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n-ALKYLMONOAMINE INTO CRYSTALLINE LAMELLAR TITANIUM PHENYLPHOSPHONATE

Intercalation enthalpies, Gibbs free energies and entropies

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Abstract

Crystalline lamellar titanium phenylphosphonate was intercalated with *n*-alkylmonoamines, $H_3C(CH_2)_n$–NH_2 (n=0 to 3), which decomposed on heating in four distinct stages. The lamellar compound was calorimetrically titrated with ethanolic amine solution at 298.15±0.02 K and the enthalpy, Gibbs free energy and entropy were calculated. With the exception of butylamine, the enthalpic values increased with the number of carbon atoms in the amine chain, as –16.20±0.22; –18.70±0.19; –23.70±0.24 and –18.30±0.22 kJ mol^{-1}, from n=0 to 3. The exothermic enthalpic values reflected a favorable energetic process of intercalation, when the solvated ethanol molecules on inorganic matrix are progressively substituted by solute. The negative Gibbs free energy results supported the spontaneity of the reactions and the positive favorable entropic values are in agreement with the increase of solvent molecules in the reaction medium, as the amine becomes bonded to the crystalline lamellar inorganic matrix.

Keywords: amine, enthalpy, intercalation, phenylphosphonate

Introduction

Synthetic procedures which prepare new materials that contain well-defined cavities are the object of many technological applications, such as catalysis. In this research field the crystalline lamellar metallic phosphonates have been received considerable attention during recent decades [1], and this field is expanding, mainly from the structural determination point of view [2].

Crystalline metallic organophosphonate compounds have a lamellar structure, being inorganic-organic hybrids, in which the inorganic backbone forms the central portion of the lamella, with organic pendant groups covalently bonded on both sides of the lamella, in an ordered infinite structural sequence [3]. The great advantage of such compounds is their preparation as polycrystalline solids, thin films or membranes, depending on the application. However, the most widely employed relate to

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host materials for many interesting intercalation reactions [2]. An important class of divalent metallic phosphonates has the general formula $M(O_3PC_6H_5)\cdot H_2O$, for M=Mg, Mn, Cd, Co, Zn, where the cations are centered in an octahedral site bonded by five oxygen phosphonate groups while the sixth position is occupied by an oxygen atom of a water molecule [4]. However, these structural features differ from those of tetravalent cations, such as zirconium and titanium, being this first metal the structure previously determined and is extensively studied and these cations are octahedrically coordinated by six oxygen atoms of the phosphonate groups [5].

The aim of this publication is to explore the intercalation process involving anhydrous titanium phenylphosphonate, $Ti(O_3PC_6H_5)_2$, with *n*-alkylmonoamines, $CH_3–(CH_2)_n–NH_2$ (n=0 to 3), from the point of view of their thermal decompositions, and also thermochemical data related to the insertion of these guest molecules into the host lamellar compound.

Experimental

All reagents employed, such as titanium trichloride (Aldrich) in hydrochloric acid in molar ratio 0.073, phenylphosphonic acid, $C_6H_5PO(OH)_2$ (Aldrich) 98% in purity as purchased and the *n*-alkylmonoamines $CH_3(CH_2)_nNH_2$ (Fluka) were used without further purification. The host compound, titanium phenylphosphonate, was synthesized as previously described [6] and the elemental analysis was obtained through inductively coupled plasma optical emission spectrometry with a Perkin Elmer model Optima 3000 DV. X-ray values were obtained on a Shimadzu model XD3A diffractometer in 2θ=1.4 to 70.0° range, with CuK_α radiation (1.54 nm). Infrared spectra of the samples in the 4000 to 400 cm^{-1} range were performed in KBr pellets, with resolution of 4 cm^{-1}, by accumulating 50 scans on a Bomem series spectrophotometer. A thermogravimetric DuPont apparatus, model 1090B, coupled with a thermobalance 951 was used to obtain the curves, in dry argon atmosphere, with a heating rate of 1.67 K s^{-1} in the range of temperature from 300 to 1073 K, with approximately 10 mg of mass.

The adsorption processes were calorimetrically monitored by titration using a heat-flow instrument LKB 2277 Thermal Activity Monitor [7]. In a typical process, 10.0 mg of host thermostated samples suspended in 2.0 cm^3 of ethanol were incrementally titrated with an original 0.5453 mol dm^{-3} amine ethanolic solution, under stirring, at 298.15±0.02 K. Such 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_r), b) solvation of the solid (Q_s) and c) dilution of amine solution (Q_{dil}). The net thermal effect is given by: $\Sigma_{int}Q=\Sigma_rQ–\Sigma_{dil}Q–\Sigma_sQ$, as the thermal effect of solvation of the inorganic lamellar compound sample suspended in the ethanol was null, then $\Sigma_{int}Q=S_rQ–\Sigma_{dil}Q$, whose butylamine intercalation results are shown in Fig. 1.

The intercalation capacities of the host were determined using batch isotherms by maintaining the same proportions as employed in the calorimetric titrations. Thus, for this procedure, 30.0 mg of titanium phenylphosphonate was suspended in 6.0 cm^3 of ethanolic amine solution, whose concentration at equilibrium varied from $4.0\cdot10^{-3}$

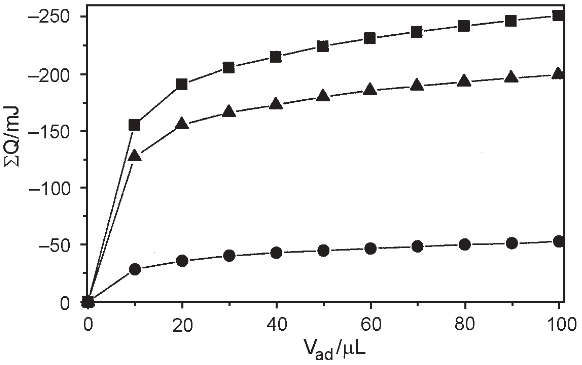

Fig. 1 Calorimetric titration of 0.0100 g of titanium phenylphosphonate suspended in 2.0 cm^3 of ethanol with 0.5453 mol dm^{-3} butylamine in the same solvent at 298.15±0.02 K. The experimental points represent the sum of the thermal effects of the direct titration $\Sigma_{tit}Q$ (– ■–), dilution $\Sigma_{dil}Q$ (–● –) and the net thermal effects $\Sigma_R Q$ (–▲–). ΣQ and V_{ad} values are the sum of the detected thermal effect and total injected volume of titrand solution, respectively

to $2.6\cdot10^{-2}$ mol dm^{-3}. The suspensions were mechanically stirred for 24 h at 298±1 K. The number of moles of amine intercalated in the inorganic backbone, N_f, on a mass, m, of the host was determined by the expression: $N_f=(N_i-N_s)/m^{-1}$, where N_i and N_s are the initial and final amount of the amine in solution. The enthalpy of interaction $\Delta_{int}h$ was obtained by an expression fitted to modified Langmuir equation [8]:

$$\frac{\sum X}{\sum_R h\Delta} = \frac{1}{(K-1)\Delta_{int}h} + \frac{\sum X}{\Delta_{int}h},$$

where ΣX is the sum of the molar fractions of the remaining amine in solution after interaction, $\Sigma_R h\Delta$ the enthalpy of intercalation obtained by dividing the thermal effect resulting from $\Sigma_{int}Q$ by the number of moles of the intercalating molecules and K a constant of proportionality that includes the equilibrium constant.

In the present case, $\Sigma X/\Sigma_R h\Delta$ *vs.* ΣX plot gave the angular and linear coefficients, which determine $\Delta_{int}h$ and K, respectively. The molar enthalpy of the interaction process was calculated by considering the enthalpy of interaction and the respective number of moles intercalated, $\Delta H^\circ_m=\Delta_{int}h/N_f$. Gibbs free energy and entropy changes were calculated from $\Delta G^\circ_m=-RT\ln K^\circ$ and $\Delta G^\circ_m=\Delta H^\circ_m-T\Delta S^\circ_m$ expressions, respectively [9].

Results and discussion

Based on the elemental analysis 11.67 and 15.27% found for titanium and phosphorus determinations, the amounts of 2.48 and 4.94 mmol g^{-1} were calculated, respectively, values which give a 2:1 molar ratio for these elements, and consequently, the molecular formula $Ti(O_3PC_6H_5)_2$ was established for this compound. An interlamellar distance of 1503 pm was calculated from the X-ray patterns, this value is normally increased as the *n*-alkylmonoamines are intercalated, to give a maximum value of

1541 pm for butylamine insertion, the longest *n*-alkyl chain. For all infrared spectra a broad weak band at 3500 cm^{-1} appeared due to the high hygroscopicity of KBr pellet preparation [10]. The appearance of weak bands in the 3295 to 2855 cm^{-1} and the 1595 to 1487 cm^{-1} ranges corresponds to the vibrational modes of the asymmetric and symmetric N–H bond [10–12], corroborating also with the success of intercalation, with great similarity for all inserted samples. However, some variations in band intensities is related to the increase in the amine alkyl chain [10]. The corresponding C–H stretching band for the phenyl ring is also weak and observed at 3055 cm^{-1}, with a thin and intense band at 1441 cm^{-1}. Other bands related to this aromatic ring are medium in intensity in the 748 to 559 cm^{-1} range [13]. All bands associated with PO_3 vibrations are observed in the 1150 to 1012 cm^{-1} range [11, 13, 14].

The intercalated n-alkylmonoamine compounds decomposed in stages as observed through thermogravimetry, part I, and the corresponding derivative, part II, of the curves in Fig. 2. Thus, four processes were detected: i) physically adsorbed amine is lost from room temperature to near 388 K, ii) the chemisorbed amine from 388 up to 653 K [15] and iii) two steps due to the loss of phenyl groups [6] in the 653 to 843 K and 843 to 1073 K ranges, respectively, to give titanium pyrophosphate [16]. These observations are clearly illustrated in the derivative curves in part II of Fig. 2. All these results are summarized in Table 1, from which are assigned the mass loss steps. The proposed formula are also listed.

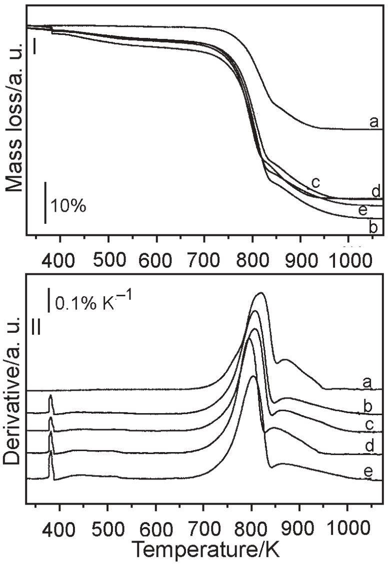

Fig. 2 Thermogravimetric (I) and derivative (II) curves for titanium phenylphosphonate (a) and intercalated compounds with methyl (b), ethyl (c), propyl (d) and butylamines (e)

Table 1 Percentage of mass (*xL* for *x*=1 to 4) obtained from thermogravimetric curves for *n*-alkylmonoamines $CH_3–(CH_2)_n–NH_2$ (*n*=0 to 3) intercalated into titanium phenylphosphonate

$CH_3–(CH_2)_n–NH_2$	1*L*/ %	2*L*/ %	3*L*/ %	4*L*/ %	Calculated formula
$CH_3–$	1.34	2.37	30.13	8.73	$(CH_5N)_{0.39}Ti(O_3PC_6H_5)_2$
$CH_3–CH_2–$	1.07	2.61	29.02	8.68	$(C_2H_7N)_{0.27}Ti(O_3PC_6H_5)_2$
$CH_3–(CH_2)_2–$	1.59	3.29	27.12	9.86	$(C_3H_9N)_{0.26}Ti(O_3PC_6H_5)_2$
$CH_3–(CH_2)_3–$	1.69	4.01	29.23	8.16	$(C_4H_{11}N)_{0.25}Ti(O_3PC_6H_5)_2$

The maximum number of moles inserted in the inorganic backbone was obtained by supernatant titration as 1.65, 1.36, 1.00 and 1.12 mmol g^{-1} for methyl, ethyl, propyl and butylamines, respectively. From the batch process the isotherms of intercalation were obtained as shown in Fig. 3. As a normal behavior, the increase in amine concentration caused a related increase in the number of moles intercalated. However, the interlamellar distances did not uniformly increase with the increase of the amine chain [10].

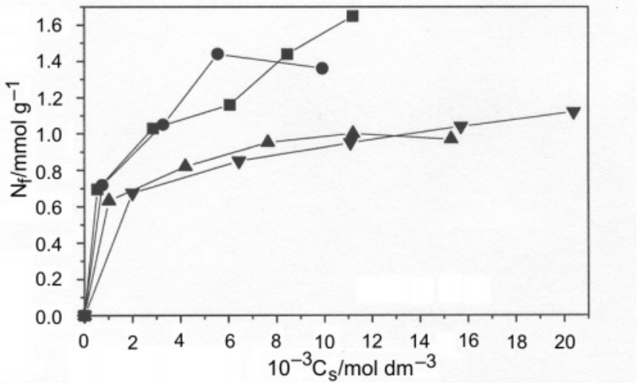

Fig. 3 Isotherms of intercalation of amines in titanium phenylphosphonate. C_s is the equilibrium concentration of the amine and N_f is the number of moles of amine per g of lamellar compound, for the *n*-alkylmonoamines: methyl- (– ■ –), ethyl- (– ● –), propyl- (–▲–) and butyl- (–▼–)

An example of the calorimetric isotherm and its linearized form is shown in Fig. 4, with a linear correlation coefficient of 0.999. The thermodynamic data related to the amine intercalation into the free cavity of the crystalline phenylphosphonate are listed in Table 2, resulting in an exothermic effect from the net interactive effects. A tendency in increasing the favorable enthalpic values as the alkyl chain size of the amine increases is inverted for butylamine, which gave a lower ΔH value than propylamine. The exothermic Gibbs free energy for all intercalations is in agreement with energetically favorable reactions. Identically, the calculated positive entropic values are also favorable for such interactive processes. The variation in entropy can be interpreted by considering that in the in-

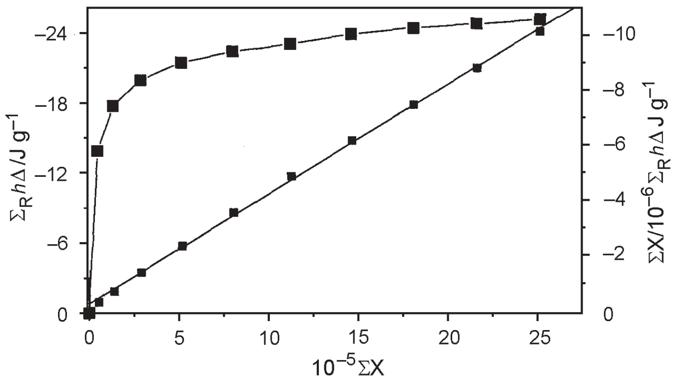

Fig. 4 Isotherm for the integral enthalpy of intercalation $\Sigma_R h\Delta$ *vs*. molar fraction, ΣX, obtained from a calorimetric titration of 0.0100 g of titanium phenylphosphonate suspended in 2.0 cm^3 of ethanol, with 0.5453 mol dm^{-3} butylamine in the same solvent at 298.15±0.02 K. The straight line is the linearized form of the isotherm

tercalation process the desolvation disturb the structure of the medium of reaction, to promote the disorganization of the system, by causing an increase in entropy, as observed for other solid/liquid interface replacements [9, 17, 18].

Table 2 Thermodynamic data for the intercalation of *n*-alkylmonoamines $CH_3–(CH_2)_n–NH_2$ (*n*=0 to 3) in ethanolic solution with titanium phenylphosphonate at 298.15±0.02 K

$CH_3–(CH_2)_n–NH_2$	$–\Delta h_{int}$/ J g^{-1}	$–\Delta H^{\circ}_m$/ kJ mol^{-1}	ln*K*	$–\Delta G^{\circ}_m$/ kJ mol^{-1}	$–\Delta S^{\circ}_m$/ J mol^{-1} K^{-1}
$CH_3–$	26.72	16.19±0.22	11.29	27.96±0.1	40±1
$CH_3–CH_2–$	25.46	18.72±0.19	11.69	28.93±0.1	34±1
$CH_3–(CH_2)_2–$	23.72	23.72±0.24	11.81	29.22±0.1	19±1
$CH_3–(CH_2)_3–$	20.50	18.31±0.22	10.97	27.18±0.1	30±1

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