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Calorimetric data on *n*-alkyldiamines intercalated into calcium phenylphosphonates

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Abstract

Layered crystalline calcium phenylphosphonate, as anhydrous $Ca(HO_3PC_6H_5)_2$, and hydrated $Ca(HO_3PC_6H_5)_2{\cdot}2H_2O$ forms were used as hosts for intercalation of *n*-alkyldiamine molecules $H_2N(CH_2)_nNH_2$ ($n = 2$–6) in water or 1,2-dichloroethane. The amount intercalated (n_f) was followed batchwise at 298 ± 1 K and the variation of the original interlayer distance (d) for hydrated calcium phenylphosphonate (1525 ppm) and anhydrous calcium phenylphosphonate (1751 ppm) was followed by X-ray powder diffraction. Linear correlations were obtained for d or n_f as a function of the number of carbon atoms in the aliphatic chain (n_c): $d = (1424 \pm 65) + (108 \pm 14)n_c$ and $n_f = (3.33 \pm 0.15) - (0.39 \pm 0.03)n_c$, for the hydrated compound and $d = (1643 \pm 60) + (108 \pm 12)n_c$ and $n_f = (3.43 \pm 0.12) - (0.39 \pm 0.01)n_c$, for the anhydrous compound. The exothermic enthalpies of intercalation increased with n_c, which derived from the monomolecular amine layer arrangement with longitudinal axis inclined by 58° to the inorganic sheets. The intercalation, followed by titration with amine at the solid/liquid interface with both matrices, gave the enthalpic/number of carbons correlation: $\Delta H^\circ = -(0.54 \pm 0.12) - (1.10 \pm 0.09)n_c$ and $\Delta H^\circ = -(1.39 \pm 0.15) - (1.56 \pm 0.10)n_c$, respectively. The exothermic enthalpic value increases with n_c are more pronounced for the anhydrous compound. The Gibbs free energies are negative while positive entropic values favor intercalation in these systems.

Keywords: Layered compounds; *n*-Alkyldiamine molecules; Intercalation reactions; Thermodynamic properties

1. Introduction

Crystalline organophosphonate compounds, mainly those derived from tetravalent metals, form a class of inorganic layered structures that consist of a sequence of alternating inorganic–organic layers. These kinds of compounds have received intense interest in recent years, not only from the structural viewpoint, but also due to their ability to insert polar molecules into the free interlamellar space [1,2]. For instance, in the zirconium compound whose layered structure was first determined, the metal atoms lie in a plane and are bridged by phosphonate groups, which are located above and below the metal atom plane. Three oxygen atoms of each tetrahedral phosphate are linked to three zirconium atoms and each metal is octahedrally coordinated by six oxygen atoms of six different phosphate groups. The fourth oxygen of each phosphate group is bonded to a proton which is located in the interlayer space [1]. This phosphate group arrangement forms a zeolitic type cavity, containing water molecules hydrogen bonded to three of the acidic phosphate groups on the same layer. Diffusion of species into the cavity is permitted if the theoretical size is limited to 264 pm [3] and the structural layers are only weakly held together by dispersion forces.

Changing to divalent cations forming crystalline structures, a simple representative example of such a compound is hydrated calcium phenylphosphonate [4], in which two water molecules are coordinated to the inorganic backbone in the available space between the inorganic layers. The weak interactive effect of those coordinating molecules is manifested when basic polar molecules are intercalated to yield new anhydrous compounds, with gradual replacement of the original water molecules [2].

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During organic molecule intercalation into this kind of layered compound, the inorganic host layers interact with the organic guest molecules by increasing the interlamellar separation. 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. For example, amines intercalated into zirconium hydrogenphosphate change their properties when in contact with water. The lamellae formed may be reconstituted to form thin films which have potential applications in the field of ion exchange, chromatography, heterogeneous catalysis and as protonic conductors [5]. On the other hand, the same intercalated materials seem to be useful as precursors in pillaring reactions [6] because the intercalation produces an increase in the interlayer space, favoring exchange between the intercalated amine and the pillaring agent.

The proposal mechanism of amine intercalation was that the basic nitrogen group is firstly protonated by the available hydrogen attached to the phosphate group and, therefore, the maximum amount of intercalated amine should be two moles per unit of metal phosphate. The intercalated amount also depends on the free area of about 20.0×10^4 pm^2 surrounding each phosphate group, which permits the accommodation of one molecule of the base per phosphate group, and on a cross-sectional area of *trans–trans* alkyl chains evaluated [7] as 18.6×10^4 pm^2.

In spite of the great number of papers devoted to studies of intercalation in inorganic lamellar structures [8–10], the use of calcium phenylphosphonate as host is restricted. However, intercalations in this compound by a variety of *n*-alkylmonoamines were recently investigated [11,12]. During the intercalation process the guest molecules are oriented inside the free lamellar cavity, causing an increase in the interlayer space [2,13], with changes in both guest and the host properties, and the resulting host–guest systems have been explored from the technological point of view [1,14]. As the guest molecule is accommodated inside the free space in the lamellar cavity, a variation in interlamellar distance takes place, which provides information about the orientation and rough estimates of the disposition of the species in the gallery [13,15–19]. The amount of alkylmonoamines intercalated into the calcium compound corresponds to two moles of amine per mole of the inorganic support with an inclination of 55° for the alkyl chain, in relation to the inorganic layer, a value which is very close to that presented by lamellar zirconium phosphate. From the point of view of the energetics involved in the host–guest interaction, the entrance of these species into the free gallery space is accompanied by an intrinsic thermal effect [15–17,19].

Although intercalation is a well-established process, the great majority of publications have focused on the structural aspects of these kinds of compounds. The main objective of this investigation is to report some calorimetric determinations of the interaction of hydrated calcium phenylphosphonate and its anhydrous derivative with *n*-alkyldiamines of the general formula $H_2N(CH_2)_nNH_2$ ($n = 2$–6), in order to contribute to the understanding of the energetic of the intercalations. The calorimetric results enable the calculation of the enthalpy of the acid–base interactions on acidic solid surfaces. Thermochemical data related to these kinds of compounds are limited [20–23]. The intercalated compounds obtained are also characterized by physical methods, in order to correlate physical properties with the energies of intercalation.

2. Experimental

2.1. Materials

All chemicals used were of reagent grade and deionized water was used throughout the experiments. Phenylphosphonic acid (Aldrich), calcium chloride (Fisher), and sodium hydroxide (Vetec) were used for all preparations. The diamines (Aldrich) of the general formula $H_2N(CH_2)_nNH_2$ ($n = 2$–6), i.e. 1,2-ethylene-, 1,3-propylene-, 1,4-butylene-, 1,5-pentamethylene- and 1,6-hexamethylenediamines, were used without further purification.

2.2. Preparations

Hydrated calcium phenylphosphonate was synthesized as before, Briefly, phenylphosphonic acid reacts with calcium chloride in aqueous solution, and the solid $Ca[(HO)O_2PC_6H_5]_2{\cdot}2H_2O$ was isolated and dehydrated to yield the anhydrous form $Ca[(HO)O_2PC_6H_5]_2$ [11].

2.3. Intercalation procedure

The intercalation was carried out by suspending about 50 mg of solid compounds in 0.50 mol dm^{-3} solutions of each amine, dissolved in water (hydrated compound) or 1,2-dichloroethane (anhydrous compound), at room temperature [11]. The isotherms of concentration versus time were obtained through the batch method [24]. For this determination, a series of flasks containing the suspension were continuously stirred in a mechanical orbital apparatus thermosted at 298 ± 1 K. The number of moles of amine intercalated into the host matrix to (n_f) can be calculated [25,26] by the difference between the initial number of moles (n_i) of added amine and that determined in the supernatant (n_s), divided by the mass (m) of the compound, i.e., $n_f = (n_i - n_s)/m$. All amine solutions were previously standardized with a 0.1570 mol dm^{-3} hydrochloric acid solution, using as indicator a 5:1 mixture of bromocresol green and methyl red [27]. After intercalation, the resulting white solid was separated by centrifugation, washed with water and ethanol, and dried at 323 K in an oven for about 8 h. The isotherms presented an increase in the number of moles of amines intercalated (n_f) with time (t) or with the concentration of the supernatant (C_s). In all cases, these intercalation processes caused a total saturation of the inorganic layered structure to establish a well-defined plateau. The batchwise experimental conditions to obtain these isotherms were as close as possible to those used in the calorimetric determinations.

2.4. Calorimetric titration

The intercalation processes were calorimetrically followed by an LKB 2277 Thermal Activity Monitor. In a typical process, 10.0 mg of host suspended in 2.0 cm^3 of water or 1,2-dichloroethane was incrementally titrated with 0.5001 mol dm^{-3} amine solution in water and 1,2-dichloromethane, respectively, under stirring, at 298.15 ± 0.20 K. The amine solutions where added in increments of 10 μL until the lamellar compound was saturated. Three independent titrations were done for the complete thermodynamic cycle: (a) thermal effects due to the host/amine interaction ($\sum Q_r$), (b) solvation of the solid ($\sum Q_s$) and (c) dilution of amine solution ($\sum Q_{dil}$). The net thermal effect of intercalation is given by: $\sum Q_{int} = \sum Q_r - \sum Q_{dil} - \sum Q_s$. The thermal effect of solvation of the inorganic lamellar compound suspended in water or 1,2-dichloroethane was 0, thus $\sum Q_{int} = \sum Q_r - \sum Q_{dil}$. An illustration for 1,4-butylenediamine is shown in Fig. 1. The enthalpy of interaction Δh_r was obtained by an expression fitted to a modified Langmuir equation [29]:

$$\mathrm{X}/\Delta h_r = 1/(K-1)\Delta h_{int} + X/\Delta h_{int} \quad (1)$$

where X is the mole fraction of the amine remaining in solution after interaction, Δh_r the enthalpy of intercalation obtained by dividing the thermal effect, Q_{int}, by the number of moles of intercalating molecules and K is a proportionality constant that includes the equilibrium constant.

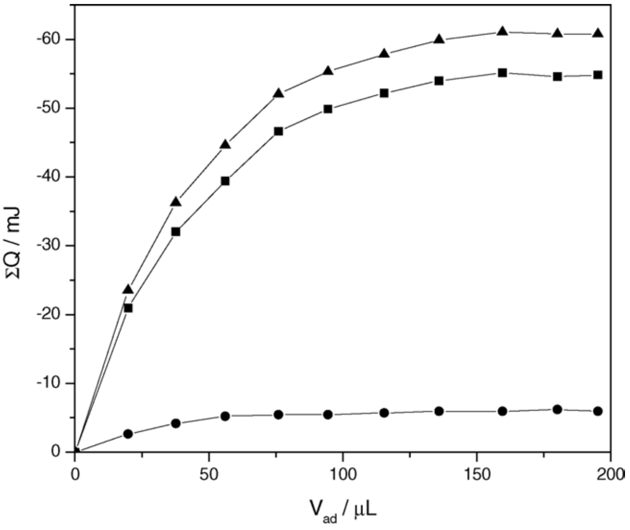

Fig. 1. Calorimetric titration of 0.0100 g of hydrated calcium phenylphosphonate suspended in 2.0 cm^3 of water with 0.5001 mol dm^{-3} of 1,4-butylenediamine in the same solvent at 298.15 ± 0.20 K. The experimental points represent the sum of the thermal effects of the direct titration $\sum Q_{int}$ (▲), dilution $\sum Q_{dil}$ (●) and the net thermal effect $\sum Q_r$ (■); $\sum Q$ and V_{ad} are the total thermal effect and total injected volume of titrant.

In the present case, a plot of $X/\Delta h_r$ versus X gave the angular and linear coefficients, Δh_{int} and K, respectively, to give $\Delta H^\circ = \Delta h_{int}/n_s$. Gibbs free energy and entropy changes were calculated from $\Delta G^\circ = -RT \ln K^\circ$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ expressions, respectively [17,19].

2.5. Characterization

Elemental analyses, X-ray diffraction patterns, infrared spectroscopy and thermogravimetry were obtained as before [11].

3. Results and discussion

Based on the elemental analysis, where 10.1% (2.52 mmol g^{-1}) and 15.6% (5.04 mmol g^{-1}) were found for calcium and phosphorus, a 2:1 molar ratio for these elements, and consequently, the molecular formulas $\mathrm{Ca(HO_3PC_6H_5)_2 \cdot 2H_2O}$ and $\mathrm{Ca(HO_3PC_6H_5)_2}$ were established.

The high degree of crystallinity of the $\mathrm{Ca(HO_3PC_6H_5)_2 \cdot 2H_2O}$ compound is shown by the presence of a sharp and intense peak that corresponds to an interlayer distance of 1525 pm, which differs from the anhydrous compound with an interlayer distance of 1751 pm [13]. This increase in distance caused by water removal was interpreted as a distortion of the original structure, as observed for similar organophosphonate compounds [28].

The infrared bands distinguish the compounds, the hydrated compound presents a weak and broad band at 3500 cm^{-1}, due to the presence of OH groups [11], which is absent in the anhydrous form. A weak band at 1438 cm^{-1} and medium bands in the 720–694 cm^{-1} range indicate the presence of phenyl rings. The bands that appear at 1340 and 1105 cm^{-1} represent P–OH vibrations and those at 1080, 1017 and 996 cm^{-1} are due to $\mathrm{PO_3}$ groups. Three bands, two of them weak, are related to the ring, in the 3000–2830 cm^{-1} region, and one at 1437 cm^{-1}, correspond to symmetrical and asymmetrical C–H stretching and to the basal stretching C–C band of the ring, respectively [3,11]. After amine intercalation, weak bands attributed to NH stretching vibrations appear at 3580 and 3077 cm^{-1}. The shift of the N–H stretching bands towards lower frequencies suggests that the guest diamine is coordinated [2] and replaces water molecules in the intercalation process.

The thermogravimetric (TG) curves for hydrated calcium phenylphosphonate presented a mass loss of 4.3% at 583 K, corresponding to the loss of water molecules, calculated value 4.1%. The release of the phenylphosphonate groups attached to the inorganic framework started around 720 K for both compounds and is completed at 900 K, but, some residual carbon is present [29]. The observed mass loss of 32.1% is assigned to the organic moiety, calculated value 34.1%. The total mass loss of 35.0% up to 1200 K is consistent with the expected value of 34.6%, coming from the conversion of $\mathrm{Ca(HO_3)PC_6H_5)_2 \cdot 2H_2O}$ to the final $\mathrm{Ca(PO_3)_2}$ residue [29].

The TG curves for the anhydrous compound showed the absence of mass loss up to 570 K. This feature emphasizes the difference between the two host compounds, confirming the anhydrous form obtained from the original hydrated compound, which, upon continued heating, also gave the same final product, $Ca(PO_3)_2$. The curves for the intercalated compounds are very similar to those observed for the calcium phenylphosphonate compounds with a difference in percentages in the decomposition stage. As discussed previously, water elimination causes a mass loss of 4.3% while, for the amine derivatives, this percentage is always larger, varying from 5.2 to 7.1%. On examining these intercalated compounds the following processes were detected: (i) physically adsorbed amine and water molecules are lost from room temperature to near 583 K, (ii) the chemisorbed amine is lost from 583 to 720 K and (iii) two steps are due to the loss of phenyl groups [30] in the 720–900 and 900–1200 K ranges, respectively, to end in with $Ca(PO_3)_2$ product [11].

The series of isotherms for *n*-alkyldiamine intercalation in hydrated calcium phenylphosphonate are illustrated in Fig. 2. The maximum number of moles of the amines intercalated was 2.48, 2.20, 1.87, 1.25 and 1.00 mmol g^{-1} for 1,2-ethylene-, 1,3-propylene-, 1,4-butylene-, 1,5-pentamethylene- and 1,6-hexamethylenediamines, respectively. For the same processes of intercalation on anhydrous calcium phenylphosphonate the corresponding isotherms are shown in Fig. 3, giving the values 2.54, 2.32, 1.95, 1.29 and 1.06 mmol g^{-1} for the same sequence of guest molecules. For both series, these values, which were obtained through a batchwise process, decreased with an increase of alkyl chain length of the diamine. Such decrease in the amount of the diamine intercalated with increasing chain length clearly demonstrates a behavior related to the size of the *n*-alkyl chain. As expected, larger diamines have reduced freedom to diffuse into the interlayer space and interact with the acidic groups on the inorganic support. Also, as the amine chain length is increased it could be supposed that a restriction to a best adjusting of the chain inside the interlayer cavity occurs.

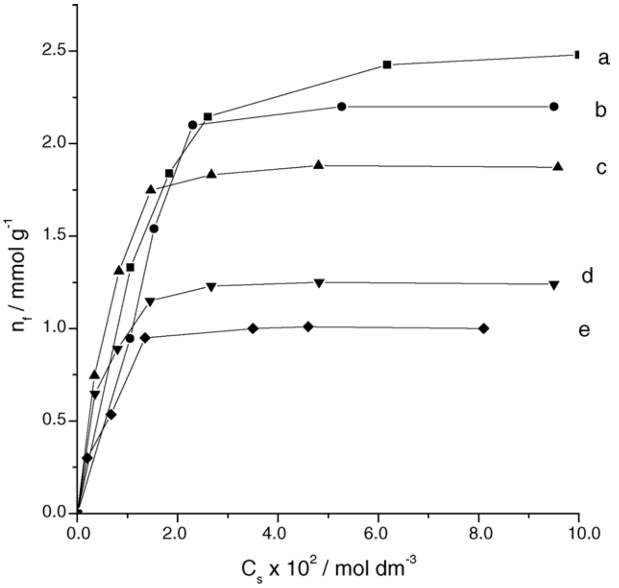

Fig. 2. Isotherms for intercalation of 1,2-ethylene- (a), 1,3-propylene- (b), 1,4-butylene- (c), 1,5-pentamethylene- (d) and 1,6-hexamethylenediamines (e) into hydrated calcium phenylphosphonate.

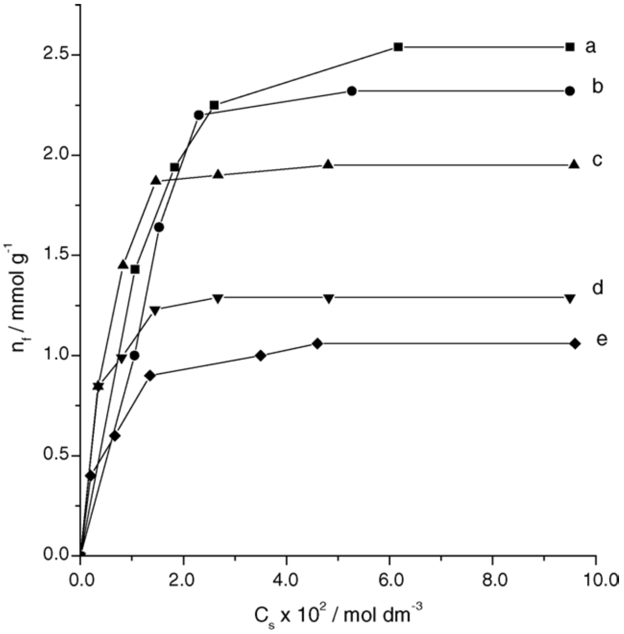

Fig. 3. Isotherms for intercalation of 1,2-ethylene- (a), 1,3-propylene- (b), 1,4-butylene- (c), 1,5-pentamethylene- (d) and 1,6-hexamethylenediamines (e) into anhydrous calcium phenylphosphonate.

The amount of the amine intercalated per gram (n_f) showed a higher value for the anhydrous calcium phenylphosphonate. This enhancement clearly reflects the increasing number of available active sites on anhydrous calcium phenylphosphonate as a consequence of water removal. Water molecule displacement was previously shown not only by thermogravimetry but also with differential scanning calorimetry [11]. In principle, after water removal, the hydrogen on free OH groups can interact with the basic amine NH_2 center. However, when the amine molecules are dissolved in water, such interactions are strongly favored as a solvation process. In such unfavorable conditions, the amine groups are highly solvated and the free available pair of electrons on the nitrogen atom is blocked, causing difficulty to bond formation in the intercalation reaction. Based on this approach, an increase in the amine intercalating process should be expected when apolar solvents are used in intercalation [31], as demonstrated by this present series of results.

During the intercalation process an increase in the interlayer distance to accommodate the diamines in the free space of the cavity occurred. This behavior can be followed via the X-ray diffraction data listed in Table 1. As observed, the interlamellar distance increased with the increase of alkyl chain length. However, this behavior is also dependent on the degree of intercalation. The number of moles of diamine

Table 1
Interlayer distance (*d*) for hydrated (CaPP) and anhydrous (CaPP1) calcium phenylphosphonates and for the respective *n*-alkyldiamine intercalated compounds

Compound	*d* (pm)
CaPP	1532
$CaPP \cdot xH_2N(CH_2)_2NH_2 \cdot (2-x)H_2O$	1640
$CaPP \cdot xH_2N(CH_2)_3NH_2 \cdot (2-x)H_2O$	1749
$CaPP \cdot xH_2N(CH_2)_4NH_2 \cdot (2-x)H_2O$	1856
$CaPP \cdot xH_2N(CH_2)_5NH_2 \cdot (2-x)H_2O$	1964
$CaPP \cdot xH_2N(CH_2)_6NH_2 \cdot (2-x)H_2O$	2072
CaPP1	1751
$CaPP1 \cdot H_2N(CH_2)_2NH_2$	1859
$CaPP1 \cdot H_2N(CH_2)_3NH_2$	1967
$CaPP1 \cdot H_2N(CH_2)_4NH_2$	2075
$CaPP1 \cdot H_2N(CH_2)_5NH_2$	2183
$CaPP1 \cdot H_2N(CH_2)_6NH_2$	2291

intercalated (n_f) and the interlamellar distance (d) correlated linearly with the number of carbons in the aliphatic chain, as illustrated in Figs. 4 and 5. The linear correlation can be expressed by Eqs. (2) and (3) for hydrated compound:

$$n_f = (3.33 \pm 0.15) - (0.39 \pm 0.03)n_c \tag{2}$$

$$d = (1424 \pm 65) + (108 \pm 14)n_c \tag{3}$$

and for anhydrous compound:

$$n_f = (3.43 \pm 0.12) - (0.39 \pm 0.01)n_c \tag{4}$$

$$d = (1643 \pm 60) + (108 \pm 12)n_c \tag{5}$$

The intercalation reaction can be fundamentally considered as an insertion of a mobile guest species A into the host solid structure [Z], maintaining the structural characteristics of the framework. The intercalation of the species takes place in the accessible empty holes (□) of the inorganic layer, or for the hydrated compound, the guest molecule replaces the Lewis base water molecule. From the interlamellar distance correlation shown in Fig. 5, the angular coefficient enables an estimate of the inclination of the diamine molecule, as well as its arrangement in either a mono or bilayer disposition inside the interlayer cavity. For a sequence of diamines the increment of 127 pm for one additional carbon atom in an all-*trans* alkyl chain can be expected. If the diamines are present as a monomolecular layer of extended molecules, their longitudinal axes are inclined at an angle of arcsin(108/127) = 58° in relation to the plane of inorganic sheet. This same angle of inclination was found for zirconium phosphonate with a series of diamines, also in a monolayer disposition [32].

All data clearly show that the process of intercalation of *n*-alkyldiamines in hydrated and anhydrous calcium phenylphosphonate can be interpreted as an acid–base solid-state reaction between a layered Lewis acid host $O_3P{-}OH$ and Lewis-base guests [20]. An illustration of the calorimetric titration related to the amine intercalation into the free cavity of the hydrated crystalline phenylphosphonate is shown in Fig. 6, and the thermodynamic data are listed in Tables 2 and 3. The results show that an increase in carbon number in the alkyl chain causes an increased exothermicity of the enthalpy change of intercalation.

The enthalpic results in anhydrous compounds are always more exothermic when compared with the hydrated

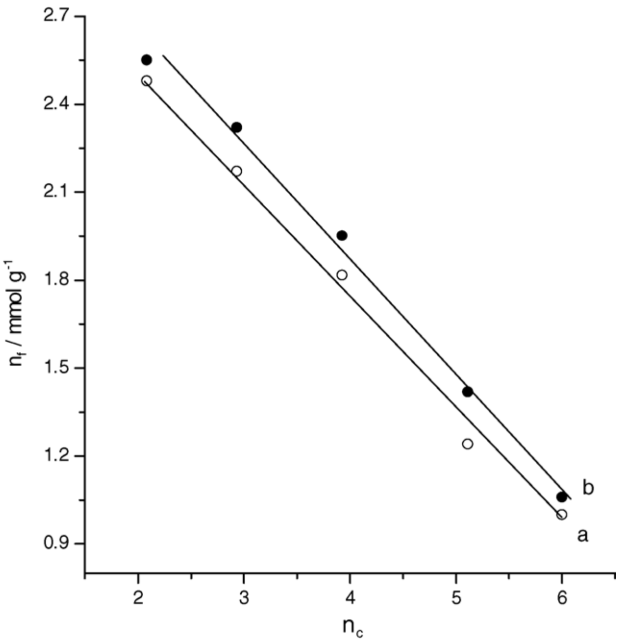

Fig. 4. Number of moles intercalated as a function of the number of carbons in the *n*-alkyldiamines intercalated into hydrated (a) and anhydrous calcium phenylphosphonates (b).

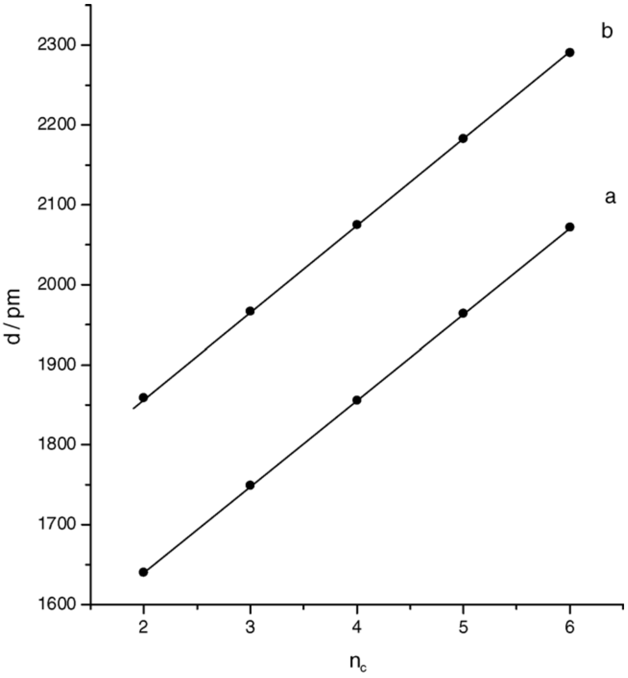

Fig. 5. Interlamellar distance as a function of the number of carbons in the *n*-alkyldiamines intercalated into hydrated (a) and anhydrous calcium phenylphosphonates (b).

Table 2
Thermodynamic data for the intercalation of *n*-alkyldiamines $(CH_2)_n(NH_2)_2$ ($n = 2$–6) in aqueous solution with hydrated calcium phenylphophonate at 298.15 ± 0.20 K

$(CH_2)_n(NH_2)_2$	$-\Delta h_{int}$ (J g^{-1})	n_s (mmol g^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	$\ln K^\circ$	$-\Delta G^\circ$ (kJ mol^{-1})	ΔS° (J mol^{-1} k^{-1})
2	6.92	2.44	2.84 ± 0.08	10.65	26.4 ± 0.1	79 ± 1
3	8.32	2.13	3.91 ± 0.23	11.42	28.3 ± 0.1	82 ± 1
4	8.82	1.75	5.04 ± 0.23	12.66	31.4 ± 0.1	89 ± 1
5	8.25	1.32	6.11 ± 0.21	13.55	33.6 ± 0.1	92 ± 1
6	8.03	1.10	7.29 ± 0.12	14.20	35.2 ± 0.1	94 ± 1

Table 3
Thermodynamic data for the intercalation of *n*-alkyldiamines $(CH_2)_n(NH_2)_2$ ($n = 2$–6) in 1,2-dichloroethane with anhydrous calcium phenylphophonate at 298.15 ± 0.20 K

$(CH_2)_n(NH_2)_2$	$-\Delta h_{int}$ (J g^{-1})	n_s (mmol g^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	$\ln K^\circ$	$-\Delta G^\circ$ (kJ mol^{-1})	ΔS° (J mol^{-1} k^{-1})
2	12.97	2.60	4.99 ± 0.08	11.34	28.1 ± 0.1	76 ± 1
3	14.60	2.41	6.06 ± 0.23	12.50	31.0 ± 0.1	84 ± 1
4	14.42	2.02	7.14 ± 0.23	13.47	33.4 ± 0.1	88 ± 1
5	13.00	1.40	9.28 ± 0.21	14.81	36.7 ± 0.1	92 ± 1
6	13.34	1.19	11.21 ± 0.12	16.09	39.9 ± 0.1	96 ± 1

compounds. The enthapic values obtained from calorimetric titration are linearly correlated with the number of carbon atoms in the *n*-alkyldiamines intercalated into hydrated calcium phenylphosphonate, as shown in Fig. 7 and given by the expression:

$$\Delta H^\circ = -(0.54 \pm 0.12) - (1.10 \pm 0.09)n_c \qquad (6)$$

The slope of the straight line represents the effect of addition of one methylene group to the aliphatic amine chain. The intercept is an estimate of the contribution of the amine head group to the enthalpy of intercalation. For a similar system, involving *n*-alkyldiamines with titanium phosphonate, a value of -2.06 kJ mol^{-1} was obtained [27], reinforcing the greater ability to intercalate in this latter matrix.

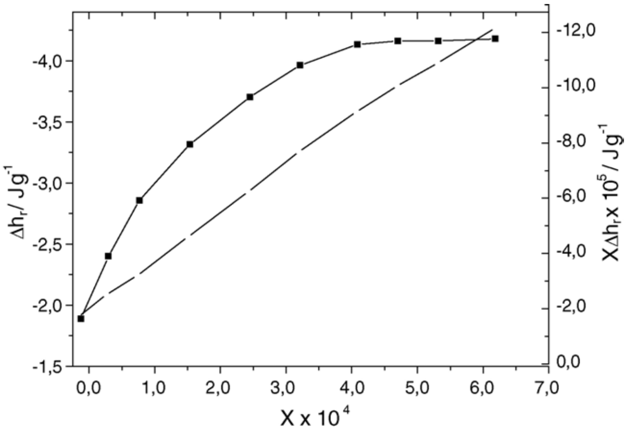

Fig. 6. Isotherm for the enthalpy of intercalation Δh_r vs. molar fraction, *X*, obtained from a calorimetric titration of 0.0100 g of hydrated calcium phenylphosphonate suspended in 2.0 cm^3 of water, with 0.5001 mol dm^{-3} of 1,4-butylenediamine in the same solvent at 298.15 ± 0.20 K. The straight line is the linearized form of the isotherm.

A linear equation was also obtained from the calorimetric titration data for intercalation for the same *n*-alkyldiamines with the anhydrous compounds (Fig. 7), as indicated by the expression:

$$\Delta H^\circ = -(1.39 \pm 0.15) - (1.56 \pm 0.10)n_c \qquad (7)$$

In this case, the intercept value of -1.39 kJ mol^{-1} reflects that the number of moles intercalated is higher than that observed with hydrated compound.

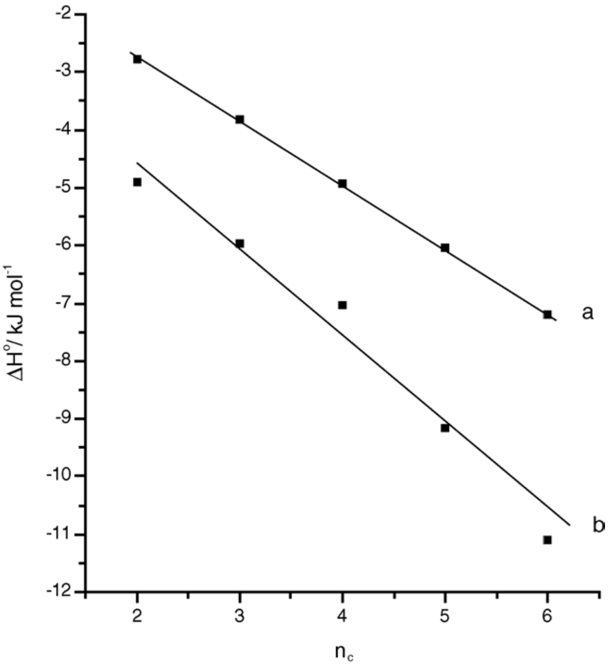

Fig. 7. Enthalpy of intercalation of *n*-alkyldiamine as a function of the number of carbons intercalated into hydrated (a) and anhydrous calcium phenylphosphonates (b).

The contribution to the enthalpy from each carbon added to the aliphatic chain of the diamine corresponds to -1.10 and $-1.56\,\mathrm{kJ\,mol^{-1}}$. Extrapolating the linear behavior of these correlations to $n_c = 0$, the enthalpy of intercalation of two moles of ammonium cations per mole of the inorganic matrix would have values of -0.54 ± 0.12 and $-1.39 \pm 0.15\,\mathrm{kJ\,mol^{-1}}$. When same procedure was used for the intercalation of alkylmonoamines into hydrated calcium phenylphosphonate, a value of $-1.74\,\mathrm{kJ\,mol^{-1}}$ was obtained [12]. However, since monoalkylamines intercalate as double layers into the host, this value should be doubled.

The sequence of the enthalpies determined here with a limited number of *n*-alkyldiamines contributes to understanding of these types of systems. The linear correlations observed suggest that enthalpic values can be inferred for other intercalated species by using these linear correlations for *n*-alkyldiamines and can be readily estimated from the number of carbons in the alkyl chain.

From the equilibrium constant the values of the Gibbs free energy and entropy changes for all intercalations were calculated. All entropic values also are consistent with the argument that the reactions are entropically favored. These values suggest that the molecules of the solvents initially bonded to the inorganic matrix are progressively disrupted as the reactions take place, causing an increasing of these free molecules to the medium. Thus, the release of these molecules of solvents to solution, as the intercalation occurred, is responsible for the increase in entropy, as represented by positive values, being nearly the same for both series of intercalations [23,33].

4. Conclusions

Anhydrous and hydrated lamellar crystalline calcium phenylphosphonates can be used as host support for organic polar molecules. Characterization of the compounds confirms the insertion of *n*-alkyldiamines into the layered structure, as demonstrated by the increase in the interlayer distances. The energetic results obtained from calorimetric determinations are consistent with processes involving the interaction of *n*-alkyldiamines into the layered phenylphosphonate compounds at the solid–liquid interface, with thermodynamically favorable values from the point of view of negative Gibbs free energy and enthalpy values and also positive entropic results.

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