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Structural, sorption and thermodynamic correlations from a layered barium phenylarsonate/n-alkyldiamine system

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ABSTRACT

The barium phenylarsonate compound, $Ba(HO_3AsC_6H_5)_2 \cdot 2H_2O$, has the ability to intercalate n-alkyldiamine molecules, $H_2N(CH_2)_nNH_2$ ($n=2$–5). The amount intercalated (n_f) from a batchwise procedure and the variation of the original basal distance (d) of 1245 ppm determined through X-ray diffractions, gave linear correlations as a function of the number of carbon atoms in the aliphatic chain (n_c): $n_f=(2.66\pm0.06)-(0.13\pm0.02)n_c$ and $d=(2168\pm65)+(114\pm14)n_c$. The intercalation process was calorimetrically followed to give exothermic enthalpy and negative Gibbs energy, reflecting spontaneous intercalation reactions at the solid/liquid interface. The displacement of solvent molecules bonded to amine and of those on the matrix during the intercalation increases the disorder to result in positive entropy, giving a favorable set of thermodynamic data for this system.

1. Introduction

A variety of crystalline inorganic nanocompounds containing well-ordered lamellar structures [1,2] comprise many natural or synthetic materials such as phyllosilicates, graphite, double layered hydroxides, transition metal oxides, silicic acids, phosphonates, phosphates, arsenates, etc. [3–11]. The insoluble crystalline class of acid salts of the general formula $M(O_3XC_2H_5)_2 \cdot H_2O$ (M = Ba, Ca, Mg, Cd, Co, Zn, Mn and X = P or As) constitute a well-studied group of compounds, mainly explored from the point of view of their ion exchange and lamellar properties [12,13].

Reactions between such lamellar compounds through the insertion of neutral polar molecules inside the layers of these insoluble compounds lead to novel characteristics. The guest molecule–host matrix interaction is strengthened and the layers are spread apart to accommodate the guest molecule. The success of this reaction depends directly on the active sites on the support that can interact with molecules of the intercalating agent to establish a stoichiometric composition, in which the active sites are exactly covered by the guest molecules [14–16]. From the viewpoint of this reaction, the guest organic molecules interact with the host acidic centers to yield new well-organized nanomaterials, while the insertion within the interlamellar space causes an expansion of the layered spacing, easily followed through the X-ray diffraction technique [17,18]. These guest–host combinations are also studied by infrared spectroscopy [19] and thermal analysis investigations [20].

The energy of intercalation is clearly associated with the interaction between the basic guest molecule and the host acidic center available inside the inorganic matrix. However, in this lamellar crystalline research field, the majority of investigations are directed to some structural features and fewer studies have been focused on the energetics of acid–base reactions. However, information about this interaction enables the determination of the thermodynamic data between the desired guest molecules with a specific inorganic host matrix. From the experimental point of view, a calorimetric technique is extremely favorable when applied to such heterogeneous systems in order to quantify the interactive effect at the solid–liquid interface [12,21].

The present investigation reports the energetics of n-alkyldiamine molecules with the general formula $H_2N(CH_2)_nNH_2$ ($n=$ 2–5), being intercalated into the void lamellar nanospace cavity available in the hydrated barium phenylarsonate structural arrangement.

2. Experimental

2.1. Materials

Reagent grade chemicals and deionized water were used throughout the experiments. Phenylarsonic acid (Aldrich) 98%, barium chloride (Merck), 99% and sodium hydroxide (Vetec) 99% were employed in all preparations. The sequence of diamines

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(Aldrich) of the general formula $H_2N(CH_2)_nNH_2$ (n=2–5), i.e., 1,2-ethylene-, 1,3-propylene-, 1,4-butylene- and 1,5-pentamethylenediamines, were used as received.

2.2. Preparation

Hydrated barium phenylarsonate was synthesized as before [22]. Briefly, 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} $BaCl_2 \cdot 2\,H_2O$ aqueous solution. The final pH of the mixture was adjusted to the range of 5–6 with sodium hydroxide. The resulting solid was filtered, washed and air-dried at 320 K. The general synthetic reaction can be written as

$$BaCl_2 \cdot 2H_2O + 2[C_6H_5AsO(OH)_2] \rightarrow Ba[(HO)O_2AsC_6H_5]_2 \cdot 2H_2O + 2HCl \qquad (1)$$

2.3. Intercalation procedure

Intercalation was carried out by suspending about 50 mg of solid barium phenylarsonate in 0.50 mol dm^{-3} aqueous solutions of each diamine at room temperature. The isotherms of concentration versus time were obtained through batch methodology [23,24]. For this determination, a series of flasks containing the suspension were continuously stirred in a mechanical orbital apparatus thermostated at 298 ± 1 K. The number of moles of diamine intercalated into the host matrix (n_f) can be calculated [25,26] by the difference between the initial number of moles (n_i) of added amine and that determined in the supernatant (n_s), divided by the mass (m) of the compound used, as illustrated by the expression $n_f=(n_i-n_s)/m$. All diamine solutions were previously standardized with a 0.1570 mol dm^{-3} hydrochloric acid solution and a 5:1 mixture of bromocresol green and methyl red was used as an indicator [27]. After intercalation, the resulting white solid was 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 the concentration of 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.

2.4. Calorimetric titration

The thermal effects of the intercalation of this series of diamines for the lamellar crystalline compound were followed in an isothermal LKB 2277 microcalorimetric system, as previously described [28]. Initially, a sample of approximately 10 mg was suspended in 2.0 cm^3 of water and vigorously stirred at 298.15 ± 0.20 K. After base line stabilization the apparatus was standardized and a microsyringe was coupled to the system connected to a stainless steel needle. Through it, increments of the diamine solution were added to the calorimetric vessel. Each thermal effect caused by the reaction was recorded after addition of the titrant. The same procedure was used to follow the thermal effect of dilution of the host and the guest solution in water [29].

The enthalpic determination for each reaction requires three independent calorimetric titrations: (a) thermal effect of reaction, Q_r, where the aqueous diamine 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_d, by adding the same aqueous diamine solution into an identical volume of water and (c) thermal effect of hydration, Q_h, which involves the addition of water to the matrix in suspension. The effects of the thermochemical cycle for this series of interactions involve suspended (sp) hydrated barium phenylarsonate (BaPAs) in water and the sequence of n-alkyldiamines (RNH_2) can be represented by

$$BaPAs_{(sp)} + RNH_{2(aq)} = BaPAs \cdot H_2NR_{(sp)};\; Q_r \qquad (2)$$

$$RNH_{2(aq)} + nH_2O = RNH_2 \cdot nH_2O_{\ (aq)};\; Q_d \qquad (3)$$

$$BaPAs_{(sp)} + nH_2O = BaPAs_{(sp)} \cdot nH_2O_{(aq)};\; Q_h \qquad (4)$$

$$BaPAs \cdot nH_2O_{(sp)} + RNH_2 \cdot nH_2O_{\ (aq)} = BaPAs \cdot H_2NR_{(sp)} + 2nH_2O;\; Q_i \qquad (5)$$

Reactions (2)–(4) represent the individual calorimetric titration experiments carried out in duplicates for each determination. The thermal effects of reaction for each experimental point of the calorimetric titration were considered for calculation of the net thermal effect (Q_i) of these interactions, as represented by reaction (5).

2.5. Characterization

Arsenic [30] and barium [31] elemental analyses were determined through atomic absorption spectroscopy using a Perkin-Elmer Model 5100 atomic absorption spectrometer and spectrophotometric methods using a Shimadzu Model MultiSpec-1501 spectrophotometer, respectively. Carbon, hydrogen and nitrogen were obtained using a Perkin-Elmer model PE 2400 instrument for the precursor and intercalated compounds.

X-ray powder diffraction measurements were obtained on a Shimadzu XD3-A diffractometer (30/20 kV/mA) with nickel-filtered CuKα radiation (λ=0.1542 nm), at a scan rate of $3.33\times10^{-2}\,^{\circ}\,s^{-1}$ at room temperature, with 2θ varying from 1.4° to 50°.

Infrared spectra were measured using a Perkin-Elmer model 1600 FTIR spectrophotometer and pressed KBr pellets with 32 scans in the 4000–400 cm^{-1} range and resolution of 4 cm^{-1}.

Thermogravimetric curves for samples varying in weight from 15.0 to 30.0 mg 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 $cm^3\,s^{-1}$.

3. Results and discussion

Barium and arsenic elemental analyses were initially determined for the precursor to be 25.5% and 27.8%, respectively. By comparing these results with the required amounts, 25.5% and 27.9%, a good agreement was established for the expected formula $Ba(O_3AsC_6H_5)_2 \cdot 2\,H_2O$ for this layered compound [13].

The host property associated with this class of lamellar metal phenylarsonates enables it, in principle, to intercalate various kinds of organic guest molecules to give, at the end of this process, a perfect accommodation of the guest molecules inside the void structural space of the crystalline inorganic matrix. The structural inorganic arrangement shows a well-ordered sequence of lamella to give a basal distance of 1245 pm obtained from X-ray measurements, a value that is very close to previous determinations [32]. For this purpose the main peak associated with the 0 0 1 reflection plane is located at a low value that corresponds to the basal distance. For example, the precursor lamellar compound with 2θ value is related to 1245 pm. Identically, the same procedure was used for all intercalated compounds and the data is listed in Table 1.

The thermogravimetric curves for the original lamellar compound and that intercalated with 1,5-pentamethylenediamine are shown in Fig. 1. The thermogravimetric curve for the original host demonstrated similar decomposition on heating to give a final $Ba(O_3As)_2$ residue. The intercalated compounds presented similar decomposition curves with mass losses varying from 5.2% to 5.9%.