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CALORIMETRIC STUDY OF AMINO MODIFIED TALC MATRICES AND COPPER SALTS

An evidence of the chelate effect

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Abstract

The surface of natural talc was modified with organosilanes $(H_3CO)_3SiR$, for $R=-(CH_2)_3NH_2$, $-(CH_2)_3NH(CH_2)_2NH_2$ and $-(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$, resulting in the inorganic-organic hybrids *TC1*, *TC2* and *TC3*. These aminated talcs contain 4.38, 2.56 and 2.03 mmol g^{-1} of immobilized organic chains for *TCx* (x=1 to 3), respectively. The chemisorption isotherm data obtained by a batchwise process were adjusted to a modified Langmuir equation, to give the maximum adsorption capacity *TC1>TC2>TC3*. The chelate effect was illustrated through calorimetric titration, giving the highest enthalpic values for *TC2* and *TC3* hybrids and favoured for sulfate counter anion. The enthalpic and entropic values indicated favourable reaction between copper-basic nitrogen center atoms on pendant chain covalently bonded to the inorganic backbone.

Keywords: adsorption, calorimetry, copper salts, talc

Introduction

In recent decades organic polymers have been rather used as support materials than inorganic oxides. Some inorganic oxides, such as silica and alumina, can still offer distinct advantages in a series of applications due to the rigidity, insolubility in a great variety of solvents, with less susceptibility to chemical or thermal degradation [1, 2].

The classical approach applied to synthesize inorganic-organic derivatives consists in exploring the ability of the reaction between the hydroxyl surfaces with a trialkoxysilane agent, $(H_3CO)_3SiR$, to produce a new coating surface. The inorganic matrices with an appropriate functionalization can be used in distinct areas such as catalysis [3], chromatography [4], electrochemistry [5], and adsorption of enzymes and metal cations [6]. The selected organic chelating groups such as ethylenediamine [7, 8], dithiocarbamate [9], acetylacetone [10], urea [11], and mercaptan [12] immobilized on silica gel demonstrated a great effectiveness of removing cations from

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aqueous and non-aqueous solutions. Although silica gel has been one of most used support for anchoring silylating agents and other inorganic surfaces such as glass or phyllosilicates were also used [13, 14].

The present investigation is focused on talc, a non-expansible lamellar hydrated magnesium silicate, $Mg_3Si_4O_{10}(OH)_2$, with a basal space of 960 pm between the layers formed from a central octahedral coordinated magnesium hydroxide in tri-octahedral arrangement sandwiched between tetrahedral coordinated Si_2O_5 silicate sheets [15].

The structure is characterized by almost completely compensated, stable and strong bonds, which can be cleavaged in silicon oxide anion planes, due to the weak van der Waals bonds between the packets. The attractive forces between the sheets give the matrix a non-expansible property and the chemical reactivity is limited to the surface [8].

Talc surface is extremely hydrophobic, when in finely ground state floats on top of water, makes it an excellent material for various applications such as paints, adhesives, sealants and other building products [16]. Other applications including reinforcing polyolefin compounds and also as an antiblock agent in polyolefin films [16].

The purpose of this publication is to report the results on talc surface after aminated silanes were anchored, mainly on adsorption. Copper-basic center nitrogen atoms interactions were calorimetrically investigated, in order to understand the influence of the counter-anion in the chelate effect on adsorption processes better.

Experimental

The talc samples used showed the following composition: loss at firing at 1273 K 4.72%, SiO_2 65.00%, MgO 27.56%, CaO 0.13%, Al_2O_3 0.037%, Fe_2O_3 2.05%, Na_2O 0.044% and K_2O ≤0.005%. The BET surface area was 2.27 ± 0.01 m^2 g^{-1}.

The silylant agents 3-aminopropyl-, N-propylethylenediamine- and N-propyldiethylenetriaminetrimethoxysilanes were reagent grade. All other reagents xylene, ethanol and copper chloride, nitrate and sulfate were used without previous purification.

The synthetic procedure consists of activating talc by heating under vacuum during 24 h at 423 K. To a stirred suspension formed by 5.0 g of talc with 250 cm^3 of dry xylene under nitrogen atmosphere at 353 K, 5.0 cm^3 of silanes were added and the reaction mixture was maintained during two days. The products were filtered, washed with ethanol and dried under vacuum for another day at 323 K. The degree of functionalization was determined by the nitrogen content by using Kjeldhal method. The new anchored materials were named as *TCx* (*x*=1 to 3), for the products of reaction with 3-aminopropyl-, N-propylethylenediamine- and N-propyldiethylenetriaminetrimethoxysilane, respectively.

The new coated materials were characterized by elemental analyses, XRD patterns, infrared spectroscopy, thermogravimetry and surface area determinations, as described before [7, 8, 11, 13].

The adsorption processes were calorimetrically monitored by titration using a heat-flow instrument LKB 2277 Thermal Activity Monitor. Thermostated aqueous solutions of copper salt were incrementally added to a suspension of 20.0 mg of talc samples in 2.0 cm^3 of water, under stirring at 298.15±0.02 K. Salt solutions were added until the surface was saturated and three independent titrations were investigated for complete thermodynamic cycle: a) thermal effects due to anchored talc/cation interface (Q_r), b) hydration of the solid (Q_s) and c) metallic solution dilution (Q_{dil}). The net thermal effect is given by: $\Sigma Q_{int}=\Sigma Q_r-\Sigma Q_{dil}-\Sigma Q_s$, as the thermal effect of hydration of talc samples suspended in the solvent was null, then $\Sigma Q_{int}=\Sigma Q_r-\Sigma Q_{dil}$.

The adsorption capacities of modified talcs were determined by using batch isotherms and the procedure used suspensions of 50 mg of modified talc in 25.0 cm^3 of copper salts, containing concentrations, varying in the $1.0\cdot10^{-3}$ to $2.0\cdot10^{-2}$ mol dm^{-3} range, which were mechanically stirred during 2 h at 298±1 K. The blue solid was removed by centrifugation, washed with deionized water and dried at 323 K. The number of moles of copper N_f adsorbed on a mass m of the modified surfaces was determined by expression: $N_f=(N_i-N_s)$ m^{-1}, where N_i and N_s are the initial and final amount of the cation in solution [11, 12]. The original activated talc did not adsorb any cation.

The interactive processes were fitted to modified Langmuir equations [11, 12, 17, 18] and from them the molar enthalpy ΔH of interaction process was calculated by $\Delta H=\Delta_{int}h/N_f$. Gibbs free energy and entropy changes were calculated from $\Delta G=-RT\ln K$ and $\Delta G=\Delta H-T\Delta S$ expressions, respectively.

Results and discussion

The chemical modification of natural phyllosilicate talc surface shows a remarkable feature related to coated inorganic matrices, which success opens a new possibility of using such a solid in other similar areas that organosilicas have been successively applied. Based on previous knowledge on this kind of surface, identical procedure enabled the organo-functionalization of talcs, in which silylant agents were incorporated in the inorganic backbone [19].

The elemental analyses data presented in Table 1, showed the results associated with the immobilization of $-(CH_2)_3NH_2$, $-(CH_2)_3NH(CH_2)_2NH_2$ and $-(CH_2)_3NH(CH_2)_2NH-(CH_2)_2NH_2$ groups on talc. From the amount of nitrogen the number of moles of pendant organic groups on the matrices *TCx* (x=1 to 3) were determined as 4.38, 2.56 and 2.03 mmol g^{-1}, respectively. The calculated and observed C/N relationships are in good agreement, however, the largest degree in the number of immobilized agents reflects the effectiveness of such kind of reactions.

The thermogravimetric curves of the original matrix showed a mass loss of 2.28% due to the release of adsorbed water in a first stage. The modified talc matrices presented similar thermal released in continuous degradation with total mass loss of 28.90; 36.36 and 34.34% for *TCx* (x=1 to 3), respectively, from 298 to 1170 K. These values are expected by the presence of organic chain length of these bonded silylant agents on the surface.

Table 1 Percentages of hydrogen (H), carbon (C) and nitrogen (N), C/N relationship observed and (calculated), and the number of pendant groups (*n*) for hybrids by elemental analysis for *TCx* (*x*=1 to 3)

TCx	H/%	C/%	N/%	C/N	*n*/mmol g^{-1}
1	4.55	18.60	6.13	3.54 (3.00)	4.38
2	4.33	19.59	7.17	3.19 (2.50)	2.56
3	4.61	19.51	8.52	2.67 (2.33)	2.03

The infrared spectrum of the original talc showed a sharp band at 3676 cm^{-1} assigned to ν(Mg–OH), a broad one at 3400 cm^{-1} due to ν(H–OH) and another related to ν(Si–O–Si) at 1000 cm^{-1} [20]. For all modified talcs ν(Mg–OH) decreases the intensity as a consequence of the reaction with the silylant agents. The ν(NH) stretching bands located at 3363 and 3293 cm^{-1} with different intensities appeared and new bands were detected at 2930 and 2867 cm^{-1} related to symmetric and asymmetric ν(C–H) bonds. Absorption associated with ν(CH_2) at 1467 cm^{-1} and for δ(N–C) bond at 1320 cm^{-1} were detected for *TC3*.

XRD data gave unchanged basal spacing for 001 reflection plane at 2θ=9.7°, to give an interlayer distance of 936 ppm. These data clearly suggested that the immobilization occurred on external surface of inorganic support, which was confirmed by low angle diffractometric measurements.

All determinations are in agreement that the aminated silanes were covalently incorporated on talc to give these new coated matrices conditions to change their adsorption capacity. The abilities in extracting copper from aqueous solutions were evaluated by measuring through sorption isotherms, as shown in Fig. 1 and the capacity order *TC1*>*TC2*>*TC3* for adsorption is shown in Table 2. This sequence confirms that the increase in nitrogen basic atom on chain caused a significant effect on adsorption, as observed for other amino derivatives [21], to form cation-amino complex and

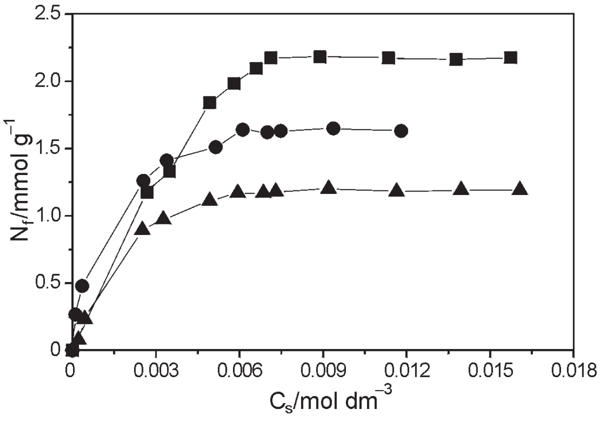

Fig. 1 Isotherms of adsorption of chloride (–■–), nitrate (–●–), and (–▲–) copper sulfate on modified *TC1* talc surface. C_s is the equilibrium concentration of cation and N_f is the number of moles of copper adsorbed per gram of adsorbent

the increase capacity of adsorption followed the order $Cl^->NO_3^->SO_4^{2-}$. This sequence is related to the ionic radio for choride 181 pm, and thermochemical radii [22] for nitrate and sulfate of 179 and 258 pm, respectively. These counter anions reflect in any steric hindrance participation due the charge counterbalance of the complex formed on surface, which behavior is evidenced from the calorimetric data.

Table 2 The maximum number of copper adsorbed (mmol g^{-1}) on *TCx* (x=1 to 3) modified matrices

Anion	*TC1*	*TC2*	*TC3*
Cl^-	2.18	1.63	1.32
NO_3^-	2.16	1.36	1.26
SO_4^{2-}	2.15	1.33	1.06

The thermal effects caused by direct cation-basic center interaction in the solid/liquid interface, the dilution of the cation solution and the net effect is shown in Fig. 2. The profile of the saturated isotherms obtained from calorimetric data is very close to that of the thermal effect of dilution of cations. An example of the calorimetric isotherm and its linearized form is exhibited in Fig. 3, with coefficient of correlation over 0.998 and all thermochemical data are listed in Table 3. The exothermic enthalpic values for the interactive processes follow the order $SO_4^{2-}>NO_3^->Cl^-$ and increased with the number of basic nitrogen atoms on organic chains, to give the order *TC3*>*TC2*>*TC1*. This behavior is associated with different kinds of complexes formed between nitrogen basic atoms/cation. The coordination compound formed

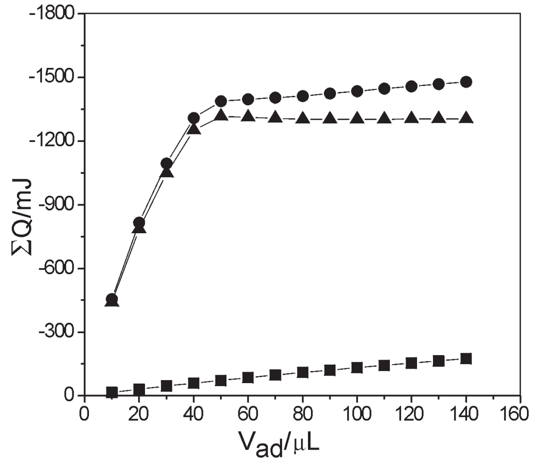

Fig. 2 Calorimetric titration of 0.01734 g of *TC2* suspended in 2.0 cm^3 of water with $CuCl_2$ 0.314 mol dm^{-3} in the same solvent at 298.15±0.02 K. The experimental points represent the sum of the thermal effects of the cation titration ΣQ_{tot} (–●–), copper dilution ΣQ_{dil} (–■–) and the net thermal effect ΣQ_{int} (–▲–). ΣQ and V_{ad} values are the sum of detected thermal effect and total injected volume of copper solution, respectively

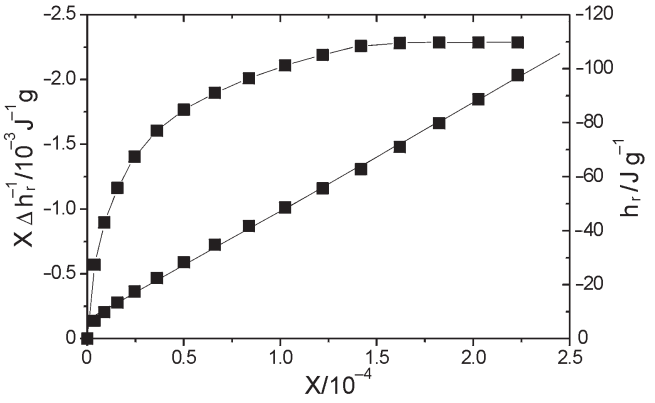

Fig. 3 Isotherm for the integral enthalpy of adsorption $\Delta_r h$ *vs.* molar fraction X obtained from a calorimetric titration of 0.01665 g of *TC3* suspended in 2.0 cm^3 of water, with $Cu(NO_3)_2$ 0.266 mol dm^{-3} in the same solvent at 298.15±0.02 K. The straight line is the linearized form of the isotherm

should be more favourable for multidentate basic nitrogen atoms, as reflected in the enthalpies results in Table 3 and this kind of contribution in function of the used material is illustrated in Fig. 4. A non-linear behavior in enthalpy was observed on passing from mono- to tridentate ligands, however, the latest pendant group even caused an increase in enthalpic values for all matrices.

Table 3 Thermodynamic data for the interaction of copper salts with modified talcs *TCx* (*x*=1 to 3) at 298.15±0.02 K

Anion	Matrix	$-\Delta H°$/kJ mol^{-1}	$-\Delta G°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
Cl^-	*TC1*	21.86±0.21	29.46±0.13	25±1
	TC2	78.40±0.78	34.04±0.91	–149±5
	TC3	97.68±0.48	29.29±0.22	–229±2
NO_3^-	*TC1*	26.76±0.27	28.19±0.34	5±2
	TC2	134.32±0.13	31.85±0.33	–344±2
	TC3	157.99±0.79	27.13±0.16	–439±3
SO_4^{2-}	*TC1*	31.85±0.32	30.60±0.22	–4±2
	TC2	138.40±0.14	30.57±0.20	–362±1
	TC3	159.73±0.16	32.39±0.23	–427±1

For all determinations the acid-base interactions on surface demonstrate spontaneity of the proposed reactions, as shown by the negative $\Delta_{int}G$ values. However, the entropic values are more favorable in the sequence $Cl^- > NO_3^- > SO_4^{2-}$. This variation is interpreted by considering the contribution of molecules of solvents previously bonded to cation, counter anion and also the inorganic support, to establish a final stage with an organization or disorganization of the system [18].

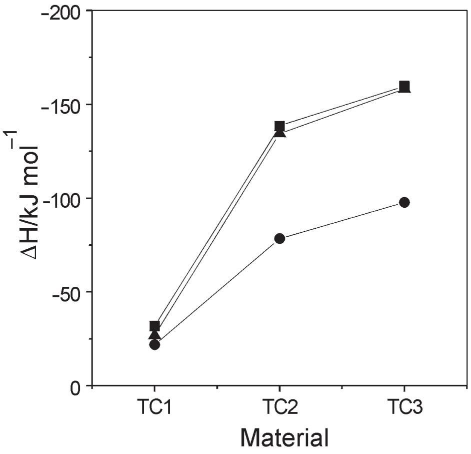

Fig. 4 Enthalpic values of chloride (–●–), nitrate (–▲–) and (–■–) copper sulfate interactions with modified talc surfaces

The water molecules associated with the basic centers on the matrix and those bonded to cation should be displaced during coordination due to the dehydration before bonding, reflecting in a possible increase in entropy [18]. Thus, this increase is followed by the largest degree of adsorption, as occurred more pronounced with copper chloride, which relative order is clearly shown for the isotherms in Fig. 1. During the complex formation, the desolvation disturbs the structure of the medium of reaction to promote the disorganization of the system, and consequently, leads to an increase in entropy [10, 11, 18], as observed for favorable condition represented by chloride, reflecting in values as shown in Table 3.

A decrease in entropy is observed for nitrate and sulfate entrance into the coordination sphere. This fact seems to be related to the enthalpy of hydration of each anion, thus, the largest value for sulfate of -1138 kJ mol^{-1} is due to its great possibility in hydrogen bonding formation with water by using all four oxygen atoms, which contrasts to the smallest variation in enthalpy of -376 kJ mol^{-1} for chloride [23]. Therefore, this process suggests that the hydration of the anion causes an organization of the molecules of solvent around the complex formed with a decrease in entropy.

In conclusion, the action of the anion to counterbalance the electrical charge in the sphere of coordination implies to consider solvation energy, lattice energy, entropy factors and kinetic parameters. However, other participations include also steric factors, non-bonded interactions and hydrogen bonding formed. Based on the series of arguments, the complete understanding of thermochemical data involves the summary of those distinct contributions.

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