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The Intercalation of Some Heterocyclic Amines into α-Titanium Hydrogenphosphate—Structural and Calorimetric Data

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The intercalation of the heterocyclic amines 2,6-lutidine, pyrazine, piperazine, and piperidine into α-titanium hydrogenphosphate gave the maximum amounts intercalated in aqueous solutions of 0.45, 0.65, 2.77, and 6.52 mmol g^{-1}, respectively, through a batch method at 298 ± 1 K. The original interlamellar distance of 760 pm increased after intercalation of piperazine and piperidine molecules, while for 2,6-lutidine and pyrazine molecules no change was observed. These results suggested that the amines were bonded only on the surface of the host. All thermochemical data were obtained on a differential isothermic microcalorimetric instrument by means of a titration procedure. From thermal effect data, the variation in enthalpy for each system gave exothermic values of -6.56 ± 0.10, -1.00 ± 0.10, -10.10 ± 0.34, and -31.44 ± 0.71 kJ mol^{-1} for intercalations of the above sequence of heterocyclic amines. The infrared spectra are in agreement with acid–base reactions, involving the layered acid host O_3P–OH of the inorganic matrix and the basic center atoms of the guest molecules.

Key Words: **layered compounds; intercalation; α-titanium hydrogenphosphate; calorimetry; heterocyclic amine.**

INTRODUCTION

Crystalline inorganic layered acid phosphate compounds of tetravalent metals, such as those formed by Zr, Ti, Sn, Hf, and so on, have been the subject of many investigations due to their ability to act as an ionic exchanger as well as their involvement in many processes of insertion of organic guest molecules containing active basic centers into the interlamellar cavities (1). These phosphates are acidic solids of intermediate strength, favoring readily the intercalation of amines (2). The intercalation behavior depends mainly on properties associated with the guest molecule such as size and polarity (3, 4).

The intercalation of polar organic molecules into this kind of layered compound can be interpreted as the interaction of the inorganic host layers with the organic guest molecules and accompanying such an operation is an increase in the interlamellar separation (5). The fully intercalated material consists of regularly alternating organic and inorganic layers and both the physical nature and the chemical reactivity of the material can be significantly altered (6–9). Titrating the inorganic support with diluted solutions of the amines to be intercalated may lead to the intercalation of amines into layered phosphates. The titration curves yield information on the saturation capacity of the intercalation toward the variation of the amount of amines at certain pH values (10, 11).

The literature reports several investigations on the intercalation of a variety of amines, such as secondary, tertiary, cyclic, or arylic amines, into these materials (6, 8, 12–15). The intercalation of these species is of interest in order to further clarify the intercalation chemistry of layered metal phosphates and also because the process leads to the preparation and characterization of a new intercalated phase. 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. However, the calorimetric technique has been used as a direct method for measuring the enthalpy of the acid–base interactions in acid solids. The thermochemical data related to these kinds of compounds are limited as described in the literature (16–21).

The aim of this publication is to report some calorimetric and structural data involving the intercalation of 2,6-lutidine (lu), pyrazine (pz), piperidine (ppe), and piperazine (ppz) into α-titanium hydrogenphosphate. Although these chosen bases contain the same basic heteroatoms attached to the rings, they differ in structural features, such as aromatic (lu, pz) or unsaturated (ppe, ppz) rings, acting potentially as mono- (lu, ppe) or bidentate (pz, ppz) groups and with large hindrance (lu). The thermal effects associated with the acidic inorganic host matrix and the basic guest

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centers are explored in order to further the understanding of the intercalation process.

EXPERIMENTAL

All chemicals used are reagent grade. Titanium trichloride 15% in hydrochloric acid solution (Carlo Erba), phosphoric acid 85% (Nuclear), and cyclic amines of 99% purity (Aldrich) were used. The crystalline titanium hydrogenphosphate in α form (TiP) was obtained through the oxidation of titanium trichloride. This synthesis was obtained by reacting 0.126 moles of titanium trichloride 15% solution with 0.50 moles of phosphoric acid 85% for 4 days in a polyethylene flask at 333 K, with periodic stirring. The solid material was separated by centrifugation and washed with double-distilled water until the wash reached the range of pH 3.5 to 4.0, and the final product was then dried at 313 K and characterized as previously described (22), to give an interlayer distance of 760 pm. The cyclic amines were carefully distilled before use.

The intercalation process for all cyclic amines was followed batchwise in an aqueous media at 298 ± 1 K. Samples of TiP were suspended in variable concentrations in the range of 2.0×10^{-3} to 0.20 mol dm^{-3} of aqueous amine solutions in polyethylene flasks with a solid:solution proportion of 1.0 g:0.10 dm^3. The suspension was mechanically stirred for 12 h. The time required to reach equilibrium was previously established for a series of intercalations with different times, by using a constant mass of the lamellar compound with a variable set of amine solutions. After the appropriate time, the solid was separated by centrifugation and dried at 313 K. With the exception of pyrazine, which was determined by UV spectroscopy, in the order of concentration of 1.0×10^{-4} mol dm^{-3}, using a quartz cell with a path length of 1.0 cm, monitoring the absorption band (23) at 259 nm, the other three amines were determined by titrating the supernatant with standard hydrochloric acid solution. The degree of intercalated heterocyclic amines was also determined by submitting the samples to termogravimetry (17).

The amount of amine inserted into the lamella (n_{int}) was determined by using 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 equilibrium, and m is the mass of TiP. For each experimental point, the reproducibility was checked by at least one duplicate run.

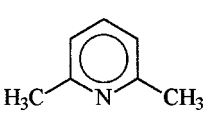
The calorimetric titration was performed in a differential isothermic microcalorimetric system LKB 2277. Approximately 20.0 mg of the host was suspended in 2.0 cm^3 of double-distilled water in a stainless steel ampoule. The system was shaken with a gold helix and thermostated at 298.15 ± 0.02 K. After stabilization of the base line, 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 of the titrant. The same procedure was used to follow the thermal effect of dilution of the host and the guest solution in water (21, 22).

Intercalated materials were characterized by using the following techniques: thermogravimetry (TG) with a DuPont model 1090B instrument, at a heating rate of 0.17 K s^{-1} and argon flux, X-ray diffractometry with Cu$K\alpha$ radiation in a Shimadzu model XD3A diffractometric apparatus, and infrared spectroscopy with a BOMEM model MB-series instrument.

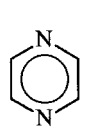
RESULTS AND DISCUSSION

The isotherms of intercalation presented in Fig. 1, showed that the host matrix exhibits a preference for the guest piperidine, when compared with the other cyclic amines. This behavior is connected to the pK_a, because piperidine is the strongest base, presenting a pK_a value of 11.12 (24). The lowest pK_a values associated with the guest molecules 2,6-lutidine and pyrazine caused weaker interactions with the matrix host and a clear distinction in intercalation is shown in the inset part of Fig. 1.

The distinct behavior presented by the cyclic amines pyrazine and 2,6-lutidine should be related to the following features: in the former amine the interaction is strongly affected by its low pK_a value, which is in the order of 0.70; however, for the latter one the main influence on the intercalation should be related to the hindrance effect of the methyl groups. This kind of disturbance caused by the methyl groups was previously observed with picoline amines, where the position of the attached group on the ring causes a drastic change in the amount of the amine intercalated (21). The respective structures of the sequence of cyclic amines used in this investigation are illustrated below. In the present case, the amount of uptake of intercalated amine gives values of 0.45, 0.65, 2.77, and 6.52 mmol g^{-1} for lu, pz, ppz, and ppe, respectively.



2,6-lutidine (lu)



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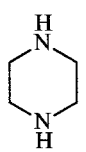
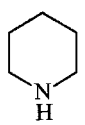


piperazine (ppz)



piperidine (ppe)

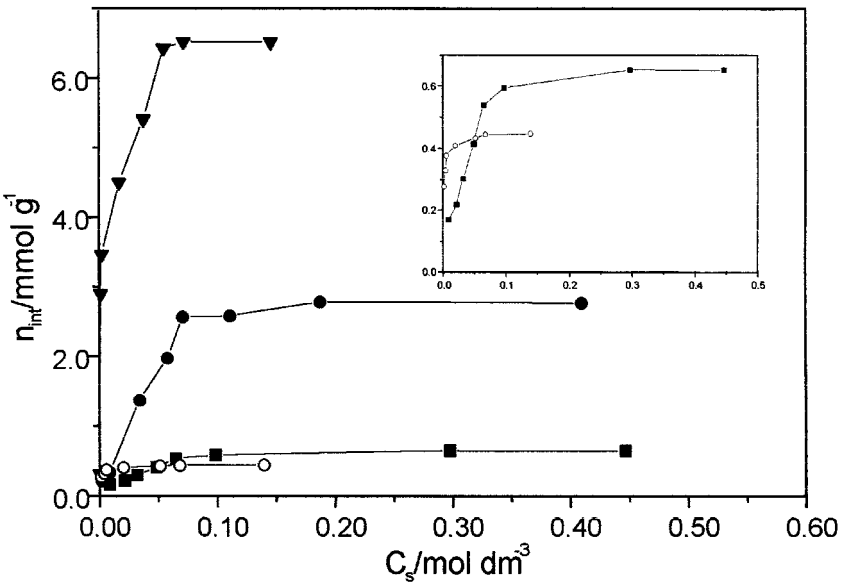


FIG. 1. Isotherms of intercalation at 298 ± 1 K of amines 2,6-lutidine (○), pyrazine (■), piperazine (●), and piperidine (▼) into $Ti(HPO_4)_2 . H_2O$. The difference in behavior between 2,6-lutidine and pyrazine shown in the inset.

X-ray diffraction patterns presented in Fig. 2 showed that the intercalation process causes an increase in the interlamellar distance of the matrix, from 760 pm to 1060 and 1660 pm for ppz and ppe, respectively. On the other hand, the guest 2,6-lutidine and pyrazine molecules did not change the original interlamellar distance. This result suggests that the basic molecules are protonated only by the available acidic hydrogenphosphate groups disposed on the host surface and consequently, an enlargement of the interlamellar distance occurred. The number of moles of these amines intercalated corroborated with this proposal. In such cases, the lower basicity of these guest molecules disfavors the intercalation and did not induce any separation of the lamella. However, the inserted amount of amine can be increased if the methodology of intercalation is altered (6). Based on the proposed mechanism of intercalation of amines into hydrogenphosphate layers, which is interpreted as being due to the occurrence of an acid–base-type reaction, for molecules with very weak basic centers, if any intercalation took place, only a small amount of the amine inserted into the interlamellar cavity can be expected (6).

The intercalation of molecules of low basicity, such as pyrazine, pyrazole, and hexamethylenotetramine, was successfully improved previously by expanding the original interlamellar distance of the matrix host through the insertion of a molecule of low polarity to establish an initial favorable condition in the structure, to accommodate the desired molecule in the next stage of intercalation (6). This procedure was applied for the direct intercalation of these three cyclic amines, after the matrix was pre-intercalated with ethanol (25,26). A proposed method to promote this kind of intercalation is based on an *in situ* reaction, where guest species are directly introduced into the free space during the synthesis of the matrix (18).

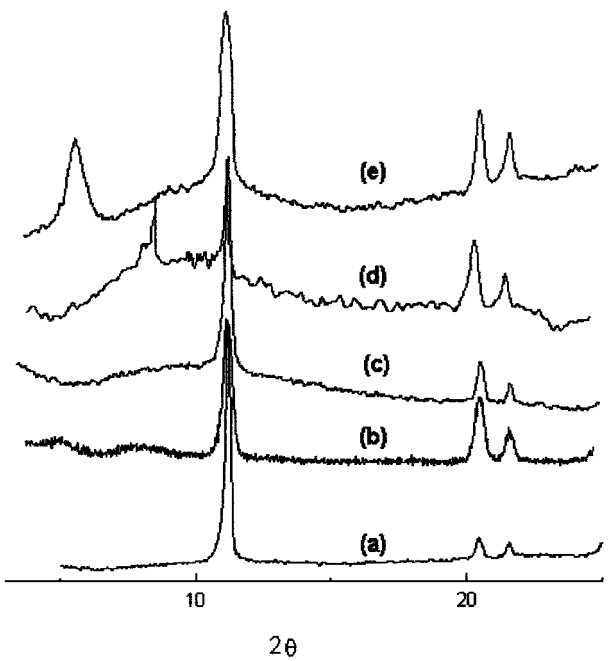


FIG. 2. X-ray diffraction patterns of $Ti(HPO_4)_2.H_2O$ host (a), and the respective intercalated compounds with guest amines: 2,6-lutidine (b), pyrazine (c), piperazine (d), and piperidine (e).

Aniline, benzylamine, cyclohexylamine, piperidine, pyrazine, and piperazine composed another series of cyclic amines that was intercalated through the batch method or by exposing this same host to a vapor of amines (27). For piperidine the interlamellar distance of 1360 pm differed from the present obtained value of 1660 pm. However, for piperidine and pyrazine the lamellar structure of the solids changed to poor crystalline materials as the time of intercalation increased (27). The decrease in crystallinity was also detected for the set pyridine and α-, β-, and γ-picolines (21). On the other hand, for pyridine the interlamellar distance of 1800 pm seemed to indicate an apparent contrast to other reports (6, 14, 28).

A first stage in the process of intercalation of pyridine involved the formation of an unsaturated phase at 1090 pm, as observed for other investigations (6, 14, 28). This interlamellar distance for this phase contained 3.75 mmol of pyridine, changing to 1800 pm as the final phase is formed. From 3.75 to 15.0 mmol of pyridine only this peak is detected due to the establishment of the final phase and the diffractogram showed the appearance of some amorphous material (21).

Based on these data, and the distinct behavior presented by this series of bases during the intercalation, two main features could be considered: (i) the amount intercalated and (ii) the arrangement of the amines into the solid matrices. Thus, with piperazine the largest amount intercalated gave an amorphous material, while with piperidine the arrangement of the amines into the lamella gave an average inclined angle of 43° between the amine chain and the hydrogenphosphate layer (27). However, in the present case the same molecules are disposed in the perpendicular position.

Piperidine and pyrazine molecules are very similar in structure and both caused different increases in the observed interlamellar distance (21), suggesting that different orientations can be expected for these inserted species. Thus, the interlamellar expansion can reflect about the possible arrangement of these amines into the free cavity of the matrix, if we consider the relationship between the interlamellar distance and the length of the molecules involved, as was previously observed for the couple pyridine and 4-aminopyridine (14, 21).

The length of pyridine is 330 and 580 pm in the parallel and perpendicular positions, respectively, while 4-aminopyridine has a length of 462 pm in the perpendicular position in relation to the inorganic layer. This last molecule gave an interlamellar distance of 1262 pm (15), in contrast to 1800 pm for the former molecule, and the value is in complete agreement with the proposed inclined position. In the present case, as the intercalation occurred, the entrance of piperazine and piperidine caused a net expansion of 300 and 900 pm, respectively. Under such conditions, the experimental values suggested that piperazine is parallel to the inorganic layer, while piperidine assumed a perpendicular orientation to the same inorganic sheet, to form a bilayer arrangement in the cavity.

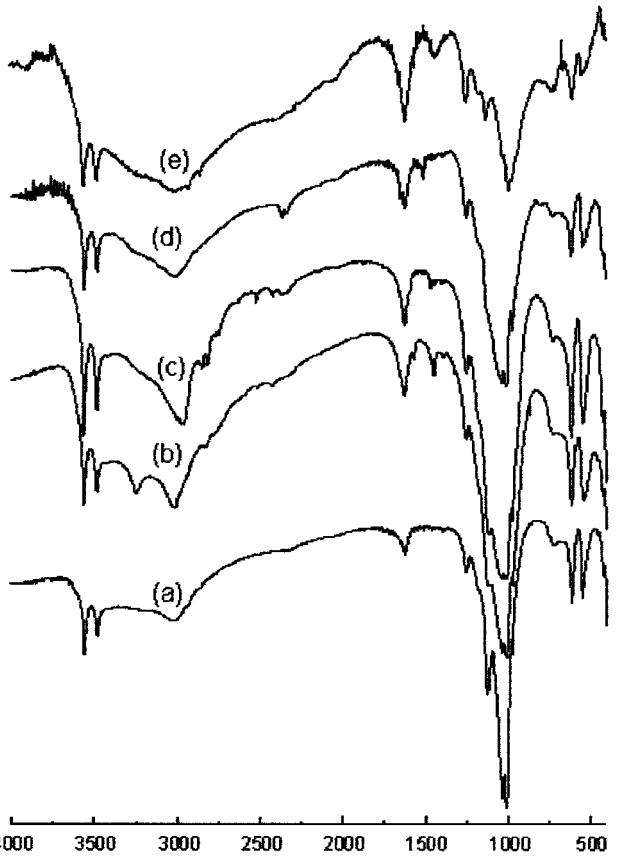


FIG. 3. Infrared spectra of $Ti(HPO_4)_2.H_2O$ host (a) and the intercalated compounds with 2,6-lutidine (b), pyrazine (c), piperazine (d), and piperidine (e).

Infrared spectra of the original and intercalated matrices are presented in Fig. 3. The band at 1250 cm^{-1} is assigned as the out-of-plane deformation of the P–OH groups (5, 13) and is also a clear diagnostic for the presence of the free monohydrogenphosphate group. When any interaction occurred, the band did not disappear, but decreased in intensity, indicating a partial amine saturation of the acidic centers by the amines. The characteristic bands (29) at 1634 and 1538 cm^{-1} for 2,6-lutidine and 1605 and 1580 cm^{-1} for pyrazine correspond to the vibration modes NH^+ due to the protonation of amines. Bands of protonation for piperidine and piperazine were observed at 1583 and 1582 cm^{-1}, which are related NH_2^+ deformation groups. The occurrence of other bands is related to vibration modes of the same groups as observed in the 2700 to 2500 cm^{-1} region.

Thermogravimetric curves of the inserted materials present a similar behavior, displaying three well-defined steps of mass loss. However, the thermodecomposition of the original matrix showed only two stages (6, 22), as shown in

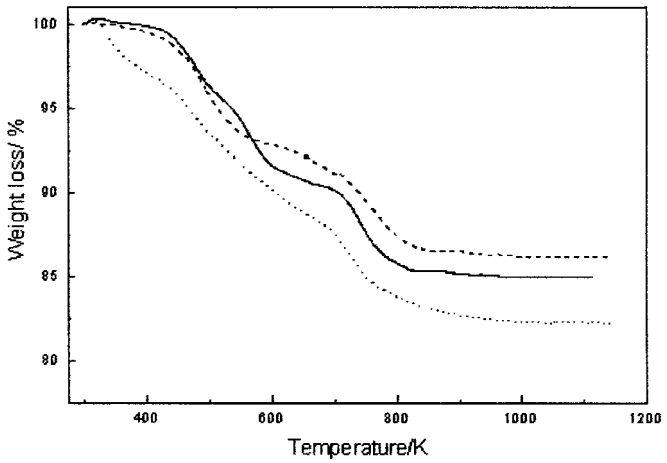


FIG. 4. Thermogravimetric curves of matrix (– –) and compounds with pyrazine (–) and piperazine (⋯) guests.

Fig. 4. For the inserted materials, the first step of mass loss occurred in the temperature range between 303 to 373 K, which corresponded to the loss of water of hydration, which was followed by the second step at 373 K. In this stage, a mass loss of 4.0, 4.5, 11.0, and 35.0% for the cyclic amines 2,6-lutidine, pyrazine, piperazine, and piperidine, respectively, was detected. The third step of mass loss occurred at a temperature over 600 K, being the loss of 1 mole of water due the reorganization of the phosphates groups, to form pyrophosphate as residue (6, 22). The decomposition curves for the heterocyclic amine pyrazine and piperazine are illustrated in Fig. 4.

The amount of inserted organic molecules was determined from the titration data of the supernatant after intercalation, and was compared to that determined by thermogravimetry, as also shown in Table 1. Smaller values are obtained by termogravimetry when compared with those values obtained by titration. This difference can be attributed to the adsorption of the amines on the surface of the matrix. Consequently, the quantification from titration can be masked, while the thermogravimetric data of the modified material were obtained after the compound was washed with the purpose of removing all the molecules adsorbed on the surface.

TABLE 1

Number of Moles of Amines Intercalated (n_{int}) of 2,6-Lutidine (lu), Pyrazine (pz), Piperidine (ppe), and Piperazine (ppz), Interlamellar Distance (d), x Values in the α-Ti$(HPO_4)_2 . x$amine$. Y H_2O$ Formula, Obtained from Volumetric Titration x_{tit}, Thermogravimetry x_{therm}, and the Moles of Water Y

Guest	n_{int}/mmol g^{-1}	d/pm	Y	x_{tit}	x_{therm}
lu	0.45	760	1.0	0.12	0.10
pz	0.65	760	1.0	0.17[a]	0.15
ppe	6.52	760 + 1660	0.4	1.68	1.64
ppz	2.77	760 + 1060	0.3	0.70	0.43

[a]Determined by UV spectroscopy.

The thermal effect of intercalation of amines into the TiP matrix was calorimetrically determined. The overall reaction may be regarded as a protonation of the basic centers of the amines, constituted by the nitrogen ring, which interacts with the acidic PO_3–OH groups of the matrix.

The thermal effect of hydration of the original matrix in the calorimetric solvent was detected as null. Thus, the resultant effect of the reaction ($\Sigma\Delta_r H$) can be calculated from the individual thermal effects of titration and dilution, by using the following expression: $\Sigma\Delta_r H = \Sigma\Delta_{tit} H - \Sigma\Delta_{dil} H$.

From the obtained set of thermal effects related to direct titration and dilution, recorded as joules per gram, the enthalpy of reaction ($\Sigma\Delta_R H$) and the enthalpy of intercalation ($\Sigma\Delta_{int} H$) can be calculated as joules per mole by using the previous data adjusted to the modified Langmuir equation (30). In such a case, a sequence of values was obtained from the calorimetric data to enable the calculation of the enthalpy of intercalation to form the monolayer per unit of mass of the host, $\Delta_{mono} H$, by using the equation below. The modified Langmuir equation was adapted to describe several types of systems (22, 31, 32).

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

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 1 gram of the matrix (J g^{-1}), K is a constant of proportionality that includes the equilibrium constant, and $\Delta_{mono} H$ is the integral enthalpy of interaction to form a monolayer, for unit of mass of the matrix (J g^{-1}). For each addition of the solute, a corresponding X value can be calculated. Thus, a plot of $\Sigma X/\Sigma\Delta_r H$ versus ΣX gives $\Delta_{mono} H$ and K values from the angular and linear coefficients, respectively, after the linearization 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 reaching the calorimetric equilibrium.

It is worth mentioning that investigations involving calorimetric techniques for detection of the thermal effects associated with intercalation processes are rare. The enthalpic results for all amines are exothermic in nature, giving the following values: -6.56 ± 0.10, -1.00 ± 0.10, -10.10 ± 0.34, and -31.44 ± 0.71 kJ mol^{-1} for 2,6-lutidine, pyrazine, piperazine and piperidine, respectively, as shown in Table 2. The small enthalpic value obtained from the calorimetric titration for pyrazine intercalation reflects the

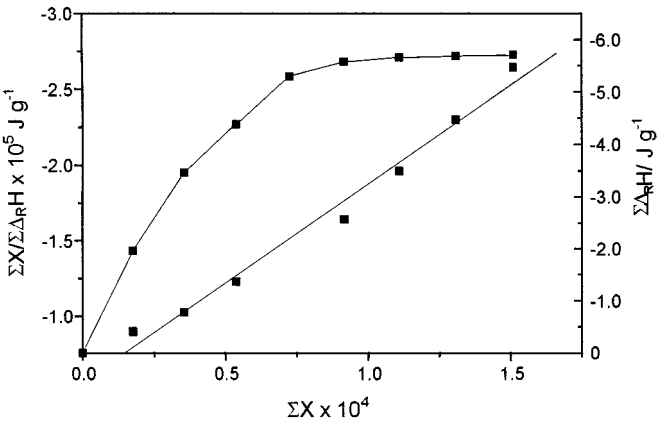


FIG 5. Isotherm for integral enthalpy intercalation ($\Sigma\Delta_r H$) versus molar fraction (ΣX) of piperazine guest in $Ti(HPO_4)_2 . H_2O$. The linearized form is given by the $\Sigma X/\Sigma\Delta_r H$ versus ΣX plot.

low affinity of this amine to fit into the interlamellar space of the inorganic phosphate structure. On the other hand, despite the low amount of 2,6-lutidine intercalated a relative high enthalpic value is observed, when compared to pyrazine. This behavior seems to be associated with a large entropic contribution to the system.

From the structural point of view, the reaction of intercalation is driven by the acid–base interaction between the heteroatom of the cyclic amine and the P–OH group of the layer. However, the energy required to expand the layer is supplied by the formation of new hydrogen bonds (6), which are connected to the protonation of the intercalated amine and this process is surely associated with an exothermic reaction (6), as observed by the listed values in Table 2.

The Gibbs free energy was calculated from the expression $\Delta G = -RT\ln K$, from which constant values were obtained from the calorimetric data shown in Table 2. The negative values for all systems indicate that the reactions are spontaneous in nature. With the exception of the guest piperidine that presents a negative value, all other entropic values, calculated from $\Delta G = \Delta H - T\Delta S$, listed in the Table 2, are also consistent with the argument that the reactions are entropically favored. These values suggested a disruption of the molecules of the solvents bonded into the interlamellar space, which were previously bonded to the inorganic matrix and also those associated with the heterocyclic amines. The increase in entropy is related to the release of these molecules to the solution after intercalation (17, 21, 22, 31).

CONCLUSIONS

The intercalation of heterocyclic amines into α-titanium hydrogenphosphate provided compounds with the general formula $Ti(HPO_4)_2(amines)_n . xH_2O$. The interlayer distance of the intercalated compounds showed a dependence on the pK_a of amines, the largest value of 1660 pm being associated with piperidine, and for pyrazine 760 pm was obtained at pK_a 11.12 and near 0.70, to give the corresponding number of moles of amines intercalated of 6.52 and 0.65 mmol g^{-1}, respectively. The low value of 0.45 mmol g^{-1} for 2,6-lutidine is also affected by the hindrance effect of the neighboring methyl groups bonded to the ring.

All the intercalation processes gave results indicating that the acidic centers of the inorganic layers were partially saturated, as indicated for the free P–OH groups by infrared spectroscopy and the original interlamellar distance of the matrix by X-ray diffraction patterns. The weight loss by thermal decomposition of intercalated matrices consists the following stages: (a) loss of the hydration water, (b) loss of the organic molecules, and (c) loss of the structural water.

A net exothermic thermal effect from the guest basic–acidic centers was observed for all interactions, with the largest enthalpic value of -36.25 ± 0.71 kJ mol^{-1} for the strongest base piperidine, whose value reflected an unfavorable entropic condition. The thermochemical data are in agreement with spontaneity of the reactions, expressed by the variation of the free Gibbs energy.

The nonaromatic basic nitrogen heteroatom guest molecules showed a great tendency to interact strongly with the acidic host centers, as expressed by the amount of moles intercalated, displacement of the lamellar layers, and also the variation in enthalpy. The structural features associated with the thermochemical data for this kind of system can

TABLE 2
Thermochemical Data for the Guest Aromatic Amines 2,6-Lutidine (lu), Pyrazine (pz), Piperidine (ppe), and Piperazine (ppz) Intercalated into α-$Ti(HPO_4)_2 . H_2O$ Host at 298.15±0.02 K

Guest	$-\Delta_{mono}H$/J g^{-1}	$-\Delta_{int}H$/kJ mol^{-1}	ln K	$-\Delta G$/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
lu	2.95 ± 0.01	6.56 ± 0.10	13.72	34.0 ± 0.3	92 ± 1
pz	0.65 ± 0.02	1.00 ± 0.10	7.74	19.2 ± 0.2	68 ± 1
ppe	236.4 ± 2.4	36.25 ± 0.71	10.00	24.8 ± 0.4	− 12 ± 1
ppz	27.98 ± 0.09	10.10 ± 0.34	11.46	28.4 ± 0.4	61 ± 1

indicate not only the interactive mechanism, but also the energetics of the guest–host interaction in an intercalation process.

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