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Thermochimica Acta 445 (2006) 57–60
thermochimica acta
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Host hydrated barium phenylphosphonate/guest heterocyclic amine intercalation energetics by calorimetric titration

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Received 12 September 2005; received in revised form 2 December 2005; accepted 2 December 2005
Available online 19 May 2006

Abstract

The heterocyclic amines 2,6-lutidine, pyrazine, piperazine and piperidine were intercalated into layered crystalline hydrated barium phenylphosphonate, $Ba(HO_3PC_6H_5)_2{\cdot}H_2O$, through a batch method in ethanolic solution, to give the maximum amounts 0.39, 0.82, 2.80 and 5.50 mmol g^{-1}, respectively. The original host interlayer distance (d) of 1532 pm increased after intercalation for piperazine (1752 pm) and piperidine (2112 pm) molecules, while for 2,6-lutidine and pyrazine molecules d values were maintained. The enthalpy of intercalation gave -5.60 ± 0.10, -1.00 ± 0.02, -9.55 ± 1.00 and -30.70 ± 0.68 kJ mol^{-1} for the sequence of heterocyclic amines. The Gibbs free energies are negative and entropies are positive for intercalation.

Keywords: Calorimetry; Heterocyclic amine; Barium phenylphosphonate; Intercalation; Thermochemistry

1. Introduction

Crystalline layered metal phosphonates constitute a class of lamellar compounds that have received increased interest over the past few years, due to molecular insertions into the free nanospace to provide self-organized nanomaterials with alternating inorganic–organic layers [1]. The intercalated nanomaterials illustrate structural changes [2], electrical [3], thermochemical [4] properties, critical temperature for superconductivity and electrode surface modifications [5]. The effectiveness of intercalation depends on the pK_a of the guest molecule [6].

Intercalation of a variety of secondary, tertiary, cyclic and arylamines into phosphonate compounds have previously been reported [7,8]. Calorimetry has been used for direct measurement of the enthalpy of the acid–base interactions at the solid/liquid interface [9]. Thermochemical data on these compounds are limited. Thus, the aim of this publication is to report calorimetric data on the intercalation of 2,6-lutidine (lu), pyrazine (pz), piperidine (ppe) and piperazine (ppz) into the crystalline structure of hydrated barium phenylphosphonate. Thermal effects associated with reaction of the acidic inorganic host matrix and the basic nitrogen atom guest centers are explored to further understanding of the intercalation process.

2. Experimental

2.1. Materials

Reagent grade chemicals and deionized water were used throughout the experiments. Phenylphosphonic acid (Aldrich), barium chloride (Merck), ethanol (Synth) and sodium hydroxide (Vetec) were employed in all preparations. The heterocyclic amines 2,6-lutidine, pyrazine, piperidine and piperazine (Aldrich) were used.

2.2. Preparation and intercalation

Hydrated barium phenylphosphonate was prepared and intercalated as previously described [10,11]. The solid was stored in a desiccator to maintain constant weight. Barium phenylphosphonate was suspended in ethanolic solutions of each amine to obtain the isotherm of intercalation [12]. The number of moles of amine intercalated (n_f) was calculated by the difference between the initial moles (n_i) of added amine and determined in the supernatant (n_s) after reaction, divided by the mass (m) of barium phenylphosphonate as expressed by $n_f = (n_i - n_s)/m$. All amine

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doi:10.1016/j.tca.2005.12.005

solutions were standardized as before [13]. The isotherms gave an increase in number of moles of amine intercalated (n_f) with increased concentration of the supernatant (C_s). After intercalation, the resulting white solids were separated by centrifugation, washed with ethanol and dried at 323 K in an oven for about 8 h.

2.3. Calorimetric titration

The thermal effects of intercalation were followed in an isothermal LKB 2277 calorimeter at 298.15 ± 0.20 K [10]. In a typical calorimetric titration, a sample of approximately 10 mg of the host was suspended in 2.0 cm^3 of ethanol and vigorously stirred. The amine solution was incrementally added with a microsyringe and the thermal effect for each increment was recorded. The same procedure was employed to follow the thermal effect of dilution of the host and the guest solution in the calorimetric solvent [10,14].

2.4. Characterization

Barium and phosphorus [10] were determined as before to give the general formula $Ba(HO_3PC_6H_5)_2{\cdot}2H_2O$. Carbon, hydrogen and nitrogen were obtained using with a Perkin-Elmer model PE 2400 instrument for the precursor and intercalated compounds. X-ray diffraction patterns, infrared spectroscopy and thermogravimetric characterizations were performed as before [10].

3. Results and discussion

The structures of thec amines are illustrated in Fig. 1. Analytical data for the host and intercalated compounds are listed in Table 1. Isotherms with distinct intercalation plateaus are presented in Fig. 2. The host shows strong preference for the guest piperidine. This behavior reflects the pK_a values of 11.12 and

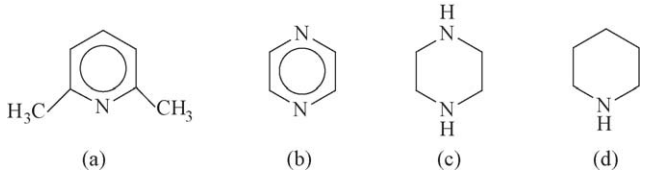

Fig. 1. Structures of 2,6-lutidine (a), pyrazine (b), piperazine (c) and piperidine (d) molecules.

Table 1
Percentages of carbon (C), hydrogen (H), nitrogen (N), interlayer distance (d) and number of moles (n_f) for hydrated barium phenylphosphonate (BaPP) and the intercalated heterocyclic amines: pyrazine (pz), 2,6-lutidine (lu), piperazine (ppz) and piperidine (ppe)

Compound	C (%)	H (%)	N (%)	d (pm)	n_f (mmol g^{-1})
BaPP	30.6	3.3	–	1532	–
BaPP·lu	33.2	3.5	1.0	1532	0.39
BaPP·pz	39.4	4.3	0.6	1532	0.82
BaPP·ppz	33.4	4.5	3.9	1752	2.80
BaPP·ppe	43.6	4.7	7.6	2112	5.50

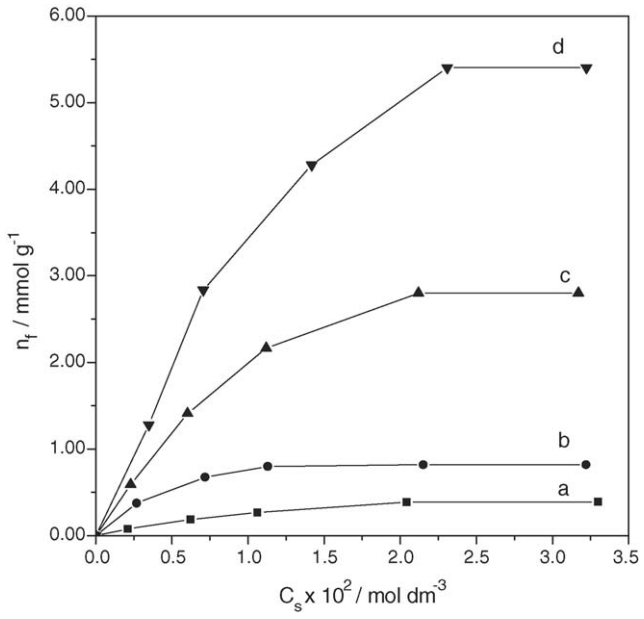

Fig. 2. Isotherms of intercalation, represented by the number of moles intercalated (n_f) into hydrated barium phenylphosphonate against the concentration of supernatant (C_s), with 2,6-lutidine (a), pyrazine (b), piperazine (c) and piperidine (d).

9.72 for piperidine and piperazine, respectively [6] and acidic centers are saturated at 5.50 mmol g^{-1}. The lowest pK_a value for 2,6-lutidine and pyrazine, 0.70, cause weaker interactions, as shown in Fig. 2. However, the two methyl groups neighboring the attached nitrogen basic center on 2,6-lutidine cause steric hindrance, lowering its effectiveness in bonding, to give 0.39 mmol g^{-1} (Table 1), as previously observed with picolines [15].

X-ray diffraction patterns showed that the intercalation process causes an increase in the interlayer distance of the matrix, from 1532 pm to 1752 and 2112 pm for piperazine and piperidine, respectively. The host maintains the original distance for 2,6-lutidine and pyrazine guest molecules. Based on the guest/host interaction it is reasonable to propose that basic molecules are protonated by the acidic hydrogenphosphonate groups on the host surface.

Piperidine and pyrazine molecules are very similar in structure, but caused different increases in the interlayer distance [6,15], suggesting distinct orientations when inserted. Thus, the interlayer expansion may reflect the arrangement of these heterocyclic amines the free cavity of the matrix. The length of pyridine disposed in parallel and perpendicular positions in relation to the inorganic layer was previously determined as 330 and 580 pm, respectively, when inserted into α-titanium hydrogenphosphate [16]. In the present case, as the intercalation occurred, piperazine and piperidine caused a net expansion of 220 and 480 pm, respectively. These values suggest that piperazine is parallel to the inorganic layer, while piperidine assumed a perpendicular orientation, as illustrated in Fig. 3.

The thermogravimetric curve for the original host demonstrated a decomposition to give the final $Ba(O_3P)_2$ residue [10]. The intercalated compounds presented similar decomposition

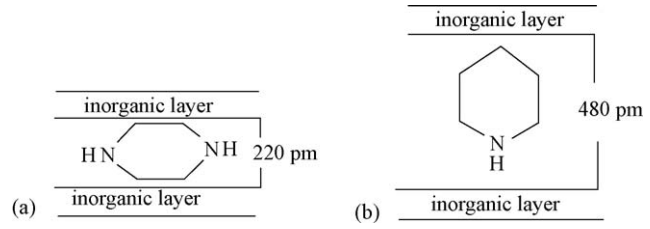

Fig. 3. Proposed model of piperazine in parallel (a) and pipridine in perpendicular (b) positions.

curves with total mass losses of 5.2, 5.4, 5.7 and 5.9% for lu, pz, ppz and ppe, respectively. The amine and remaining water molecules are lost from room temperature to 700 K and the phenyl groups are lost from 750 to 990 K to give the residue $Ba(O_3P)_2$ [17].

The infrared vibrational bands for these compounds are associated with water bonded to the inorganic layer containing the attached organophosphate at 3500 cm^{-1} [10]. Weak bands at 1438 cm^{-1} and medium bands in the 720–694 cm^{-1} range indicate the presence of phenyl rings and the bands at 1080, 1017, 996 cm^{-1} are due to PO_3 groups. Three bands are related to the ring in the 3000–2830 cm^{-1} region, and one at 1437 cm^{-1}, correspond to the symmetrical and asymmetrical C–H stretch and to the C–C stretch of the ring, respectively. The band at 1250 cm^{-1} is assigned as P–OH group out-of-plane deformations [18], indicating the existence of the remaining unreactive groups during compound formation, which acts as acidic sites in the lamella. The other expected bands, associated with guest molecule vibrations, are superimposed on the phenylphosphonate bands.

Determining the enthalpy of reaction requires three independent calorimetric titrations: (a) thermal effect of reaction, Q_r, where the ethanolic amine solution is added to a suspension of the inorganic matrix in ethanol, (b) thermal effect of dilution, Q_{dil}, by adding the same ethanolic amine solution into an identical volume of ethanol, and (c) thermal effect of hydration, Q_h, that involves the addition of ethanol to a matrix suspension. The thermal effects of reaction for each experimental point of the calorimetric titration were considered for calculation of the net thermal effect (Q_{int}) of these interactions: $\Sigma Q_{int} = \Sigma Q_r - \Sigma Q_{dil} - \Sigma Q_h$. The sequence of values enables calculation of the net enthalpy of interaction to form a monolayer per unit mass of matrices, by using a modified Langmuir model, which was adjusted to several types of systems [6]. The enthalpy of monolayer and the constant of equilibrium derived the linearized from of the experimental data plot are shown in Fig. 4. Calculation of the enthalpy was based on the expression $\Delta H = \Delta h_{int}/n_s$, were n_s is the number of adsorbed moles after reaching calorimetric equilibrium [4,8,10].

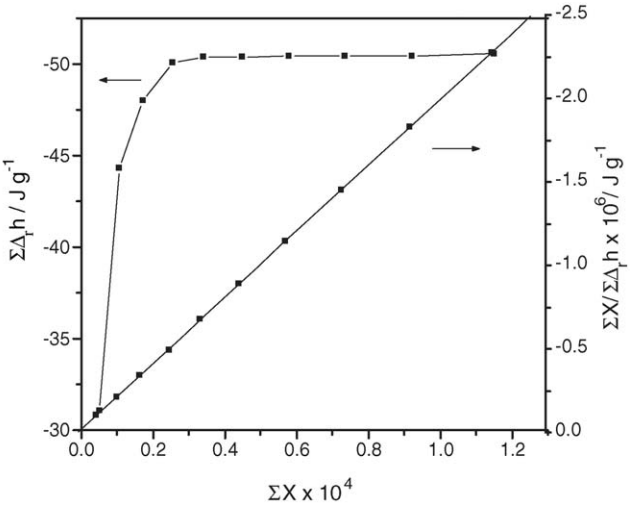

Fig. 4. Isotherm for the integral enthalpy of intercalation $\Sigma\Delta h_r$ vs. molar fraction, ΣX, obtained from a calorimetric titration of 0.0100 g of hydrated barium phenylphosphonate suspended in 2.0 cm^3 of ethanol, with 0.5001 mol dm^{-3} piperazine in the same solvent at 298.15 ± 0.20 K. The linearized form is given by $\Sigma X/\Sigma\Delta h_r$.

The results are all exothermic in nature as shown in Table 2 with small ΔH value for pyrazine intercalation reflects the low affinity of this amine. On the other hand, despite the low amount of 2,6-lutidine intercalated, a relatively large ΔH value is observed.

Intercalation is driven by the acid–base interaction between the heteroatom of the heterocyclic amine and *P*–OH group attached to the inorganic layer. The energy required to expand the layer is thus supplied by the formation of new hydrogen bonds and this process is surely associated with an exothermic reaction [5], as observed from values listed in Table 2.

The Gibbs free energies calculated from the expression $\Delta G = -RT \ln K$, with the K values obtained from the calorimetric data are shown in Table 2, indicating that the reactions are all spontaneous. The ΔS calculated from $\Delta G = \Delta H - T\Delta S$, also listed in Table 2, are consistent with the argument that the reactions are entropically favored. These values suggest a disruption of the solvent molecules initially bound to the inorganic matrix and associated with the heterocyclic amines. The increase in entropy is related to the release of

Table 2
Thermodynamic data for the intercalation of heterocyclic amines (HA) in ethanolic solution into hydrated barium phenylphosphonate at 298.15 ± 0.20 K

HA	n^s (mmol g^{-1})	$-\Delta_{int}h$ (J g^{-1})	$-\Delta H$ (kJ mol^{-1})	K ($\times 10^{-6}$)	ln K	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
pz	0.89	0.89	1.00 ± 0.02	0.01	9.42	23.4 ± 0.1	92 ± 1
lu	0.41	2.29	5.60 ± 0.10	0.15	11.92	29.6 ± 0.1	81 ± 1
ppz	2.94	28.17	9.55 ± 1.00	6.99	15.76	39.1 ± 0.1	99 ± 1
ppe	5.70	175.00	30.70 ± 0.68	3.36	15.03	39.3 ± 0.1	22 ± 1

these molecules into solution during the intercalation process [13,15].

4. Conclusion

The nanocompounds formed showed a dependence on pK_a values. The most effective, piperazine, with pK_a 11.12 inserts the largest amount of 5.50 mmol g^{-1} and expands the lamellar structure to 2112 pm. In contrast to pyrazine with pK_a 0.70 that intercalated only 0.82 mmol g^{-1} and caused an interlayer distance of 1532 pm. Intercalation of 2,6-lutidine is also affected by steric hindrance by the methyl groups, affecting the nitrogen basic center/host hydrogen bond formation. The largest exothermic ΔH value, -30.70 ± 0.68 kJ mol^{-1}, was for the strongest base, piperidine.

Acknowledgement

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

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