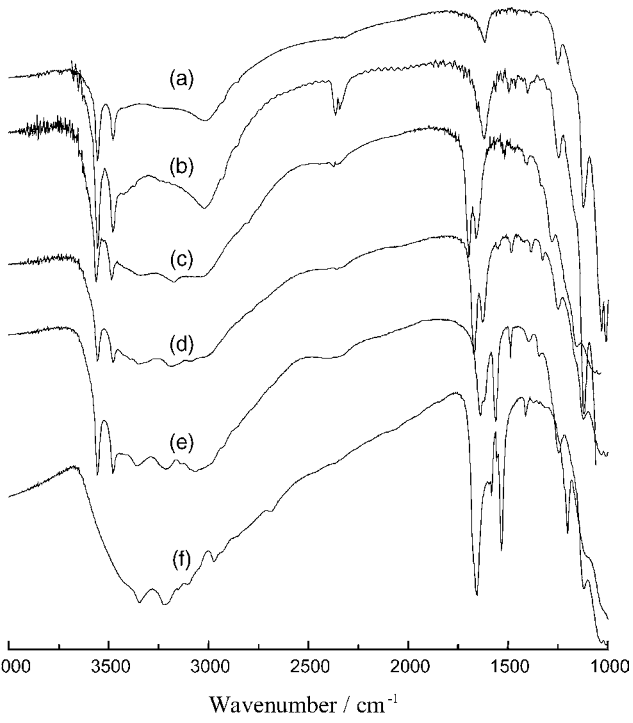


Fig. 3. Infrared spectra of $\mathrm{Ti(HPO_4)_2\cdot H_2O}$ host (a) and the respective intercalated compounds with guest amines: abza (b), ammp (c), 2amp (d), 3amp (e) and 4amp (f).

to the participation of the canonical form located at 1670, 1655, and 1664 $cm^{-1}$ for the same sequence of cations.

The guest 3amp molecule showed one band at 1637 $cm^{-1}$, assigned to the $NH_2$ group [18,19] and two others at 1560 and 1487 $cm^{-1}$ are attributed to the protonated nitrogen of the aromatic ring in the interlayer region of the phosphate structure. The absence of the $NH_3^+$ group could be explained by the absence of such tautomerism.

The intercalated abza compound showed bands at 1560 and 1656 $cm^{-1}$ associated with: (i) $-NH_2$ bending vibration mode, or (ii) symmetric and asymmetric $-NH_3^+$ deformation [18,19]. Another band at 1399 $cm^{-1}$ is assigned to $NH_3^+$ bending, while the weak band at 1614 $cm^{-1}$ could be attributed to angular water deformation or to $NH_2$ deformation. The stretching vibration of this group in the 3400–3250 $cm^{-1}$ region is masked by the OH stretching vibration mode of the inorganic matrix.

The number of intercalated organic molecules determined from the titration data is in agreement with the thermogravimetric results listed in Table 1 and ammp did not show defined stages of decomposition. The thermogravimetric curves presented four steps of decomposition for 2, 3, 4amp and abza intercalated compounds, corresponding to 2.5, 1.8, 5.5 and 4.2% of loss of mass, to give 0.50, 0.30, 1.0 and 0.60 mol of water of hydration, respectively. The intercalated ammp molecule presented overlapped stages in the curve that did not permit the quantification of the decomposition. The second and third steps, from 373 to 700 K corresponding to the release of amines, gave 23.0, 20.0, 35.0 and 17.0% of weight for 2, 3 and 4amp and abza. These data give 0.79, 0.76, 1.47 and 0.42 mol of amine intercalated per each mole of the host matrix, respectively. The last loss of mass is attributed to the release of 1 mol of water, due to the condensation of the vicinal hydrogenphosphate groups of the inorganic structure to form the pyrophosphate as residue.

To obtain better information on the energetics of the intercalation processes for cyclic amines, represented here as $N{\sim}NH_2$, calorimetric titrations were carried out in aqueous solution. On entrance of the amine into the lamellar cavity, it interacts with the monohydrogenphosphate group, ($O_3P$–OH), enabling proton transfer to the base to form the organic cation. This species is electrostatically bonded to the inorganic sheets with the aromatic amine in the original free interlamellar space. Thus, the overall reaction is related to the protonation of the amine basic centers by the acidic groups of the inorganic layer, in a typical acid–base interaction [7], represented by the following series of reactions:

$$\begin{aligned}&O_3P\text{–}OH = O_3P\text{–}O^- + H^+\\&N \sim NH_2 + H^+ = N \sim NH_3{}^+\\&O_3P\text{–}O^- + N \sim NH_3{}^+ = O_3P\text{–}O^- + H_3N \sim N\\&O_3P - OH + N \sim NH_2 = O_3P - O^- + H_3N \sim N\end{aligned} \tag{1}$$

In the course of the calorimetric titration, the thermal effects observed ($\Delta_{tit}h$) are related to overall reaction in the preceding scheme. For completeness the thermal effect of hydration of the host ($\Delta_{hyd}h$) and that related to dilution ($\Delta_{dil}h$) should also be considered. Thus, the net enthalpy change of the reaction ($\Delta_r h$) can be calculated by means of the expression: $\Sigma\,\Delta_r h = \Sigma\,\Delta_{tit}h - \Sigma\,\Delta_{dil}h$, due to the fact that a null effect was found for hydration of the host matrix [10,15,16]. These values are represented as a function of the volume added ($V_{ad}$), as exemplified for 3amp in Fig. 4.

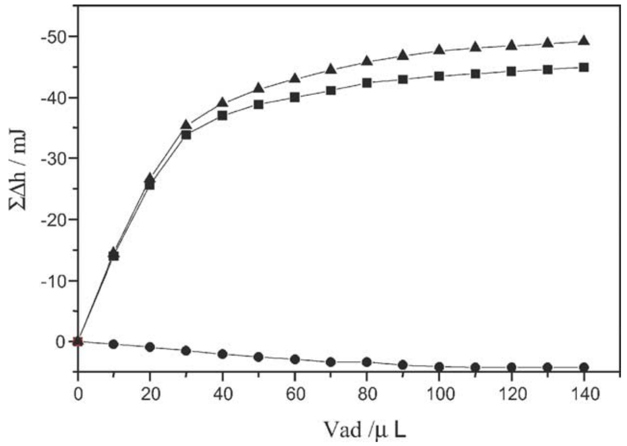


Fig. 4. The experimental curve represents the sum of the thermal effects $\Sigma\,\Delta_{tit}h$ (■), $\Sigma\,\Delta_{dil}h$ (●), $\Sigma\,\Delta_r h$ (▲) for calorimetric titration of 3-aminopyridine into $Ti(HPO_4)_2{\cdot}H_2O$.

From the thermal effects related to direct titration and the recorded dilution, the enthalpy of reaction ($\Sigma\Delta_R H$) and also the enthalpy of intercalation ($\Sigma\Delta_{int}H$) can be calculated (J $mol^{-1}$) by the modified Langmuir equation [20]. The calorimetric data enable the calculation of the enthalpy of intercalation to form a monolayer per unit mass of the host, $\Delta_{mono}H$. For this modified Langmuir equation was adapted to describe heterogeneous systems [14,15,21-25].

$$\frac{\Sigma X}{\Sigma\,\Delta_R H} = \frac{1}{(K-1)\Delta_{mono}H} + \frac{\Sigma X}{\Delta_{mono}H} \tag{2}$$

where $X$ is the fraction, in moles, of the amine in solution after the interaction, $\Delta_R H$ is the integral enthalpy of interaction for one gram of the matrix (J $g^{-1}$), K is a proportionality constant that includes the equilibrium constant, and $\Delta_{mono}H$ is the integral enthalpy of interaction to form a monolayer for a unit of mass of the matrix (J $g^{-1}$). For each incremental solute addition, a corresponding $X$ value can be calculated. Thus, a plot of $\Sigma X/\Sigma\,\Delta_r H$ versus $\Sigma X$ gives $\Delta_{mono}H$ and $K$ values from the angular and linear coefficients, respectively, using the linearized form of the equation, as shown in Fig. 5. The calculation of $\Delta_{int}H$ was based on the expression: $\Delta_{int}H = \Delta_{mono}H/n_{int}$ where $n_{int}$ is the number of intercalated moles, after establishing calorimetric equilibrium in the solid/liquid interface [21–25]. The enthalpic results for the intercalation of these heterocyclic amines are exothermic, as shown in Table 2.

The presence of a substitute group on pyridine ring affects the effectiveness of heterocyclic nitrogen atom through a Bronsted acid–base interaction [13,14]. Such energetic

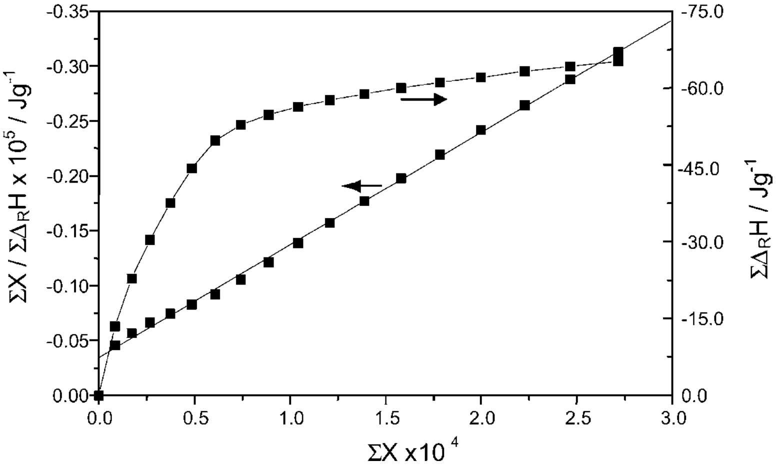


Fig. 5. Isotherm of the integral enthalpy of intercalation ($\Delta_{\text{int}}H$) of 2-amine-4-methylpyridine guest given by $\Sigma\,\Delta_r H$ vs. $\Sigma X$ plot. The linearized form is represented by $\Sigma X/\Sigma\,\Delta_r$ vs. $\Sigma X$ plot.

effects of monoamine groups when intercalated in monolayer should be related to features associated with the structural arrangement of the active group bonded on ring. However, the enthalpy of interaction listed in Table 2 gave very close values for amine groups on carbons 2 and 4. These values suggested that: (i) the inclined arrangement of 2amp favors the interaction of amino group with the acidic center beyond that one with the heterocyclic nitrogen atom, (ii) the amino group on position 4 of the ring causes also a favorable canonical condition [14] to intercalate as demonstrate through the partial saturation of acidic P–OH groups on each lamella, and (iii) neither of these favorable conditions were available for 3amp, which gave the smallest enthalpic value. Based on the restricted thermodynamic data on such systems, comparison with aminopicoline molecules [13] can be done. For example, the aminopyridine molecules showed a relative dependency of intercalation on the attached amine groups on heterocyclic ring in bond formation. Such behavior contrasted with that observed with picoline molecules, in which the methyl steric hindrance can superimpose on the favorable inductive effect for bond formation, as observed with 2-aminopicoline, to give the smallest adsorption and thermodynamic values [13,26,27].

The association of the favorable methyl inductive effect on the amine heterocyclic ring of 2-amino-4-methylpyridine caused a high degree of adsorption, 4.52 mmol g$^{-1}$, with a large lamellar expansion to 1577 pm, in a proposed double guest layer formation inside the lamellar cavity. The lowest enthalpic value, $-14.02 \pm 0.07$ kJ mol$^{-1}$, can be interpreted by considering the unfavorable thermal effect caused simultaneously as the interlamellar space is expanded, during bond formation. Such endothermic effects on lamellar expansion decrease the expected favorable exothermic value.

The entrance of abza molecules in parallel position within the lamellar space gave the lowest number of moles intercalated, 1.70 mmol g$^{-1}$. When this molecule is bound the available acidic centers are covered and the reactivity of the neighborhood sites is obligatorily blocked, to give the smallest interlamellar distance of 1060 pm. This aromatic molecule does not contain a heteroatom in the ring and both amine primary basic centers differ in coordinating behavior from the other molecules. Consequently, the obtained enthalpy, $-29.77 \pm 0.29$ kJ mol$^{-1}$, is not comparable with that of the other guest molecules, which contain a heteroatom nitrogen basic center.

The Gibbs free energy was calculated from the expression $\Delta G = -RT\ln K$ and the equilibrium constant value was obtained from the calorimetric data [13–16] by Eq. (2) and the results are shown in Table 2. The negative values for all systems indicate that the reactions are spontaneous in nature. The entropic values were calculated from the expression $\Delta G = \Delta H - T\Delta S$. With the exception of

Table 2
Integral enthalpy of intercalation to form a monolayer per unit mass of the host ($\Delta_{\text{mono}}H$), enthalpy ($\Delta_{\text{int}}H$), Gibbs free energy ($\Delta G$) and entropy ($\Delta S$) for the intercalation

| Guest | $-\Delta_{\text{mono}}H$ (J g$^{-1}$) | $-\Delta_{\text{int}}H$ (kJ mol$^{-1}$) | ln $K$ | $-\Delta G$ (kJ mol$^{-1}$) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|
| 2amp | 123.84 ± 0.07 | 36.75 ± 0.78 | 12.42 | 30.8 ± 0.3 | −20 ± 1 |
| 3amp | 68.81 ± 0.01 | 20.42 ± 0.28 | 12.02 | 29.8 ± 0.1 | 32 ± 1 |
| 4amp | 225.76 ± 0.87 | 35.23 ± 0.07 | 10.29 | 25.5 ± 0.1 | −33 ± 1 |
| ammp | 63.37 ± 0.01 | 14.02 ± 0.07 | 10.33 | 25.6 ± 0.1 | 39 ± 1 |
| abza | 50.61 ± 0.02 | 29.77 ± 0.29 | 14.28 | 35.4 ± 0.4 | 19 ± 1 |

2amp and 4amp, the heterocyclic amines presented unfavorable entropic contribution to $\Delta G$ values. However, this effect is compensated by the large favorable enthalpic values. The positive favorable entropic results are in agreement with the replacement of the water molecule initially bonded to the matrix or those associated with the aromatic amine through hydrogen bonding, which causes a disorganization of the system, and are free as the intercalation takes place [28,29].

## 4. Conclusion

The series of aromatic amines intercalated into crystalline α-titanium hydrogenphosphate causes interlamellar expansion in accord with the structural features of each polar molecule. The non-heterocyclic aromatic molecule, 2-aminobenzylamine, was arranged in a position parallel to the inorganic layer. Such disposition of the organic ring restricts intercalation reflect in a low number of inserted molecules. When the basic nitrogen atom is within the aromatic ring the set of molecules is intercalated in inclined or in perpendicular positions in relation to the inorganic backbone. However, due to the favorable condition established for both basic nitrogen centers, supported by an increase in the methyl inductive effect, as in 2-amino-4-methylamine, a double layer of this molecule is arranged within the free cavity, as shown by the largest interlamellar distance.

The thermochemical data reflect the facility of intercalation of such molecules as spontaneous as expressed by a negative Gibbs free energy and exothermic reactions. The lowest enthalpic value for 2-amino-4-methylamine molecule may be related to the endothermic contribution of the expansion of the layers as the intercalation takes place.

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