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Calorimetric investigation of metal ion adsorption on 3-glycidoxypropyltrimethylsiloxane + propane-1,3-diamine immobilized on silica gel

José A.A. Sales, Claudio Airoldi*

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

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Abstract

The silylant precursor agent 3-glycidoxypropyltrimethoxysilane was covalently anchored onto a silica gel surface followed by propane-1,3-diamine molecule incorporation using a heterogeneous route (SiHT). On another series, the precursor agent was previously reacted with diamine to give the silylant agent in homogeneous condition, before immobilization (SiHM). The degrees of immobilization were 0.80 and 1.53 mmol g^{-1} for SiHT and SiHM, respectively. Both grafting surfaces were employed to extract the divalent cations nickel, copper, cobalt and zinc from aqueous solutions. This cation/nitrogen interactive process was calorimetrically followed to give exothermic enthalpy, negative free Gibbs energy and positive entropy values. These favorable thermodynamic data are more pronounced for copper on both surfaces, with a higher tendency for SiHM, due to the larger amount of available nitrogen atoms in the pendant chain covalently attached to the inorganic silica backbone.

Keywords: Silica; Propane-1; 3-Diamine; Immobilization; Adsorption; Thermodynamic

1. Introduction

A significant interest on the chemical industry in recent years is to develop more environmentally friendly methodologies [1]. The area of concern is the large volumes of waste and toxic effluents produced by a variety of chemical processes [2]. Potential benefits have been related to the use of silica gel modified with organic compounds in different application areas [3], taking into account the properties associated with the new synthetic materials, such as good mechanical strength, swelling stability and fast metal exchange kinetics required for use in different types of systems. For appropriate employment principally the structural characteristics of the organic compound, the nature of the functional group present and the basicity of the incorporated donor atoms bonded on the pendant chain attached to the inorganic backbone have been explored [4].

Specially designed molecules covalently bonded onto silica gel surface perform specific functions in a series of practical applications such as catalysts [5], in modifying electrode surfaces [6], to increase the chromatographic separation of herbicides [7] or other organic molecules [8]. As a consequence, their uses have been extended to environmental problems [9,10]. For example, molecules such as ethylenediamine [11], 8-hydroxyquinoline [12], substituted pyrazole [13], dithiocarbamate [14] and aminothiol [15] were grafted onto silica surfaces and explored for preconcentration and/or elimination of metal ions from dilute aqueous solutions [16].

From the experimental point of view, two grafting methods can be successfully applied [17]: (a) the most common procedure consists in a direct grafting of the desired silylant agent directly onto the silica surface and (b) a synthesized molecule containing the alkoxide moiety is attached due to

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* Corresponding author. Tel.: +55 19 3788 3023; fax: +55 19 3788 3055.
E-mail address: airoldi@iqm.unicamp.br (C. Airoldi).

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the available silanol groups disposed on silica surface [18]. Both procedures illustrate the versatility of the immobilization, showing distinct and elegant routes for the same attached final product of reaction.

Pristine or chemically modified polymeric inorganic surfaces suspended in a given solution behave as adsorbents in physical or chemical processes, which depend on the nature of the available groups attached on the surfaces [19]. However, the presence of free basic atoms on pendant organic chains produces cation complexing abilities, favoring metal adsorption at the solid/liquid interface in such heterogeneous systems.

The present investigation is focused on the silylant agent 3-glycidoxypropyltrimethoxysilane, by exploring the ability of the epoxide group opening, in the presence of nucleophiles, allowing facile incorporation of nucleophilic amines, such as propane-1,3-diamine. The final grafted organic molecules were employed for chelation of divalent nickel, copper, cobalt and zinc from dilute aqueous solutions. The coordination performances of the attached ligands were followed by using calorimetric measurements. This quantification enables an understanding of the cation–surface interactions from the thermodynamic data obtained.

2. Experimental

2.1. Chemicals

Reagent grade solvents were purified and distilled just before use. Silica gel with particle sizes in the range 0.072–0.174 mm, average pore diameter 6.0×10^{-7} cm and pore volume 0.75 $cm^3\,g^{-1}$, was treated and activated as before [11]. The silylant agent 3-glycidoxypropyltrimethoxysilane (GPTS) was used without further purification, propane-1,3-diamine (pda) was distilled under reduced pressure. Hydrated divalent nitrates for copper, nickel, cobalt and zinc were used in all adsorption process. Deionised water from a Millipore Milli-Q (18.2 MΩ cm) was used in all experimental procedures.

2.2. Immobilization

Heterogeneous route: 20.0 g of activated silica gel reacted with 20.0 cm^3 (91.0 mmol) of GPTS in toluene under reflux of the solvent in dry nitrogen [11,20]. After filtering and washing, the solid (SiG) was dried. Then, 5.0 g of this product was reacted with 8.5 cm^3 (102.0 mmol) of propane-1,3-diamine and the solid was filtered, washed and dried [17], to obtain the product, SiHT, as shown in Fig. 1.

Homogeneous method: 5.0 cm^3 (23.0 mmol) of GPTS was reacted with 1.9 cm^3 (23.0 mmol) of the diamine in dry methanol. The mixture was refluxed under dry nitrogen and the product was reacted with 5.0 g of silica suspended in toluene. The final solid was filtered, washed and dried [17], to give the product, SiHM, as shown in Fig. 2.

2.3. Characterization

Elemental analyses were performed with a Perkin-Elmer 2400 Series II microelemental analyzer. The surface area was obtained by using the BET equation, through nitrogen adsorption isotherms, by means of a Flowsorb 2300 analyzer [21]. The mass loss determinations were performed under nitrogen on a DuPont instrument, Model 951, using 8.0–12.0 mg of the sample at a heating rate of 0.17 $K\,s^{-1}$. Infrared spectra were obtained in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1}, by accumulating 32 scans using a MB-Bomem FTIR spectrophotometer. KBr pellets were used for solid samples and NaCl windows for liquid samples [17].

2.4. Isotherms of adsorption

The adsorption was followed batchwise in aqueous solution for divalent nickel, copper, cobalt and zinc nitrates at 298 ± 1 K. For these adsorption measurements, samples of 50 mg of silica derivatized were suspended in 20.0 cm^3 of aqueous solution containing variable amounts of each cation, whose concentrations varied over the 2.0–14.0 mmol dm^{-3} range, in a orbital shaker thermostated for 12 h [22]. After equilibrium was established, the suspension was centrifuged, aliquots of

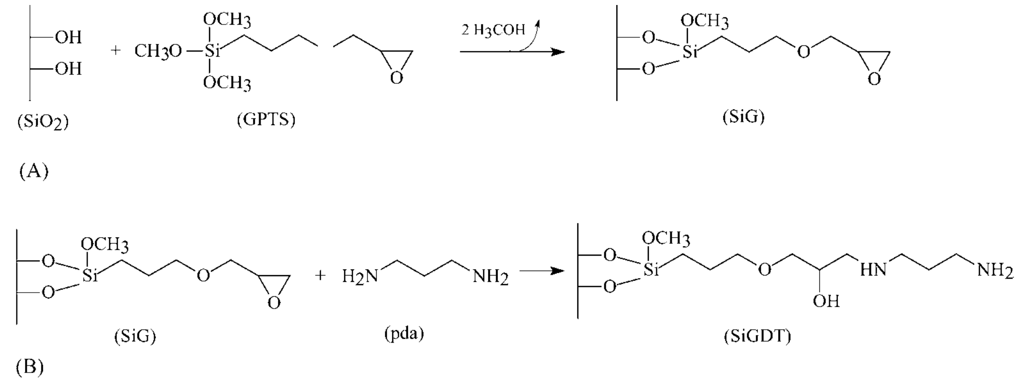

Fig. 1. Reaction of silica gel with silylant agent GPTS, to yield the anchored SiG (A) and incorporation of propane-1,3-diamine in a heterogeneous route SiHT (B).

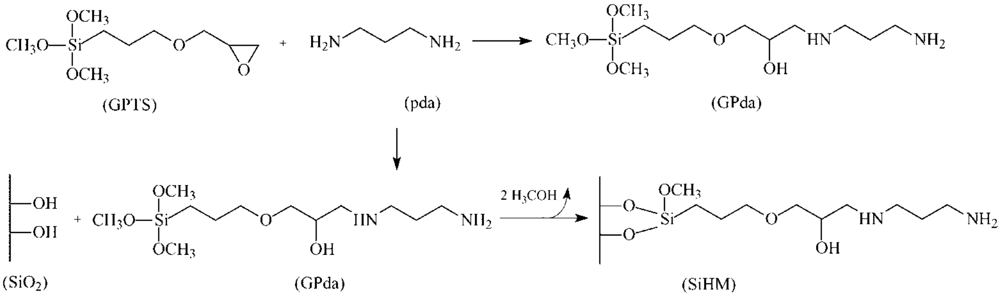

Fig. 2. Reaction of the silylant agent GPTS with diamine dpa to form the new silylant agent GPda, followed by silica gel immobilization to give SiHM in a homogeneous route.

the supernatant were carefully pipetted and the amounts of metallic cations remaining in solution were determined by ICP-OES with a Perkin-Elmer 3000 DV apparatus.

2.5. Calorimetry

The calorimetric titrations were followed on a differential isothermal LKB 2277 microcalorimetric system [23]. For each titration, a sample of about 20 mg was suspended in 2.0 cm^3 of deionized water in a steel ampoule and was vigorously stirred in a thermostat bath at 298.15 ± 0.02 K. After equilibrium, increments of metallic cation solution were added through a microsyringe, coupled to the calorimetric vessel. For each increment the thermal effect ($\Delta_{tit}Q$) was recorded until saturation of the surface was reached, which was indicated by a constant thermal effect. The same procedure was used to monitor the thermal effect of the titration of the cation solution in water ($\Delta_{dil}Q$) without the solid and also to monitor the water anchored to the suspension surface. The thermal effect of hydration of the modified matrix gave a null value. By combining the thermal effect values, the resulting integral thermal effect ($\Sigma\Delta_rQ$) can be determined by the expression $\Sigma\Delta_rQ = \Sigma\Delta_{tit}Q - \Sigma\Delta_{dil}Q$. The calorimetric titration data for copper on the SiHM immobilized surface is shown in Fig. 3.

2.6. Thermodynamic of interaction

The interactive adsorption cation–surface processes were fitted to a modified Langmuir Eq. (1):

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

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 adsorption sites, and b is a parameter associated with the equilibrium constant for the reaction. N_s and b values can be estimated from the coefficients after linearization of the isotherm [24]. The agreement of both methods reflected in very close N_s values obtained from batch and calorimetric techniques.

The enthalpy of interaction $\Delta_{int}h$ was obtained by an expression derived from the modified Langmuir Eq. (2):

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

where X is the sum of the molar fractions of the metallic cation remaining in solution after interaction, $\Delta_r h$ the integral enthalpy that is obtained by the quotient between ΣQ_r per mass of the matrix and K a proportionality constant that includes the equilibrium constant. Here, a $X/\Delta_r h$ versus X plot gave the angular and linear coefficients, which determine $\Delta_{int}h$ and K, respectively. The molar enthalpy of interaction process can be calculated the by expression $\Delta H^0 = \Delta_{int}h/N_s$. The K value is used to obtain the Gibbs free energy through the expression, $\Delta G = -RT \ln K$, and the entropy value is calculated by means of the expression: $\Delta G = \Delta H - T\Delta S$.

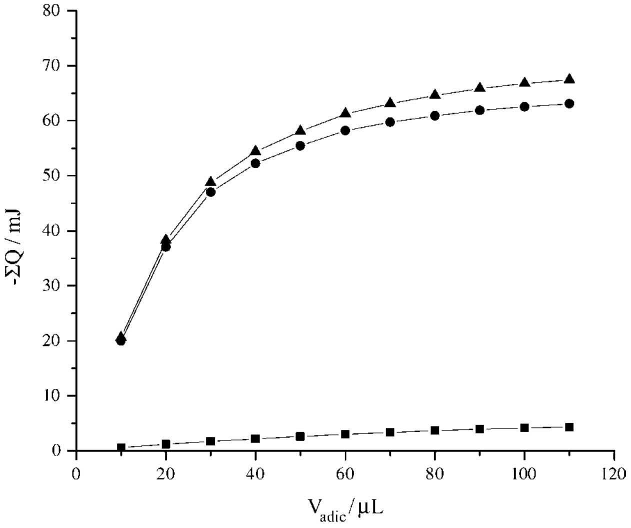

Fig. 3. Calorimetric titration of a suspension of 20.0 mg of silica SiHM in water with 0.0515 mol dm^{-3} copper nitrate. The thermal effects are represented by titration $\Sigma_{tit}Q$ (▲), diluition $\Sigma_{dil}Q$ (■) and the net Σ_rQ (●) values.

Table 1
Percentages (%) of carbon (C), hydrogen (H) and nitrogen (N) from elemental analysis of chemically modified silicas, density (*d*) of immobilized groups per gram of silica (mmol g^{-1}) and surface area (*S*) (m^2 g^{-1})

	C (%)	H (%)	N (%)	*d* (mmol g^{-1})	*S* (m^2 g^{-1})
SiG	8.62 ± 0.01	1.75 ± 0.01	–	1.03 ± 0.01	334 ± 17
SiHT	11.59 ± 0.02	2.46 ± 0.04	2.22 ± 0.01	0.80 ± 0.01	154 ± 12
SiHM	20.76 ± 0.53	4.39 ± 0.08	4.28 ± 0.24	1.53 ± 0.04	133 ± 2

3. Results and discussion

The synthesized silylant agent consisted of incorporating a propane-1,3-diamine molecule in the precursor epoxide agent [17], as shown in Figs. 1 and 2. From the elemental percentages based on carbon, hydrogen and nitrogen, the amount of 3-glycidoxypropyltrimethoxysilane anchored on the silica surface was established and also the amount of organic molecule immobilized, as listed in Table 1. The increase of these elements as the reaction takes place is in agreement with the increase of the silane organic chain being anchored. For example, the amount of nitrogen using the homogeneous route, SiHM, gave a value of 1.53 mmol g^{-1} and the same material obtained through the heterogeneous route, SiHT, gave 0.80 mmol g^{-1}. Based on these values it is clear that when the reaction occurred under homogeneous conditions the effectiveness is nearly twice that of heterogeneous one. The density of the pendant groups covalently attached to the inorganic silica backbone changes the original characteristics of the surface. Thus, the initial specific surface area of 421 ± 3 m^2 g^{-1} decreases as the immobilization takes place, to give 155 ± 12 and 133 ± 2 m^2 g^{-1} for these routes, respectively. As expected, those anchored pendant groups reduced nitrogen adsorption in the silica pores during the area measurement process [25]. On the other hand, the presence of the basic atoms attached to the pendant groups is potentially useful to remove metallic cations from aqueous or non-aqueous solutions [26].

From the grafting process, the molecular design can be executed on a surface, with the anchored species being identified by infrared spectroscopy. The spectra of individual components and the final silylant agent synthesized by the homogeneous route presented the N–H and C–H stretching bands for diamine and the precursor silylant agent compound. The bands at 1250 and 820 cm^{-1} for the epoxide moiety in the precursor silylant agent vanished completely in the final compound, showing the opening of the three member cycle as the diamine nitrogen nucleophilic center interacts to incorporate in the precursor silylant agent [17]. The original silica, when anchored with the precursor silylant agent and after the inclusion of propane-1,3-diamine molecule, obtained from heterogeneous SiHT and homogeneous SiHM routes presented great similarities of bands. The band at 3500 cm^{-1} for the pure silica is assigned to OH stretching and the band at 1050 cm^{-1} is attributed to the Si–O–Si siloxane stretching with a strong shoulder that varies in function of the chemical surface modification. Another characteristic band assigned to ≡Si–OH group corresponds to the silanol deformation observed near 965 cm^{-1}, which is very sensitive to the immobilization process [17]. After silylant agent (GPTS) immobilization, a new band appeared at 2940 cm^{-1} that corresponds to the ν(C–H) stretching frequency, due to the presence of the carbon chain of the pendant group attached to the inorganic matrix. The band at 965 cm^{-1} for the δ(Si–OH) silanol groups was considerably reduced due to the organic functionalization by means of the use of the silane alkoxide groups, as expected in such immobilization processes [27].

3.1. Thermogravimetry

The thermogravimetric curves reflect the thermal stability of these new materials. Based on the mass losses the quantity decomposed in each stage can be calculated, in order to compare with the analytical results. Thus, curves of original silica, when chemically modified with the precursor silylant agent and after diamine incorporation by heterogeneous (SiHT) and homogeneous (SiHM) routes are presented in Fig. 4. The original silica presented a loss of adsorbed water mass of 0.70% that was followed by a new event due to the condensation of free silanol groups to cause siloxane bond formation, ≡Si–O–Si≡, in the final structure of the inorganic oxide of 2.0% [28].

The curve involving 3-glycidoxypropyltrimethoxysilane funcionalization, SiG, gave a mass loss of 17.9% in the 473–923 K interval of temperature, after physisorbed

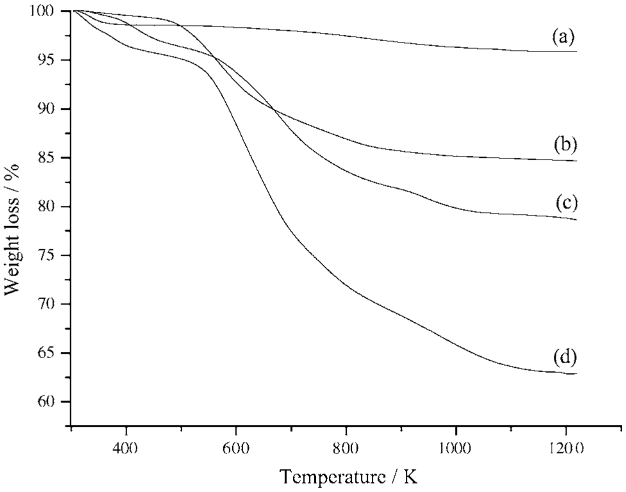

Fig. 4. Thermogravimetric curves of pure silica (a), chemically modified with the epoxide SiG (b) and incorporated with 1,3-propanediamine through heterogeneous SiHT (c) and homogeneous SiHM (d) routes.

Table 2
Percentages of mass losses (Δm) obtained from thermogravimetric curves in the temperature intervals (ΔT) of silica and immobilized silica

Compound	Δm (%)	ΔT (K)
SiO_2	0.7	298–408
	2.0	408–1208
SiG	17.9	298–913
	1.4	913–1223
	3.7	298–493
SiHT	14.4	493–878
	3.4	878–1218
SiHM	2.9	298–473
	33.5	473–1223

water elimination (Table 2). This loss is related to the decomposition of the immobilized organic silylant chain, and also included the condensation of the remaining silanol groups. The decomposition process is responsible for the increase of siloxane bonds as the temperature increases. The immobilized silicas with propane-1,3-diamine through the heterogeneous, SiHT, and the homogeneous, SiHM, routes presented from room to 450 K, a second physically adsorbed water mass loss. Both materials in the interval of temperature from 450 to 1000 K showed an increase of mass loss that was attributed to the decomposition of the immobilized organic chain molecule, together with the condensation of the remaining silanol groups. The pronounced increase in mass loss for the SiHM matrix, in relation to SiHT, reflects the higher amount of the anchored organic groups, which corroborates with the elemental analysis results [29].

3.2. Cations adsorption

Covalent propane-1,3-diamine molecule incorporation in the precursor agent 3-glycidoxypropyltrimethoxysilane produces variable amounts of pendant groups as a function of the anchoring process. As observed in Table 1, the density of the groups is larger when the immobilization occurred though homogeneous route. The facile epoxide ring opening causes the appearance of Lewis base centers attached to the pendant chain moieties, which, in potential, can extract cations from dilute water solution. Thus, divalent nickel, copper, cobalt and zinc cations were assayed through the batch method and the quantitative interaction effects were obtained via calorimetric titration.

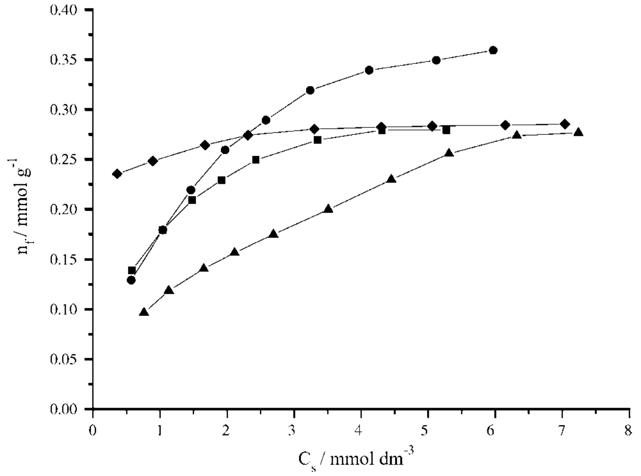

Fig. 5. Isotherms of interaction of cations Cu^{2+} (■), Co^{2+} (●), Ni^{2+} (▲) and Zn^{2+} (♦) with the SiHT matrix.

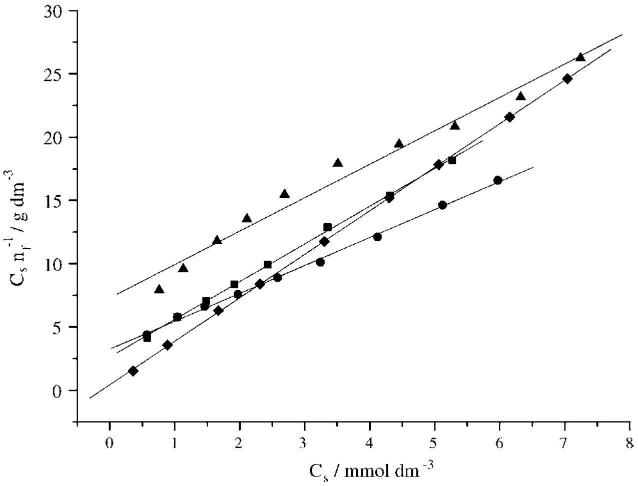

Fig. 6. Linearization of the interaction of cations Cu^{2+} (■), Co^{2+} (●), Ni^{2+} (▲) and Zn^{2+} (♦) with SiHT matrix.

A common characteristic for this adsorption process with these cations is the change in color of the matrices when the solid contacts the salt of all these cations in aqueous solution in the batch process, showing the complexing ability of the modified silicas, to give the characteristic color that varies from intense green for copper, to dark pink for cobalt.

With the purpose of evaluating the complexing effect of the chemically modified silica with the silylant agent 3-glycidoxypropyltrimethoxysilane, the silica obtained was employed in the adsorption process for all cations, which gave a low capacity in the order of 1.0–4.0 μmol g^{-1}. These data

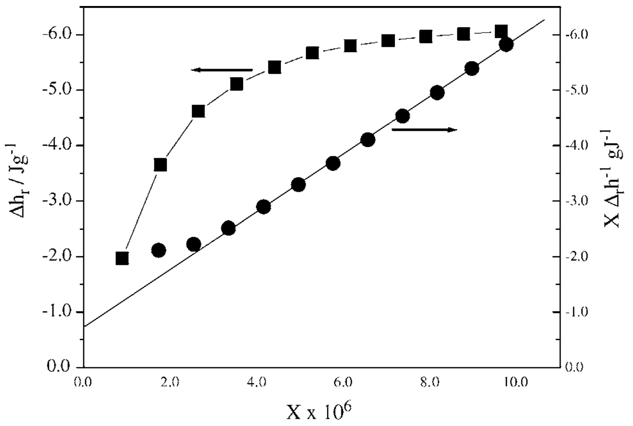

Fig. 7. Calorimetry of the interaction of a suspension of SiHT with 0.0147 mol dm^{-3} copper nitrate, represented by $\Delta_R h$ vs. X plot. The linearization is given by $X/\Delta_R h$ vs. X.

Table 3
Termodynamic data of the interaction of SiHT and SiHM surfaces with divalent nickel, copper, cobalt and zinc nitrates in aqueous solution at 298.15 ± 0.02 K

	M^{2+}	$\Delta_{int}h$	K (10^3)	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	N_s (mmol g^{-1})
SiHT	Ni	4.37 ± 0.2	3.56 ± 0.2	19.88 ± 0.10	8.8 ± 0.4	96 ± 2	0.22 ± 0.06
	Cu	3.48 ± 0.1	2.70 ± 0.1	5.20 ± 0.11	7.2 ± 0.4	42 ± 1	0.67 ± 0.10
	Co	17.50 ± 0.4	3.76 ± 0.2	20.84 ± 0.66	9.3 ± 0.4	101 ± 2	0.84 ± 0.40
	Zn	3.19 ± 0.1	3.30 ± 0.1	7.98 ± 0.01	8.2 ± 0.3	54 ± 1	0.40 ± 0.40
SiHM	Ni	11.09 ± 0.1	3.98 ± 0.2	9.65 ± 0.12	10.0 ± 0.1	66 ± 1	1.15 ± 0.05
	Cu	25.30 ± 0.4	4.32 ± 0.4	15.62 ± 0.57	10.7 ± 0.1	88 ± 2	1.62 ± 0.08
	Co	9.44 ± 0.2	3.87 ± 0.2	10.15 ± 0.15	9.6 ± 0.1	66 ± 1	0.93 ± 0.03
	Zn	8.63 ± 0.1	3.58 ± 0.1	11.98 ± 0.66	8.9 ± 0.4	70 ± 1	0.72 ± 0.01

indicate that the silica chemically modified with epoxysilane did not interfere in the adsorption capacity of the silicas containing the amino group [13].

The outlined adsorption isotherms are very similar for all cations studied, with variation in adsorption intensity, which reflects the availability of the Lewis basic centers attached to the pendant groups, as represented by the diamine molecule matrix incorporated under homogeneous conditions, as shown in Fig. 5. The adsorption isotherm data was adjusted to the modified Langmuir model, expressed by Eq. (2). From the C_s/n_f versus C_s plot, as exemplified in Fig. 6, N_s and b values can be calculated from linear and angular coefficients of the straight line, which gave 0.84; 0.67; 0.40 and 0.22 mmol g^{-1} for cobalt, copper, zinc and nickel, respectively. Based on these data the sequence of adsorption Co > Cu > Zn > Ni were obtained and the SiHT matrix presented the largest cation adsorption capacity, suggesting its use in pre-concentration and separation of cations [30]. For the incorporated diamine molecule matrix from the homogeneous route, SiHM, the higher chelating ability for complexing cations is demonstrated by the values 1.62; 1.15, 0.93 and 0.72 mmol g^{-1}, to give the cation sequence Cu > Ni > Co > Zn. Such interactions can be interpreted due to the transference of cation from solution to the basic centers of the inorganic structures, with simultaneous complexation by using the available amine groups.

3.3. Calorimetry

The useful calorimetric titration technique enables the understanding of the interaction process concerning the cations with the available pendant basic groups attached to an inorganic surface at the typical solid/liquid interface equilibrium, from which the thermodynamic data of the system can be determined [24].

The resulting adsorption thermal effect from the calorimetric titration $\Sigma_r Q$ was calculated by considering the thermal effects of direct titration and those related to the dilution processes, as represented by: $\Sigma_r Q = \Sigma_{tit} Q - \Sigma_{dil} Q$. The thermodynamic data obtained through these titrations were based on adjusting the experimental results to Eq. (2), as represented for copper with the immobilized silica, obtained in a heterogeneous condition, as shown in Fig. 7. The complete data are listed in Table 3. The exothermic enthalpic values reflect the favorable interactive process by using the hard nitrogen Lewis basic centers [31] with the series of divalent cations. The negative free Gibbs energy is in agreement with a spontaneous interaction and the positive entropy also corroborates with the favorable condition for such interactions, as observed before for other systems [23].

The sequence of the enthalpy follows defined orders: Ni > Cu > Co > Zn and Cu > Ni > Co > Zn for the surfaces obtained via heterogeneous and homogeneous routes, respectively. For such kinds of system an Irving–Williams series [32] is expected, which was not observed for the latter case. However, this behavior was detected for other systems [11,33].

The favorable entropic positive values calculated were interpreted as a net effect caused by solvent being released from the inorganic matrices and also those previously found in cation solvation. Thus, the highly solvated cations release water in order to bond with the available nitrogen basic centers and, simultaneously, the water molecules hydrogen bonded to such coordinated centers are also free to the medium, with an increase in entropy. The same behavior was also observed for similar systems, whose interaction processes occurred at the solid/liquid interface [34,35]. By comparing the entropic values, the homogeneous incorporation process gave higher values in comparison to the heterogeneous route. This statement can be coherently interpreted due to the larger number of pendant groups attached in the first process, which needs an increased amount of cations to interact and, consequently, causes an increased number of solvent molecules freed to the medium.

4. Conclusions

Silica gel previously modified with the silylant agent 3-glycidoxypropyltrimethoxysilane incorporated propane-1,3-diamine due to action of the nucleophile nitrogen basic centers, to cause an opening of the epoxide ring. The homogeneous route results in the larger amount of such molecules, which were located on the inorganic support, to enable a better condition to extract cations from aqueous solution. These chemically modified surfaces have the ability to bond through the basic nitrogen atoms to give a good sorption capacity for the divalent cations nickel, copper, cobalt and zinc in the extraction process, simulating the extraction of toxic cations from aqueous solutions. From the thermodynamic point of view, all values are favorable, such as the exothermic enthalpy, the negative free Gibbs energy and positive entropy. The pendant groups covalently attached to the inorganic support act as chelating agents, whose behavior suggests their application as new materials for cation removal from aqueous solutions.

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