

SILICIC ACID MAGADIITE AS A HOST FOR N-ALKYLDIAMINE GUEST MOLECULES AND FEATURES RELATED TO THE THERMODYNAMICS OF INTERCALATION

THAÍS R. MACEDO, GIOVANNI C. PETRUCCELLI AND CLAUDIO AIROLDI

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

Abstract—Some n-alkyldiamines with the general formulae $H_2N(CH_2)_nNH_2$ ($n = 2–5$) were intercalated into the layered silicic acid magadiite, from aqueous solution, causing an increase in the original interlayer distance of 1172 pm. The synthetic magadiite and all intercalated compounds were characterized by elemental analysis, infrared vibrational spectroscopy, X-ray diffractometry, ^{29}Si nuclear magnetic resonance in the solid state, thermogravimetry, scanning electron microscopy, surface area and porosity. The intercalation was followed through a batch-wise method at 298 ± 1 K and gave the maximum amounts 3.70, 2.80, 1.75 and 1.18 mmol g^{-1} , for n varying from 2 to 5, respectively. The well characterized magadiite was calorimetrically titrated in a heterogeneous medium, to obtain the thermodynamic data of intercalation at the solid/liquid interface. Linear correlations were obtained for the number of moles intercalated (N_f), the interlamellar distance (d) and the specific enthalpy ($\Delta_{int}h$) values of the interactive process as a function of the number of C atoms of the aliphatic organic chains (n_C) for n-alkyldiamine: $N_f = (5.36 \pm 0.25) - (0.86 \pm 0.07)n_C$, $d = (1406.6 \pm 1.9) + (20.9 \pm 0.5)n_C$ and $\Delta_{int}h = (5.96 \pm 0.25) + (0.06 \pm 0.01)n_C$. The basic N guest atom/silanolic acid center interactions inside the host nanospace gallery gave exothermic enthalpies, positive entropies and negative Gibbs free energy values. This set of data suggests the spontaneity of these intercalation reactions.

Key Words—Calorimetry, Intercalation, Magadiite, n-alkyldiamines, Silicic Acid.

INTRODUCTION

The many layered inorganic crystalline compounds originating from natural sources (Fonseca *et al.*, 2005) or synthesized in the laboratory (Lima and Airoldi, 2004), are very important in our understanding of new nanomaterials and their deployment in numerous applications (Cheetham *et al.*, 1999). The well ordered inorganic atom combinations of such compounds derived from the original sheets are distanced in an equilibrium condition, maintained by weak van der Waals interactive forces. This void interlayer nanospace can, in principle, be occupied by a guest molecule in a typical intercalation reaction (Clearfield, 1998; Čapková and Schenk, 2003).

The reversible insertion of guest molecules into the crystalline structure does not cause any damage to the host (Ruiz-Hitzky *et al.*, 2001; Ruiz and Airoldi, 2004). The change that occurs during the insertion is the increase in interlayer spacing, during which the intercalating agents are organized into ordered molecular assembly arrangements, as elucidated by X-ray diffraction (XRD) (Čapková and Schenk, 2003; Ruiz and Airoldi, 2004; Fonseca *et al.*, 2005). Control of how the intercalant is organized within the interlayer nanospace, using specific physical or chemical environments, may

give rise to new material with desirable properties (Alberti and Bein, 1996). The inclusion of synthetic functional pendant molecules within the interlayer nanospace is a practice which can be used for many nanomaterials (Richard-Plouet *et al.*, 2004; Fonseca *et al.*, 2005), *e.g.* the phyllosilicates with multifunctional layered organoclay-silicates (Guillot *et al.*, 2002; Fujii *et al.*, 2003). The resulting nanomaterials reflect the limited interlayer space which will give rise to specific intercalation reactions, and these are normally favorable for extracting cations from aqueous solution (Fonseca and Airoldi, 2000a; Fonseca *et al.*, 2000, 2004; Minet *et al.*, 2004).

A significant class of compounds, involving a series of layered materials, originating from silicic acid, formed the silicate, makatite; this is represented by $Na_2O(4–22)SiO_2(5–10)H_2O$; it has a unique structure, different from those of kanemite, octosilicate, magadiite and kenyaite (Almond *et al.*, 1997; Feng and Balkus, 2003, 2004). These compounds were obtained naturally from very alkaline conditions; the suggested laboratory procedure is based on a typical hydrothermal synthesis employing silica gel as the principal reagent at high alkaline pH (Eypert-Blaison *et al.*, 2001a). Through controlled changes in time, pressure, temperature, stoichiometry and reagent ratios, the aforementioned series of compounds can be obtained, mainly in the Na form, which is preferred (Almond *et al.*, 1997).

The present investigation is concerned with the most common layered silicate of this series, sodic magadiite,

* E-mail address of corresponding author:

airoldi@iqm.unicamp.br

DOI: 10.1346/CCMN.2007.0550204

prepared with the ideal chemical composition of $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot x\text{H}_2\text{O}$ (Almond *et al.*, 1997; Wang and Pinnavaia, 2003). This natural (Beneke and Lagaly, 1975a) crystalline silicate was first discovered in 1967 at Lake Magadi, Kenya, and has since been successfully synthesized in the laboratory (Schwieger *et al.*, 1988).

In spite of the great importance of this compound, its crystal structure remains unknown. Nevertheless, it is believed to comprise regular sheets of SiO_4 tetrahedra containing terminal O atoms neutralized by Na ions (Almond *et al.*, 1997; Feng and Balkus, 2003, 2004). After acidic treatment, these original cations can be ion-exchanged to form the crystalline silicic acid magadiite (Eypert-Blaison *et al.*, 2001b). As expected for any silica derivative surface (Fonseca and Airoidi, 2000b, 2001; Fonseca *et al.*, 2001; Babel and Kurniawan, 2003), a large number of silanol groups is available to react with a huge number of organic polar basic compounds (Wang and Pinnavaia, 2003; Shindachi *et al.*, 2004) in order to achieve an intercalation reaction (Beneke and Lagaly, 1975b).

The amines are a common class of compounds suitable for intercalation in layered nanomaterials due to their polarity, ease of handling and solubility in a variety of solvents, including water (Kwon *et al.*, 1996). The monoamines, as well as the diamines, can form mono or bilayer structural arrangements within the interlayer nanospace (Danjo *et al.*, 1999; Airoidi *et al.*, 2000; Lima and Airoidi, 2002). Alkanediamines and polyamines can be intercalated to normally form a monolayer structure with the guest molecules disposed in an inclined position in relation to the inorganic sheet (Airoidi *et al.*, 2000). The inclusion of such guest molecules gives new properties to the original compound and these can be useful as adsorbent agents, and can also be used to pillar the compounds which would favor intercalation of large molecules (Alberti and Bein, 1996; Nakayama *et al.*, 2002).

Although intercalation is a well established process, the majority of investigations have considered mainly structural features of these kinds of compounds. The aim of the present study is to report some calorimetric determinations involving the intercalation of some n-alkyldiamines ($\text{C}_2\text{--C}_5$) into host magadiite in the acidic form, with the objective of understanding the energetics of interaction, taking into account that thermodynamic data related to intercalation into the cavities of layered compounds are rare in the literature. The advantage in obtaining these data is to correlate some physical properties associated with structural features of the layered host magadiite.

EXPERIMENTAL

Materials

The n-alkyldiamines (Aldrich) with the general formulae $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($n = 2\text{--}5$): 1,2-ethylenedia-

mine, 1,3-propylenediamine, 1,4-butylenediamine and 1,5-pentamethylenediamine were used without further purification. The concentration of those amine solutions in doubly distilled water was 0.50 mol dm^{-3} , and these were diluted when performing the experiments. For the synthesis of the layered material, silica gel (Merck), NaOH (Vetec) and HCl (Merck) were used.

Synthesis of magadiite

Magadiite in the Na form (Namag) was synthesized as described previously (Almond *et al.*, 1997; Kwon and Park, 2004). Briefly, a suspension of $\text{SiO}_2\text{:NaOH:H}_2\text{O}$ in a molar proportion of 9:2:75 was heated in a sealed Teflon vessel for 72 h at 423 K. The suspension was first filtered and the solid was washed with 0.10 mol dm^{-3} NaOH solution, followed by water, to pH 9. The excess water in the suspension was eliminated after transferring the solid paste to a special flask for centrifugation. Then, the resulting solid was dried at 323 K for 24 h. This dried product was suspended in 0.20 mol dm^{-3} HCl solution (pH 2.0) for 24 h, filtered and dried at 340 K, to yield magadiite in the acidic form (Hmag).

Intercalation

The n-alkyldiamine $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($n = 2\text{--}5$) intercalation reactions were followed through a batch-wise method in aqueous solution at $298\pm 1 \text{ K}$. Samples of $\sim 50 \text{ mg}$ of acidic magadiite in a series of flasks were suspended in 20.0 cm^3 of water and with various volumes of n-alkyldiamine solutions, varying from 1.0 to 2.0 cm^3 . All samples were stirred in an orbital thermostated bath for 72 h, to ensure maximum intercalation. At the end of that time, the solid was separated from the supernatant solution by filtration, washed with doubly distilled water and air dried, before analysis. Samples of the supernatant solutions were titrated with standard HCl and the amount of n-alkyldiamine intercalated (N_f) was determined using the equation: $N_f = (N_i - N_s)/m$, where N_i is the initial number of moles of guest molecule in solution, N_s is the number of moles of n-alkyldiamines in solution in equilibrium with the solid phase, and m is the mass of Hmag used for each determination (Ruiz and Airoidi, 2004).

Calorimetry

The calorimetric titrations were carried out in an isothermal LKB 2277 microcalorimetric system (Fonseca and Airoidi, 2000a). For each titration, $\sim 15 \text{ mg}$ of the inorganic lamellar compound was suspended in 2.0 cm^3 of doubly distilled water in a steel ampoule. The suspension was strongly stirred with a gold helix at $298.15\pm 0.20 \text{ K}$. After equilibrium, aliquots of aqueous n-alkyldiamine solution were incrementally added through a coupled microsyringe. Each thermal effect caused by the interaction of the n-alkyldiamines into the crystalline lamellar compound

Table 1. The interlayer distance (d) obtained, from XRD patterns, after n-alkyldiamine (Diamine) intercalation; percentages of carbon (C), hydrogen (H) and nitrogen (N) from elemental analyses, the number of diamines calculated from nitrogen content (N_{int}) and those obtained from the batch-wise method (N_{f}).

Diamine	d (nm)	C (%)	H (%)	N (%)	N_{int} (mmol g ⁻¹)	N_{f} (mmol g ⁻¹)
H ₂ N(CH ₂) ₂ NH ₂	1.45	3.04	1.28	2.98	3.69	3.67
H ₂ N(CH ₂) ₃ NH ₂	1.47	5.24	1.80	3.86	2.78	1.99
H ₂ N(CH ₂) ₄ NH ₂	1.49	4.14	1.53	2.42	1.75	1.41
H ₂ N(CH ₂) ₅ NH ₂	1.51	5.41	1.79	2.54	1.17	1.18

was recorded, as the increments of solution occurred. The same procedure was used to obtain the thermal effects of the dilution of the Hmag support in water and of each n-alkyldiamine solution diluted in water in the absence of the inorganic matrix. The thermal effect caused by the hydration of the original inorganic host gave a null value.

Characterization

The C, N and H contents were determined using a Perkin-Elmer 2400 Series II microelemental analyzer, and at least two independent determinations were performed for each sample. The XRD patterns were obtained on a Shimadzu model XD3A diffractometer using Ni-filtered CuK α radiation. The nuclear magnetic resonance (NMR) spectra were recorded from a Bruker AC300/P solid-state high-resolution spectrometer, using cross-polarization and magic angle spinning (CP-MAS), at a frequency of 59.6 MHz with a rotation frequency of 15 kHz and an acquisition time of 3 ms for the ²⁹Si nucleus. Infrared (IR) spectra were obtained in the 4000 to 400 cm⁻¹ range at a resolution of 4 cm⁻¹, by accumulating 32 scans using a MB-Bomem FTIR spectrometer, with pressed KBr pellets. The mass-loss determinations were performed under a nitrogen flow on a TA, TGA 2050 model 5100 device, with a heating rate of 0.167 K s⁻¹, with the samples varying in weight from 10.0 to 30.0 mg. The samples were dried rigorously before scanning electron microscopy (SEM) using a Jeol JSM-6360 LV microscope.

RESULTS AND DISCUSSION

Unequivocal proof of the success of these syntheses is the powder XRD patterns for Na- and the acidic compounds, in agreement with previously reported data (Wang and Pinnavaia, 1998; Feng and Balkus, 2003, 2004). Other important features that enabled us to understand the inorganic framework related to the structure of these lamellar compounds came from IR spectroscopy, solid-state Si NMR and SEM. The surface area determined by the BET method gave 25.1 \pm 0.1 and 16.9 \pm 0.1 m²g⁻¹, respectively, and the average pore diameter, measured by the BJH method, was 25 \pm 1 and 19 \pm 1 nm, for Na- and acidic magadiite, respectively.

When a series of acidic magadiite samples is suspended in aqueous solutions of n-alkyldiamine for 72 h, intercalation takes place, causing an increase in the interlayer distance (Table 1).

The XRD patterns for all intercalated compounds are presented in Figure 1. As observed, the original interlayer distance (d) of 1.17 nm for the acidic Hmag compound increases with the intercalation process. When this crystalline inorganic lamellar nanomaterial is suspended with the series of n-alkyldiamine solutions, the expected increase in the interlayer distance occurred, in order to accommodate the selected guest molecules inside the free nanospace of the cavity. This expansion increases with the length of the alkyl chains. Therefore, this behavior is dependent on the orientation of the guest molecule in the cavity. In the present case, the basic N atoms attached to the end of organic chains are expected to bond simultaneously to the acidic centers of two successive lamellar layers, to give, for the smallest 1,2-ethylenediamine and the longest, 1,5-pentamethylenediamine molecules, d values of 1.45 and 1.51 nm, respectively (Table 1).

Based on the percentage of N determined for these compounds (Table 1), the number of moles of each n-alkyldiamine was calculated and these values decrease as the length of the guest molecules increased. The highest value of 3.69 mol g⁻¹ for the first member of this series contrasts with 1.17 mmol g⁻¹ value found for the

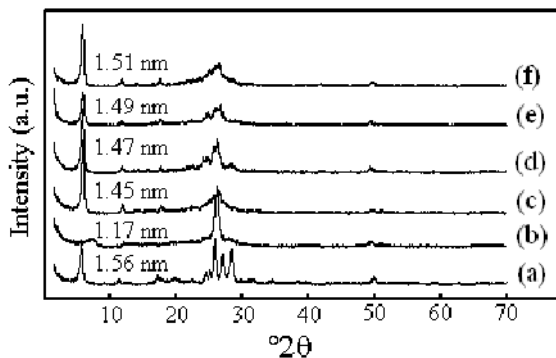


Figure 1. XRD patterns for Na magadiite (a), acidic magadiite (b) and intercalated compounds with 1,2-ethylenediamine (c), 1,3-propylenediamine (d), 1,4-butylenediamine (e) and 1,5-pentamethylenediamine (f). CuK α radiation.

largest molecule. This behavior could be attributed to the difficulty of accommodating the largest guest molecule within the lamellar cavity.

The IR spectra for acidic magadiite and for all intercalated compounds are shown in Figure 2. The weak stretching vibrations in the 1300 to 1550 cm^{-1} region are assigned to the presence of the guest molecule in the lamellar compound. Other weak peaks are related to the angular asymmetric and symmetric N-H deformation bands from the NH_3^+ group, confirming that these groups are bonded to the inorganic layer. The characteristic bands associated with the presence of aliphatic bridging moieties appear in the 2850–2980 cm^{-1} range and are related to asymmetric and symmetric C–H bonds with C in sp^3 hybridization (Miyamoto *et al.*, 2001). The weak peak at 700 cm^{-1} is assigned to the remaining silanol groups on inorganic lamella, in agreement with an incomplete saturation of the acidic centers by the guest molecules. The bands in the 3400–3650 cm^{-1} region can be attributed to the simultaneous stretching that corresponds to the presence of the N-H of the guest molecule and also to the available silanols bonded to the inorganic structure (Eypert-Blaison *et al.*, 2001b).

The thermogravimetric curves for magadiite in the Na and acidic forms differ considerably in the extent of mass loss that corresponds to released water, an amount of 8.2 and 0.8%, respectively. This expected difference may be associated with the facility of the Na cation to coordinate water inside the lamellar nanospace. However, for all intercalated compounds a total mass loss near 15% was observed (Figure 3). Based on the individual mass loss found for the displaced organic molecules, the amount intercalated per mole of magadiite was calculated. With the exception of 1,2-ethylenediamine, all other values are very close to those determined from titration methodology, obtained from the free guest molecules in the supernatant solution

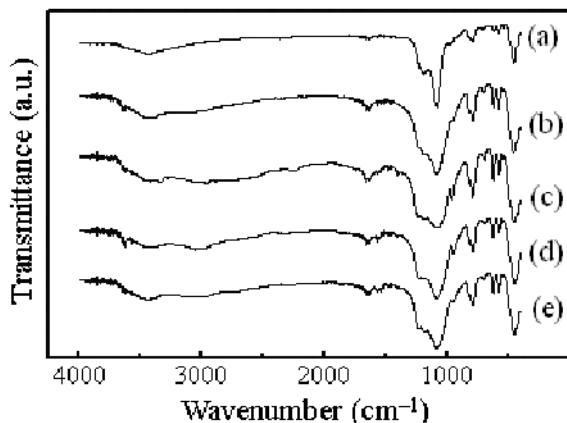


Figure 2. IR spectra of acidic magadiite (a) and the intercalated compounds with 1,2-ethylenediamine (b), 1,3-propylenediamine (c), 1,4-butylenediamine (d) and 1,5-pentamethylenediamine (e).

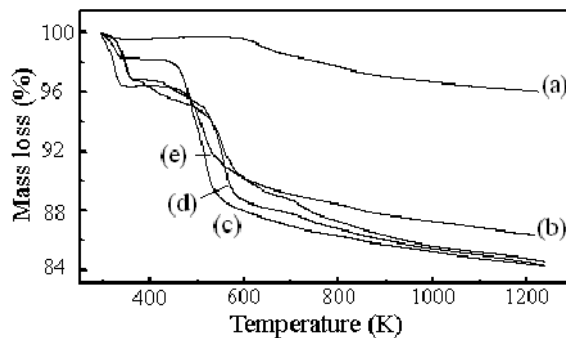


Figure 3. Thermogravimetric curves for acidic magadiite (a) and the intercalated compounds with 1,2-ethylenediamine (b), 1,3-propylenediamine (c), 1,4-butylenediamine (d) and 1,5-pentamethylenediamine (e).

after the batch-wise process of intercalation, by considering the number of moles of *n*-alkyldiamine intercalated per mole of the inorganic support (Table 2). Thus, these data conform to a general equation $\text{Hmag}_x(\text{diamine})_y(\text{water})$ that expresses this intercalation process. The mass losses for the intercalated compounds in the 315–364 K interval depend on the individual *n*-alkyldiamine intercalated, corresponding to waters of hydration. The second stage, starting at 365 K, refers to the loss of the organic molecule; the final temperature depends on the particular guest molecule. The last step between 700 and 1250 K comprises the loss of water molecules due to the condensation of the remaining silanol groups in the inorganic structure, to yield the siloxane units on the surface.

One relevant contribution to the understanding of the group distributions on layered magadiite in Na and acidic forms, and also their respective intercalated compounds, comes from the ^{29}Si solid-state NMR cross polarization (CP) spectra (Figure 4). The data are summarized in Table 3. During polysilicate formation, the SiO_4 unit condenses and a series of acidic sites is generated, with the Si species having different connectivities. Considering the relative proportion of Q_3 , $(\text{SiO})_3\text{SiO}$, and Q_4 , $(\text{SiO})_4\text{Si}$, species, NMR is a powerful technique for identifying each particular inorganic polymer (Almond *et al.*, 1997; Komori *et al.*, 2000). This procedure enabled establishment of features related to the distribution of the Si tetrahedra in the structure.

Table 2. Number of moles of *n*-alkyldiamine (diamine) intercalated per mole of Hmag, obtained by titration (x_{tit}) and thermogravimetry (x_{therm}) and moles of water (y), conforming to the general formula $\text{Hmag}_x(\text{diamine})_y(\text{water})$.

Diamine	x_{tit}	x_{therm}	y
$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$	3.20	2.02	1.00
$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$	1.74	1.82	0.94
$\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$	1.23	1.26	1.78
$\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$	1.03	0.91	2.48

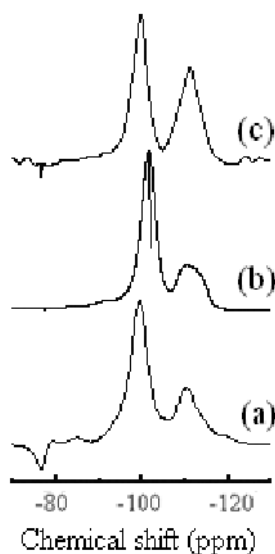


Figure 4. ^{29}Si NMR of Namag (a), Hmag (b) and intercalated with 1,4-butylenediamine (c).

For the Na magadiite spectrum only the Q_3 signal observed at -99.2 ppm is related to the stoichiometry of the silicate, and the strongly H-bonded water molecules give a broad peak (Almond *et al.*, 1997). Each magadiite layer presented equal numbers of Na cations or protons to counter the charge on the oxygen atoms. For acidic magadiite, distinguishable siloxane and silanol groups, with a difference in chemical shift, predicted to be near 3.5 ppm, are seen. In the present case the Q_3 signal is located at -101.1 ppm, a value within the proposed interval (Almond *et al.*, 1997). The intercalated compounds showed the presence of a peak near this value. For example, for 1,5-pentamethylenediamine, this peak was sited at -100.0 ppm. On the other hand, the same set of three peaks for the Q_4 signal are observed in Na magadiite at -109.6 , -111.1 and -115.5 ppm and at -110.1 , -110.9 and -113.5 ppm for the acidic form. When this last polysilicate was intercalated with 1,5-pentamethylenediamine, the signals were found at -110.1 , -112.8 and 114.6 ppm (Table 3). After intercalation, a signal shift could be expected because of the possible change in the Si atom neighborhood. However, the Q_3 peak was shifted upfield while the three Q_4 signals were not affected, and the set of peaks is in agreement with the maintenance of the crystalline structure of the magadiite after intercalation, with a change of relative intensity in the Q_3 peak (Almond *et al.*, 1997).

The number of moles of n-alkyldiamine intercalated (N_f) are listed in Table 1, and the isotherms for all intercalated guest molecules are shown in Figure 5. As observed, N_f decreased in value as the alkyl chain length of the guest molecule increased, showing a preference for the shortest molecules. For example, 1,2-ethylenediamine and 1,5-pentamethylenediamine gave values of

Table 3. Chemical shifts (ppm), obtained using ^{29}Si NMR, for magadiite and the intercalated compounds with 1,2-ethylenediamine (ethyl), 1,3-propylenediamine (propyl), 1,4-butylenediamine (butyl) and 1,5-pentamethylenediamine (pentyl).

Compound	CP MAS	
	Q_3	Q_4
Namag	-99.2	-109.6 -111.1 -115.5
Hmag	-101.1	-110.1 -110.9 -113.5
Hmag.ethyl	-99.9	-110.4 -111.6 -114.3
Hmag.propyl	-99.8	-112.1
Hmag.butyl	-98.1 -100.2	-109.4 -112.1 -114.6
Hmag.pentyl	-100.0	-110.1 -112.8 -114.6

3.67 and 1.18 mmol g^{-1} , respectively. This behavior should be correlated with the freedom of diffusing the shortest n-alkyldiamine into the interlayer space. As the guest molecules increase in length, the interactive process becomes more difficult. These interactive intercalation/magadiite values at the solid/liquid interface processes (Langmuir, 1918) were fitted to a modified Langmuir equation (equation 1):

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b}$$

where C_s (mol dm^{-3}) is the concentration of n-alkyldiamine remaining in solution after equilibrium, N_s (mol g^{-1}) is the maximum number of moles intercalated

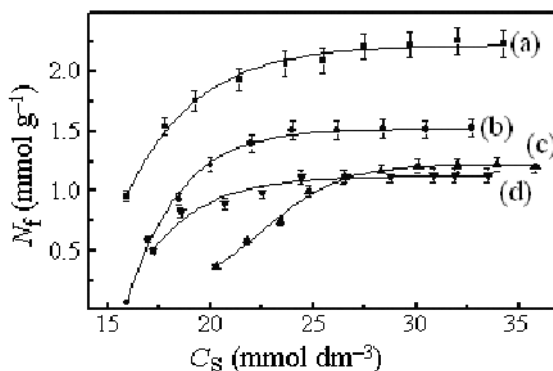


Figure 5. Isotherms of concentration for n-alkyldiamine intercalations into acidic magadiite, by considering the number of moles intercalated (N_f) against supernatant concentration (C_s) plot, for 1,2-ethylenediamine (a), 1,3-propylenediamine (b), 1,4-butylenediamine (c) and 1,5-pentamethylenediamine (d).

per gram of host, which depends on the number of acidic sites, a process that leads to the formation of a monolayer and b a parameter related to the equilibrium constant for the reaction. The N_s and b values can be calculated through the coefficients after linearization of the isotherm (Langmuir, 1918). The agreement of both methods is reflected in the very close values obtained from the batch-wise and calorimetric techniques.

The variation in interlayer distance (d) depends directly on the size of each guest molecule accommodated into the free nanocavity of the inorganic layers, the physical effects of which can be clearly related to the number of molecules thus inserted (N_f). By considering the change in length for the sequence of guest molecules simultaneously bonded to two inorganic layers, the increase in size is inevitably dependent on the number of carbon atoms (n_C) attached to the aliphatic chains. A linear correlation between these values was obtained, as expressed by the following equations (Figure 6). Based on these good linear correlations, the unknown properties related to these nanocompounds can be determined, by considering only the number of C atoms of a given n-alkyldiamine. This principle can be a very useful means of determining these important properties of nanomaterials, without measurements.

$$N_f = (5.36 \pm 0.25) - (0.86 \pm 0.07)n_C$$

$$d = (1406.6 \pm 1.9) + (20.9 \pm 0.5)n_C$$

The entrance of the guest molecule into the well organized lamellar structure can disturb its original arrangement, by expanding the interlayer distance, which depends on the n-alkyldiamine molecule, also affecting the amount intercalated. These detailed structural modifications can be followed using SEM, in which some features associated with the distribution of lamella in the organized solid can be observed. For example, magadiite in the acidic form retains spherical aggregates of platelets (Figure 7a). However, the intercalation process causes changes in the morphology of these compounds, although the main lamellar characteristics continue to be present (Figure 7b) (Okutomo *et al.*, 1999).

The thermal effect of the intercalation of the guest n-alkyldiamines molecules with acidic magadiite centers

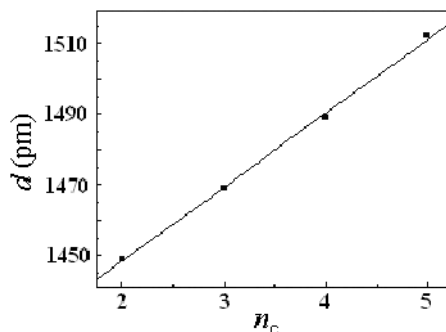
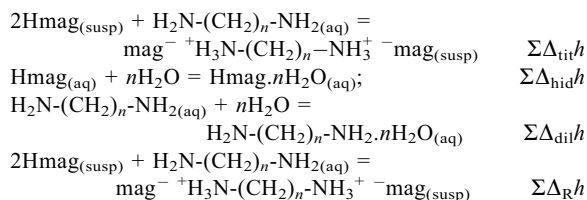


Figure 6. Interlamellar distance (d) as a function of the number of carbons (n_C) in the aliphatic chain of the n-alkyldiamines.

was determined by a sequence of calorimetric titrations. The interaction may be understood as a neutralization of both basic N centers of each guest molecule by the acidic silanol groups available in two successive lamellae of the inorganic layers. The complete calorimetric titration enables us to understand the thermal effects of interactions at the solid/liquid interface, by considering the n-alkyldiamines with acidic magadiite (Hmag) suspended in doubly distilled water, followed by dilution of the titrand and also the original inorganic matrix, as expressed by the sequence of equations:



The thermal effect of hydration of the original matrix ($\Sigma\Delta_{\text{hid}}h$) as previously observed for other systems, gave a null value (Fonseca and Airoidi, 2000a; Ruiz and Airoidi, 2004) and the resultant effect of the reaction ($\Sigma\Delta_{\text{R}}h$) can be calculated by the equation:

$$\Sigma\Delta_{\text{R}}h = \Sigma\Delta_{\text{tit}}h - \Sigma\Delta_{\text{dil}}h$$

A representative calorimetric curve for titration is illustrated by 1,3-propylenediamine, plotting the isotherm of the variation in thermal effects (ΣQ) vs. the

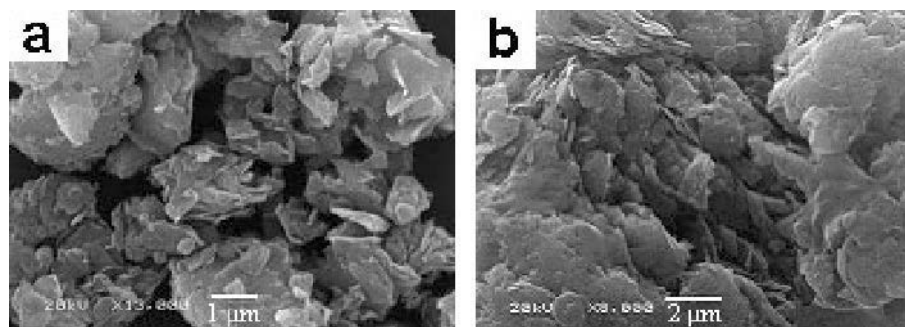


Figure 7. SEM images for acidic magadiite (a) and the intercalated compound with 1,4-butylenediamine (b).

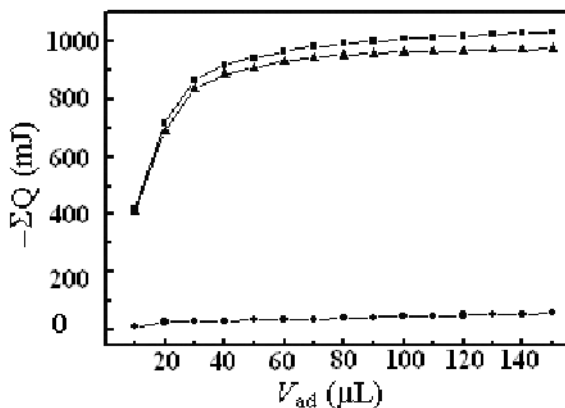


Figure 8. Isotherm obtained by calorimetric titration of a suspension of 15.0 mg of Hmag in water with $0.5190 \text{ mol dm}^{-3}$ 1,3-propylenediamine. Thermal effect of interaction $\Sigma\Delta_{\text{int}}h$ (\blacksquare), dilution $\Sigma\Delta_{\text{dil}}h$ (\bullet) and net effect $\Sigma\Delta_{\text{R}}h$ (\blacktriangle).

increment of volume (V_{ad}) for a complete sequence of the calorimetric reactions involved in this process. From these values the net thermal effect is easily obtained (Figure 8).

From the net thermal effect obtained for all guest molecules intercalated, $\Delta_{\text{int}}h$, and the amount of the titrant used, these values were adjusted to a modified Langmuir equation (Airoldi *et al.*, 2000) as successfully applied to similar systems:

$$\frac{X}{\Delta_{\text{R}}h} = \frac{1}{(K-1)\Delta_{\text{int}}h} + \frac{x}{\Delta_{\text{int}}h}$$

In this equation X is the sum of the molar fractions of n-alkyldiammonium ions remaining in solution after intercalation, $\Delta_{\text{R}}h$ the integral enthalpy obtained from the quotient between the sum of the resulting effect per mass of the acidic magadiite ($\Sigma Q/m$) and K a proportionality constant, which includes the equilibrium constant of the system at each point of titration. Then, a plot of $X/\Delta_{\text{R}}h$ vs. X gave $\Delta_{\text{int}}h$ and K values from the angular and linear coefficients, respectively, after linearization of the calorimetric data (Figure 9).

The molar enthalpy of the intercalation process can be calculated by the expression: $\Delta H = \Delta_{\text{int}}h/N_{\text{S}}$. The Gibbs free energy from $\Delta G = -RT \ln K$, and the entropy

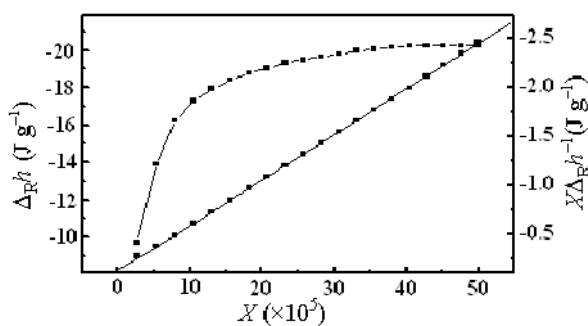


Figure 9. Calorimetry of the intercalation of a suspension of Hmag with $0.4790 \text{ mol dm}^{-3}$ 1,5-pentamethylenediamine, represented by a $\Delta_{\text{R}}h$ vs. X plot. The linearized form of the isotherm is given by $X/\Delta_{\text{R}}h$ vs. X .

value (ΔS) can be obtained by means of the expression $\Delta G = \Delta H - T\Delta S$ (Table 4). For all intercalation processes the enthalpic values are exothermic in nature, which, combined with the respective negative Gibbs free energy values, enable calculation of the entropy. These small positive entropic values for the sequence of guest molecules, null in case of 1,3-propylenediamine, reflect the increase in the free water molecules that were initially associated with the inorganic surface, summed up with those molecules H-bonded to amine groups, during the progress of intercalation, due to the silanol-basic formation of N bonds. Thus, these water molecules freed to the medium can disorganize the system with a consequent increase in entropy. As observed, this set of results from this heterogeneous system gave favorable thermodynamic data, indicating that the interaction of the chosen n-alkyldiamine molecules with the acidic crystalline lamellar compound should occur as a spontaneous reaction.

Another feature to be observed from this series of thermodynamic data and other properties associated with the physical behavior of such intercalations is again related to the length of the n-alkyldiamine organic chains, which could be expressed by the number of C atoms. Thus, the specific enthalpy due to the interactive process ($\Delta_{\text{int}}h$) can be linearly correlated with the increase in the carbon chain, as indicated by the equation:

$$\Delta_{\text{int}}h = -(101.38 \pm 5.84) + (16.88 \pm 1.59)n_{\text{C}}$$

Table 4. The specific enthalpy ($\Delta_{\text{int}}h$), the number of moles intercalated (N_{S}), the variation in enthalpy (ΔH), equilibrium constant (K), Gibbs free energy (ΔG) and entropy (ΔS) values for intercalation of n-alkyldiamines (Diamine) into acidic magadiite.

Diamine	$-\Delta_{\text{int}}h$ (J g^{-1})	N_{S} (mmol g^{-1})	$-\Delta H$ (kJ mol^{-1})	$K (\times 10^4)$	$-\Delta G$ (kJ mol^{-1})	$+\Delta S$ ($\text{J mol}^{-1} \text{K}^{-1}$)
$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$	69.78	3.67 ± 0.02	19.01 ± 0.01	5.58	27.1 ± 0.1	27 ± 1
$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$	49.14	1.99 ± 0.06	24.70 ± 0.02	1.94	24.5 ± 0.2	-1 ± 1
$\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$	30.60	1.41 ± 0.02	21.70 ± 0.01	2.75	25.3 ± 0.1	12 ± 1
$\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$	19.70	1.18 ± 0.01	16.70 ± 0.05	2.58	24.9 ± 0.2	28 ± 1

As mentioned before, enthalpic data for undetermined guest molecules can be inferred by considering only the number of C atoms attached to the respective n-alkyldiamine organic chains.

CONCLUSIONS

The synthetic lamellar polysilicate magadiite in Na and acidic forms presented interlayer distances of 1.55 and 1.17 nm, respectively. The acidic silanol groups distributed on each lamella enabled a series of intercalations of n-alkyldiamine, by bonding simultaneously through basic N atoms in two successive lamellae, thus changing the interlayer distance. This insertion is less than the maximum expected for the exchange capacity of the inorganic matrix, to give a number of moles (N_f) and lamellar expansion distances (d) that correlate linearly with the number of C atoms (n_C) attached to the amine organic chains, as represented by:

$$N_f = (5.36 \pm 0.25) - (0.86 \pm 0.07)n_C$$

$$d = (1406.6 \pm 1.9) + (20.9 \pm 0.5)n_C$$

Throughout the investigation of the interactive effect of intercalation reactions by calorimetry, at the solid/liquid interface, the thermodynamic data for that heterogeneous condition was determined. The enthalpy of interaction ($\Delta_{int}h$) also correlates linearly with the number of C atoms:

$$\Delta_{int}h = -(101.38 \pm 5.84) + (16.88 \pm 1.59)n_C$$

The importance of these correlations is to infer properties without experimental assays, by only considering the number of carbon atoms of a given n-alkyldiamine, to propose the number of moles intercalated, the interlayer distance and the enthalpic effect of interaction. In addition, the interactive process that generated the thermodynamic data, such as exothermic enthalpic, negative Gibbs free energy and positive entropy, indicate the existence of spontaneous intercalation reactions.

ACKNOWLEDGMENTS

The authors are indebted to FAPESP for financial support and a fellowship to TRM. CNPq is also acknowledged for fellowships to GCP and CA.

REFERENCES

- Alberti, G. and Bein, T. (1996) *Comprehensive Supramolecular Chemistry*. Pergamon, Oxford, UK, Vol. 7, Chapter 5, pp. 151–156.
- Almond, G.G., Harris, R.K. and Franklin, K.R. (1997) A structural consideration of kanemite, octosilicate, magadiite and kenyaite. *Journal of Materials Chemistry*, **7**, 681–687.
- Airoldi, C., Nunes, L.M. and Farias, R.F., (2000) The intercalation of n-alkyldiamines into crystalline layered titanate. *Materials Research Bulletin*, **35**, 2081–2090.
- Babel, S. and Kurniawan, T.A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, **97**, 219–243.
- Beneke, K. and Lagaly, G. (1975a) Magadiite and H-magadiite. 1. Sodium magadiite and some of its derivatives. *American Mineralogist*, **60**, 642–649.
- Beneke, K. and Lagaly, G. (1975b) Magadiite and H-magadiite. 2. H-magadiite and its intercalation compounds. *American Mineralogist*, **60**, 650–658.
- Čapková, P. and Schenk, H. (2003) Host-guest complementarity and crystal packing of intercalated layered structures. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **47**, 1–10.
- Cheetham, A.K., Ferey, G. and Loiseau, T. (1999) Open-framework inorganic materials. *Angewandte Chemie International Edition*, **38**, 3269–3292.
- Clearfield, A. (1998) Metal phosphonate chemistry. *Progress in Inorganic Chemistry*, **47**, 371–510.
- Danjo, M., Hayashi, A., Nakayama, H., Kimura, Y., Shimizu, T., Mizugushi, Y., Yagita, Y., Tshako, M., Nariai, H. and Motooka, I. (1999) Structure and organic gas-adsorption properties of some polyamine intercalated alpha-zirconium phosphates. *Bulletin of the Chemical Society of Japan*, **72**, 2079–2084.
- Eypert-Blaison, C., Sauzéat, E., Pelletier, M., Michot, L.J., Villieras, F. and Humbert, B. (2001a) Hydration mechanisms and swelling behavior of Na-magadiite. *Chemistry of Materials*, **13**, 1480–1486.
- Eypert-Blaison, C., Humbert, B., Michot, L. J., Pelletier, M., Sauzéat, E. and Villieras, F. (2001b) Structural role of hydration water in Na- and H-magadiite: A spectroscopic study. *Chemistry of Materials*, **13**, 4439–4446.
- Feng, F.X. and Balkus Jr, K.J. (2003) Synthesis of kenyaite, magadiite and octosilicate using poly(ethylene glycol) as a template. *Journal of Porous Materials*, **10**, 5–15.
- Feng, F.X. and Balkus Jr, K.J. (2004) Recrystallization of layered silicates to silicalite-1. *Microporous and Mesoporous Materials*, **69**, 85–96.
- Fonseca, M.G. and Airoldi, C. (2000a) Mercaptopropyl magnesium phyllosilicate – thermodynamic data on the interaction with divalent cations in aqueous solution. *Thermochimica Acta*, **359**, 1–9.
- Fonseca, M.G. and Airoldi, C. (2000b) New layered inorganic-organic nanocomposites containing n-propylmercapto copper phyllosilicates. *Journal of Materials Chemistry*, **10**, 1457–1463.
- Fonseca, M.G. and Airoldi, C. (2001) New amino-inorganic hybrids from talc silylation and copper adsorption properties. *Materials Research Bulletin*, **36**, 277–287.
- Fonseca, M.G., Silva, C.R., Barone, J.S. and Airoldi, C. (2000) Layered hybrid nickel phyllosilicates and reactivity of the gallery space. *Journal of Materials Chemistry*, **10**, 789–795.
- Fonseca, M.G., Simoni, J.A. and Airoldi, C. (2001) Some thermodynamic data about amino chrysotile derivatives with nickel and cobalt cation interactions in aqueous solution. *Thermochimica Acta*, **369**, 17–24.
- Fonseca, M.G., Silva Filho, E.C., Machado Jr, R.S.A., Arakaki, L.N.H., Espinola, J.G.P. and Airoldi, C. (2004) Zinc phyllosilicates containing amino pendant groups. *Journal of Solid State Chemistry*, **177**, 2316–2322.
- Fonseca, M.G., Oliveira, M.M., Arakaki, L.N.H., Espinola, J.G.P. and Airoldi, C. (2005) Natural vermiculite as an exchanger support for heavy cations in aqueous solution. *Journal of Colloid and Interface Science*, **285**, 50–55.
- Fujii, K., Hayashi, S. and Kodama, H. (2003) Synthesis of an alkylammonium/magnesium phyllosilicate hybrid nanocomposite consisting of a smectite-like layer and organosiloxane layers. *Chemistry of Materials*, **15**, 1189–1197.
- Guillot, M., Richard-Plouet, M. and Vilminot, S. (2002) Structural characterisations of a lamellar organic-inorganic nickel silicate obtained by hydrothermal synthesis from nickel acetate and (aminopropyl)triethoxysilane. *Journal of*

- Materials Chemistry*, **12**, 851–857.
- Komori, Y., Miyoshi, M., Hayashi, S., Sugahara, Y. and Kuroda, K. (2000) Characterization of silanol groups in protonated magadiite by H-1 and H-2 solid-state nuclear magnetic resonance. *Clays and Clay Minerals*, **48**, 632–637.
- Kwon, O.Y. and Park, K.Y. (2004) Synthesis of layered silicates from sodium silicate solution. *Bulletin of the Korean Chemical Society*, **25**, 25–26.
- Kwon, O.Y., Jeong, S.Y., Suh, J.K., Ryu, B.H. and Lee, J.M. (1996) Effects of organic solvents in the intercalation of octylamine into H-magadiite. *Journal of Colloid and Interface Science*, **177**, 677–680.
- Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, **40**, 1361–1403.
- Lima, C.B.A. and Airoldi, C. (2002) Layered crystalline calcium phenylphosphonate – synthesis, characterization and n-alkylmonoamine intercalation. *Solid State Science*, **4**, 1321–1329.
- Lima, C.B.A. and Airoldi, C. (2004) Topotactic exchange and intercalation of calcium phosphate. *Solid State Science*, **6**, 1245–1250.
- Minet, J., Abramson, S., Bresson, B., Sanchez, C., Montouillout, V. and Lequeux, N. (2004) New layered calcium organosilicate hybrids with covalently linked organic functionalities. *Chemistry of Materials*, **16**, 3955–3962.
- Miyamoto, N., Kawai, R., Kuroda, K. and Ogawa, M. (2001) Intercalation of a cationic cyanine dye into the layer silicate magadiite. *Applied Clay Science*, **19**, 39–46.
- Nakayama, H., Hayashi, A., Eguchi, T., Nakamura, N. and Tshako, M. (2002) Unusual adsorption mechanism for carboxylic acid gases by polyamine-intercalated alpha-zirconium phosphate. *Journal of Materials Chemistry*, **12**, 3093–3099.
- Okutomo, S., Kuroda, K. and Ogawa, M. (1999) Preparation and characterization of silylated-magadiites. *Applied Clay Science*, **15**, 253–264.
- Richard-Plouet, M., Vilminot, S. and Guillot, M. (2004) Synthetic transition metal phyllosilicates and organic-inorganic related phases. *New Journal of Chemistry*, **28**, 1073–1082.
- Ruiz-Hitzky, E. and Airoldi, C. (2004) Thermochemical data for n-alkylmonoamine intercalation into crystalline lamellar zirconium phenylphosphonate. *Thermochimica Acta*, **420**, 73–78.
- Ruiz-Hitzky, E., Casal, B., Aranda, P. and Galvan, J.C. (2001) Inorganic-organic nanocomposite materials based on macrocyclic compounds. *Reviews in Inorganic Chemistry*, **21**, 125–159.
- Schwieger, W., Heyer, W. and Bergk, K.H. (1988) The hydrothermal magadiite crystallization. 1. The kinetic of the crystallization – possibilities of their description. *Zeitschrift für Anorganische und Allgemeine Chemie*, **559**, 191–200.
- Shindachi, I., Hanaki, H., Sasai, R., Shichi, T., Yui, T. and Takagi, K. (2004) The effect of layered sodium-magadiite on the photochromic reversibility of diarylethene immobilized on its surfaces. *Chemistry Letters*, **33**, 1116–1117.
- Wang, Z. and Pinnavaia, T.J. (1998) Hybrid organic-inorganic nanocomposites: Exfoliation of magadiite nanolayers in an elastomeric epoxy polymer. *Journal of Materials Chemistry*, **10**, 1820–1826.
- Wang, Z. and Pinnavaia, T.J. (2003) Intercalation of poly(propyleneoxide) amines (Jeffamines) in synthetic layered silicas derived from ilerite, magadiite, and kenyaite. *Journal of Materials Chemistry*, **13**, 2127–2131.

(Received 13 June 2006; revised 3 August 2006; Ms. 1181; A.E. James E. Amonette)