

Thermochemistry of intercalation of *n*-alkylmonoamines into lamellar hydrated barium phenylarsonate

Angélica M. Lazzarin, Claudio Airoidi*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, São Paulo, Brazil

Received 18 September 2006; received in revised form 13 December 2006; accepted 19 December 2006

Available online 3 January 2007

Abstract

Hydrated layered crystalline barium phenylarsonate, $\text{Ba}(\text{HO}_3\text{AsC}_6\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$ was used as host for intercalation of *n*-alkylmonoamine molecules $\text{CH}_3(\text{CH}_2)_n\text{-NH}_2$ ($n=1-4$) in aqueous solution. The amount intercalated (n_f) was followed batchwise at 298 ± 1 K and the variation of the original interlayer distance (d) for hydrated barium phenylarsonate (1245 ppm) was followed by X-ray powder diffraction. Linear correlations were obtained for both d and n_f as a function of the number of carbon atoms in the aliphatic chain (n_c): $d = (2225 \pm 32) + (111 \pm 11)n_c$ and $n_f = (2.28 \pm 0.15) - (11.50 \pm 0.03)n_c$. The exothermic enthalpies of intercalation increased with n_c , which was derived from the monomolecular amine layer arrangements with the longitudinal axis inclined by 60° to the inorganic sheets. The intercalation was followed by titration with amine at the solid/liquid interface and gave the enthalpy/number of carbons correlation: $\Delta H = -(7.25 \pm 0.40) - (1.67 \pm 0.10)n_c$. The negative Gibbs free energies and positive entropic values reflect the favorable host/guest intercalation processes for this system.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Material composite; Chemical synthesis; Chemical techniques; Thermodynamic properties

1. Introduction

The insertion process of organic neutral polar molecules into the nanospace void of sheets of layered insoluble nanocompounds leads to well-organized inorganic/organic structural materials. The guest molecule–host matrix interaction is strengthened and the layers are spread apart to accommodate the entrance of the guest molecule. Such dynamic guest/host interactions occupy the available active sites disposed on the inorganic support and the intercalation of molecules result in a stoichiometric composition, in which the active sites are exactly covered by the guest agents [1–3]. The class of compounds involving layered nanomaterials have diverse activities with participation of phosphonates [4–6], phosphates [7,8], arsonates [9], vanadates [10], smectite [11], etc and are susceptible to intercalating various species. The insoluble crystalline acidic salts of the general formula $\text{M}(\text{O}_3\text{XR})_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Ba}, \text{Ca}, \text{Mg}, \text{Cd}, \text{Co}, \text{Zn}, \text{Mn}, \text{X} = \text{P}, \text{As}$ and $\text{R} = \text{organic moiety}$) constitute a well-studied group of compounds from the view point of ion exchange and lamellar properties [12].

Advances in the intercalation field have been obtained by observing if any property of the lamellar nanocompound changes, by comparing these with those related to the host, as well as to the inserted guest molecules at the end of the process [13]. The intercalation behavior depends on several factors such as the compounds employed, their sizes and the pK_a values of the guest molecules [1,5]. Moreover, an increase in temperature or the use of an appropriate solvent can accelerate the intercalation process several times [14]. However, the success in intercalating weak bases and or even large molecules is strongly dependent on a prior expansion of the interlamellar distance by an appropriate molecule, in order to make the final insertion easier [14].

The expansion of the original interlayer distance to accommodate the inserted molecule and some details associated with guest–host interactions are easily detected by X-ray diffraction powder patterns and vibrational features of the formed compound through infrared spectroscopy [15]. After insertion, thermal analyses constitute a set of helpful technique to follow the reaction by comparing the successive stages on heating [16].

The great majority of the investigations related to the crystalline lamellar research field are devoted to some structural features [13,14] with only limited studies focused on the

* Corresponding author. Fax: +55 19 35213023.

E-mail address: airoidi@iqm.unicamp.br (C. Airoidi).

energetics [1,4–6] of acid–base reactions for this class of compounds. Thermodynamic data involved with the host/guest interaction of a chosen molecule or with a series of guest molecules and the inorganic polymeric lamellar matrix can give information of the acid–base reactions. From the experimental view point, calorimetric techniques can be successfully applied to such kinds of heterogeneous systems and the effectiveness of the interactive effect that is established at the solid–liquid interface can be determined [1,4–6].

The present investigation reports calorimetric determinations involving the interaction of barium phenylarsonate with *n*-alkylmonoamines, $\text{CH}_3(\text{CH}_2)_n\text{-NH}_2$ ($n = 1\text{--}4$), in order to study the energetics of the intercalation. These new intercalated compounds were characterized through physical and thermal methods and some correlations of these data correlate with the energetics of intercalation were observed.

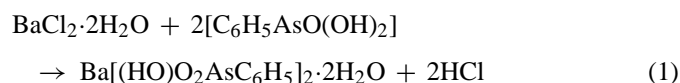
2. Experimental

2.1. Materials

Reagent grade chemicals and deionized water were used throughout the experiments. Phenylarsonic acid (98%, Aldrich), barium chloride (99%, Merck) and sodium hydroxide (99%, Vetec) were employed in all preparations. Amines (Aldrich) of the general formula $\text{H}_3\text{C}(\text{CH}_2)_n\text{-NH}_2$ ($n = 1\text{--}4$), i.e., ethyl, propyl, butyl and pentylamines were used.

2.2. Preparation

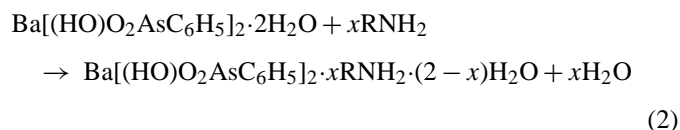
Hydrated barium phenylarsonate was prepared by reacting 60.0 cm^3 of a 1.0 mol dm^{-3} aqueous solution of phenylarsonic acid with 25.0 cm^3 of a 0.50 mol dm^{-3} aqueous $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution to give an initial pH 1. The final pH of the mixture was adjusted in the 5–6 range with sodium hydroxide 0.10 mol dm^{-3} , by using a volume of near 1 cm^3 . The resulting solid was filtered, washed and air dried at 320 K . The general synthetic reaction can be written as:



2.3. Intercalation

The intercalation was carried out by suspending about 50 mg of barium phenylarsonate in 0.50 mol dm^{-3} aqueous solutions of each amine and the concentration versus time curve was obtained through the batch method. This assay consisted in stirring a series of flasks with variable guest/host ratios in a mechanical orbital stirring apparatus at $298 \pm 1\text{ K}$. The time required to saturate the host by each guest molecule was determined by observing the formation of a well-defined plateau in the isotherm of intercalation [1,4–6]. The interactive process at the solid–liquid interfaces involving all *n*-alkylmonoamines, RNH_2 ,

can be generally represented as follows:

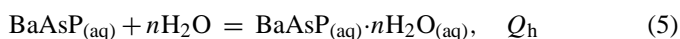
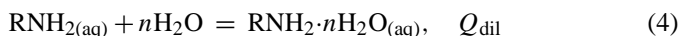


The number of moles of amine intercalated (n_f) was calculated [1,4–6] by the difference between the initial number of moles (n_i) of amine added and those determined in the supernatant (n_s) after reaction, divided by the mass (m) of the compound used, as expressed by $n_f = (n_i - n_s)/m$. All amine solutions were previously standardized with $0.1570\text{ mol dm}^{-3}$ hydrochloric acid [1]. In all cases, the isotherms presented an increase in the number of moles of amine intercalated (n_f) with increasing concentrations of the free amine in the supernatant (C_s), in agreement with a total saturation of the inorganic layered structure, as demonstrated by the plateau. After intercalation, the resulting white solids were separated by centrifugation 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 free amine in 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 thermal effects of the intercalation of the series of *n*-alkylmonoamines into the crystalline lamellar compound were followed in an isothermal LKB 2277 microcalorimetric system [1,4–6]. The typical calorimetric titration consisted in dissolving or suspending the samples in the calorimetric solvent with vigorous stirring at $298.15 \pm 0.02\text{ K}$. After baseline stabilization, the titrand solution was incrementally added through a microsyringe coupled to the microcalorimeter by a stainless steel needle. For each increment, the respective thermal effect was recorded during the progress of the reaction, up to its completion [1,4–6,17].

The enthalpic determination for each reaction required three independent calorimetric titrations: (a) thermal effect of reaction, Q_r , where the aqueous amine solution is added to a suspension of about 10 mg of the inorganic host matrix in 2.0 cm^3 of water, (b) thermal effect of dilution, Q_{dil} , by adding the same aqueous amine solution to the same volume of pure water and (c) the thermal effect of hydration, Q_h , that involves the addition of water to the matrix in suspension. The effects of the thermodynamic cycle for this series of interactions involving hydrated barium phenylarsonate (BaAsP) and the sequence of *n*-alkylmonoamines (RNH_2) can be represented by:



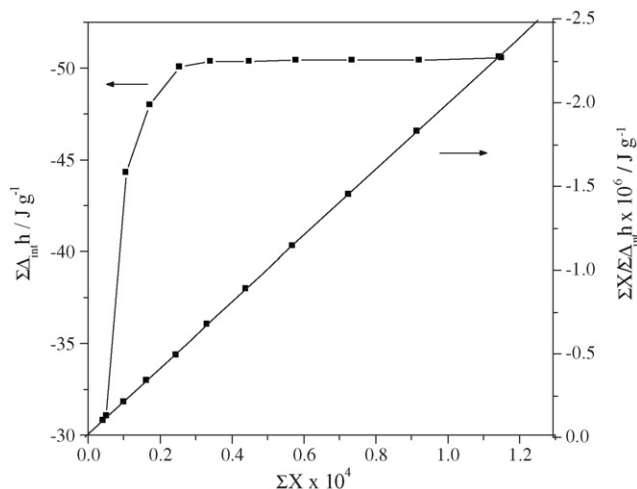
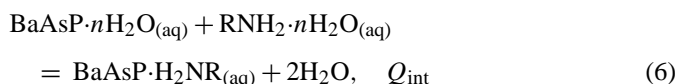


Fig. 1. Isotherm for the integral enthalpy of intercalation $\Sigma\Delta h_{\text{int}}$ vs. molar fraction, ΣX , obtained from a calorimetric titration of 0.0100 g of hydrated barium phenylarsonate suspended in 2.0 cm³ of water, with 0.5001 mol dm⁻³ ethylamine in the same solvent at 298.15 ± 0.02 K. The linearized form is given by $\Sigma X/\Sigma\Delta h_{\text{int}}$.



Reactions (3)–(5) represent the individual calorimetric titration experiments carried out in duplicate for each determination. The thermal effects of reaction for each experimental point of the calorimetric titration were considered in the calculation of the net thermal effect (Q_{int}) of these interactions, as represented by reaction (6) to give $\Sigma Q_{\text{int}} = \Sigma Q_{\text{r}} + \Sigma Q_{\text{dil}} + \Sigma Q_{\text{h}}$, in which ΣQ_{h} is null [4–6].

From the set of thermal effects related to direct titration and dilution, the enthalpy of reaction can be calculated by using these data adjusted to the modified Langmuir equation. The sequence of values obtained from the calorimetric data enabled the calculation of the net enthalpy of interaction to form a monolayer per unit mass of matrices, Δh_{int} , by using Eq. (7), a modified Langmuir model adjusted to describe several types of systems [1,5,18,19].

$$\frac{\Sigma X}{\Sigma\Delta h_{\text{r}}} = \frac{1}{(K-1)\Delta h_{\text{int}}} + \frac{\Sigma X}{\Delta h_{\text{int}}} \quad (7)$$

where ΣX is the sum of the molar fractions of the titrand remaining in solution after interaction, $\Sigma\Delta h_{\text{r}}$ is the enthalpy of intercalation obtained by dividing the thermal effect resulting from ΣQ_{int} by the number of moles of the intercalating molecules and K is a proportionality constant that includes the equilibrium constant. Therefore, a $\Sigma X/\Sigma\Delta h_{\text{r}}$ against ΣX plot gives Δh_{int} and K values from the angular and linear coefficients, respectively, after linearization of the equation, as shown in Fig. 1. The calculation of ΔH was based on the expression $\Delta H = \Delta h_{\text{int}}/n_{\text{s}}$, where n_{s} is the number of adsorbed moles after reaching calorimetric equilibrium [18]. Gibbs free energy and entropy changes were calculated from $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$ expressions, respectively.

Table 1

Percentages of carbon (C), hydrogen (H) and nitrogen (N) for hydrated barium phenylarsonate (BaAsP) and intercalated *n*-alkylmonoamine compounds

Compound	C (%)	H (%)	N (%)
BaAsP	26.9	1.9	–
BaAsP· <i>x</i> CH ₃ CH ₂ NH ₂ ·(1- <i>x</i>)H ₂ O	27.2	3.4	3.0
BaAsP· <i>x</i> CH ₃ (CH ₂) ₂ NH ₂ ·(1- <i>x</i>)H ₂ O	31.7	3.5	2.8
BaAsP· <i>x</i> CH ₃ (CH ₂) ₃ NH ₂ ·(1- <i>x</i>)H ₂ O	33.0	3.7	2.7
BaAsP· <i>x</i> CH ₃ (CH ₂) ₄ NH ₂ ·(1- <i>x</i>)H ₂ O	34.3	3.9	2.6

2.5. Characterization

Arsenic [20] and barium elemental analyses were determined through atomic absorption spectroscopy using a Perkin-Elmer Model 5100 atomic absorption spectrometer and phosphorus [21,22] was determined using a spectrophotometric method with a Shimadzu Model MultiSpec-1501 spectrophotometer. Carbon, hydrogen and nitrogen were obtained using a Perkin-Elmer model PE 2400 instrument, applied to the precursor and to the intercalated compounds.

X-ray diffraction patterns were obtained with nickel-filtered Cu K α radiation on a Shimadzu XD3-A diffractometer (30/20 kV/mA).

Infrared spectra were performed on a Perkin-Elmer model 1600 FTIR spectrophotometer by using pressed KBr pellets, with 4 cm⁻¹ of resolution.

Thermogravimetric curves were recorded using a DuPont model 1090 B apparatus coupled to a model 951 thermobalance, on heating from room temperature to 1273 K at a heating rate of 0.17 K s⁻¹ in an argon flow of 1.67 cm³ s⁻¹. The samples varied in weight from 15 to 30 mg.

The surface area measurements were performed on a Micromeritics Flow-Sorb 2300 instrument through gaseous nitrogen adsorption at 77 K, by applying the BET method.

Scanning electron microscopic (SEM) images were obtained for samples dispersed on a double-faced conducting tape adhered to an aluminum support. The samples were coated with gold using a low voltage sputtering Balzer MED 020 apparatus, and the measurements were carried out on a JEOL JSM-T300 scanning electron microscope.

3. Results and discussion

Barium, arsenic, carbon and hydrogen were determined for the layered crystalline host to give 25.5, 27.8, 26.9 and 1.9% which are in excellent agreement with the required amounts, 25.5, 27.9, 26.8 and 1.9% for the expected formula Ba(O₃AsC₆H₅)₂·2H₂O. The complete percentages for carbon, hydrogen and nitrogen for host and their intercalated compounds are listed in Table 1.

The high degree of crystallinity of the host compound was reflected by the well-formed X-ray diffraction powder patterns, which presented a sharp and intense peak attributed to the 001 plane at 7.1°, corresponding to an interlayer distance of 1245 pm. The series of amine-intercalated nanocompounds obtained from aqueous solutions clearly displayed an increase in the interlayer distances due to the entrance of these guest molecules and

Table 2
Interlayer distance (d) and surface area (S) for hydrated barium phenylarsonate (BaAsP) and the intercalated n -alkylmonoamine compounds

Compound	d (pm)	S (m ² g ⁻¹)
BaAsP	1245	125.7 ± 1.1
BaAsP· x CH ₃ CH ₂ NH ₂ ·(1- x)H ₂ O	2337	115.3 ± 1.0
BaAsP· x CH ₃ (CH ₂) ₂ NH ₂ ·(1- x)H ₂ O	2447	111.5 ± 1.0
BaAsP· x CH ₃ (CH ₂) ₃ NH ₂ ·(1- x)H ₂ O	2559	108.7 ± 1.3
BaAsP· x CH ₃ (CH ₂) ₄ NH ₂ ·(1- x)H ₂ O	2670	100.1 ± 1.1

always presented larger interlayer values than those observed for the original matrix. These increases in interlayer distance correlate with the number of carbon atoms of the organic amine chains, a behavior that was also observed for other systems [19,23,24]. The sequence of values for these distances is listed in Table 2. The linear relationship between the interlayer distance (d) and the number of carbons in the amine molecules (n_c) is shown in Fig. 2 and is correlated by the following expression:

$$d = (2225 \pm 32) + (111 \pm 11)n_c \quad (8)$$

Based on this expression, the mean increase in interlayer distance from two subsequent carbon atoms attached to the organic amine chain reflected in an addition of 111 pm. However, by considering the straight alkylmonoamine chain in a normal *trans-trans* arrangement, the successive additions of each methylene group causes an increase in the chain length estimated as 127 pm [25]. Then, the increased range per carbon atom of 111 pm observed for the present compounds indicates that the alkyl chains must be arranged in bilayers tilted at a 60° angle ($\sin^{-1} \theta = 111/127$), in relation to the inorganic basal plane [26].

The surface area values for the present host and all intercalated nanocompounds are listed in Table 2. As expected, the

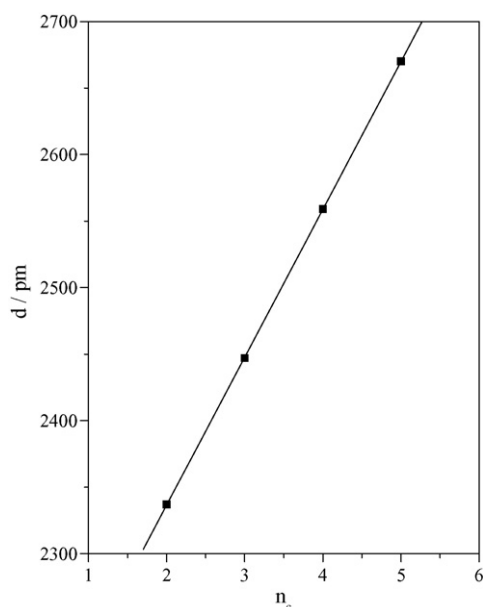


Fig. 2. Interlamellar distance as a function of the number of carbon atoms intercalated.

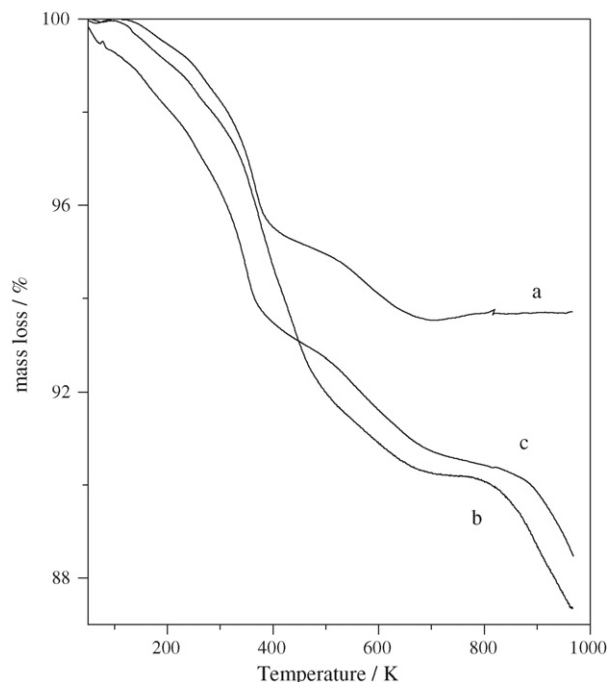


Fig. 3. Percentage of mass loss as a function of temperature for hydrated barium phenylarsonate (a), and when intercalated with ethylamine (b) and pentylamine (c) molecules.

presence of molecules inside the free lamellar cavity inevitable causes a decrease in these values. This for the amine chain molecule insertion show that a progressive increase in interlayer distance is occurring in going from ethylamine to the largest pentylamine molecule. Under these conditions, the decrease in surface area can be interpreted as a consequence of the difficulty of the gaseous nitrogen molecules to cover the free space as the intercalation takes place. For such kind of synthetic materials, a high surface area is an advantage in some technological applications [27].

All infrared spectra presented characteristic bands at 3500 cm⁻¹, demonstrating the existence of water molecules bonded to the inorganic matrix. When intercalated, the original broad band changed in shape with a slight maximum displacement to the 3676–3140 cm⁻¹ interval, which was attributed to N–H bond formation. Another vibrational mode that appeared in the 2984–2824 cm⁻¹ range corresponds to amine C–H bonds. The small peak at 3047 cm⁻¹ corresponds the C–H bond of the phenyl group, followed by a sharp and intense peak at 1430 cm⁻¹ and also peaks at 748 and 690 cm⁻¹. As expected, all bands in the 1147–1033 cm⁻¹ region are related to the vibrations associated with the arsonate group [9].

The thermogravimetric curve for the host and those obtained for all intercalated nanocompounds with n -alkylmonoamines are shown in Fig. 3. The hydrated host compound presented a mass loss of 4.0% up to 400 K, which corresponds to the release of water molecules. The loss of the organic groups started around 700 K and is completed at 990 K, to yield a final Ba(O₃As)₂ residue. The observed mass loss of 34.0%, corresponding to the organic moiety, is in agreement with the calculated value of 34.1% [28]. Based on these results, a possible mechanism of

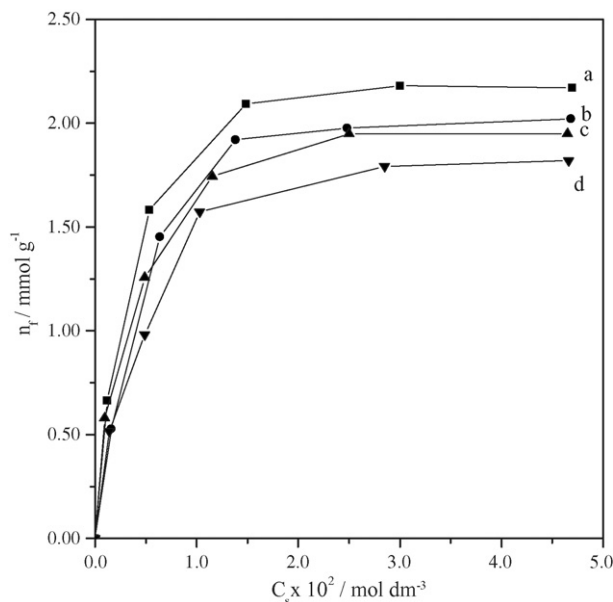
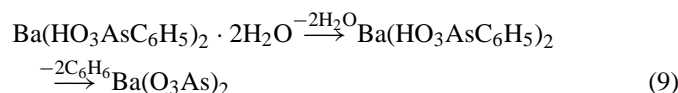


Fig. 4. Isotherms of intercalation, represented by the number of moles intercalated (n_f) into hydrated barium phenylarsonate against the concentration of supernatant (C_s), with ethyl (a), propyl (b), butyl (c) and pentylamines (d).

decomposition can be formulated as follows:



The thermogravimetric curves for all intercalated nanocompounds are very similar to those observed for the precursor hydrated crystalline compound with a difference in percentages of the decomposition stages which reflects the degree of each guest molecule intercalated. The similar shape of all curves presented the continuous mass loss in parallel decreasing, where the extreme amine nanocompounds are shown in Fig. 3. As previously discussed, water elimination from the parent compound causes a mass loss of 4.0%, while for the amine derivatives higher percentages of 5.2, 5.4, 5.7 and 5.9% for ethyl, propyl, butyl and pentylamines, respectively, were observed. On examining these intercalated compounds, the following processes were detected: (i) amine and the remaining water molecules are lost from room temperature to 700 K and (ii) two phenyl groups are lost, by possible combine to give diphenyl molecule, from 750 up to 990 K range, to give the residue $\text{Ba}(\text{O}_3\text{As})_2$ [28].

The scanning electron microscopic (SEM) photographs (not shown) of barium phenylarsonate and also the intercalated samples showed that the crystal morphology of these nanocompounds is clearly lamellar, in agreement with the expected structural characteristics. The morphology of intercalated pentylamine is very similar to that observed in the image for the host matrix. These results are very important in order to obtain pillared nanocompounds with a high degree of crystallinity [26].

The series of isotherms involving n -alkylmonoamine intercalations on hydrated barium phenylarsonate are shown in Fig. 4. The maximum numbers of moles of the amines intercalated were 2.18, 2.02, 1.95 and 1.82 mmol g^{-1} for ethyl, propyl, butyl and pentylamines, respectively. To evaluate the data obtained from

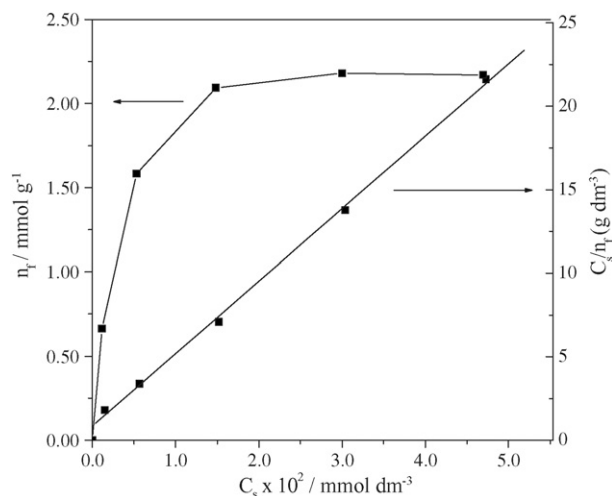


Fig. 5. Isotherm of intercalation of ethylamine indicating (n_f) vs. concentration (C_s). The straight line is the linearization C_s/n_f vs. C_s with coefficient correlation 0.999.

the isotherms in order to determine the amine molar fraction in solution, the results were adjusted to a Langmuir model, in which it is assumed that a monolayer of amines is formed on the inorganic matrix [1,5]. The data were adjusted to the expression:

$$\frac{C_s}{n_f} = \frac{C_s}{n_s} + \frac{1}{bn_s} \quad (10)$$

where C_s and n_f are the number of moles of the amine in the supernatant and intercalated, per gram of the host, n_s is the amount of amine necessary to form a monolayer and b is a constant related to the intensity of the reaction [1,5]. The intercalated isotherm for ethylamine and its linearized form C_s/n_f versus C_s are shown in Fig. 5.

These values obtained from the batchwise procedure decreased with an increase of alkyl chain length of the amine. Such decreases in the amount of the amine intercalated clearly demonstrate a behavior related to the chain size of the guest n -alkyl molecule. As expected, larger amines have reduced freedom to diffuse into the interlayer space when interacting with the acidic groups on the inorganic support. In addition, as the amine chain length increases it could be supposed that a certain restriction to a best adjusting of the chain inside the interlayer nanocavity can occur. Consequently, the number of moles decreased with the increase of alkyl chain length and this behavior is dependent on the degree of intercalation. The number of moles of amine intercalated (n_f) correlated linearly with the number of carbons in the aliphatic chain, as is illustrated in Fig. 6. The linear correlation can be expressed by equation:

$$n_f = (2.28 \pm 0.15) - (11.50 \pm 0.03)n_c \quad (11)$$

The intercalation reaction can be considered as an insertion of a mobile guest species into the host solid structure, while maintaining the framework structural characteristics and an acid/base reaction of the guest species takes place in the accessible empty holes of the inorganic layer.

The thermal effect of amine intercalations inside the barium phenylarsonate matrix was calorimetrically determined. This

Table 3
Thermodynamic data for the intercalation of *n*-alkylmonoamines $\text{CH}_3(\text{CH}_2)_n\text{-NH}_2$ ($n=1\text{--}4$) in aqueous solution into hydrated barium phenylarsonate at 298.15 ± 0.02 K

Amine	n_s (mmol g^{-1})	$-\Delta_{\text{int}}h$ (J g^{-1})	$-\Delta H$ (kJ mol^{-1})	K ($\times 10^{-5}$)	$\ln K$	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Ethyl	2.39	22.8	9.51 ± 0.21	1.64	12.01	29.8 ± 0.1	68 ± 1
Propyl	2.20	25.4	11.5 ± 0.10	4.79	13.08	32.4 ± 0.1	70 ± 1
Butyl	2.05	26.3	12.8 ± 0.15	8.73	13.68	33.9 ± 0.1	71 ± 1
Pentyl	1.97	28.9	14.7 ± 0.08	18.86	14.45	35.8 ± 0.1	71 ± 1

technique consists in following a sequence of individual thermal effects that occur during solute–substrate interactions when the titrand is added to a given solution. By considering the presence of a solid in the system, each thermal effect value is obtained by the injection of titrand solution to a confined suspension of the desired matrix in the calorimetric vessel. The total thermal effect of interaction at each point of titration is then determined by the sum of all thermal effects obtained during the calorimetric titration.

The thermodynamic data related to amine intercalation into the free nanocavity of the hydrated crystalline phenylarsonate are listed in Table 3. The results show that an increase in carbon number in the alkyl chain causes an increased exothermicity of the change in enthalpy of intercalation. The enthalpic values obtained from calorimetric titration are linearly correlated with the number of carbon atoms in the intercalated *n*-alkylmonoamines, as shown in Fig. 7 and is given by the expression:

$$\Delta H = -(7.25 \pm 0.40) - (1.67 \pm 0.10)n_c \quad (12)$$

The slope of the straight line represents the effect of addition of one methylene group to the aliphatic amine chain. The intercept is an estimative of the amine group contribution to the

enthalpy of intercalation. For a similar system involving this same sequence of guest molecules with calcium phenylphosphonate, a value of -1.30 kJ mol^{-1} was obtained [29], which indicates the effectiveness in intercalation with this present inorganic host.

The sequence of the enthalpies determined here with a limited number of *n*-alkylmonoamines contributes to an 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 an unknown guest molecule, in order to readily estimate this desired value from the number of carbons present in the alkyl chain moiety.

From the equilibrium constant, the values of the Gibbs free energy and entropy changes for all intercalation were calculated. All entropic values are also 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, as well as the water molecules hydrogen bonded to the amine groups, causing an increasing of these free molecules in

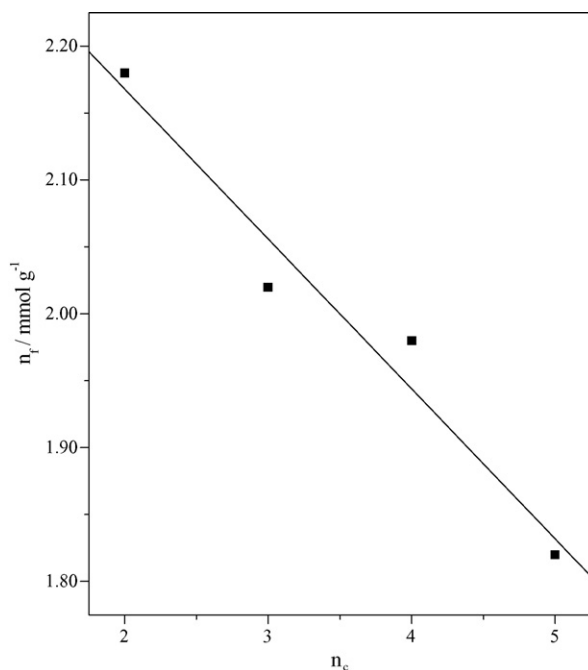


Fig. 6. Number of moles intercalated as a function of the number of carbons in the *n*-alkylmonoamines intercalated into hydrated barium phenylarsonate.

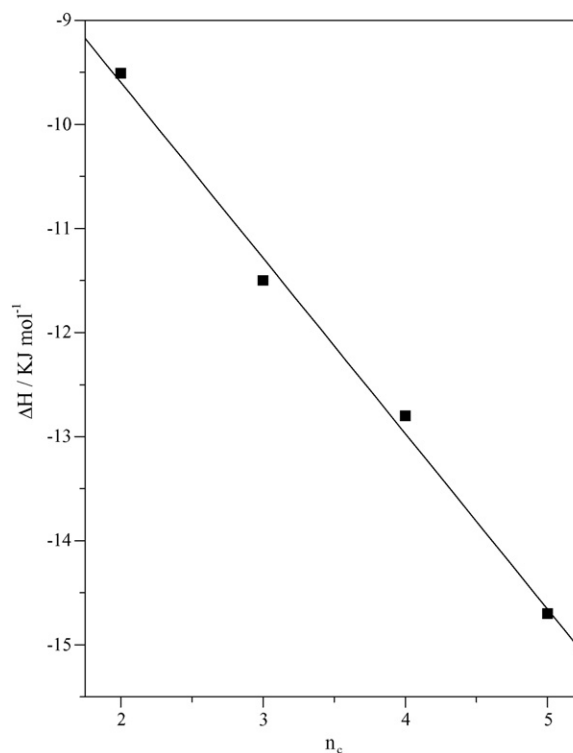


Fig. 7. Enthalpy of intercalation of *n*-alkylmonoamine as a function of the number of carbons intercalated into hydrated barium phenylarsonate.

the medium [6,30,31]. Thus, the release of these molecules of hydration to solution, as the intercalation occurred, is responsible for the increase in entropy, as represented by positive values, which are nearly the same for all intercalations [20,32], as shown in Table 3.

4. Conclusion

Hydrated lamellar crystalline barium phenylarsonate can be used as host support for organic polar molecules. Characterization of the compounds confirms the insertion of *n*-alkylmonoamines into the layered structure, as demonstrated by the increase in the interlayer distance. The data obtained from calorimetric determinations are consistent with processes involving *n*-alkylmonoamines and the phenylarsonate nanocompound at the solid–liquid interface, with thermodynamically favorable values from the viewpoint of negative Gibbs free energy, exothermic enthalpy values and also positive entropic results. The correlations between interlayer distances of guest/host enthalpy and interactions with the carbon atom numbers of the aliphatic amine chain can be useful to infer properties for intercalation of undetermined *n*-alkylmonoamines.

Acknowledgements

The authors are indebted to FAPESP for a fellowship to A.M.L. and for financial support, and to CNPq for a fellowship to C.A.

References

- [1] T.R. Macedo, C. Airoidi, *Micropor. Mesopor. Mater.* 94 (2006) 81.
- [2] I.P.S. Silva, J.C.O. Santos, M.M. Conceição, L.M. Nunes, I.M.G. Santosa, A.G. Souza, *Mater. Lett.* 59 (2005) 2510.
- [3] B. Ramajo, A. Espina, S.A. Khainakov, J.R. Garcia, *J. Incl. Phenom.* 49 (2004) 241.
- [4] V.S.O. Ruiz, C. Airoidi, *Thermochim. Acta* 420 (2004) 73.
- [5] A.M. Lazarin, C. Airoidi, *Thermochim. Acta* 445 (2006) 57.
- [6] A.M. Lazarin, C. Airoidi, *J. Chem. Thermodyn.* 37 (2005) 247.
- [7] T. Takei, K. Sekijima, D. Wang, N. Kumada, N. Kinomura, *Solid State Ionics* 170 (2004) 111.
- [8] M.O. Machado, A.M. Lazarin, C. Airoidi, *J. Chem. Thermodyn.* 38 (2006) 130.
- [9] V.S.O. Ruiz, C. Airoidi, *J. Braz. Chem. Soc.* 16 (2005) 1030.
- [10] S. Dasgupta, M. Agarwal, A. Datta, *Micropor. Mesopor. Chem.* 67 (2004) 229.
- [11] C.C. Chou, Y.C. Chang, M.L. Chiang, J.J. Lin, *Macromolecules* 37 (2004).
- [12] V.S.O. Ruiz, S.L.P. Dias, Y. Gushikem, C. Airoidi, R.E. Bruns, *J. Solid State Chem.* 177 (2004) 675.
- [13] P. Capková, H. Schenk, *J. Incl. Phenom.* 47 (2003) 1.
- [14] G. Alberti, T. Bein (Eds.), *Comprehensive Supramolecular Chemistry*, 7, Pergamon Press, New York, 1996.
- [15] M.A. Bizeto, V.R.L. Constantino, *Mater. Res. Bull.* 39 (2004) 1811.
- [16] L. Benes, V. Zima, K. Melanova, M. Trchova, P. Matejka, *J. Incl. Phenom.* 45 (2003) 235.
- [17] J.A.A. Sales, C. Airoidi, *Thermochim. Acta* 427 (2005) 77.
- [18] G.C. Petrucelli, M.A. Meirinho, T.R. Macedo, C. Airoidi, *Thermochim. Acta* 450 (2006) 16.
- [19] M. Jorianec, R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, New York, 1988.
- [20] V.S.O. Ruiz, A.S. Ribeiro, C. Airoidi, *Curr. Anal. Chem.* 1 (2005) 171.
- [21] D.M. Poojary, B. Zhang, A. Cabeza, M.A.G. Aranda, S. Bruque, A. Clearfield, *J. Mater. Chem.* 6 (1996) 639.
- [22] A.M. Lazarin, C. Airoidi, *Anal. Chim. Acta* 523 (2004) 89.
- [23] C. Airoidi, S. Roca, *J. Mater. Chem.* 6 (1996) 1963.
- [24] C. Airoidi, S.F. Oliveira, *Struct. Chem.* 2 (1991) 41.
- [25] C.B.A. Lima, C. Airoidi, *Int. J. Inorg. Chem.* 3 (2001) 907.
- [26] A.M. Lazarin, C. Airoidi, *J. Incl. Phenom.* 51 (2005) 33.
- [27] Y. Israëli, C. Besse, J. Morel, J.N. Desrosiers, *J. Chem. Soc., Dalton Trans.* (2000) 791.
- [28] S.F. Oliveira, C. Airoidi, *Mikrochim. Acta* 110 (1993) 95.
- [29] C.B.A. Lima, C. Airoidi, *Thermochim. Acta* 400 (2003) 51.
- [30] A.M. Lazarin, I.S. Lima, J.A. Simoni, C. Airoidi, *J. Mater. Res.* 21 (2006) 2191.
- [31] L.M. Nunes, C. Airoidi, *Chem. Mater.* 11 (1999) 2069.
- [32] A.M. Lazarin, C. Airoidi, *Thermochim. Acta* 437 (2005) 122.