# Thermochemical data for *n*-alkylmonoamine intercalation into crystalline lamellar zirconium phenylphosphonate

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## Abstract

Layered crystalline zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, changed its interlamellar distance of 1481 pm after intercalation of *n*-alkylmonoamines, $CH_3-(CH_2)_n-NH_2$ ($n = 0$–6). The infrared spectra of the precursor host and the corresponding intercalated compounds presented vibrations associated with $PO_3$ groups in the 1163–1039 $cm^{-1}$ range and additional bands related to C–H stretching bands in the 2950–2850 $cm^{-1}$ interval were observed after amine insertion. The thermogravimetric curves showed a mass loss assigned to the phenyl group; however, the amine intercalated fraction was not quantitatively determined. A peak in the $^{31}P$ NMR spectrum centered at $-6$ ppm for the host was observed. The surface area was $42.0 \pm 0.2$ $m^2 g^{-1}$ and the scanning electron micrograph gave images consistent with lamellar structural features. The layered compound was calorimetrically titrated with amine in ethanol, requiring three independent operations: (i) titration of matrix with amine, (ii) matrix salvation, and (iii) dilution of the amine solution. From those thermal effects the variation in enthalpy was calculated as: $-41 \pm 1.00$, $-33.28 \pm 0.50$, $-34.40 \pm 0.80$, $-10.40 \pm 0.40$, $-12.40 \pm 0.42$, $-16.10 \pm 0.08$ and $-7.0 \pm 0.04$ $kJ\,mol^{-1}$, for $n = 0$–6, respectively. The exothermic enthalpic values reflected a favorable energetic process of amine–host intercalation in ethanol. The negative Gibbs free energy results supported the spontaneity of all these intercalation reactions. The positive favorable entropic values, as carbon chain size increased, are in agreement with the free solvent molecules in the medium, as the amines are progressively bonded to the crystalline lamellar inorganic matrix at the solid/liquid interface.
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## 1. Introduction

The earliest reported data on the intercalation chemistry described the insertion of sulfuric acid into lamellar graphite in 1841. However, a large stimulation in this field came in the last three decades, when a great variety of inorganic lamellar backbone structural compounds were employed as hosts to accommodate guest molecules in their void cavities. This class of solids, with layered arrangements, has many important features associated with adsorption, ion-exchange, catalyst, proton and ion-conductor processes, beyond its function as a convenient inorganic matrix for chemical modification. The availability of use is connected with the high thermal stability, resistance to chemical oxidation and selectivity to ions and molecules [1]. One of the most important properties of this kind of layered material is availability in expanding the interlamellar space, when guest molecules are inserted [2,3].

Normally, lamellar compounds containing identical composition are isostructural in nature, being considered as excellent matrices for intercalation and as well as ion-exchange reactions [1,4–6]. Thus, great attention was previously devoted as this exchange property, whose main purpose was related to phosphate compounds, without mentioning the intercalation process. Nevertheless, as the first intercalation took place, this new methodology opened a considerable increase in investigations, as denoted by a large number of publications [1,4,7]. From this remarkable insight in investigation, there was great impulse on designing compounds, which were successfully synthesized, such as phosphonates, which zirconium phenylphosphonate is the focus of the present study.

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Metal (IV) phosphonates with α- or γ-layered structures are usually obtained from the reaction between a phosphonic acid and the correspondent metal (IV) salt. This preparative method was extended to other metal oxidations, and also for the equivalent phosphonates. In every case, such compounds are obtained at low temperatures often from aqueous solutions and are good illustrations of soft chemistry routes. A large variety of molecules can be intercalated in these interlayer cavities due to the fact that these metal phosphonates offer new possibilities for interlayer chemistry [1,4].

Great attention has been devoted to the variety of investigations focused on lamellar organophosphonates, mainly based on structural features [1], whose synthetic procedures enabled the formation of compounds commonly represented by the general formula $M(O_3PR)_x \cdot H_2O$, for various metals (M), with R representing aliphatic or aromatic radicals and $x$ the valence of the cations. The water molecule can be carefully eliminated to yield the anhydrous compounds on heating. The relevant organophosphonate basic structural features are similar for those found for phosphates, with the advantage in the synthesis to fasten the organic pendant groups derived from the organophosphonate acids, distributed in the internal free spaces of the sequence of lamella.

The aim of this investigation is focused on lamellar organophosphonates, which can form commonly a set of compounds represented by general formula $M(O_3PR) \cdot nH_2O$, which the related anhydrous compounds can be obtained on heating. The basic structural features are similar to that found with phosphates, whose synthetic procedures enabled the possibility to imbed an organic pendant group into the internal part of the lamellar space [7,8–10]. In this context, some structural features associated with zirconium phenylphosphonate are now described and the first calorimetric data related to $n$-alkylmonoamines $R–NH_2$ ($n = 0$–$6$) intercalation are now reported.

## 2. Experimental

### 2.1. Materials

Phenylphosphonic acid $C_6H_5PO(OH)_2$ (Aldrich) and hydrated zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ (Riedel) were used without further purification. Methyl- (Across) and ethylamines (Fluka) were distilled from stock aqueous solutions, passing the amines through a column containing sodium hydroxide to eliminate possible water vapor and bubbling the distillate into dry ethanol. Propyl- (Fluka), butyl- (Riedel), pentyl- (Across), hexyl- (Fluka) and heptylamines (Fluka) were also purified by distillation.

### 2.2. Synthesis of zirconium phenylphosphonate

Anhydrous zirconium phenylphosphonate was synthesized by three distinct procedures. Sample 1 was prepared

by adding to a polyethylene flask containing $1.0 \, \text{mol dm}^{-3}$ phenylphosphonic acid, hydrated zirconium oxychloride and concentrated hydrofluoric acid solutions in order to attain $(C_6H_5PO(OH)_2/[Zr] = 10$ and $[F]/[Zr] = 30$ ratios [11]. The clear solution of zirconium–fluor complex was slowly formed by heating at 333 K for 7 days, periodically adding water in order to maintain the volume of solution. Samples 2 and 3 were prepared by using the preceding method, but in sample 2 the hydrofluoric acid was introduced some days after the start of the synthesis and sample 3 was prepared in the absence of the hydrofluoric acid. These three samples were analyzed by X-ray diffraction and sample 3 showed a low degree of crystallinity. With this information, either sample 1 or 2 could be chosen for this continuing investigation, but sample 1 was selected for all subsequent operations.

### 2.3. Characterization

The synthesized and intercalated compounds were characterized through phosphorus nuclear magnetic resonance, $^{31}P$ NMR, by using the MAS technique in an INOVA-500 spectrophotometer, with the contact time 1 ms, frequency 75.47 MHz, 2 s of interval, 11 ms for the time of acquisition, using phosphoric acid as external reference. Carbon, hydrogen and nitrogen were analyzed by a Perkin-Elmer, model PE-2400 elemental analyzer. The X-ray diffraction patterns were obtained in a Shimadzu, model XD3A diffractometer with $2\theta$ in the 1.4–70° range, with Cu Kα (1.54060 Å) radiation. The infrared spectra were performed on a Bomem FTIR, model MB spectrophotometer, using KBr pellets with 50 scans in the 4000–400 cm$^{-1}$ region. The thermogravimetric curves were obtained on a DuPont instrument, model 1090 B, in an argon atmosphere, coupled with a thermobalance 951, maintaining a heating rate of $1.18 \times 10^{-2} \, \text{K s}^{-1}$ for the matrix. For the intercalated compounds this condition was changed to $1.18 \times 10^{-2} \, \text{K s}^{-1}$ up to 390 K, and $1.67 \times 10^{-2} \, \text{K s}^{-1}$ from this temperature up to 1270 K. A Jeol JSTM-300 scanning electron microscope studied the morphology of the compounds obtained after sputter coating layer, a thin conducting layer of gold. The surface area was obtained using the BET equation, through the nitrogen adsorption isotherms at 77 K, on a Flowsorb II 300 Micromeritics analyzer.

### 2.4. Amine intercalation

From batch intercalation process the corresponding isotherms were obtained. The number of moles intercalated per gram of the 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: $n_f = (n_i - n_s)/m$ [12]. The intercalation process was carried about by suspending about 30.0 mg of the lamellar crystalline solid in $6.0 \, \text{cm}^3$ of $1.50 \, \text{mol dm}^{-3}$

ethanolic solutions of each amine at room temperature. For each isotherm, a series of flasks containing the suspensions received additions of 10 μL of the amine solutions, which were continuously stirred in an orbital mechanical apparatus thermostated at 298 ± 1 K. After 24 h the number of moles of amine that were intercalated was obtained by titrating aliquots of supernatant with standardized hydrochloric acid solution. The number of amine molecules intercalated increased with the concentration of the supernatant, until at the plateau the total saturation of the layered structure was reached an experimental optimization which established the best condition to apply for calorimetric procedure.

The collected data for the isotherms of intercalation can be fitted to a modified Langmuir equation [13]:

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b}$$

where $C_s$ is the concentration of the amine (mol dm$^{-3}$) at equilibrium, $N_f$ is as defined previously and $N_s$ is the maximum amount of solute intercalated per gram of adsorbent (mol g$^{-1}$), which depends on the amount of intercalation sites, and $b$ is a constant. From the angular and linear coefficients, $N_s$ and $b$ values are obtained by plotting $C_s/N_f$ as a function of $C_s$.

## 2.5. Calorimetry

The intercalation processes were calorimetrically monitored by titration using a LKB 2277 Thermal Activity Monitor heat-flow instrument [14–16]. In a typical process, 10.0 mg of thermostated host samples suspended in 2.0 cm$^3$ of ethanol were incrementally titrated with an originally 0.50 mol dm$^{-3}$ amine solution, under stirring, at 298.15 ± 0.02 K. Amine solutions were added in increments of 10 μL until the lamellar compound was saturated and three independent titrations were investigated for the complete thermodynamic cycle: (a) thermal effects due to the host–amine interaction ($Q_{int}$), (b) hydration of the solid ($Q_s$) and (c) dilution of amine solution ($Q_{dil}$). The net thermal effect is given by $\sum Q_r = \sum Q_{int} - \sum Q_{dil} - \sum Q_s$. As the thermal effect of hydration of the suspended inorganic lamellar compound sample in ethanol was null, then $\sum Q_{int} = \sum Q_r - \sum Q_{dil}$, whose methylamine intercalation results are shown in Fig. 1. The enthalpy of interaction $\Delta_{int}h$ was obtained by an expression fitted to the modified Langmuir equation [8] $\sum X / \sum \Delta_R h = 1/(K-1)\Delta_{int}h + \sum X / \Delta_{int}h$, where $\sum X$ is the sum of the molar fractions of the remaining amine in solution after intercalation, $\sum \Delta_R h$ the enthalpy of intercalation obtained by dividing the thermal effect resulting from $\sum Q_{int}$ by the number of moles of the molecules and $K$ a proportionality constant that includes the equilibrium constant. $\Delta_{int}h$ and $K$ were determined from $\sum X / \sum \Delta_R h$ versus $\sum X$ plots. The molar enthalpy, $\Delta H$, of the interaction process was calculated by considering the enthalpy of intercalation and the respective number of moles inserted, $\Delta H = \Delta_{int}h/N_s$.

Gibbs free energy and entropy changes were calculated from $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$ expressions, respectively [14].

## 3. Results and discussion

The X-ray diffraction patterns for samples showed at low angle the characteristic reflections related to the lamellar solids [17], with a basal spacing that corresponds to the interlamellar distance of 1481 pm for zirconium phenylphosphonate, a value which is close to other results [1,18–20]. With the exception of the pentyl- to hexylamines, that increase this distance to 1510 pm, the other amines did not change the original interlamellar distance.

By considering the matrix basal distance of 1481 pm, in which the opposite sides of the interior of the same lamella can be occupied by two phenylic rings with individual lengths of 585 pm inserted into a given inorganic layer [11]. By considering this proposed arrangement a free lamellar space of 311 pm remained. As expected, during the amine–metal interaction the total space can be used for any amine. In case of the longer chain length of 979 pm for pentylamine, when bonded to opposing zirconium acid centers inside of the same lamella, an expansion could be expected, as observed for the subsequent n-alkylmonoamines. The diffraction patterns for intercalated matrices are shown in Fig. 2.

The infrared spectra displayed in Fig. 3 illustrate the similarity of the samples. The vibrations assigned to N–H can be defined in the 3700–3100 cm$^{-1}$ interval, due to the presence of broad bands in this region, which could be masked by an
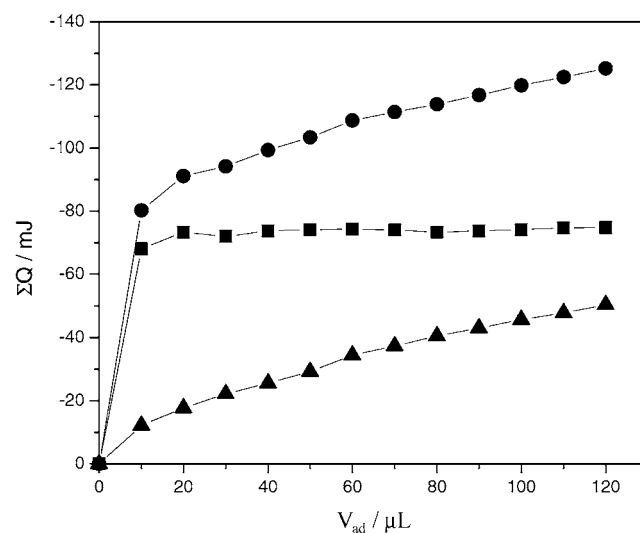


Fig. 1. Calorimetric titration of 0.0100 g of zirconium phenylphosphonate suspended in 2.0 cm$^3$ of ethanol with 0.5453 mol dm$^{-3}$ of methylamine in the same solvent at 298.15 ± 0.02 K. The experimental points represent the sum of the thermal effects of the direct titration $\sum_{tit} Q$ (●), dilution $\sum_{dil} Q$ (▲) and the net thermal effects $\sum Q_R$ (■). $\sum Q$ and $V_{ad}$ values are the sum of the detected thermal effect and total injected volume of titrand solution, respectively.
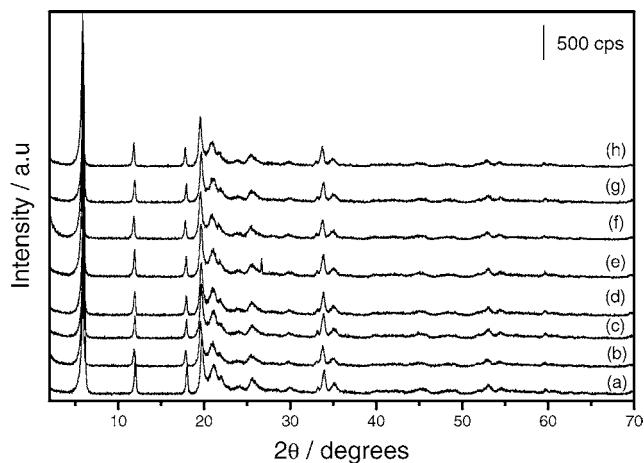
Fig. 2. X-ray diffraction patterns for zirconium phenylphosphonate (a) and the intercalated compounds with methyl- (b), ethyl- (c), propyl- (d), butyl- (e), pentyl- (f), hexyl- (g) and heptylamines (h).

OH group derived from hydration process. From hexyl- to heptylamines the vibration assigned to C–H is clear in the 2959–2853 cm$^{-1}$ range. The stretching attributed to C–H for the phenylic ring is observed at 3062 cm$^{-1}$, with a sharp and intense peak located at 1438 cm$^{-1}$ and PO$_3$ vibrations were observed in the 1163–1039 cm$^{-1}$ range.

The $^{31}$P NMR spectrum for zirconium phenylphosphonate is shown in Fig. 4. A main peak centered at −6 ppm with side bands is in agreement with having phosphorus atoms disposed in the inorganic layer in an equivalent environmental situation [1,17].

The surface area for the original crystalline lamellar host gave $42.0 \pm 0.2$ m$^2$ g$^{-1}$ and, after aliphatic amine intercalations, an increase to $52.5 \pm 3.3$ m$^2$ g$^{-1}$ was detected. This behavior in increasing the area was previously observed for a similar compound of titanium [17,18].



Fig. 4. $^{31}$P NMR spectrum of the Zr(O$_3$PC$_6$H$_5$)$_2$ compound.

The presence of details in the scanning electron microscopic image should be associated with the lamellar structural features, which was firstly interpreted for manganese oxide layered material [21]. However, after intercalation the original zirconium phenylphosphonate changes the morphology.

The synthesized crystalline host, as well as the intercalated compounds, showed high thermal stability [1,17,18,22,23]. The thermogravimetric and the corresponding derivative curves are shown in Fig. 5. These related thermogravimetric curves presented a plateau up to 670 K, in which interval of temperature no mass loss is observed. From this temperature the organic moiety started to decompose, as can be observed through the decrease of mass, indicated by the increase in temperature; however, the loss in mass was not suitable to quantify amine release although it is proposed that pyrophosphate is left as residue.

By the batch process the number of moles inserted into the lamellar structure was calculated as 0.23, 0.21, 0.17,
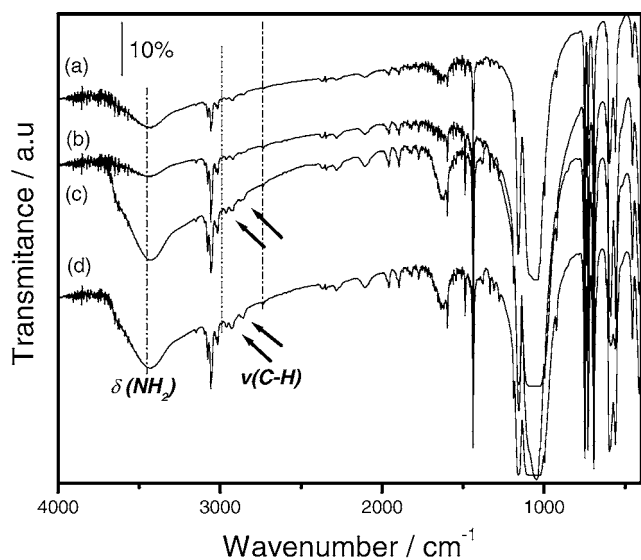


Fig. 3. Infrared spectra of zirconium phenylphosphonate (a) and the intercalated compounds with ethyl- (b), butyl- (c) and heptylamines (d).
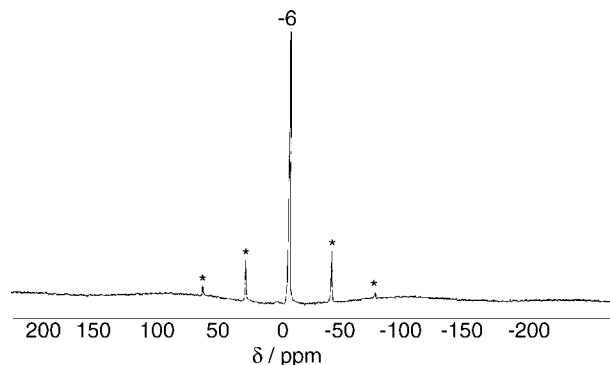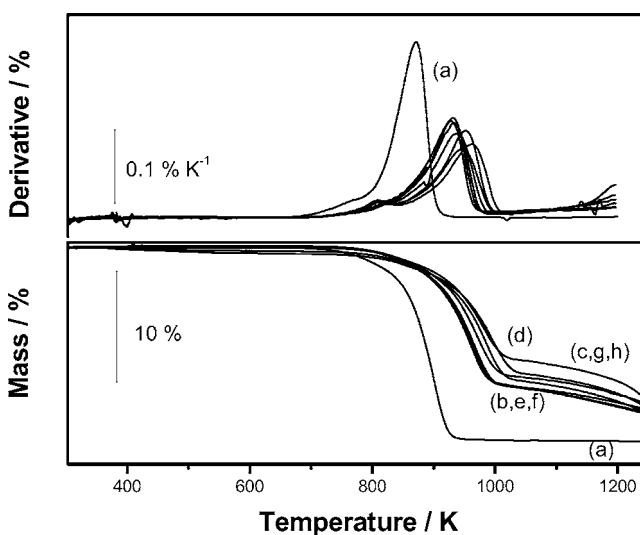


Fig. 5. Thermogravimetric and derivative curves for zirconium phenylphosphonate (a), and the corresponding intercalated compounds with methyl- (b), ethyl- (c), propyl- (d), butyl- (e), pentyl- (f), hexyl- (g) and heptylamines (h).
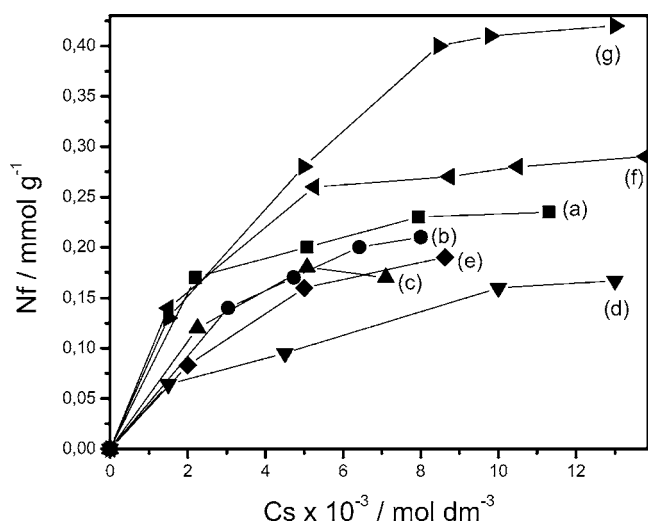
Fig. 6. Isotherms of concentration for *n*-alkylmonoamine intercalations into zirconium phenylphosphonate, by considering the number of moles intercalated ($N_f$) vs. supernatant concentration ($C_s$) plot, for methyl- (a), ethyl- (b), propyl- (c), butyl- (d), pentyl- (e), hexyl- (f) and heptylamines (g).

Table 1
Number of moles of *n*-alkylmonoamines, $CH_3–(CH_2)_n–NH_2$ ($R–NH_2$) intercalated into zirconium phenylphosphonate in the batch process

| R | $N_f$ (mmol g$^{-1}$) |
|---|---|
| $CH_3–$ | 0.23 |
| $CH_3–CH_2–$ | 0.21 |
| $CH_3–(CH_2)_2–$ | 0.17 |
| $CH_3–(CH_2)_3–$ | 0.17 |
| $CH_3–(CH_2)_4–$ | 0.19 |
| $CH_3–(CH_2)_5–$ | 0.29 |
| $CH_3–(CH_2)_6–$ | 0.42 |

these procedures are relevant to compare both types of values, obtained from different techniques.

The summary of the set of data obtained for the energetic of intercalation are listed in Table 3, showing the decrease in enthalpy values when the number of carbon atoms in the amine chains increased. These results can be interpreted due to the difficulty of the amines in intercalating, as seen by the low amount found for each compound. In fact, this kind of argument is also supported by small variations of the interlamellar distance seen through X-ray diffraction, by the absence of mass loss in the expected range of temperature in the thermogravimetric curves and also by the low surface area found. The negative Gibbs free energy corroborated the spontaneity of this kind of reaction. By comparing this set of intercalated amines, the increase in size increased the entropic values, as observed for butyl- to hexylamines. In examining this set of thermodynamic values, the lower entropic values are compensated by higher enthalpic values [24], to promote a negative Gibbs free energy.

0.17, 0.19, 0.29 and 0.42 mmol g$^{-1}$ for the sequence from methyl- to heptylamines, as shown in Fig. 6 and Table 1. The results obtained from the isotherms of intercalation are in agreement with the preference of this inorganic layered matrix in inserting heptylamine. The number of moles adsorbed was also calculated from the elemental results determined, which are added in Table 2. These results are very similar to those obtained by the batch process, as 0.22, 0.22, 0.19, 0.17, 0.21, 0.46 and 0.29 mmol g$^{-1}$, indicating that

Table 2
Percentages of carbon (C), nitrogen (N), hydrogen (H) and number of moles intercalated ($N_f$) determined through elemental analysis, for *n*-alkylmonoamines, $CH_3–(CH_2)_n–NH_2$ ($R–NH_2$), intercalated into zirconium phenylphosphonate

| R | C (%) | N (%) | H (%) | $N_f$ (mmol g$^{-1}$) |
|---|---|---|---|---|
| $CH_3–$ | 33.88 | 0.31 | 2.37 | 0.22 |
| $CH_3–CH_2–$ | 30.54 | 0.31 | 2.35 | 0.22 |
| $CH_3–(CH_2)_2–$ | 35.40 | 0.26 | 2.33 | 0.19 |
| $CH_3–(CH_2)_3–$ | 32.01 | 0.24 | 2.48 | 0.17 |
| $CH_3–(CH_2)_4–$ | 31.54 | 0.29 | 2.34 | 0.21 |
| $CH_3–(CH_2)_5–$ | 24.75 | 0.64 | 2.41 | 0.46 |
| $CH_3–(CH_2)_6–$ | 33.67 | 0.41 | 2.85 | 0.29 |

Table 3
Thermochemical data for *n*-alkylmonoamines, $CH_3–(CH_2)_n–NH_2$ ($R–NH_2$), intercalation into zirconium phenylphosphonate from ethanolic solution at $298.15 \pm 0.02$ K

| R | $-\Delta h_{int}$ (J g$^{-1}$) | $N_f$ (mmol g$^{-1}$) | $N_s$ (mmol g$^{-1}$) | $-\Delta H$ (kJ mol$^{-1}$) | $K$ ($\times 10^4$) | $\ln K$ | $-\Delta G$ (kJ mol$^{-1}$) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $CH_3–$ | 9.84 | 0.23 | 0.24 | $41.00 \pm 1.0$ | 1.7 | 9.74 | $24.1 \pm 0.1$ | $-56 \pm 1$ |
| $CH_3–CH_2–$ | 6.99 | 0.21 | 0.21 | $33.28 \pm 0.50$ | 39.0 | 12.87 | $31.9 \pm 0.1$ | $-4.5 \pm 1$ |
| $CH_3–(CH_2)_2–$ | 6.19 | 0.17 | 0.18 | $34.40 \pm 0.80$ | 10.4 | 11.55 | $28.6 \pm 0.1$ | $-19 \pm 1$ |
| $CH_3–(CH_2)_3–$ | 1.97 | 0.17 | 0.19 | $10.40 \pm 0.40$ | 2.58 | 10.16 | $25.2 \pm 0.1$ | $50 \pm 1$ |
| $CH_3–(CH_2)_4–$ | 2.61 | 0.19 | 0.21 | $12.40 \pm 0.42$ | 3.81 | 10.55 | $26.2 \pm 0.1$ | $46 \pm 1$ |
| $CH_3–(CH_2)_5–$ | 4.82 | 0.29 | 0.30 | $16.10 \pm 0.08$ | 9.4 | 11.45 | $27.3 \pm 0.1$ | $37 \pm 1$ |
| $CH_3–(CH_2)_6–$ | 4.33 | 0.42 | 0.62 | $7.00 \pm 0.04$ | 49.6 | 13.11 | $30.2 \pm 0.1$ | $78 \pm 1$ |

## 4. Conclusions

The intercalation of *n*-alkylmonoamines into zirconium phenylphosphonate provided compounds with the general formula $Zr(O_3PC_6H_5)_2(amines)_n$, with a maximum interlayer distance of 1510 pm for hexylamine. From these first calorimetric determinations involving zirconium organophosphonate, the calculated enthalpic values did not follow the increase sequence of the amine carbon length chains, as previously observed for similar systems [25–27]. However, the negative free Gibbs energy values indicate the spontaneity of this kind of adsorption, in which the unfavorable entropic values are compensated by the corresponding enthalpic ones. Based on the number of moles inserted into the layered matrix, which demonstrate a large tendency for accepting smallest amine chains, it is supposed that the phenyl groups attached to the inorganic layers block access of the basic amine molecule to the acidic zirconium center into the lamella.

## Acknowledgements

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