**n-ALKYLMONOAMINE INTO CRystalline Lamellar Titanium Phenylphosphonate**

**Intercalation enthalpies, Gibbs free energies and entropies**

_V. S. O. Ruiz and C. Airoldi*_

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970 Campinas, São Paulo, Brazil

(Received April 23, 2002; in revised form October 30, 2002)

**Abstract**

Crystalline lamellar titanium phenylphosphonate was intercalated with _n_-alkylmonoamines, H₃C(CH₂)ₙ–NH₂ (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...
host materials for many interesting intercalation reactions [2]. An important class of divalent metallic phosphonates has the general formula $M(O_3PC_6H_5)_{215}H_2O$, 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$_6$H$_5$PO(OH)$_2$ (Aldrich) 98% in purity as purchased and the $n$-alkylmonoamines CH$_3$–(CH$_2$)$_n$–NH$_2$ (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 20 range of 1.4 to 70.0°, with CuK$_\alpha$ 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: $\Delta_nQ=\Delta_rQ-\Delta_dilQ$, as the thermal effect of solvation of the inorganic lamellar compound sample suspended in the ethanol was null, then $\Delta_nQ=\Delta_rQ-\Delta_dilQ$, 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 4.0×10$^{-3}$