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Crystalline polysilicate magadiite with intercalated *n*-alkylmonoamine and some correlations involving thermochemical data

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Abstract

Synthesized hydrated lamellar acidic crystalline magadiite ($H_2Si_{14}O_{29}\cdot 2H_2O$) nanocompound was used as host for intercalation of polar *n*-alkylmonoamine molecules of the general formula $H_3C(CH_2)_nNH_2$ ($n = 1$–6) in aqueous solution. The original interlayer distance (*d*) of 1500 pm, determined by X-ray powder diffraction patterns, increases after intercalation. The values correlated with the number of aliphatic amine carbon (n_c) atoms: $d = [(1312 \pm 11) + (21 \pm 2)]n_c$. The amount of intercalated amines (N_s), decreased as n_c increased: $N_s = [(5.82 \pm 0.04) - (0.45 \pm 0.01)]n_c$. The acidic layered nanocompound was calorimetrically titrated with the amines and the thermodynamic data gave exothermic values for all guest molecules, as shown by the correlation: $\Delta_{int}H = -[(24.45 \pm 0.49) - (1.91 \pm 0.10)]n_c$ and $d = [(1576 \pm 16) - (10.8 \pm 1.0)]\Delta_{int}H$. The negative values of the Gibbs energies and the positive entropies also presented the correlations: $\Delta_{int}G = -[(22.8 \pm 0.2) - (0.2 \pm 0.1)]n_c$ and $\Delta_{int}S = [(6 \pm 1) + (5 \pm 1)]n_c$, respectively.
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1. Introduction

A great variety of crystalline inorganic nanocompounds have lamellar structures [1,2]. Many natural or synthetic materials, such as clay minerals, phylosilicates, graphite, double layered hydroxides, transition metal oxides and silicic acids, show this layered property [3–5].

The natural crystalline sodium silicate magadiite $Na_2Si_{14}O_{29}\cdot xH_2O$ ($x = 7$–10) was first discovered at Magadi Lake in Kenya [6–9]. This crystalline sodic polysilicate displays interesting properties associated with the ability of interlamellar sorption of polar organic molecules in aqueous solution. The resulting intercalated compounds change their physical and chemical properties, such as capacity for ion exchange in which sodium ions can be replaced by protons and other cations. A synthetic design can derive new nanocompounds with potential as catalyst supports, detergent systems, chemistry of fermentation agents, enzymes, chromatographic columns, water decontamination, pre-concentration, etc. [10–16]. Organic guest species intercalation into layered inorganic materials is a promising

focus to construct ordered inorganic/organic nanostructural assemblies controlled by the host–guest interactions [2,17,18].

The present investigation reports the energetics of *n*-alkylmonoamine molecules with the general formula $H_3C(CH_2)_n$–NH_2 ($n = 1$–6), being intercalated into the void lamellar nanospace cavity available in the acidic crystalline magadiite structural arrangement.

2. Experimental

2.1. Reagents

All chemicals were of reagent grade and deionized water was used in the experiments. Silica (Fluka), sodium hydroxide (Vetec) and hydrochloric acid (Vetec) were employed in all preparations. The *n*-alkylmonoamines (Aldrich) were purified before use.

2.2. Preparations

The hydrated sodium polysilicate magadiite, $Na_2Si_{14}O_{29}\cdot xH_2O$ (Namag) was prepared by reacting 20.00 g (0.33 mol) of SiO_2 with 75.0 cm^3 of aqueous NaOH solution 0.95 mol dm^{-3}.

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The mixture was sealed in a Teflon-lined autoclave and hydrothermally heated at 423 ± 1 K for 72 h. The product was washed with $1.0 \, \text{mol dm}^{-3}$ aqueous NaOH solution, deionized water until pH 9.0 and dried at 333 ± 1 K for 24 h. The protonated host $H_2Si_{14}O_{29} \cdot x - yH_2O$ (Hmag) was prepared by stirring the product obtained with $200.0 \, \text{cm}^3$ of $0.10 \, \text{mol dm}^{-3}$ hydrochloric acid for 12 h, washing with the same hydrochloric acid solution, then deionized water to pH 2.0 and dried at 333 ± 1 K for 24 h [18–20].

2.3. Analytical procedures

X-ray powder patterns were obtained with nickel-filtered Cu Kα radiation on a Shimadzu model XRD 600 diffractometer (40 kV/30 mA) with a speed of 3.33×10^{-2} degree s^{-1} and the interlayer spacings of the compounds were calculated from the (0 0 1) plane. Infrared spectra were obtained with a Bomen MB series instrument with KBr pellets. The spectra were obtained in the 4000–400 cm^{-1} region with an accumulation of 30 scans and 4.0 cm^{-1} of resolution. Carbon, nitrogen and hydrogen contents were determined with a Perkin-Elmer model 5100 elemental analyzer.

2.4. Intercalation

The intercalation of all aliphatic n-alkylmonoamines was carried out in a water bath thermostated at 298 ± 1 K. For each intercalation an individual amine dissolved in water at a concentration of $0.50 \, \text{mol dm}^{-3}$ was stirred with Hmag. The time required to reach the equilibrium was obtained by a series of intercalations as a function of the time. The resulting isotherms showed a clear indication of completeness indicating that 4–5 h were enough to reach intercalation equilibrium. The complete isotherm of intercalation consists in mixing 0.050 g of Hmag with various concentrations, varying from 1.92×10^{-2} up to $7.70 \times 10^{-2} \, \text{mol dm}^{-3}$ for a given amine in $25.0 \, \text{cm}^3$ of water with continuous stirring. The number of moles intercalated per gram (N_f) is calculated by difference between the initial (N_i) and the supernatant (N_s) number of moles of the amine divided by mass (m) of the host used $N_f = (N_i - N_s)/m$. All supernatant contents were determined with $0.10 \, \text{mol dm}^{-3}$ hydrochloric acid, a mixed bromocresol green/methyl red 5:1 indicator. The number of amines for monolayer formation can be obtained from a modified Langmuir model [21–24]:

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

where C_s is the amine concentration (mmol dm^{-3}) remaining in solution after equilibrium, N_f the maximum amount of amine intercalated (mmol g^{-1}), N_s the amount of amine for monolayer formation (mmol g^{-1}) and b is a parameter associated with the equilibrium constant for the reaction.

2.5. Calorimetric titration

The thermal effects of amine adsorptions on Hmag were followed in an isothermal LKB 2277 calorimeter. A sample of

approximately 20 mg was suspended in $2.0 \, \text{cm}^3$ of water and vigorously stirred at 298.15 ± 0.20 K. After thermal equilibrium, a solution of each amine with an initial concentration of $0.50 \, \text{mol dm}^{-3}$, contained in a microsyringe, was incrementally added in aliquots of $20.0 \, \text{mm}^3$, normally in 15 increments. For each increment of solution the thermal effect ($\sum Q_{tit}h$) was recorded until saturation was reached, indicated by a constant thermal effect. Identically, the titrations of the amine solutions were monitored in water ($\sum Q_{dil}h$). The thermal effect of hydration of the host suspended in water gave a null value. By combining the two thermal effect values the resulting integral thermal effect $\sum Q_r h = (\sum Q_{tit}h) - (\sum Q_{dil}h)$ can be calculated. The change in enthalpy associated with amine/Hmag ($\sum \Delta_{int}h$) intercalation can be determined by the modified Langmuir equation [25–28]:

$$\frac{X}{\Delta_r h} = \frac{1}{(K-1)\Delta_{int}h} + \frac{X}{\Delta_{int}h} \tag{2}$$

where X is the molar amine fractions remaining in solution, $\Delta_r h$ the enthalpy obtained from the quotient between the sums of the resulting effect per mass of Hmag ($\sum Q_r h/m$), $\Delta_{int}h$ is the enthalpy for monolayer formation and K a parameter associated with the equilibrium constant. $\Delta_{int}h$ and K values can be determined from the coefficients after linearization of the isotherm. The molar enthalpy of the interaction process can be calculated through the expression $\Delta_{int}H = \Delta_{int}h/N_s$. From K value the Gibbs energy is calculated by the expression: $\Delta_{int}G = -RT \ln K$ and the entropy value by considering: $\Delta_{int}G = \Delta_{int}H - T\Delta_{int}S$.

3. Results and discussion

The X-ray powder diffraction patterns for Namag and acidic Hmag nanocompounds are shown in Fig. 1, and those for the n-alkylmonoamines intercalated in the host support are illustrated in Fig. 2. The original interlamellar distance (d) of 1530 pm for sodic magadiite decreased when all available sodic groups in the polysilicate layered structure are replaced by protons inside the gallery region, to give a new interlayer distance of 1150 pm [29].
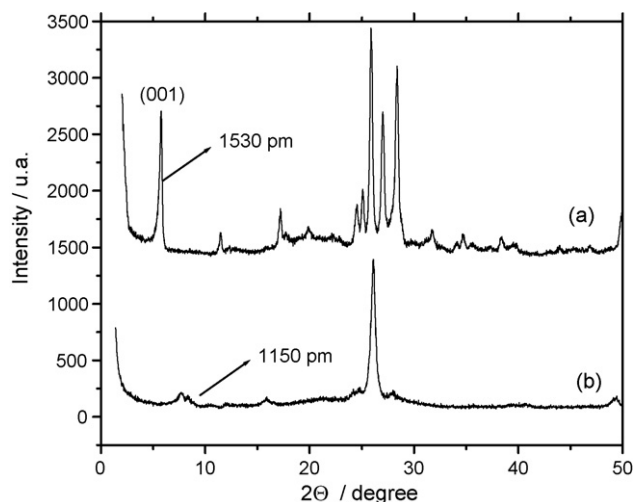

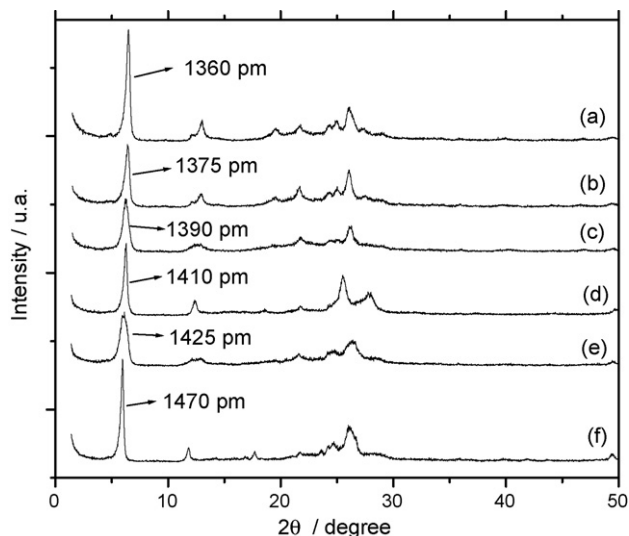Fig. 1. XRD patterns for Namag (a) and Hmag (b).

Fig. 2. XRD patterns for Hmag intercalated with ethyl- (a), propyl- (b), butyl- (c), pentyl- (d), hexyl- (e) and heptylamines (f).

This decrease in interlayer distance is caused by the elimination of hydrated sodium cation from the original cavity.

The intercalation process with *n*-alkylmonoamines resulted in an increase in interlayer distances to 1360, 1375, 1390, 1410, 1425 and 1470 pm for ethyl-, *n*-propyl-, *n*-butyl-, *n*-pentyl-, *n*-hexyl- and *n*-heptylamines, respectively. These interlayer distances depend on the length of the intercalated amine; the behavior is correlated with the number of carbon atoms (n_c) of the hydrocarbon chains, as represented by $d = [(1312 \pm 11) + (21 \pm 2)]n_c$, as shown in Fig. 3.

The expected basal distance expansion was firstly calculated by supposing that all amines are disposed at a perpendicular angle α in relation to the inorganic lamella. The amines with chain lengths of 309, 430, 675, 860, 1045 and 1231 pm [30] added to the original host interlayer distance of 1150 pm give an increase to 1459, 1580, 1825, 2010, 2195 and 2381 pm, respec-
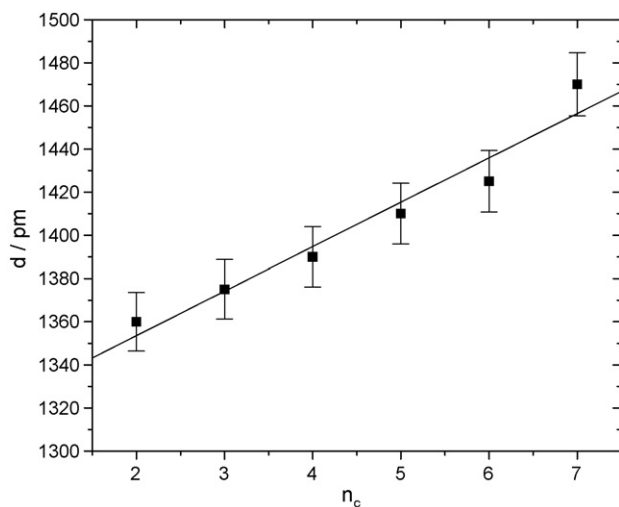
tively. It is clear that the amines must be accommodated in inclined positions, resulting in calculated distances (d_c) with angles $\alpha = \arcsin(d_c/d)$ of 68°, 57°, 49°, 44°, 38° and 38°. The high inclination observed for the largest amines agree with the low intercalation values due to coverage of the acidic silanol groups of the lamellar surface, obstructing the amine bonding.

The infrared spectra of the initial compounds are exhibited in Fig. 4 and the spectra of the intercalated compounds in Fig. 5. The presence of low stretching bands around 2800–3000 cm^{-1} are assignable to the existence of asymmetric and symmetric C–H (sp^3), respectively, in the lamellar nanospace. The asymmetric and symmetric angular deformation of N–H from NH$_3^+$ group is shown near the 1300–1500 cm^{-1} region. The weak peak at 700 cm^{-1} was attributed to the remaining Si–OH groups, which confirms a partial saturation of the acidic Hmag centers with the amines [20,31–33].

Based on carbon, nitrogen and hydrogen analyses, the amount of the amine inserted into the lamellar cavity of HMag

Fig. 4. Infrared spectra of Namag (a) and Hmag (b).

Fig. 3. The correlation between interlayer distance (*d*) of the *n*-alkylmonoamine intercalations into Hmag as a function of the number of carbon atoms (n_c) of the aliphatic chains.
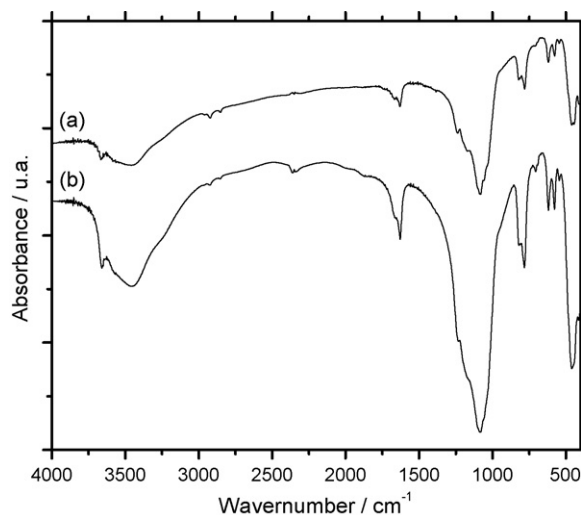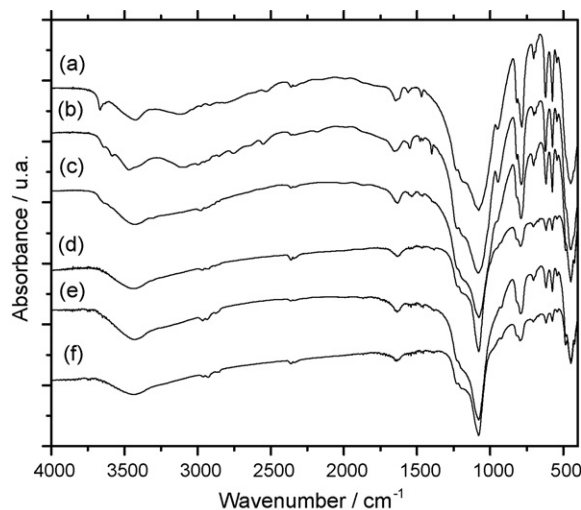

Fig. 5. Infrared spectra of Hmag intercalated with aliphatic ethyl- (a), propyl- (b), butyl- (c), pentyl- (d), hexyl- (e) and heptylamines (f).

Table 1
Percentages of carbon, nitrogen and hydrogen of adsorbed amines intercalated by Hmag, determined from elemental analysis $N_s{}^1$ and from the batch method using the Langmuir modified isotherm $N_s{}^2$

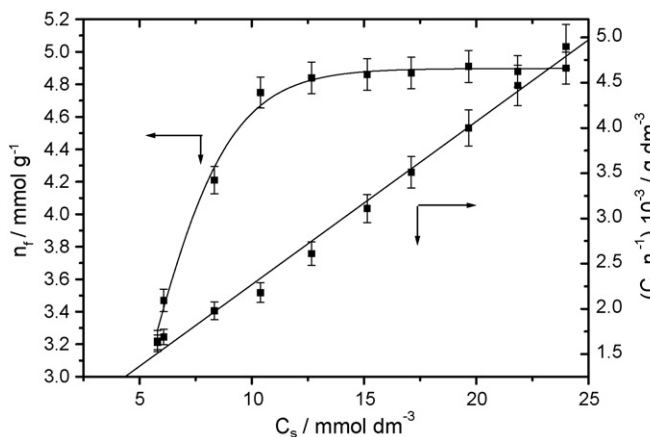| $CH_3(CH_2)_nNH_2$	C (%)	N (%)	H (%)	$N_s{}^1$ (mmol g^{-1})	$N_s{}^2$ (mmol g^{-1})
$n = 1$	11.35	6.85	3.50	4.81 ± 0.29	4.90 ± 0.04
$n = 2$	16.51	6.19	4.10	4.51 ± 0.10	4.65 ± 0.06
$n = 3$	19.29	5.60	4.58	4.01 ± 0.31	4.22 ± 0.05
$n = 4$	21.58	5.16	4.75	3.64 ± 0.11	3.87 ± 0.04
$n = 5$	22.01	4.40	4.69	3.11 ± 0.10	3.30 ± 0.09
$n = 6$	22.35	3.77	4.65	2.68 ± 0.10	2.80 ± 0.04

Fig. 6. Isotherm for ethylamine intercalation in Hmag, represented by N_f values vs. concentration C_s. The linearization C_s/N_f vs. C_s is given by the straight line.

to form a monolayer was determined. Similar values were obtained from the modified Langmuir adsorption equation. These values are listed for all nanocompounds in Table 1 and a representation of N_s values for ethylamine is shown in Fig. 6. The amount inserted for this series of amines decreased with the increase of the carbon chain length of the guest molecules, $N_s = [(5.82 \pm 0.04) - (0.45 \pm 0.01)]n_c$, as demonstrated in Fig. 7.
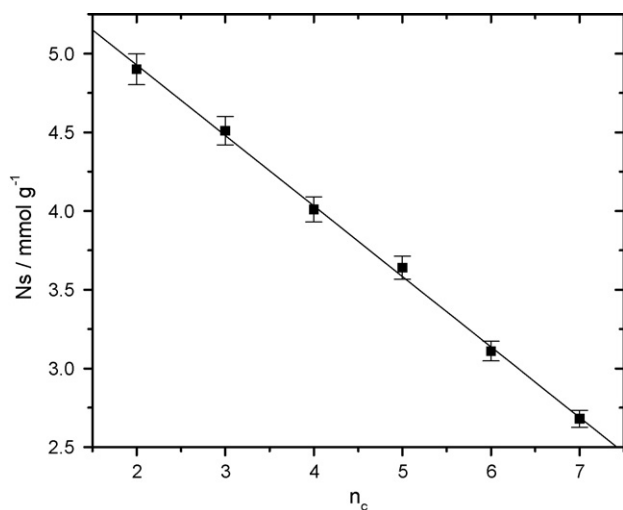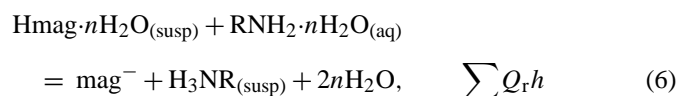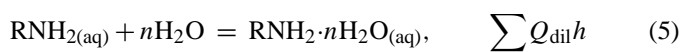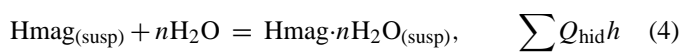
Determination of the net enthalpy of reaction requires three independent series of measurements [17,18]:

$$Hmag_{(susp)} + RNH_{2(aq)} = mag^- + H_3NR_{(susp)}, \qquad \sum Q_{tit}h \tag{3}$$

$$Hmag_{(susp)} + nH_2O = Hmag \cdot nH_2O_{(susp)}, \qquad \sum Q_{hid}h \tag{4}$$

$$RNH_{2(aq)} + nH_2O = RNH_2 \cdot nH_2O_{(aq)}, \qquad \sum Q_{dil}h \tag{5}$$

$$Hmag \cdot nH_2O_{(susp)} + RNH_2 \cdot nH_2O_{(aq)}$$
$$= mag^- + H_3NR_{(susp)} + 2nH_2O, \qquad \sum Q_r h \tag{6}$$

Reactions (3)–(6) represent the individual calorimetric experiments, which were carried out in duplicate for each determination. The molar fractions of amine in equilibrium were obtained by using $X/\Delta_r h$ versus X plots to give simultaneously the enthalpy of interaction $\Delta_{int}H$ and K values, respectively, as represented in Fig. 8. The enthalpy and the equilibrium constant are obtained from the angular and linear coefficients of straight lines [22–28].

The thermodynamic values for amine accommodation into the gallery are listed in Table 2. The exothermic enthalpic data suggest a favorable neutralization between the acidic cen-
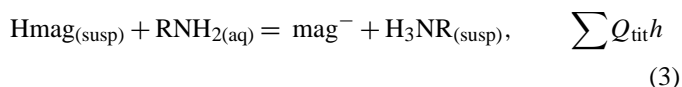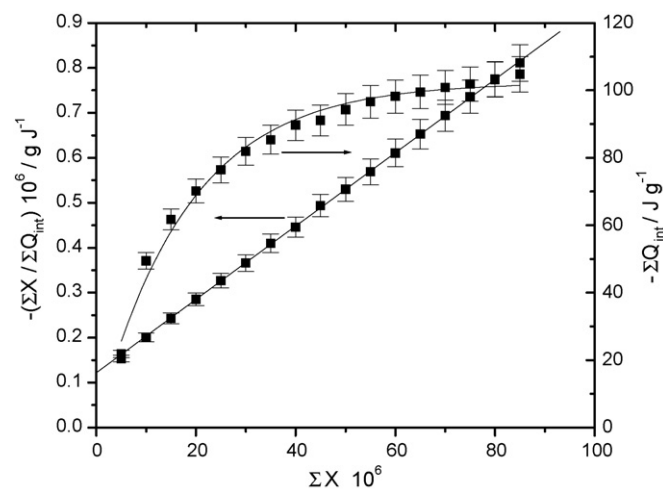

Fig. 7. Correlation of the amount of n-alkylmonoamines (N_s) intercalated into Hmag as a function of the number of carbon atoms (n_c) of the aliphatic chain.

Fig. 8. Isotherm obtained from calorimetric titration of 20.00 mg of Hmag suspended in water with 0.50 mol dm^{-3} of ethylamine at 298.15 ± 0.20 K. This isotherm shows the integral enthalpy of intercalation vs. molar fraction. The straight line is the linearized form.

Table 2
Thermodynamic data for *n*-alkylmonoamine intercalation into Hmag

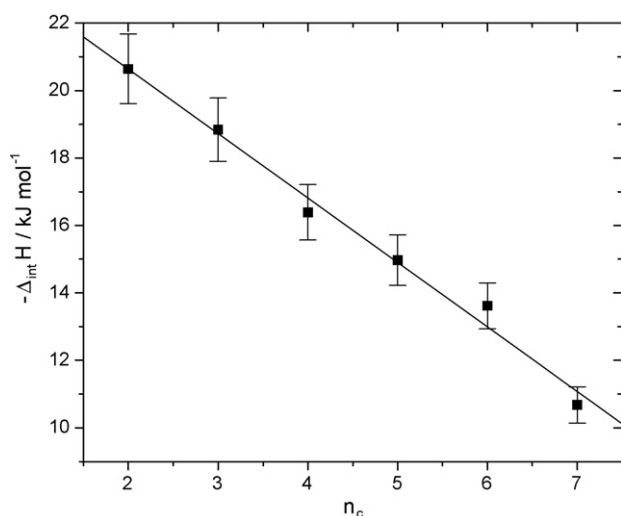| $CH_3(CH_2)_n NH_2$	$-\Delta_{int}H$ (kJ mol^{-1})	K (10^3)	$-\Delta_{int}G$ (kJ mol^{-1})	$\Delta_{int}S$ (J K^{-1} mol^{-1})
$n = 1$	20.64 ± 0.62	6.8 ± 1.4	21.9 ± 1.3	4 ± 1
$n = 2$	18.84 ± 0.57	5.0 ± 1.2	21.1 ± 1.2	8 ± 1
$n = 3$	16.39 ± 0.49	4.2 ± 1.2	20.7 ± 1.2	14 ± 1
$n = 4$	14.97 ± 0.45	3.5 ± 1.2	20.2 ± 1.2	18 ± 1
$n = 5$	13.62 ± 0.41	3.1 ± 1.2	19.9 ± 1.2	21 ± 1
$n = 6$	10.68 ± 0.32	2.3 ± 1.1	19.2 ± 1.1	29 ± 1

Fig. 9. Correlation of the enthalpy of intercalation ($\Delta_{int}H$) of *n*-alkylmonoamines into Hmag as a function of the number of carbon atoms (n_c) of the aliphatic chain.

Fig. 11. Correlation of entropy of intercalation ($\Delta_{int}S$) for *n*-alkylmonoamines into Hmag as a function of the number of carbon atoms (n_c) of the aliphatic chain.

ters on the lamellar surface and the basic nitrogen atom of the *n*-alkylmonoamine molecules. The negative Gibbs energy demonstrates that a favorable equilibrium condition was established in the intercalation. The positive entropic values are in agreement with the displacement of water molecules: (i) those bonded to the lamella, which are reinforced by (ii)
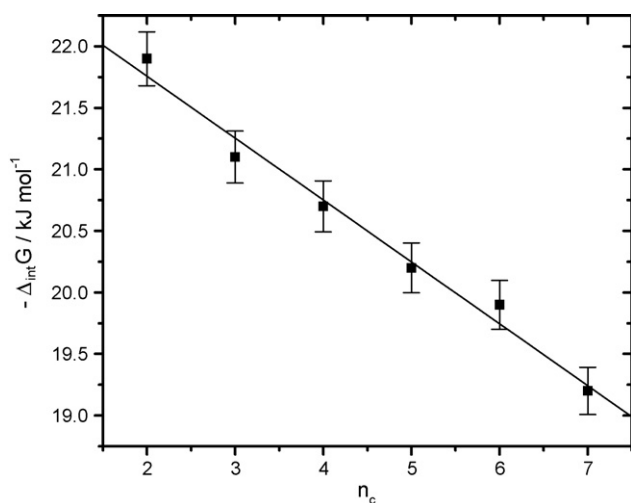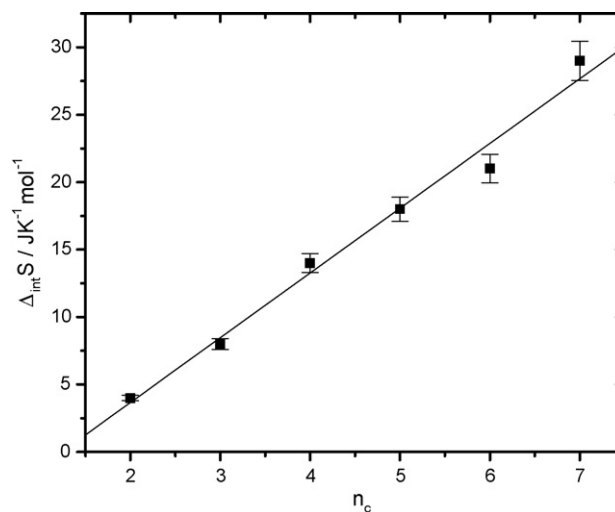

Fig. 10. Correlation of the Gibbs energy ($\Delta_{int}G$) of intercalation of *n*-alkylmonoamines into Hmag as a function of the number of carbon atoms (n_c) of the aliphatic chain.

those hydrogen molecule bonded to the active basic center, to favor the acid/base interaction at the liquid/solid interface, as the intercalations are in progress [22–28]. A close view of the dependence of these properties associated with the *n*-alkylmonoamine chains can be shown by the correlations involving the number of carbon atoms belonging to the chain for: (i) enthalpy $\Delta_{int}H = -[(24.45 \pm 0.49) - (1.91 \pm 0.10)]n_c$ in Fig. 9, or $d = [(1576 \pm 16) - (10.8 \pm 1.0)]\Delta_{int}H$, (ii) Gibbs energy $\Delta_{int}G = -[(22.8 \pm 0.2) - (0.5 \pm 0.1)]n_c$, in Fig. 10, and (iii) entropy $\Delta_{int}S = -[(6 \pm 1) + (5 \pm 1)]n_c$, in Fig. 11. These sets of thermodynamic data are in complete agreement with the favorability of amine intercalation in acidic magadiite. On the other hand, these correlations are a useful tool to infer thermodynamic data for undetermined *n*-alkylmonoamines.

4. Conclusion

The as-synthesized crystalline magadiite had the sodium easily exchanged by proton under acidic conditions the available silanol groups distributed on the lamellar surface have the ability to hydrogen bond to the basic nitrogen atom of the *n*-alkylmonoamines, with a consequent interlayer expansion. Such acid–base interactions at the solid/liquid interface were calorimetrically followed and the thermodynamic data correlated with the number of carbon atoms of the aliphatic amine chains. Ther-

modynamic data for a given *n*-alkylmonoamine not studied in this series can be inferred from the well-established correlations.

Acknowledgements

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