

Crystalline calcium phenylphosphonate—thermodynamic data on *n*-alkylmonoamine intercalations

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Abstract

Lamellar crystalline calcium phenylphosphonate, as anhydrous $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2$ and hydrated $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ compounds, were used as hosts for intercalation of polar *n*-alkylmonoamine molecules of the general formula $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$ ($n = 0-4, 7$) in water or 1,2-dichloroethane. An increase in the interlayer distance was observed. The exothermic enthalpic values for intercalation increased with the number of carbon atoms and with increasing concentration of the amines. The intercalation followed by a titration procedure in the solid/liquid interface with $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2$ gave the enthalpy/number of carbons correlations: $\Delta_{\text{int}}H = -(1.74 \pm 0.43) - (1.30 \pm 0.13)n_c$ and $\Delta_{\text{int}}H = -(4.15 \pm 0.15) - (1.07 \pm 0.03)n_c$, for water and 1,2-dichloroethane, respectively. A similar correlation $\Delta_{\text{int}}H = -(4.27 \pm 0.80) - (1.85 \pm 0.21)n_c$ was obtained in water by using the ampoule breaking procedure for $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$. The increase in exothermic enthalpic values with the increase in *n*-aliphatic carbon atoms is more pronounced for the anhydrous compound and also when using the ampoule breaking procedure. The Gibbs free energies are negative. Positive entropic values favor intercalation in these systems.

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1. Introduction

There is considerable interest in synthesis of new layered metal phosphonate salts due to their robust and yet flexible structural properties. This class of layered inorganic–organic hybrid compounds presents an inorganic backbone with pendant organic groups on both sides of the central layer. This kind of structural arrangement was first synthesized with tetravalent metals and more recently with a series of divalent cations. Polymeric units, containing the metallic cations between phosphonate groups, form

the overlapping lamella. Applications of these materials include catalysis, sorption and ion exchange, as well as uses in intercalation chemistry [1–3].

Calcium phenylphosphonate was first synthesized [4,5] through reaction of an aqueous solution of calcium ion with an organophosphonic acid, followed by addition of aqueous sodium hydroxide solution. However, the success of this procedure is largely dependent on the occurred pH. The chemical formula of the anhydrous calcium phosphonate [6] was previously proposed as $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2$.

The present investigation is focused on the hydrated compound, $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$, in which two water molecules are coordinated to the inorganic backbone. When basic polar molecules are intercalated,

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these water molecules are gradually replaced [7]. During the intercalation process the guest molecules are oriented inside the free lamellar cavity, causing an increase in the interlamellar distance to accommodate them inside the interlayer space [7,8]. Thus, intercalation changes both guest and host properties. The resulting host–guest systems have been explored from the technological point of view [1–3]. The variation in interlamellar distance permits extraction of information about the orientation and rough estimates of the disposition of the species in the gallery space [1,9–13]. Entrance of these species into the free gallery space is accompanied by a thermal effect [9–13].

The energetic of intercalation is associated with the interaction between the basic guest molecule and the host acidic center located on the inorganic matrix. Studies of *n*-alkyldiamines with an α -titanium hydrogenphosphate system established the mechanism of the gradual substitution of solvent molecules initially bonded to the inorganic layer by the intercalating molecule [14]. Linear correlations between the enthalpy of the reaction and interlayer distance or with the number of carbon atoms in the aliphatic chain can be used to infer properties for other non-intercalated species [7]. Some other investigations involving *n*-alkylmonoamines, *n*-alkyldiamines and some heterocyclic amines with inorganic layer compounds have also been reported [9,10,15].

The present study reports calorimetric data, based on calorimetric titration [16,17] and the breaking thin-glass ampoules [18], on intercalation between hydrated $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ and anhydrous $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2$ crystalline calcium phenylphosphonates and *n*-alkylmonoamines, $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$ ($n = 0\text{--}4, 7$), to establish correlations between the physical properties of the host inorganic matrix and the guest molecules.

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 amines (Fluka) of the general

formula $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$ ($n = 0\text{--}4, 7$), i.e. methyl-, ethyl-, propyl-, butyl-, pentyl- and octylamines, were used without further purification.

2.2. Preparations

Hydrated calcium phenylphosphonate, $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$, was prepared by reacting 60.0 cm^3 of a 1.0 mol dm^{-3} aqueous solution of organophosphonic acid with 25.0 cm^3 of 0.50 mol dm^{-3} $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. To this mixture, maintained with vigorous stirring, 0.30 mol dm^{-3} of a NaOH solution was added dropwise, to adjust the pH to 5–6. An abundant white solid immediately precipitated. The compound was isolated by filtration, washed with doubly distilled water and air dried at 320 K [19]. This compound was dehydrated by heating the sample at 573 K in vacuum for 8 h to give the final anhydrous compound, $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2$.

2.3. Intercalation procedure

The intercalation process was carried out by suspending about 70.0 mg of the lamellar crystalline solid in 0.10 mol dm^{-3} aqueous solutions of each amine at room temperature. The isotherms of concentration versus time were obtained through a batch method [17]. For this determination a series of flasks containing the suspension were continuously stirred in an orbital mechanical apparatus thermostated at $298 \pm 1 \text{ K}$. Thus, the number of moles adsorbed per gram of the intercalated compound (n_f) is calculated by the difference between the initial (n_i) and the supernatant (n_s) number of moles of amine divided by the mass (m) of the compound used, $n_f = (n_i - n_s)/m$ [16,17]. All solutions were standardized with $0.1079 \text{ mol dm}^{-3}$ hydrochloric acid, using an indicator made by mixing bromocresol green and methyl red in a 5:1 proportion. The number of moles of amine intercalated (n_f) increased with time (t) and with the concentration of the supernatant (C_s), until the plateau related to total saturation of the layered structure was obtained.

2.4. Calorimetric titration

The thermal effects of the intercalation of the series of amines for both crystalline lamellar compounds were followed in an isothermal LKB 2277 microcalorimetric system, as previously described

[13]. A sample of approximately 20 mg was suspended in 2.0 cm³ of water or 1,2-dichloroethane and vigorously stirred at 298.15 ± 0.02 K. After equilibrium, a solution of amine in the chosen solvent was added through a microsyringe. For each increment of solution the thermal effect ($\Sigma_{\text{int}}Q$) was recorded until saturation was reached, indicated by a constant thermal effect. Identically, titrations of the amine solutions in each solvent ($\Sigma_{\text{dil}}Q$) without the solid were monitored as was also the solution with calcium phenylphosphonate suspended in the calorimetric solvent, which gave a null value. Combining these thermal effects gives the thermal effect for intercalation: $\Sigma_{\text{int}}Q = \Sigma_{\text{tit}}Q - \Sigma_{\text{dil}}Q$. From ΣQ_{int} the change in enthalpy associated with the amine–matrix interaction can be determined by fitting the intercalation data to a modified Langmuir equation [13–17].

2.5. Ampoule breaking calorimetry

An LKB 8700-1 isoperibolic precision calorimetric system and a Thermometric 2225 precision solution calorimeter were used for reaction–solution measurements for the intercalation of amines into lamellar host solid. The thermal effects caused by breaking thermostated thin-glass ampoules containing the solid matrix (ca. 50 mg) into 0.090 dm³ of amine solutions of variable concentration, varying from 0.10 to 0.50 mol dm⁻³, were recorded. The response of ampoule breaking in well-stirred solutions indicated a kinetically favorable system, whose baseline was reached in a few minutes [13–17]. As observed with other lamellar compounds, a null thermal effect resulted when anhydrous or hydrated calcium phosphonate samples were broken into the calorimetric solvent in the absence of amine [18]. The standard molar enthalpies of intercalation were obtained by breaking at least five ampoules in the calorimetric solvent at 298.15 ± 0.02 K. Moreover, the thermal effect of empty ampoule breaking was found to be negligible [18,20]. For the Thermometric system, Sol Cal software was used to calculate the enthalpy, which was given by considering the net thermal effect produced during the ampoule breaking divided by the number of moles of the amine intercalated $\Delta H = \Sigma Q/n_f$ [16,17]. The results obtained in both calorimetric systems showed identical enthalpic values. At the end of each ampoule breaking, the resulting solution

was filtered and aliquots of supernatant were titrated with standard hydrochloric acid solution to obtain n_f values.

3. Results and discussion

The synthesized compounds were characterized by means of a complexometric titration for calcium [21] and a spectrophotometric method for phosphorus [22,23], and also by carbon, hydrogen and nitrogen elemental analysis. X-ray diffraction patterns, infrared spectroscopy, thermogravimetry and nuclear magnetic resonance were also used for characterization [24]. The hydrated compound was heated to determine the water content of the solid.

The isotherm of intercalation of all *n*-alkylmonoamines using the batch method measured the acceptance by host solid, Ca(HO₃PC₆H₅)₂·2H₂O in the present case, of the amines, as illustrated with propylamine in Fig. 1. To linearize the results obtained in the isotherms the data were fitted to the Langmuir model, in which it is assumed that a monolayer of amine is formed on the crystalline layered inorganic compound [25]. The values are fitted to the expression:

$$\frac{C_s}{n_f} = \frac{C_s}{n^s} + \frac{1}{b}$$

where C_s is the remaining amine concentration in solution after intercalation equilibrium, n_f as defined previously, n^s the maximum amount of amine intercalated to form a monolayer, per gram of the host, and b is a parameter associated with the thermodynamic equilibrium of intercalation [13,17,26]. These n^s and b values can be estimated from angular and linear coefficients after linearizing the isotherm, as represented in Fig. 1.

In an attempt to understand the energetics of intercalation, the *n*-alkylmonoamines CH₃(CH₂)_{*n*}NH₂ (*n* = 0–4, 7) were inserted into hydrated Ca(HO₃PC₆H₅)₂·2H₂O and anhydrous Ca(HO₃PC₆H₅)₂, calcium phenylphosphonates, whose interactive effect was calorimetrically followed through ampoule breaking or titration methods. The first procedure consisted of breaking a series of ampoules in a given calorimetric solvent and recording the corresponding thermal effects. In the titration procedure the thermal effects due to solute–substrate interaction were obtained in

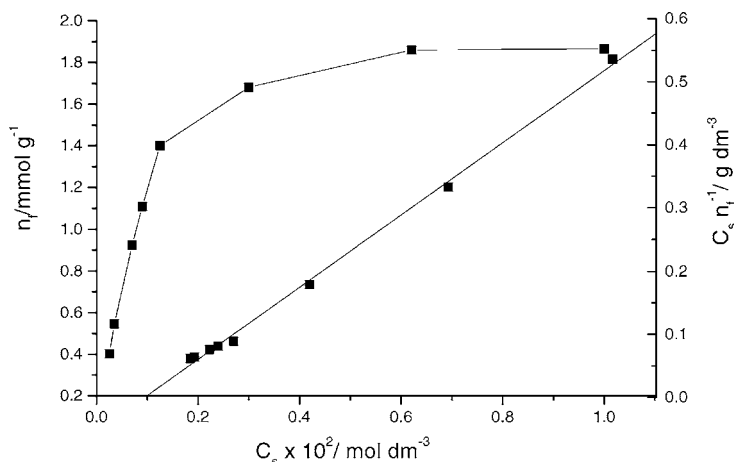
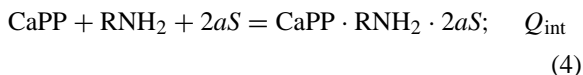
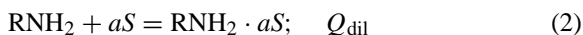
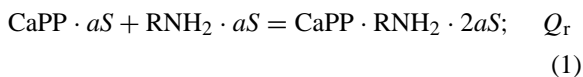


Fig. 1. Isotherm of intercalation of propylamine in $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$, indicating n_f values versus concentration C_s . The straight line represents the linearization C_s/n_f vs. C_s . The linear correlation coefficient r is 0.999.

a sequence of incremental titrand additions. In both cases, these data were used to calculate the variation of enthalpy [17,18].

Determination of the enthalpy of reaction requires three independent series of measurements, which are applied to ampoule breaking or titration procedures and also to the particular calorimetric solvent (S) employed, from which a considerable number of molecules (a) are used in the solvation process. The sequence of reactions (1)–(3) yields the main reaction (4), as represented here for anhydrous host solid, represented by CaPP:



Reactions (1)–(3) represent individual calorimetric experiments which were carried out in duplicate for each determination [13]. The net thermal effect ($\Sigma_{\text{int}}Q$) of those interactions, i.e. $\Sigma_{\text{int}}Q = \Sigma_rQ - \Sigma_{\text{dil}}Q$, for the net reaction (4) was calculated for each experimental point.

With the exception of n -butylamine, where 13.0 mg of hydrated calcium phenylphosphonate were used, all other n -alkylmonoamines used 20.0 mg when titrating a suspension of the host solid in the calorimetric titration, as shown in Table 1. For these identical series of calorimetric determinations, the number of additions and the volumes of amine solution to saturate the mass of the matrix are also listed in Table 1. For example, 13 identical additions of 10 μl of 0.450 mol dm^{-3} propylamine were used to saturate the sample. The individual thermal effects obtained for the calorimetric titration of the host with this same n -alkylmonoamine are shown in Fig. 2.

From the calorimetric titration procedure, better information about the energetic process involving all investigated systems can be obtained, as shown in Fig. 2. The incremented addition of amine solution to the

Table 1

Experimental conditions established by calorimetric titration of 2.0 cm^3 of a suspension of $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ with amines (RNH_2) having concentrations (C) in aqueous solution with a sequence of identical additions (N) of 10 μl , to give the number of moles intercalated n_f for mass (m) of the guest compound

RNH_2	C (mol dm^{-3})	N (μl)	n_f (mmol)	m (mg)
CH_3-	0.41	13	2.67	20.0
CH_3-CH_2-	0.55	10	2.22	20.0
$\text{CH}_3-(\text{CH}_2)_2$	0.45	13	1.86	20.0
$\text{CH}_3-(\text{CH}_2)_3$	0.54	11	1.56	20.0
$\text{CH}_3-(\text{CH}_2)_4$	0.34	10	1.39	13.0

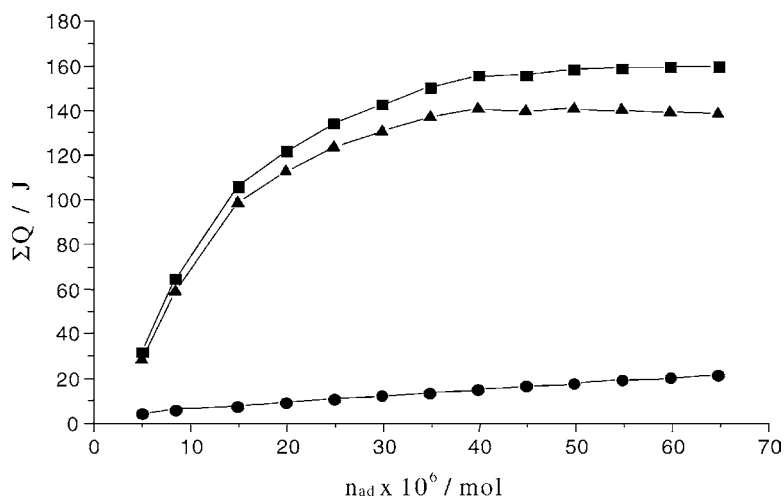


Fig. 2. Calorimetric titration curves for 20.0 mg of $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ suspended in 2.0 cm^3 of water with $0.498 \text{ mol dm}^{-3}$ propylamine at $298.15 \pm 0.02 \text{ K}$. The thermal effects of the reaction (■), dilution (●) and net value (▲) are shown.

host solid leads to its saturation. In such conditions the maximum amount of the titrand causes the accommodation of the amine in the free interlamellar space, with formation of a monolayer inside the lamella. Using the isotherm data through a batch method, the molar fractions of amine in equilibrium were obtained, by using $X/\Delta_r H$ versus X plots, to give the enthalpy of interaction $\Delta_{\text{int}} H$ and K values, from the angular and linear coefficients of the straight lines, respectively. The following equation describes this process:

$$\frac{X}{\Delta_r H} = \frac{1}{K-1} \Delta_{\text{int}} H + \frac{X}{\Delta_{\text{int}} H} \quad (5)$$

where X is the sum of molar fractions of the remaining amine in solution after intercalation, X is obtained for each point of titrand addition by using the modified Langmuir equation, which was previously shown to be a good adjustable model for such systems [13,14,18]. $\Delta_r H$ is the integral enthalpy of intercalation obtained by dividing the thermal effect resulting from intercalation by the number of moles of the lamellar host, $\Delta_r H = \Delta_{\text{int}} H/n^s$, with n^s being calculated from the batch process intercalation results [13,15,17,27] (Fig. 3). From these and K values, the other thermodynamic data, such as Gibbs free energy, by the

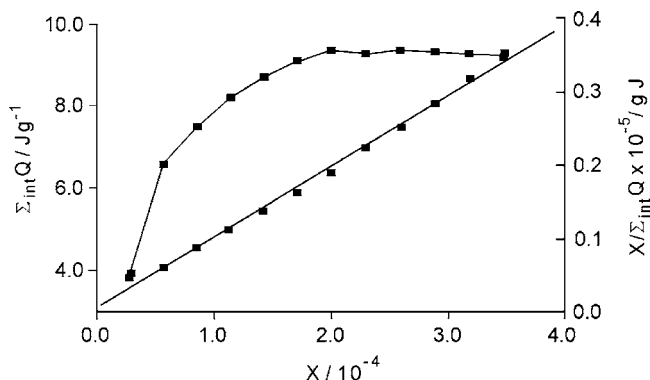


Fig. 3. Isotherm obtained from calorimetric titration of 20.0 mg of $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ suspended in water with $0.450 \text{ mol dm}^{-3}$ propylamine. The molar fraction $\Sigma_{\text{int}} Q$ vs. X plot and its linearized $X/\Sigma_{\text{int}} Q$ vs. X form are also shown.

Table 2

Thermodynamic values for intercalation through calorimetric titration of aqueous amines (RNH₂) solutions into the hydrated or anhydrous (a) form of calcium phenylphosphonate, with linear correlation (*r*)

RNH ₂	−Δ <i>H</i> (kJ mol ^{−1})	−Δ <i>G</i> (kJ mol ^{−1})	Δ <i>S</i> (J K ^{−1} mol ^{−1})	<i>r</i>
CH ₃ −	3.18 ± 0.06	31.4 ± 0.1	21 ± 1	0.982
CH ₃ −CH ₂ −	4.41 ± 0.07	39.8 ± 0.1	28 ± 1	0.997
CH ₃ −(CH ₂) ₂ −	5.55 ± 0.06	35.3 ± 0.1	30 ± 1	0.997
CH ₃ −(CH ₂) ₃ −	6.41 ± 0.04	19.6 ± 0.1	28 ± 1	0.997
CH ₃ −(CH ₂) ₄ −	8.70 ± 0.03	19.6 ± 0.1	36 ± 1	0.990
CH ₃ −(CH ₂) ₃ − (a)	8.03 ± 0.06	13.4 ± 0.1	31 ± 1	0.982

equation $\Delta G = -RT \ln K$, and the variation in entropy, is obtained by employing the expression $\Delta G = \Delta H - T\Delta S$, and the values are listed in Table 2. The variation in enthalpy increases as the aliphatic amine chain length increases for this energetically favorable system, as expressed by negative ΔG values. A similar behavior was also observed when 1,2-dichloroethane was used as solvent, as listed in Table 3.

For the guest molecule *n*-butylamine intercalated in the matrix in aqueous solution, the enthalpic values changed from -6.41 ± 0.04 to -8.03 ± 0.06 kJ mol^{−1} for the hydrated and anhydrous hosts, respectively. This observed increase in enthalpic values shows a favorable condition of intercalation. This fact suggested that immersion of the anhydrous compound in water does not replace the solvent molecules in the lattice, as indicated by distinguishable enthalpic values. Support for this behavior was obtained when the anhydrous compound Ca(HO₃PC₆H₅)₂ was intercalated in dry apolar 1,2-dichloroethane. The enthalpic results in this solvent for a given amine are always higher when compared with water as solvent. However, similar results of enthalpic intercalation were obtained for anhydrous host in water and 1,2-dichloroethane, as illustrated for *n*-butylamine, which gave -8.19 ± 0.10 kJ mol^{−1} with this apolar solvent.

Table 3

Thermodynamic data for intercalation of amine (RNH₂) solutions through calorimetric titration into Ca(HO₃PC₆H₅)₂ in 1,2-dichloroethane, with linear correlation (*r*)

RNH ₂	−Δ <i>H</i> (kJ mol ^{−1})	−Δ <i>G</i> (kJ mol ^{−1})	Δ <i>S</i> (J K ^{−1} mol ^{−1})	<i>r</i>
CH ₃ −	5.34 ± 0.20	32.2 ± 0.1	29 ± 1	0.997
CH ₃ −CH ₂ −	6.35 ± 0.30	23.5 ± 0.1	29 ± 1	0.997
CH ₃ −(CH ₂) ₂ −	7.44 ± 0.20	35.8 ± 0.1	38 ± 1	0.998
CH ₃ −(CH ₂) ₃ −	8.19 ± 0.10	23.5 ± 0.1	35 ± 1	0.998
CH ₃ −(CH ₂) ₇ −	12.9 ± 0.10	12.3 ± 0.1	47 ± 1	0.997

The enthalpic values obtained from calorimetric titration are linearly correlated with the number of carbon atoms (*n_c*) on the aliphatic *n*-alkylmonoamines intercalated in water into Ca(HO₃PC₆H₅)₂·2H₂O [11,13–15], as shown in Fig. 4, and expressed by

$$\Delta H = -(1.74 \pm 0.43) - (1.30 \pm 0.13)n_c \quad (6)$$

The slope represents the effect of addition of one methylene group to the aliphatic amine chain. The intercept, -1.74 kJ mol^{−1}, is an estimate of the contribution to the enthalpy of intercalation of the amine bonding to the matrix. For a similar system, involving *n*-dialkylmonoamines with titanium phosphate, a value of -2.06 kJ mol^{−1} was previously obtained [15].

A linear equation was also obtained from the calorimetric titration data for intercalation of the same series of *n*-alkylamines with Ca(HO₃PC₆H₅)₂ in 1,2-dichloroethane:

$$\Delta H = -(4.15 \pm 0.15) - (1.07 \pm 0.03)n_c \quad (7)$$

In this case, for each carbon atom added to the *n*-alkylamine, the increase in the enthalpy change is -1.07 kJ mol^{−1}, while the intercept of -4.15 kJ mol^{−1}, suggests that the number of moles intercalated is greater than that obtained during the same process in water.

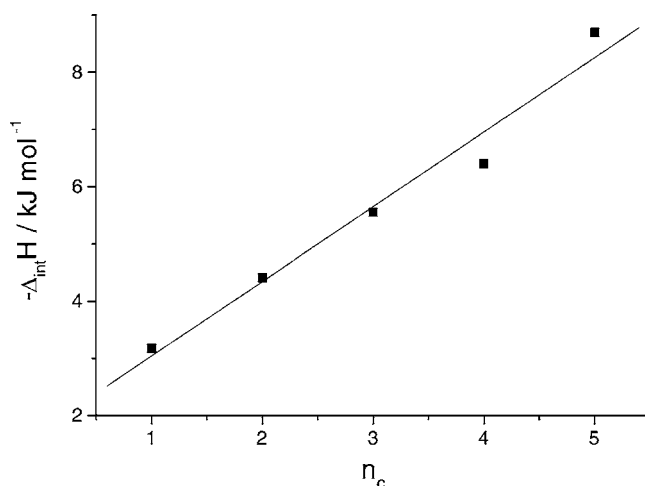


Fig. 4. Correlation between the enthalpy of intercalation ($\Delta_{\text{int}}H$) in aqueous solution and the number of carbon atoms (n_c) on the aliphatic chain for ethyl-, propyl-, butyl and pentylamines. These values were obtained from calorimetric titration on the hydrated $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ compound.

The other method used to determine the variation in enthalpy for the host–guest interaction was based on the ampoule breaking process. Table 4 shows the experimental values when five ampoules with similar mass (m) of hydrated calcium phenylphosphonate were broken into aqueous propylamine solutions. In such experiments the corresponding net thermal effects ΣQ were determined and the intercalated amount (n_f) was obtained by difference, through the titration of the amine in the supernatant. The linearization [28,29] of n_f versus the quotient $\Sigma Q/m$ gives the enthalpic value for the process of intercalation of the hydrated host with propylamine, which was $\Delta_{\text{int}}H = -9.80 \pm 0.70 \text{ kJ mol}^{-1}$, with a correlation coefficient of 0.992.

Table 4

The thermal effects (Q) obtained from the ampoule breaking process for mass (m) of $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ with propylamine in 90.0 cm^3 of aqueous solution, the number of moles intercalated, n_f , and the ratio Q/m , to obtain the enthalpy $-9.80 \pm 0.70 \text{ kJ mol}^{-1}$, with a linear correlation coefficients of 0.992

m (mg)	$-\Sigma Q$ (J)	n_f (mmol)	$-\Sigma Q/m$ (J g^{-1})
46.60	1.30	9.75	27.9
48.45	1.98	8.12	40.87
58.68	2.90	7.87	49.42
52.22	4.00	5.17	76.59
53.87	4.70	3.48	87.24

The set of enthalpic values is listed in Table 5 for $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$, obtained in aqueous solution with the ampoule breaking method for this series of aliphatic n -alkylmonoamine. A correlation was calculated as expressed by the following expression, represented in Fig. 5.

$$\Delta_{\text{int}}H = -(4.27 \pm 0.80) - (1.85 \pm 0.21)n_c \quad (8)$$

The slope of $-1.85 \text{ kJ mol}^{-1}$ represents the effect of addition of a methylene group to the aliphatic n -alkylamine on the enthalpic value. On the other hand, the intercept, $-4.27 \text{ kJ mol}^{-1}$, corresponds to the enthalpy change for reaction of the amino group. This value is high in comparison to that obtained by calorimetric titration, as observed in Fig. 4, of $-1.74 \text{ kJ mol}^{-1}$.

Table 5

Variation of enthalpy for intercalation (ΔH_{int}) of n -alkylmonoamines (RNH_2) with $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ in aqueous solution, obtained by the ampoule breaking method, with the corresponding linear correlation coefficients (r)

RNH_2	$-\Delta H_{\text{int}}$ (kJ mol^{-1})	r
$\text{CH}_3\text{-CH}_2\text{-}$	8.17 ± 1.06	0.97
$\text{CH}_3\text{-(CH}_2)_2\text{-}$	9.80 ± 0.70	0.99
$\text{CH}_3\text{-(CH}_2)_3\text{-}$	11.13 ± 0.98	0.98
$\text{CH}_3\text{-(CH}_2)_4\text{-}$	13.90 ± 1.31	0.98

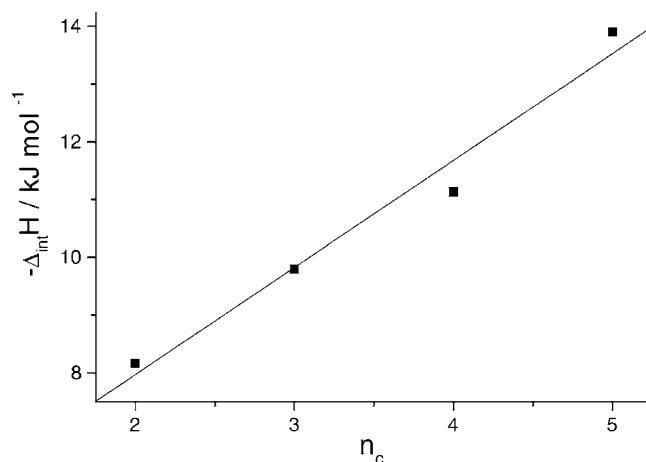


Fig. 5. Correlation between the enthalpy of intercalation (ΔH_{int}) in aqueous solution and the number of carbon atoms (n_c) on the aliphatic chain for ethyl-, propyl-, butyl and pentylamines. These values were obtained by the ampoule breaking process with the anhydrous $\text{Ca}(\text{HO}_3\text{PC}_6\text{H}_5)_2$ compound.

Such difference should be associated with the kinetic of intercalation in both conditions. Although the ampoule breaking process is rapid and favorable for strong stirring, however, the expected equilibrium can not be reached. Thus, the more appropriated results are those from calorimetric titration, as expressed by Eq. (8).

4. Conclusion

The intercalation of a series of *n*-alkylmonoamines into hydrated or anhydrous lamellar crystalline phenylphosphonate followed through calorimetric or ampoule breaking procedures gave thermodynamically favorable values from the point of view of negative Gibbs free energy and enthalpy values and also positive entropic results. Both solid hosts present an increase in enthalpy values as the number of carbon atoms of the aliphatic amine size increased, from either titration or ampoule breaking methods. From the linear correlations established, the enthalpy value for an unknown amine can be inferred, by considering the corresponding methylene group associated with each guest molecule. However, the kinetic of intercalation is more favorable for calorimetric titration, in which procedure the equilibrium condition is reached.

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