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Mercaptopropyl magnesium phyllosilicate — thermodynamic data on the interaction with divalent cations in aqueous solution

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Abstract

Magnesium phyllosilicate (SILMgSH) was obtained by the sol–gel process involving the reaction of magnesium cation and mercaptotrialkoxysilane in aqueous basic solution at 298 K. The inorganic–organic hybrid was characterized by elemental analysis to give a presence of 4.88 mmol g^{-1} of organic chains, and X-ray diffraction (XRD) patterns gave basal peaks associated with an interlayer distance of 1300 pm. The interactions between the terminal thiol groups of the organic chains of a silylating agent attached to magnesium phyllosilicate and the divalent cations copper, nickel, cobalt and zinc in aqueous solution were followed through calorimetric titrations. After subtracting the thermal effect of dilution, the net thermal effects were adjusted to a modified Langmuir equation, and the enthalpy of the interaction calculated to give the following exothermic values: -47.06 ± 1.00, -27.63 ± 0.50, -21.92 ± 0.50 and -14.66 ± 0.52 kJ mol^{-1}, for copper, nickel, cobalt and zinc cations, respectively. The distinct behavior of the copper cation involves the formation of a more organized compound. Gibbs free energy values changes are negative. With the exception of copper, all reactions were entropically favoured and the final products of adsorption presented an increased crystallinity clearly detected by XRD.

Keywords: Adsorption; Phyllosilicates; Modified clays; Enthalpy

1. Introduction

The interactive processes involving metallic cations with inorganic or organically modified matrices have been explored in recent years [1–7]. Due to the presence of acidic centres on inorganic matrices, bases can be adsorbed on the surface. Also, covalent attachment of organic molecules to inorganic surfaces can yield new inorganic–organic hybrids, such as for silica gel, where a great variety of chelating agents are used to complex cations from aqueous or non-aqueous solutions [1,5,8–11]. The properties of these materials are of importance in many applications such as electrochemistry, chromatography, pre-concentration of species or cations, and decontamination of water [2,12–15]. With relation to the last feature, investigations are focused on highly selective and specific processes for cations such as cobalt, nickel, copper and zinc, which are human hazards in the environment [2]. Exploration of these chemical interactions by spectroscopic techniques and calorimetric procedures

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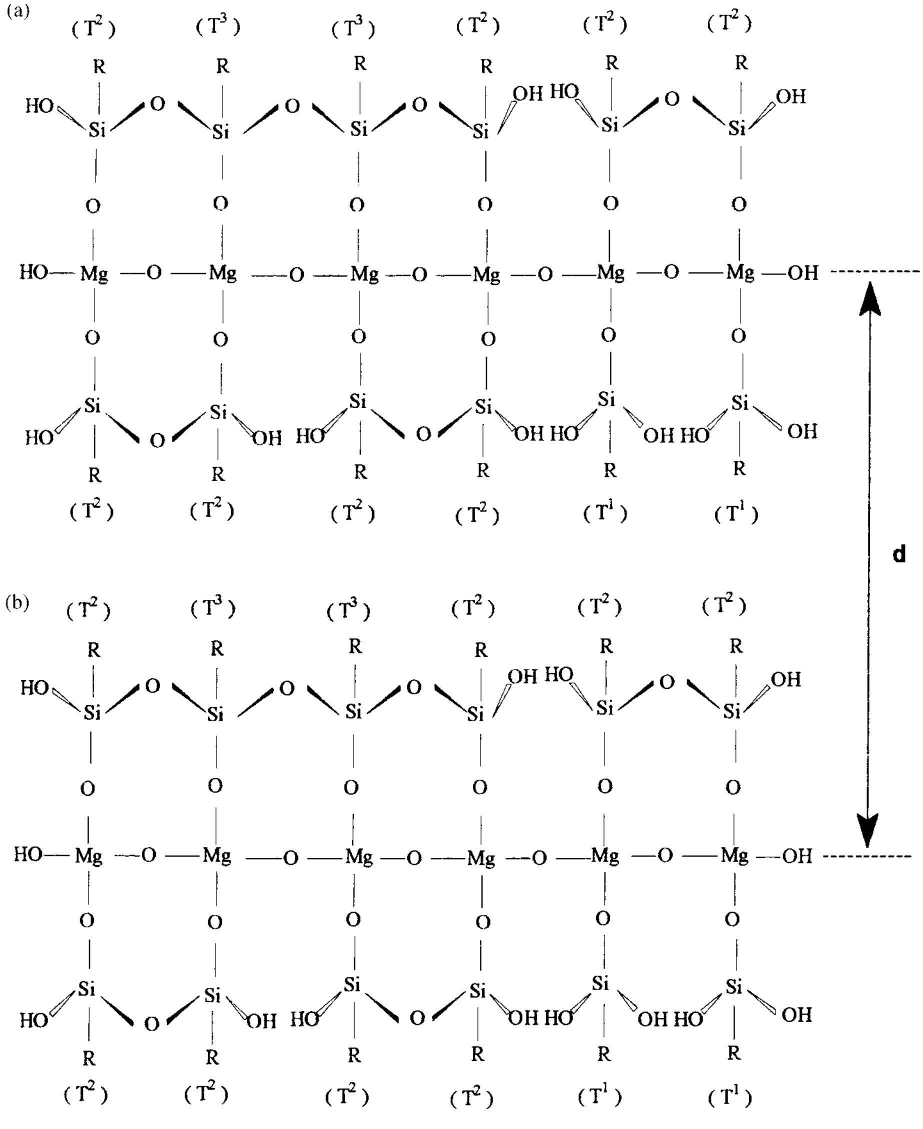

Fig. 1. Structure of the nanohybrid magnesium phyllosilicate; R is the organic radical and *d* the interlayer spacing planar representation. The network consists of a tetrahedral–octahedral–tetrahedral arrangement with a basal spacing *d*. T^1, T^2 and T^3 species are associated with the silicon species $RSi(SiO)_n(OH)_{3-n}$ for $n=3$ down to $n=1$, respectively.

can produce information about the specificity and selectivity of these matrices [16,17].

A large variety of synthetic techniques are used to obtain hybrid surfaces, with reactions in sequence or in one-step direct-synthesis procedures [11,18–21]. In this connection, inorganic–organic hybrids formed by phyllosilicates have been obtained through the polymerization of magnesium cations with trialkoxysilanes under alkaline conditions [22–28]. These structures are very close to that found for natural talc, as shown in Fig. 1a. Each organic chain is covalently attached to the polymeric silica-type structure of the layer to yield $O_3Si–C$ groups in the inorganic backbone, as is represented in Fig. 1b. Magnesium cations are located between both silicate tetrahedral sheets and are completely coordinated by oxygen atoms centred in octahedral sites, as shown in Fig. 1b. These new synthetic hybrids have a layered structure, whose interlayer space depends not only on the type but also on the length of the organic chain molecule R incorporated into the phyllosilicate in these self-assembled systems [24,26–28].

The present investigation involves a magnesium phyllosilicate modified with mercaptopropyl groups and named SILMgSH. Such surfaces containing immobilized thiol groups on silica gel, and the corresponding oxidized form, interact strongly with divalent cations in aqueous and non-aqueous solutions [29–31]. The aim of this publication is to report on the adsorption of cobalt, nickel, copper and zinc cations on mercaptopropyl magnesium phyllosilicates in aqueous solution; thermochemical data on the adsorption processes were obtained. The calorimetric titration technique was chosen to study the interaction due to the previous success obtained for a similar system [31].

2. Experimental

2.1. Materials

The silylating agent 3-mercaptopropyltrimethoxisilane, $HS(CH_2)_3Si(OCH_3)_3$ (Aldrich), magnesium chloride hexahydrate (Fluka), methanol and sodium hydroxide (Merck) were all reagent grade, and were used without further purification. Hydrated divalent copper (Merk), nickel (Nuclear) and zinc (Nuclear) nitrates were also used without purification. Bidistilled water was used in all experimental procedures.

2.2. Synthesis of mercaptopropyl magnesium phyllosilicates

The first step of this synthesis consisted of dissolving 0.052 mol of hexahydrated magnesium chloride in 300 cm^3 of bidistilled water at room temperature under stirring. To this mixture, 50.0 cm^3 of a solution of 1.39 mol dm^{-3} of 3-mercaptopropyltrimethoxisilane dissolved in methanol was added slowly, which caused an immediate formation of a white suspension. This stoichiometry gives an Si/Mg molar ratio of 1.33, which is the same as that found in natural talc. To this suspension, 500.0 cm^3 of aqueous solution of 0.10 mol dm^{-3} sodium hydroxide was added slowly under stirring, after which the reaction mixture was aged. After 24 h at room temperature, a white powder precipitated that was filtered, washed with water and dried under vacuum at 323 K.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were obtained with nickel-filtered Cu Kα radiation on a Shimadzu model XD3A diffractometer (30/20 kV/mA) at a speed of 3.33×10^{-2} degree s^{-1}. Infrared spectra were obtained with 1% KBr pressed pellets. The spectra were obtained in the 400–4000 cm^{-1} region with an accumulation of 30 scans and 4 cm^{-1} of resolution on a Bomen series MB spectrometer. Nuclear magnetic resonance (NMR) spectroscopy of the solid materials was carried out on an AC 300/P Bruker spectrometer at room temperature. The measurements were made at frequencies of 75.5 and 59.6 MHz for carbon and silicon, respectively. For carbon CP/MAS, the spectra were obtained with a pulse repetition time of 3 s and a contact time of 3 ms. The ^{29}Si NMR spectra were obtained by high-power proton decoupling with a pulse repetition time of 60 s. Thermogravimetric curves were obtained with a DuPont model 1090 B apparatus coupled with a thermobalance 951 by heating the samples from room temperature to 1273 K at a heating rate of 0.16 K s^{-1} under an argon atmosphere flowing at 1.67 cm^3 s^{-1}, with samples varying in weight from 15.0 to 30.0 mg. Carbon, nitrogen and hydrogen contents were determined with a Perkin-Elmer microelemental Model PE 2400 analyser. The amount of magnesium cation was determined by atomic absorption spectroscopy, after dissolving the samples in a mixture of hydrofluoric and nitric acids.

2.4. Adsorption of cations

A batchwise method was used for the adsorption measurements. For each cation, samples of approximately 20 mg of the phyllosilicate were suspended in 25.0 cm^3 of aqueous solution of the divalent cation in increasing concentrations, varying from 4.0×10^{-3} to 0.14 mol dm^{-3}. The suspension was stirred mechanically in a thermostated bath at 298±1 K. A period of 5 h was necessary for maximum adsorption; thus, to ensure equilibrium adsorption for all experiments, a total time of 6 h was adopted. For each point of the isotherm, at least two aliquots of 0.50 cm^3 were removed from the supernatant and the amount of metal remaining in solution determined by a conventional complexometric titration with standard EDTA solution (Ni^{2+}, Co^{2+}) or by the iodometric thiosulfate method (Cu^{2+}). Zinc concentrations were determined by atomic absorption. The amount of cations adsorbed was determined by the expression $N_f=(N_i-N_s)/m$, where N_i is the initial number of moles of cation in solution, N_s is the number of moles of cation in solution after equilibrium and m is the mass of phyllosilicate used in each run.

2.5. Calorimetry

Calorimetric titrations were carried out in a differential isothermic LKB 2277 microcalorimetric system, at 298.15±0.02 K, as described previously [12]. A sample of approximately 20 mg of the phyllosilicate was suspended in 2.0 cm^3 of bidistilled water in a stainless steel ampoule and stirred vigorously. After equilibrium, aliquots of the solution of metallic cation were added with a microsyringe. For each added increment of solution, the thermal effect was recorded until saturation of the process was reached, indicated by a constant thermal effect ($\sum Q_{tot}$). The same procedure was used to monitor the thermal effect of titration of the cation solution into water ($\sum Q_{dil}$) without the solid and that of titration of water into suspended solid, which gave a null value. The resulting integral thermal effect ($\sum Q_{int}$) was determined by the expression $\sum Q_{int} = \sum Q_{tot} - \sum Q_{dil}$. The change in enthalpy associated with the cation–matrix interaction ($\Delta_{int}h$) was obtained by adjusting batch process data to a modified Langmuir equation.

3. Results and discussion

The elemental analysis for CHS gave 17.80% C, 4.50% H and 15.7% S, indicating the presence of 4.88 mmol g^{-1} of pendant groups in the SILMgSH matrix. The C/S molar ratio obtained (1.13) is very close to the calculated one, showing that the organic moieties did not decompose during the synthetic process.

The infrared bands characterize the organic moieties in the gallery space. Thus, bands at 2930 cm^{-1} ν (C–H), 2562 cm^{-1} ν (S–H), 1250 cm^{-1} ν (Si–C) and at 1040 and 990 cm^{-1} associated with Si–O–Si and Si–O–Mg groups, respectively, were observed. A broad band near 3600 cm^{-1} was assigned to the presence of water and Si–OH stretching bands [32–34] and a sharp band at 3700 cm^{-1} was related to ν (Mg–OH) [35–38]. However, a band at 1628 cm^{-1} was associated with the bending vibration mode of water. A band at 700 cm^{-1} is assigned to the overlap of Si–O and δ 3Mg(OH) vibration modes as observed in trioctahedral magnesium-clays [39].

Solid state ^{13}C NMR spectrometry is an important auxiliary tool to elucidate structures of the silylating agent attached to the silicate. Thus, ^{13}C CP/MAS spectra for the solid SILMgSH hybrid showed signals in good agreement with previously reported data on corresponding silica hybrids [29,31]. These data confirmed the presence of the organic moiety $-CH_2-CH_2-CH_2-SH$ bonded to the inorganic layer. The spectrum (Fig. 2) for the hybrid gave two intense peaks, one at 28.7 ppm that was assigned to methylene carbon atoms 1 and 2, and another peak at 13.3 ppm related to the methylene group No. 3. A less intense peak at 44.7 ppm corresponds to the carbon of the methoxy group. The presence of this last peak is an indication that the hydrolysis of precursor silane was incomplete.

^{29}Si NMR spectra can also provide information about the nature of the attachments of pendant groups on silicate hybrids. Assignments are based on previous results for analogous systems, which involved modified silicas and other phyllosilicates [40–44]. Three

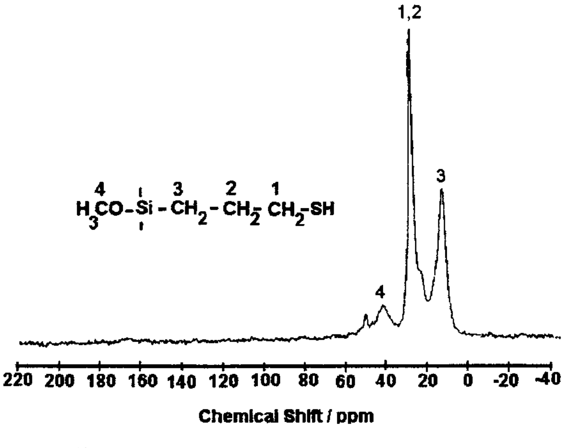

Fig. 2. ^{13}C NMR spectrum of mercaptopropyl magnesium phyllosilicate.

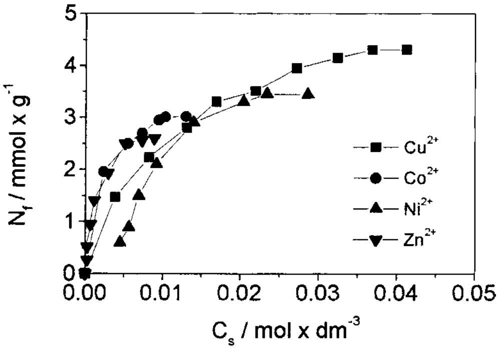

Fig. 3. Isotherms of interaction of cations on SILMgSH.

signals at −66.5, −56.0 and −48.4 ppm are associated with R–Si*–(OSi)$_3$, R–Si*–(OSi)$_2$–OH and R–Si*–(OSi)–(OH)$_2$ groups, respectively, which were quantified by deconvolution of the peaks to give 39.8, 26.4 and 17.5%. This fact suggested the presence of a high degree of silanol groups on the phyllosilicate inorganic framework.

The adsorption isotherms are illustrated in Fig. 3, indicating that the maximum capacity adsorption increased in the sequence $Cu^{2+}>Ni^{2+}>Co^{2+}>Zn^{2+}$.

Magnesium elemental analysis, XRD and infrared spectroscopy were used to obtain additional information about the interactive processes. The contents of magnesium in all products derived from this interaction at maximum concentration of metal ion are presented in Table 1. The values are consistent with the partial elimination of this cation from the original matrix; however, this process is not connected to a simple reaction involving only the cations and magnesium phyllosilicate. The proposed model for these interactions is (a) dissolution of the precursor phyllosilicate causing the transference of magnesium cations to solution, (b) reformation of the inorganic structure around the metallic cations and (c) simultaneous complexation of mercaptopropyl groups in the interlayer space by cations. These different amounts are also listed in Table 1. The sequence of the number of metallic cation that enters into the inorganic sheet decreases in the order $Zn^{2+}<Co^{2+}<Ni^{2+}<Cu^{2+}$. This sequence is the opposite of that of hydrated cation size (cm^3 mol^{-1} in parenthesis): Cu^{2+} (147.8)≈Ni^{2+} (147.8)<Co^{2+} (169.6)<Zn^{2+} (178.2) [45–47]. The observed sequence for complexation of cations by thiol groups was $Cu^{2+}<Ni^{2+}<Co^{2+}<Zn^{2+}$, which is the same as the order observed for mercaptopropyl silica gel [31].

The powder XRD patterns presented in Fig. 4 show a substantial change in the crystallinity of the original matrix. The results suggest the formation of 1:1 copper phyllosilicate and a sauconite-like structure for the copper and zinc systems [48,49]. Cobalt and nickel yield amorphous compounds.

The infrared spectrum of the original matrix showed a sequence of bands in agreement with the presence of organic moieties bonded to the inorganic backbone with absorptions at 2900 and 1180 cm^{-1} associated with ν (C–H) and ν (Si–C), respectively, as shown in Fig. 5 [32–34]. The absence of the original band at 2550 cm^{-1} due to ν (S–H) is in agreement with the complexation of thiol groups by the metallic cation [50]. The characteristic bands at 1340 cm^{-1} suggest the presence of nitrate ion in the coordination sphere of the complexes [32]. The absorption related to Si–O–Si groups was still observed at 1000 cm^{-1} in all spectra. The band for δ (Si–O) group was observed at 510, 540, 530 and 560 cm^{-1} for hybrids with Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}, respectively. These results support the initial idea that the interaction of mercap-

Table 1
Amounts of remaining magnesium cation (N_{Mg}), total cation adsorbed (N_f), cation on inorganic sheet (N_{oct}) and complexed to –SH moieties (N_{ads})[a]

Hybrid	N_{Mg} (mmol g^{-1})	N_f (mmol g^{-1})	N_{oct} (mmol g^{-1})	N_{ads} (mmol g^{-1})
SILMgSH	4.04	–	–	–
SILMgSH/Cu^{2+}	0.11	4.31	3.93	0.38
SILMgSH/Ni^{2+}	1.19	3.44	2.86	0.58
SILMgSH/Co^{2+}	1.36	3.03	2.68	0.35
SILMgSH/Zn^{2+}	1.90	2.60	2.14	0.46

[a] The last quantities were obtained by the equations N_{oct}=4.04−N_{Mg} and N_{ads}=N_f−N_{oct}.

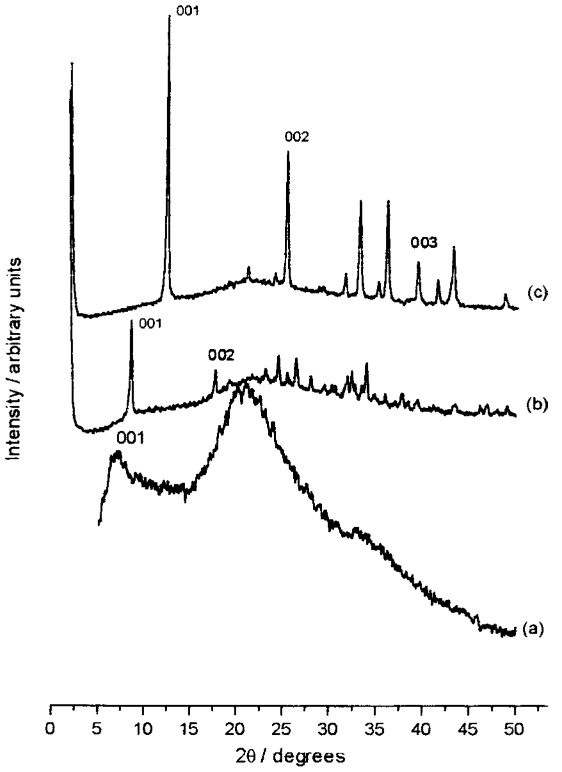

Fig. 4. Comparative XRD patterns for (a) SILMgSH; (b) SILMgSH/Zn^{2+} and (c) SILMgSH/Cu^{2+}.

topropyl magnesium phyllosilicate with metallic cations is a complex reaction involving both formation of complexes and reformation of the inorganic sheets.

These interactive processes were fitted to a modified Langmuir equation (1):

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

where C_s is the remaining cation concentration (mol dm^{-3}) in solution after equilibrium, N_f the amount of cation adsorbed (mol g^{-1}), N_s the maximum amount of adsorbed cation per gram of adsorbent matrix (mol g^{-1}), which depends on the number of adsorption sites and b a parameter associated with the equilibrium constant for the reaction. N_s and b values can be estimated from coefficients after linearization of the isotherm [51]. The N_s values obtained from batch and calorimetric techniques are very close.

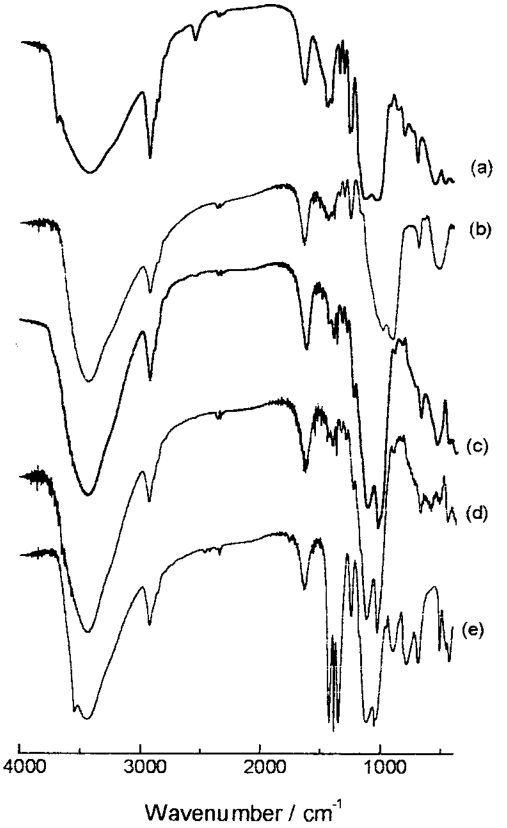

Fig. 5. Infrared spectra for (a) SILMgSH; (b) SILMgSH/Zn^{2+}; (c) SILMgSH/Co^{2+}; (d) SILMgSH/Ni^{2+} and (e) SILMgSH/Cu^{2+} hybrids.

Information on the energetics of the processes in all investigated systems was obtained from the calorimetric titration procedure. Calorimetric titration of the suspended mercaptopropyl magnesium phyllosilicate in aqueous solution with $Cu^{2+}_{(aq)}$ is illustrated in Fig. 6 by plotting the sum of thermal effect ($\sum Q$) as a function of the volume of titrand added (V_{ad}). The enthalpy of interaction $\Delta_{int}h$ was obtained by an expression derived from the modified Langmuir equation (2):

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

where $\sum X$ is the sum of the molar fractions of the remaining metallic cation in solution after interaction, $\Delta_r h$ the integral enthalpy obtained as the quotient

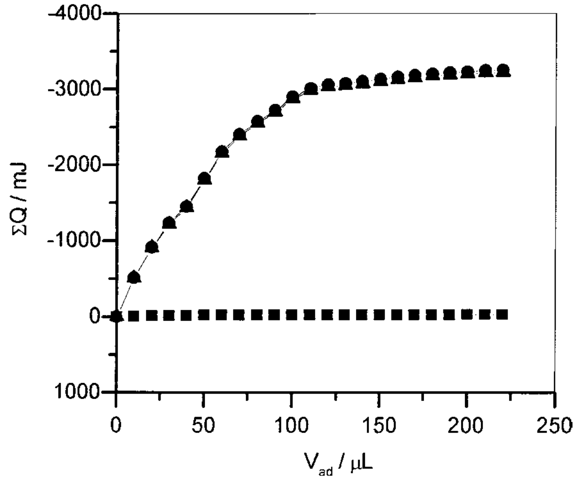

Fig. 6. Calorimetric titration of a suspension of 0.01813 g of SILMgSH in 2.0 cm^3 of water with $Cu(NO)_3$ (0.70 mol dm^{-3}) in the same solvent at 298.15±0.02 K. The experimental points represent the sum of the thermal effects of cation titration $\sum Q_{tot}$ (—●—), cation dilution $\sum Q_{dil}$ (—■—) and the net thermal effect of interaction $\sum Q_{int}$ (—▲—). $\sum Q$ and V_{ad} values are the sum of detected thermal effect and total injected volume of copper solution, respectively.

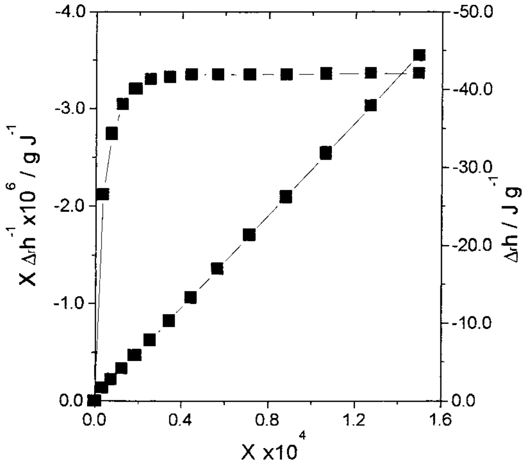

Fig. 7. Isotherm for the integral enthalpy of adsorption ($\Delta_r h$) vs. molar fraction (X) obtained from a calorimetric titration of a suspension of 0.01078 g of SILMgSH, in 2.0 cm^3 of water, with $Co(NO_3)_2$ (0.37 mol dm^{-3}) in the same solvent at 298.15±0.02 K. The straight line is the linearized form of the isotherm.

of $\sum Q_{int}$ and mass of the phyllosilicate used and K a constant of proportionality that includes the equilibrium constant [1,4]. $\Delta_{int}h$ and K were determined from $\sum X/\Delta_r h$ versus X plots, as illustrated in Fig. 7. The molar enthalpy change of the interaction process was calculated by $\Delta H^0 = \Delta_{int}h/N_f$, the Gibbs free energy change by $\Delta G = -RT \ln K$, and the entropy change from $\Delta G = \Delta H - T\Delta S$. The results are listed in Table 2.

The enthalpy changes are exothermic, decreasing in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$; this sequence is the same as that obtained for N_f values. Again, a different behaviour for copper is observed and the large value indicates formation of a stable complex. The free energy change indicates spontaneous processes, in the order $Cu^{2+} < Zn^{2+} < Ni^{2+} < Co^{2+}$. The free energy of solvation of the metallic ions is a major contribution to these processes because the hybrid matrix contains the dehydrated cation. Thus, there is a correlation between the Gibbs free energy of hydration and the correspondent energy obtained for each reaction. Consider the system with cobalt that showed the largest free energy change, −34.11±0.46 kJ mol^{-1}, with the lowest cation hydration free energy of −1963 kJ mol^{-1} [45,46]. The largest free energy of hydration is for copper, −2016 kJ mol^{-1}, and results in the lowest free energy change of −24.11±0.19 kJ mol^{-1} for the processes studied [45,46].

With the exception of copper, all other systems presented exothermic entropic values, which are also consistent with the occurrence of favoured reactions. Thus, this value suggested that the presence of cation

Table 2
Thermodynamic data for the interaction of metallic nitrates with mercaptopropyl magnesium phyllosilicate at 298.15±0.02 K

M^{2+}	$-\Delta_{int}h$ (J g^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
Cu^{2+}	202.84±3.23	47.06±1.00	24.01±0.19	−77±4
Ni^{2+}	41.44±0.32	27.63±0.50	29.65±0.70	7±4
Co^{2+}	42.30±0.08	21.92±0.50	34.11±0.46	41±3
Zn^{2+}	34.89±0.48	14.66±0.52	28.94±0.33	48±3

in the hybrid causes an ordering in the structure by decreasing the entropic value. However, this effect contributes to an increase in crystallinity of the final solid. This rearrangement in structure should give a contribution to entropy, which surpasses the same effect originating from the transference of water of hydration to the medium of the reaction. The highest entropic values were observed for other cations with the largest hydration volumes and illustrate the principle that the loss of water of hydration leads to a disorganization of the final system. For instance, zinc with a volume of hydration of 178.2 $cm^3 mol^{-1}$ gave an entropic value of 45 ± 3 J mol^{-1} K^{-1}.

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References

[1] C. Airoldi, E.F.C. Alcântara, Thermochim. Acta 95 (1995) 259.

[2] S. Komarneni, N. Kozai, R. Roy, J. Mater. Chem. 8 (1998) 1329.

[3] J.F. Diaz, J.B. Kenneth Jr., Chem. Mater. 9 (1997) 61.

[4] C. Airoldi, S. Roca, Thermochim. Acta 284 (1996) 289.

[5] C. Airoldi, M.R.M.C. Santos, J. Mater. Chem. 4 (1994) 1479.

[6] C. Airoldi, S. Roca, J. Chem. Soc., Dalton Trans. (1997) 2517.

[7] S.F. Oliveira, J.G.P. Espinola, W.E.S. Lemus, A.G. Souza, C. Airoldi, Colloids Surf. A- Physicochem. Eng. Aspects 136 (1998) 151.

[8] T.P. Lishko, L.V. Glushchenko, Y.V. Kholin, Z.N. Zaitev, A. Bugaevskii, N.D. Donskaya, Russ. J. Phys. Chem. 65 (1991) 1584.

[9] C. Airoldi, E.F.C.J. Alcântara, J. Chem. Thermodyn. 27 (1995) 623.

[10] M.G. Fonseca, J.G.P. Espinola, S.F. Oliveira, L.C.R. dos Santos, A.G. Souza, C. Airoldi, Colloids Surf. A- Physicochem. Eng. Aspects 133 (1998) 205.

[11] A.R. Cestari, C. Airoldi, J. Braz. Chem. Soc. 6 (1995) 291.

[12] B. Buszewski, M. Jezierska, M. Welniak, D. Berek, J. High Resol. Chromatogr. 21 (1998) 267.

[13] C.R. Silva, C. Airoldi, J. High Resol. Chromatogr. 22 (1999) 103.

[14] N.L. Dias, Y. Gushiken, V.W. Polito, Talanta 42 (1995) 1625.

[15] Y. Gushikem, C.R.M. Peixoto, U.P.R. Filho, L.T. Kubota, E. Stadler, J. Colloid Interface Sci. 184 (1996) 236.

[16] E.F.S. Vieira, A.R. Cestari, J.A. Simoni, C. Airoldi, Thermochim. Acta 328 (1999) 247.

[17] L.M. Nunes, C. Airoldi, Thermochim. Acta 328 (1999) 297.

[18] C.R. Silva, C. Airoldi, J. Colloid Interface Sci. 195 (1997) 381.

[19] A.R. Cestari, C. Airoldi, Langmuir 13 (1997) 2681.

[20] M.G. Fonseca, C. Airoldi, J. Mater. Chem. 9 (1999) 1375.

[21] C.J. Brinker, G.W. Scherer, Sol–Gel Science — The Physics and Chemistry of Sol–Gel Processing, Academic Press, New York, 1990.

[22] Y. Fukushima, M. Tami, J. Chem. Soc., Chem. Commun. (1995) 241.

[23] Y. Fukushima, M. Tami, Bull. Chem. Soc. Jpn. 69 (1996) 3667.

[24] S.L. Burkett, A. Press, S. Mann, Chem. Mater. 9 (1997) 1071.

[25] Y.-S. Hong, S.-J. Kim, Bull. Korean Chem. Soc. 18 (1997) 236.

[26] L. Ukrainczyk, R.A. Bellman, A.B. Anderson, J. Phys. Chem. B 101 (1997) 531.

[27] S. Whilton, S.L. Burkett, S. Mann, J. Mater. Chem. 8 (1998) 1927.

[28] M.G. Fonseca, C.R. Silva, C. Airoldi, Langmuir 15 (1999) 5048.

[29] A.R. Cestari, C. Airoldi, J. Colloid Interface Sci. 195 (1997) 338.

[30] N.L. Dias, Y. Gushikem, Sep. Sci. Technol. 15 (1997) 2535.

[31] E.F.S. Vieira, J.D. Simoni, C. Airoldi, J. Mater. Chem. 11 (1997) 2249.

[32] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986.

[33] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy: A Guide for Students of Organic Chemistry, Saunders College Publishing, Orlando, 1996.

[34] R.M. Silverstein, G.C. Bassler, T.C. Morrel, Spectrometric Identification of Organic Compounds, Wiley/Interscience, London, 1991.

[35] P.J. Launer, Am. Min. 37 (1952) 764.

[36] B.D. Sarsena, Am. Min. 47 (1960) 242.

[37] V.C. Farmer, J.D. Russel, Spectrochim. Acta 20 (1964) 1149.

[38] R.W.T. Wilkins, J. Ito, Am. Min. 52 (1967) 1649.

[39] C. Mosser, M. Mestdagh, A. Decarreau, A. Herbillon, Clay Min. 25 (1990) 271.

[40] K. Albert, B. Pfleiderer, E. Bayer, in: D.E. Leyden, W.T. Collins (Eds.), Chemically Modified Surfaces in Science and Industry, Gordon Breach Science Publishers, New York, 1988.

[41] C.A. Fyfe, Y. Zhang, P. Aroca, J. Am. Chem. Soc. 114 (1992) 3252.

[42] S. Nakata, Y. Tanaka, S. Asaoka, M. Nakamura, J. Mol. Struct. 441 (1998) 267.

[43] J. Sanz, J.M. Serratosa, J. Am. Chem. Soc. 106 (1984) 4790.

[44] B.L. Sherriff, H.D. Grundy, J.S. Hartman, Eur. J. Miner. 3 (1991) 751.

[45] Y. Marcus, Ion Solvation, Wiley, London, 1985.

[46] A. Bem-Naim, Solvation Thermodynamics, Plenum Press, New York, 1987.

[47] G.A. Krestov, Thermodynamics of Solvation: Solution and Dissolution; Ions and Solvents; Structure and Energetics, Ellis Horwood, London, 1991.

[48] G.W. Brindely, G. Brown, Crystal Structures of Clay Minerals and their X-Ray Identification, Mineralogical Society, London, 1980.

[49] D.M. Moore, R.C. Reynolds, X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford Press, London, 1997.

[50] R.J. Gale, C.A. Winkler, Inorg. Chim. Acta 21 (1976) 151.

[51] A.W. Adamson, Physical Chemistry of Surfaces, Wiley, New York, 1990.