

# Useful aminoalcohol molecules incorporated in an epoxide silylating agent for silica organofunctionalization and thermodynamics of copper removal

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Ethanolamine (E) and diethanolamine (D) molecules were incorporated onto a precursor 3-glycidyloxypropyltrimethoxysilane (G) agent, followed by organofunctionalization of the silica gel through homogeneous (A) and heterogeneous (B) routes, to yield SiEA, SiDA, SiEB and SiDB hybrids. These chemically organofunctionalized silicas were characterized by several techniques, including infrared spectroscopy (FTIR), solid-state nuclear magnetic resonance ( $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR using CP/MAS), thermogravimetry and elemental analysis. Based on the obtained nitrogen percentages, the amount of pendant organic groups attached to the inorganic matrices SiEB, SiEA, SiDB and SiDA were calculated as  $0.22 \pm 0.04$ ,  $1.05 \pm 0.03$ ,  $0.29 \pm 0.02$  and  $0.89 \pm 0.01$ , respectively. The infrared spectra presented characteristic bands attributed either to the inorganic framework or to the immobilized chains. Solid-state  $^{13}\text{C}$  NMR results clearly demonstrated that the organic moieties are covalently bonded to the inorganic framework, while  $^{29}\text{Si}$  NMR revealed the silicon atoms with distinct environments, Q and T, in agreement with the covalent attachment of organic moieties. The basic centers attached on the pendant groups have the ability to sorb copper from aqueous solution. This process was adjusted to the Langmuir model, to obtain maximum sorption values of  $0.28 \pm 0.02$ ,  $0.40 \pm 0.02$ ,  $0.29 \pm 0.03$ ,  $0.76 \pm 0.02 \text{ mmol g}^{-1}$  for SiEB, SiEA, SiDB and SiDA hybrids, respectively, from the isotherms. Thermodynamic data obtained from calorimetric titrations reflected the spontaneity of the reactions, which are also enthalpically and entropically favorable for the proposed cation/basic center interactions for these chelating processes at the solid/liquid interface.

## Introduction

Metal pollutant contaminations of water sources is a worrisome feature associated with environmental concerns, due to the fact that a variety of species can affect the ecosystem. An efficient procedure for metal removal is desirable to permit favorable uses of waste water, instead of discharging it to the environment.<sup>1</sup> One of the most widely applied methodologies for such removal is the sorption process.<sup>2</sup> Useful procedures for metal uptake from contaminated water can be obtained by using chemically and mechanically stable solids containing organic pendant chains covalently bonded to them.<sup>3</sup> For this purpose, an intense search has been initiated for synthesizing such new materials, normally denoted inorganic–organic hybrids, that combine distinct properties due to the covalent grafting of organic units onto the inorganic surface, that may be associated with their improvements in many uses, not only for cation removal.<sup>4</sup> The success of these chemically organofunctionalized materials is closely related to a variety of applications such as catalysis,<sup>5</sup> chromatographic determinations,<sup>6</sup> use as chemical

sensors<sup>7</sup> and also as sorbents for hazardous species from solution, such as metallic elements,<sup>8</sup> pesticides,<sup>9</sup> surfactants<sup>10</sup> and dyes.<sup>11</sup>

Silica gel,<sup>12</sup> glass,<sup>13</sup> inorganic phosphates<sup>14</sup> and phyllosilicates<sup>15</sup> are some illustrative examples of supports applied in the synthesis of these hybrid compounds. Among these inorganic polymeric matrices, silica gel deserves special attention, due to the fact that this amorphous oxide presents high thermal, chemical and mechanical stabilities, and offers favorable conditions to chemical modification with appropriate compounds containing desirable organic functions, through the reactions of the large quantity of available silanol groups dispersed on the surface.<sup>12</sup>

To act as a cation sorbent the synthesized hybrid must contain Lewis base centers attached to the pendant chains, covalently bonded to the inorganic structure with chelating properties to permit cation sorption from aqueous or non-aqueous solutions as efficiently as possible.<sup>16</sup> Organic molecules such as ethanolamine and diethanolamine are aminoalcohols that contain basic nitrogen and oxygen centers in their structures and, in principle, have chemical affinity to bond cations. These structural characteristics make these molecules good choices to functionalize inorganic surfaces to produce new materials able to remove specific metal contaminants.

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To design a specific hybrid on silica gel, organofunctionalization with a chosen precursor silylating molecule is required, which must contain trialkoxy groups at the end of the organic chain in order to react with free silanol groups disposed on the silica gel surface.<sup>12</sup> To explore the effect of increase in chain length, followed by the inclusion of basic centers, ethanolamine and diethanolamine were incorporated into the three-membered ring precursor 3-glycidypropyltrimethoxysilane, that enabled synthesis of two new silylating agents.<sup>17</sup>

The anchoring of aminoalcohols on the silica surface has been explored by two different immobilization methodologies: homogeneous and heterogeneous routes. The first process is performed by reacting the precursor organosilane with the desired functional molecule, to yield the new agent. The product of this reaction is then immobilized on the silica surface through the condensation of the alkoxide groups with the silanol groups available on the inorganic surface. In the heterogeneous method the precursor silylating agent is first immobilized onto silica before reacting with the functional molecule to lead to the same final product.<sup>12</sup> These hybrids have the ability to coordinate copper from aqueous solution and the thermodynamic results of cation/basic center interactions were determined through calorimetric titration at the solid/liquid interface.

## Results and discussion

### Characterization

Ethanolamine (E) and diethanolamine (D) molecules inserted into the three-membered ring precursor 3-glycidypropyltrimethoxysilane (G) generate two new silylating agents, which organofunctionalized the silica surface in both the homogeneous (A) and the heterogeneous (B) routes to form new modified hybrids, as shown in Fig. 1.

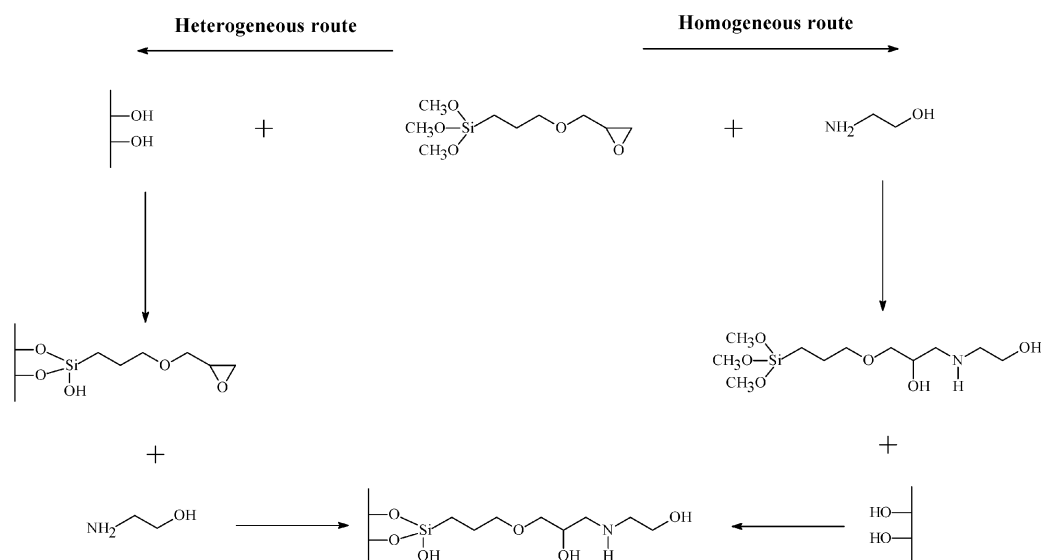
The immobilization of these carbonic chains onto the inorganic polymeric structures was supported by elemental analysis. The amounts of carbon, hydrogen and nitrogen in

**Table 1** Percentages of carbon (C), hydrogen (H), nitrogen (N) and degree of immobilization (*d*) on synthesized compounds (SiX)

SiX	C (%)	H (%)	N (%)	<i>d</i> /mmol g <sup>-1</sup>
SiG	7.73 ± 0.08	1.45 ± 0.03	—	1.07 ± 0.01
SiEB	2.40 ± 0.02	0.68 ± 0.01	0.31 ± 0.06	0.22 ± 0.04
SiEA	10.31 ± 0.10	1.80 ± 0.06	1.47 ± 0.04	1.05 ± 0.03
SiDB	5.46 ± 0.29	1.24 ± 0.06	0.40 ± 0.02	0.29 ± 0.02
SiDA	11.86 ± 0.05	2.50 ± 0.09	1.24 ± 0.01	0.89 ± 0.01

the resultant solids demonstrate the success of the synthesis with the presence of immobilized organic pendant chains being evident. The percentages of nitrogen were used to calculate the quantities of the organic molecules immobilized, which can be expressed as the density of immobilized functional groups or functionalization degree (*d*), as listed in Table 1.

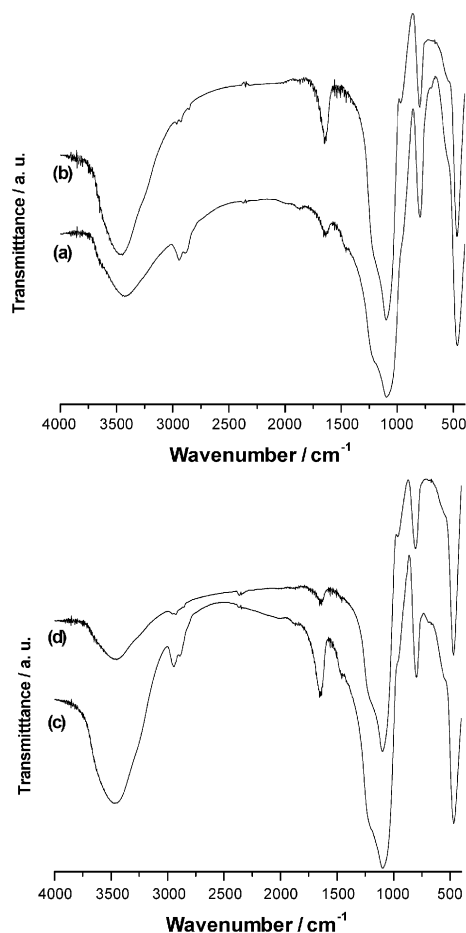
The organofunctionalized silicas prepared through the homogeneous route presented higher degrees of immobilization, indicating also higher efficiency when compared with the heterogeneous process. For example, this tendency is clearly observed for incorporated ethanolamine that gave for homogeneous SiEA and heterogeneous SiEB routes, densities of organic groups of 1.05 ± 0.03 and 0.22 ± 0.04 mmol g<sup>-1</sup>, respectively. Similarly, the same behavior was observed for the hybrids synthesized with diethanolamine, SiDB and SiDA, as given by *d*-values of 0.29 ± 0.02 and 0.89 ± 0.01 mmol g<sup>-1</sup>. This tendency was previously obtained with other similar systems, in spite of the operational facility of the heterogeneous route.<sup>18,19</sup> Another feature to be mentioned is the higher densities of pendant organic chains obtained for the incorporated ethanolamine molecule, when compared with the same synthetic route for diethanolamine. For instance, the density of organic groups with ethanolamine of 1.05 ± 0.03 mmol g<sup>-1</sup> from the homogeneous methodology is higher than that with diethanolamine of 0.89 ± 0.01 mmol g<sup>-1</sup>. This difference could be associated with the higher volume of diethanolamine molecule that creates a steric hindrance in the modification processes as the hybrids are synthesized.



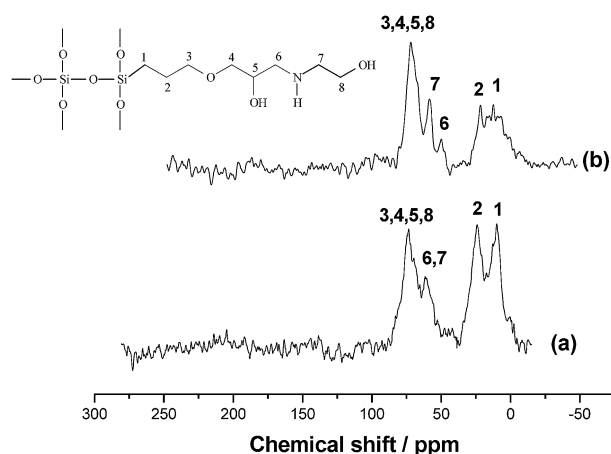
**Fig. 1** Immobilization of ethanolamine molecule onto the silica gel surface by heterogeneous and homogeneous routes.

All the chemically modified silicas from homogeneous and heterogeneous processes present quite similar infrared spectra, showing typical bands associated with the inorganic backbone, as well as with the new functional organic groups attached to them. These spectra are shown in Fig. 2. The large broad bands in the  $3500\text{ cm}^{-1}$  region are attributed to the O–H stretching frequency due to the presence of water molecules sorbed on solid surfaces through hydrogen bonds and those corresponding to unreacted silanol groups, and also those formed from hydrolysis of the free alkoxy groups of the silylating agents.<sup>20</sup> However, in these cases, the bands are enhanced due to the presence of the hydroxyl groups from the original compositions of the ethanolamine and diethanolamine molecules, which are now incorporated in the inorganic structures. Another band present in the spectra is observed at  $1630\text{ cm}^{-1}$  related to the presence of water molecules sorbed on surfaces. The intense band at  $1100\text{ cm}^{-1}$  is attributed to siloxane bond (Si–O–Si) stretching that constitutes the structural skeleton of the inorganic support. The presence of this band suggests that the composition of the initial inorganic skeleton is maintained after the modification processes.<sup>21</sup>

The spectra of chemically modified surfaces containing ethanolamine and diethanolamine molecules from the heterogeneous route, SiEB and SiDB, presented bands in the  $965\text{ cm}^{-1}$  region that are attributed to free silanol group (Si–OH)



**Fig. 2** Infrared spectra of SiEA (a), SiEB (b), SiDA (c) and SiDB (d) hybrids.

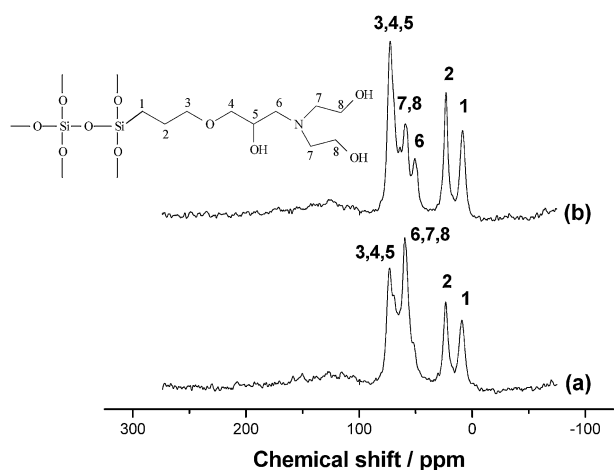


**Fig. 3** Solid-state  $^{13}\text{C}$  NMR spectra of SiEA (a) and SiEB (b) hybrids.

bending, which are more evident than those in SiEA and SiDA spectra. The relationship between the intensities of these bands with the amount of silanol groups dispersed on the surfaces lead to the conclusion that the homogeneous process was more effective than the heterogeneous one, because the modifications on such surfaces were performed through reactions between silanol groups and the available alkoxy groups of the silylating agents. The bands located at  $2945$  and  $2869\text{ cm}^{-1}$  are attributed to symmetric and asymmetric stretching of the C–H bonds.<sup>22</sup> These bands are of fundamental importance to conclude about the success of the immobilization of the silylating agents onto silica surfaces. Bands related to N–H stretching bonds were expected to appear in the spectra of the functionalized hybrids with ethanolamine, but are not observed due to their probable overlap with the broad O–H stretching bands.

Some relevant features associated with the attachment of pendant groups on the inorganic backbone structure of silica gel were achieved through solid-state  $^{13}\text{C}$  NMR spectroscopy, as shown for SiEB and SiEA in Fig. 3. The numbered signals assigned in the inserted formula are in good agreement with the proposed structures of the silylating agents covalently attached to the inorganic framework. For both hybrids, signals at  $10.7$ ,  $24.2$ ,  $61.6$  and  $74.2\text{ ppm}$  were observed, whose peaks were attributed to carbon atoms 1–8.<sup>23</sup> These peaks corroborate the proposals that both materials were obtained as proposed, taking into account that the sequence of peaks are related to the carbons of the pendant groups of the organic moiety of these synthesized hybrids, again confirming the success of the synthetic processes for these materials. The SiEB spectrum presented a signal at  $50\text{ ppm}$  attributed to carbon bonded to the oxygen of the epoxide ring that is not observed in the corresponding spectrum for the SiEA hybrid. This fact might reflect the existence of the epoxy groups that did not react with the basic centers of the ethanolamine molecule. This result confirmed that there are fewer organic groups containing nitrogen atoms attached to the synthesized hybrids through the heterogeneous route, as also indicated by elemental analysis.

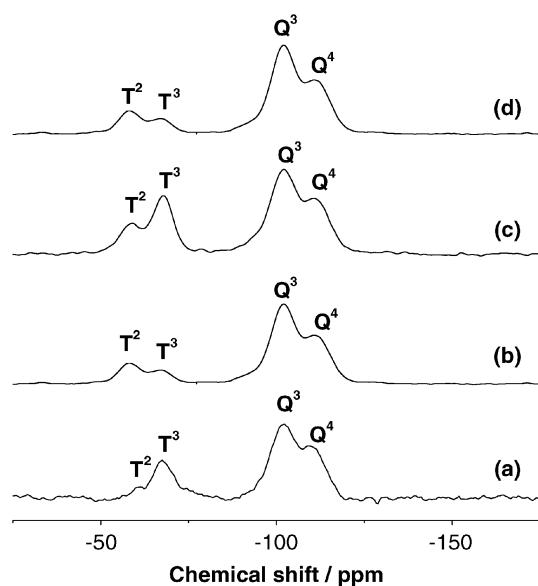
The proposed diethanolamine molecule attachment to the precursor spacer modified agent through the homogeneous and heterogeneous routes is confirmed by  $^{13}\text{C}$  NMR spectra of



**Fig. 4** Solid-state  $^{13}\text{C}$  NMR spectra of SiDA (a) and SiDB (b) hybrids.

SiDB and SiDA, as shown in Fig. 4. The assigned carbon atoms 1–8 related to the organic pendant groups gave signals at 5.5, 23.3, 58.8 and 72.8 ppm in good agreement with a previous report.<sup>17</sup> The spectrum of the hybrid obtained through the heterogeneous route again presented one signal in the 50 ppm region, attributed to the presence of a residual epoxide ring.

Solid-state  $^{29}\text{Si}$  NMR spectroscopy was performed to confirm the covalent bond formed between the silylating agents and the silica gel surface. The spectra for all synthesized hybrids are shown in Fig. 5. A series of signals are attributed to  $[\text{Si}(\text{OSi})_4]$ ,  $\text{Q}^4$ , at  $-110$  ppm and  $[\text{Si}(\text{OSi})_3\text{OH}]$ ,  $\text{Q}^3$ , at  $-100$  ppm. These values are related to the inorganic framework of the silica gel and were essentially identical for all samples with similar chemical shifts.<sup>24</sup> Two signals from T-type silicon atoms appeared at  $-64$  and  $-56$  ppm, the first being attributed to the presence of silicon atoms bonded to aminosilane groups,  $[\text{RSi}(\text{OSi})_3]$ , where R represents the



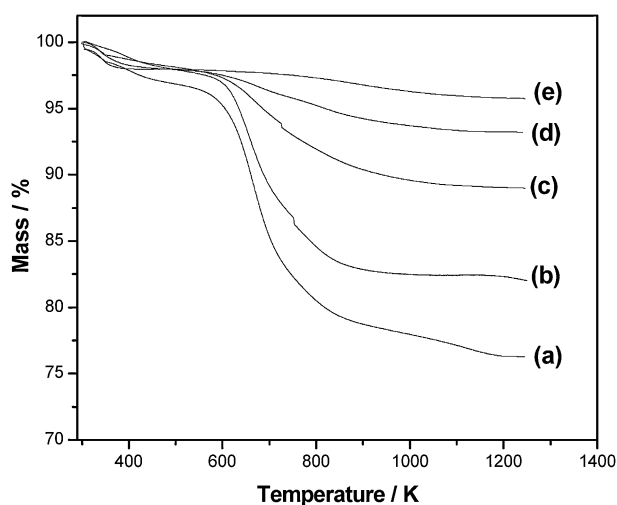
**Fig. 5** Solid-state  $^{29}\text{Si}$  NMR spectra of SiEA (a), SiEB (b), SiDA (c) and SiDB (d) hybrids.

pendant organic chains. Small shoulders observed in the  $-56$  ppm region are attributed to silicon atoms of  $[\text{RXSi}(\text{OSi})_2]$  species, where X is  $-\text{OH}$  or  $-\text{OCH}_3$  groups that were not hydrolyzed. Thus, these two T signals can be assigned to the presence of  $\text{T}^2$  and  $\text{T}^3$  species, respectively,<sup>15</sup> which show the presence of the modified silylating agents attached to the surface of silica and also illustrate the manner in which they are bonded to the surface.

All chemically modified hybrids presented quite similar decomposition patterns, as shown by the thermogravimetric curves in Fig. 6. A small initial 1.0% mass loss in activated silica gel from 298 to 473 K is attributed to the release of water physically sorbed on the surface. The following mass loss of 2.6% reached at 1170 K is related to the condensation of free silanol groups on the surface to form siloxane groups.<sup>25</sup>

The thermogravimetric curve of the SiEA hybrid indicates a first mass loss of 2.1% between 356 to 478 K due to the release of original water molecules physically sorbed on the matrix surface. The second mass loss corresponding to 15.4% from 502 to 930 K is mainly due to the decomposition of the organic group covalently bonded on the silica surface. A total mass loss of 18.0 and 6.8% were then observed for SiEA and SiEB hybrids. The steps of decomposition for SiEA are also illustrated by the derivative curve, as shown in Fig. 7.

The complete thermogravimetric data found for all solids are summarized in Table 2. Based on these values a comparison of these hybrids obtained from homogeneous and heterogeneous methodologies is in agreement with the higher degree of functionalization of SiEA, which corresponds to the better anchoring process on the silica surface when compared to SiEB, as also indicated by elemental analysis. The same comparison can be made between the results obtained for SiDA and SiDB hybrids, which presented total mass losses of 23.7 and 11.0%, respectively. In spite of the lower uptake, the surfaces modified with diethanolamine presented higher total mass loss values because this molecule has a higher intrinsic molar mass value. Again, from the thermogravimetric results



**Fig. 6** Thermogravimetric curves of the chemically organo-functionalized silicas SiDA (a), SiEA (b), SiDB (c), SiEB (d) and pure silica (e).

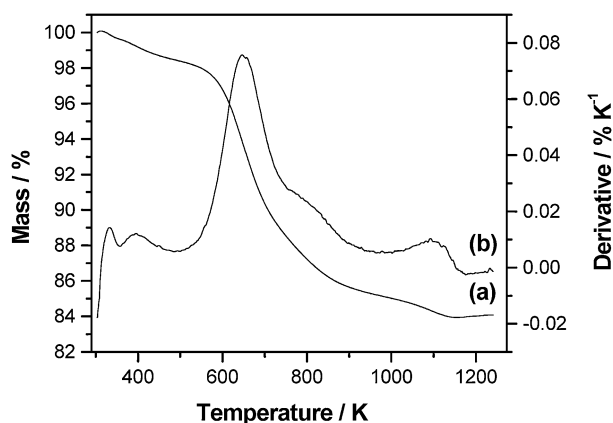


Fig. 7 Thermogravimetric (a) and derivative (b) curves of silica with ethanalamine incorporated through the homogeneous route (SiEA).

Table 2 Values of mass losses ( $\Delta m$ ) undergone by modified silicas (SiX) at specific temperature intervals ( $\Delta T$ )

SiX	$\Delta m$ (%)	$\Delta T/K$
SiEB	2.2	304–489
	4.0	519–950
	0.6	987–1144
SiEA	2.1	356–478
	15.4	502–930
	0.5	1002–1176
SiDB	2.0	323–479
	7.8	528–959
	1.2	1005–1189
SiDA	3.2	312–442
	18.2	517–947
	2.3	980–1187

it is possible to observe that the homogeneous route enabled better organofunctionalization on this inorganic polymeric surface.

### Sorption

The ability of the chemically modified silicas for extracting copper cations was evaluated by measuring the sorption capacities, after stirring the suspension of the functionalized solids with aqueous copper solutions at constant temperature. As expected, the initially white solids changed their original color to blue after sorption. These sorption capacities are related to the availability of nitrogen and oxygen basic centers attached to the pendant chains that act as Lewis centers. Such available pendant chains covalently bonded onto the inorganic surface can chelate cations from aqueous solutions.<sup>26</sup>

Under equilibrium conditions, exchange processes take place at the solid/liquid interface and can be characterized through the number of moles sorbed ( $N_f$ ) per gram of a chosen material. This value is then calculated from the initial number of moles of cation in solution ( $n_i$ ) and those at the equilibrium condition ( $n_s$ ) for a given mass ( $m$ ) of the sorbent, by applying the expression:  $N_f = (n_i - n_s)/m$ .

The sorption isotherm models, represented by the number of moles sorbed ( $N_f$ ), vs. the number of moles at equilibrium per volume of solution ( $C_s$ ) is shown in Fig. 8. Normally, the Langmuir equation is largely used to adjust the sorption data and also is considered as the best fit for these kinds of

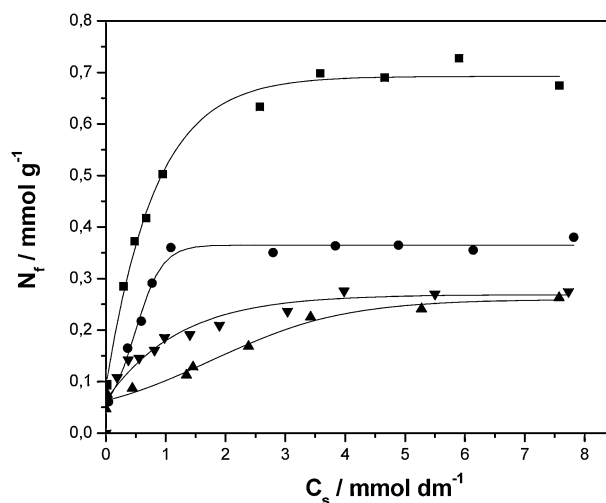


Fig. 8 Isotherms of copper interactions on SiEB (▲), SiDB (▼), SiEA (●) and SiDA (■) surfaces at 298 + 1 K.

isotherms. The Langmuir equation was actually formulated for gas–solids system, which regards that all sorption sites are homogeneously located to form a monolayer with the same probability to sorb gas molecules on the solid surface. However, these assumptions for this model are widely applied and accepted also for liquid–solid systems, when heterogeneous surfaces are considered,<sup>27</sup> as represented by eqn (1).

$$N_f = \frac{N^s b C_s}{1 + b C_s} \quad (1)$$

In this expression  $N_f$  is the number of moles sorbed on the surface per gram,  $N^s$  is the maximum quantity of cations per gram necessary to form a monolayer on the modified surface,  $b$  is a proportionality factor that includes the equilibrium constant for the reaction and  $C_s$  is the equilibrium concentration of the sorbate in solution.

Another widely used descriptive model for sorption applications is the Freundlich-type isotherm, however the equation applied to this process does not give any limit to the sorption capacity, making the amount sorbed reach infinity when the concentration increases, which thus restricted ranges of sorption.<sup>28</sup>

Although widely used, the linear transformation of the Langmuir equation to obtain sorption parameters  $N^s$  and  $b$ , has also been strongly criticized for sorption isotherm fitting.<sup>29</sup> Linearization, while convenient, can create distortions in the error distribution of the data and not yield fully reliable data. On the other hand, several publications describe non-linear regression adjustment as being more suitable for obtaining more correct parameter values and the best isotherm fitting. Also since the development of computer technology the application of non-linear optimization methodology is more amenable,<sup>30</sup> which avoids the creation of any distortion in the original error distribution.

For this present case, the non-linear fitting procedure was thus used in order to acquire the maximum capacity of copper sorption to form a monolayer on the modified surfaces, and enabled the determination of the equilibrium constant values,



**Table 3** Maximum sorption ( $N^s$ ) and thermodynamic data for copper interaction with basic centers attached on inorganic–organic hybrids

Hybrid	$N^s/\text{mmol g}^{-1}$	$r^2$	$-\Delta_{\text{ads}}H/\text{kJ mol}^{-1}$	$10^{-3}K$	$-\Delta G/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
SiEB	$0.28 \pm 0.02$	0.9967	$11.04 \pm 0.03$	$2.1 \pm 0.7$	$16.1 \pm 0.1$	$17 \pm 1$
SiEA	$0.40 \pm 0.02$	0.9987	$19.67 \pm 0.05$	$2.8 \pm 0.6$	$25.4 \pm 0.1$	$19 \pm 1$
SiDB	$0.29 \pm 0.03$	0.9972	$3.70 \pm 0.01$	$0.7 \pm 0.2$	$18.9 \pm 0.1$	$51 \pm 1$
SiDA	$0.76 \pm 0.02$	0.9945	$13.05 \pm 0.01$	$2.0 \pm 0.2$	$18.5 \pm 0.5$	$18 \pm 1$

with  $r^2$  of 0.9867, 0.9836, 0.9529 and 0.9818 for SiEB, SiEA, SiDB and SiDA, respectively.

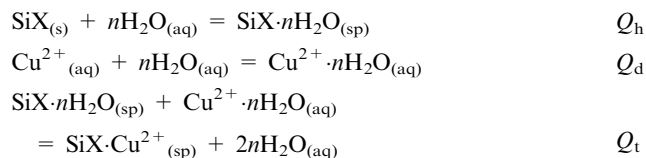
Although a higher degree of grafting was obtained for SiEA of  $1.05 \pm 0.03 \text{ mmol g}^{-1}$ , the total amount of cation sorbed,  $0.40 \pm 0.02 \text{ mmol g}^{-1}$ , was lower than that obtained for the SiDA sample with a degree of immobilization  $0.89 \pm 0.01 \text{ mmol g}^{-1}$ , with sorbed amount of  $0.76 \pm 0.02 \text{ mmol g}^{-1}$ . The maximum sorption capacities for all organofunctionalized hybrids are listed in Table 3. This behavior can be explained, in principle, by the higher number of oxygen basic centers available on the pendant diethanolamine chains. On the other hand, the position of the oxygen atoms at the extremities of the incorporated diethanolamine molecule creates a favorable condition to complex cations. Again, the same kind of comparisons can be observed for the metal uptake capacity of SiEB and SiDB hybrids.

### Calorimetric titration

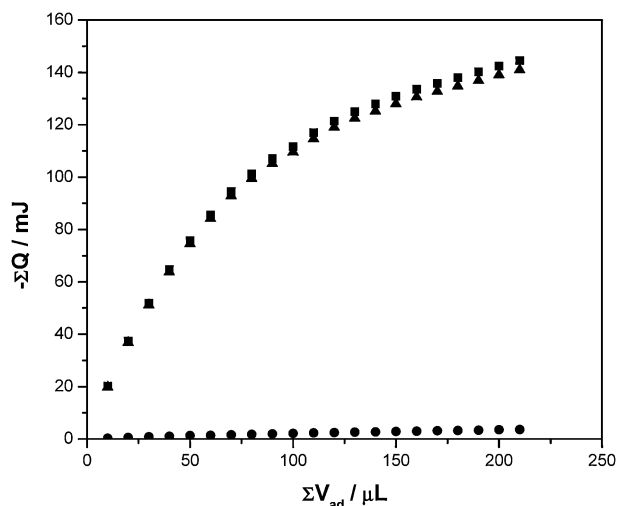
To follow the interactions of the basic centers attached to the organic pendant chains with metallic cation at the solid/liquid interface, samples of all synthesized hybrids were calorimetrically titrated with divalent copper. During each titration the cation solution was gradually added to a suspension of the chemically modified silica until saturation of the surface formed a monolayer. The net thermal effect of sorption ( $Q$ ) was expressed by the difference between the thermal effect of the titration ( $Q_t$ ) and the dilution processes ( $Q_d$ ), since the thermal effect of the hydration of the support ( $Q_h$ ) was null.<sup>31</sup> Under such experimental conditions the net thermal effect of sorption is given by eqn (2). The calorimetric curves of thermal effects of cation titration, cation dilution and the net thermal effect of interaction for sorption process on SiEA are shown in Fig. 9.

$$\sum Q = \sum Q_t - \sum Q_d \quad (2)$$

The thermal effects involved in each step of the titration for any hybrid SiX in suspension (sp) with copper  $\text{Cu}^{2+}$  in aqueous (aq) solution can be represented by the following calorimetric reactions:



The resulting calorimetric values were adjusted to a modified Langmuir equation to calculate the integral enthalpy change involved in the formation of a monolayer per unit of mass of the sorbate,  $\Delta_{\text{mono}}H$ . The Langmuir equation behavior is shown to be a good adjustable model for such heterogeneous systems, as illustrated in Fig. 10 for copper sorption on SiEA

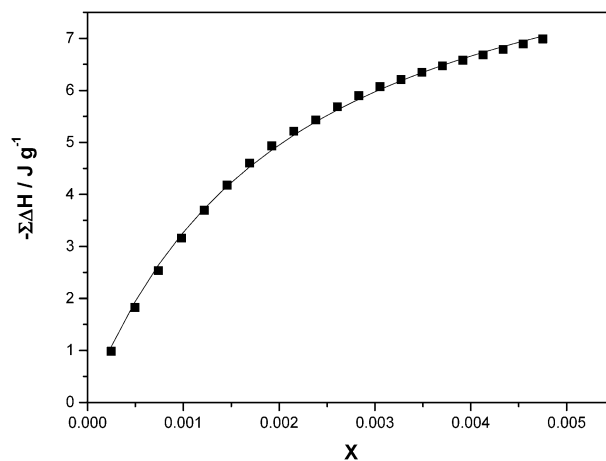


**Fig. 9** Calorimetric titration of 0.02115 g of SiEA in 2.0 cm<sup>3</sup> of deionized water with 0.050 mol dm<sup>-3</sup>  $\text{Cu}(\text{NO}_3)_2$  in the same solvent at  $298.15 \pm 0.20 \text{ K}$ . The experimental points represent the sum of the thermal effects of titration (■), dilution (●) and the net thermal effect (▲).

hybrid.<sup>32</sup> Eqn (3) shows a modified model of Langmuir equation adjusted for calorimetry, as proposed by previous reports.<sup>33,34</sup>

$$\sum \Delta_r H = \frac{\Delta_{\text{mono}} H \theta \sum X}{1 + \theta \sum X} \quad (3)$$

Here  $\sum X$  is the sum of the molar fractions of the remaining metallic cation in solution after interaction,  $\Delta_r H$  is the integral enthalpy of sorption ( $\text{J g}^{-1}$ ) obtained as the quotient of the net



**Fig. 10** Langmuir isotherm obtained from calorimetric titration of 0.02115 g of SiEA with 0.050 mol dm<sup>-3</sup> aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  at  $298.15 \pm 0.20 \text{ K}$ .

thermal effect of sorption and the mass of the sorbate, and  $\Theta$  is a constant of proportionality that also includes the equilibrium constant. Again non-linear regression analysis was used to determine the values of  $\Delta_{\text{mono}}H$  and  $\Theta$ , with the coefficient of correlation  $r^2$  to adjust the curve, as listed in Table 3. The enthalpy change of the interaction process,  $\Delta_{\text{ads}}H$  (Table 3), can be calculated by the expression  $\Delta_{\text{ads}}H = \Delta_{\text{mono}}H/N^s$ .

The Gibbs free energy changes were calculated by the expression  $\Delta G = -RT \ln K$ , where  $K$  is the equilibrium constant for the sorption process, and the entropy change was calculated from  $\Delta G = \Delta H - T\Delta S$ . All these thermodynamic data for the sorption processes for all synthesized hybrids are listed in Table 3.

For all determinations the cation–basic center interactions on the surfaces demonstrated the spontaneity of the proposed reactions, as indicated through the calculated negative  $\Delta G$  values and all  $\Delta_{\text{ads}}H$  values are exothermic in nature, which decrease in the order SiEA > SiDA > SiEB > SiDB, as shown in Table 3.

Taking into account the highest exothermic value,  $-19.67 \pm 0.05 \text{ kJ mol}^{-1}$ , obtained with the SiEA hybrid than for all other materials, it is expected to show the most favorable copper/basic center interaction at the solid/liquid interface. Indeed, the elemental analyses and thermogravimetric data demonstrated a higher degree of organofunctionalization on SiEA followed by SiDA (hybrids both synthesized through the homogeneous route). However, this sequence is also evidenced when energetic values of  $\Delta_{\text{ads}}H$  are evaluated. In addition to the functionalization degree, SiEA presented a higher exothermic value than SiDA because nitrogen is a softer basic center when compared with oxygen and it is expected that copper ions are sorbed preferentially to the former.<sup>35</sup> Thus interaction should be more effective in SiEA than in SiDA, although the latter hybrid possesses one more oxygen basic site and it is able to sorb a higher amount of cations, due to the greater availability in SiEA of the nitrogen atoms in the organic chain attached to the surface. The presence of two oxygen atom at the extremity of the organic chain might generate a steric hindrance in SiDA, making it more difficult for copper to interact with the nitrogen basic sites of pendant organic chains.

The same tendency is observed when the energetic data of SiEB and SiDB are compared. Again, the organofunctionalized hybrid with ethanolamine presented a higher exothermic value, leading to the conclusion that energetic effects of copper sorption on these surfaces are directly related to the density of pendant organic groups and to the availability of nitrogen basic centers.

The entropic results presented positive values suggesting an increase of the disorder of the final systems after the sorption processes. The entropic contribution for this system is closely related to solvent displacement (i) of molecules initially hydrogen bonded to nitrogen and oxygen basic centers attached to the pendant chains and (ii) water molecules bonded to the copper coordination sphere. As the cation/basic center interactions take place during the progress of reaction at the solid/liquid interface, the amount of free water molecules increases so leading to an increase in entropy. Similar behavior has also been observed for interactive effects involving similar heterogeneous systems.<sup>33</sup>

This set of thermodynamic data is in agreement with the favorable condition of copper/basic center interactions for all organofunctionalized synthesized hybrids, with highest preference of the reaction with SiEA hybrid, despite the less favored entropic gain in this case.

## Experimental

### Chemicals

Silica gel (Fluka) with particle sizes of 0.063 to 0.200 mm, with average pore diameters of 6.0 nm and pore volumes of  $0.75 \text{ cm}^3 \text{ g}^{-1}$  was activated by refluxing  $1.0 \text{ mol dm}^{-3}$  with hydrochloric acid for 4 h to remove any impurities, then filtered, repeatedly washed with water until the filtrate was neutral, and dried under vacuum at 423 K for 12 h to remove sorbed surface water. Further, it was heated in a stream of dry nitrogen for 2 h and was immediately used. The precursor silylating agent 3-glycidoxypolytrimethoxysilane (Aldrich) and ethanolamine (Vetec) were reagent grade. Diethanolamine (Vetec) was purified by distillation under reduced pressure. All other reagents, such as copper nitrate hexahydrate (Vetec), methanol and toluene were also used without prior purification. Copper nitrate solutions were prepared in deionized water (ultra-pure Milli-Q Millipore,  $18.2 \text{ M}\Omega \text{ cm}$ ).

### Synthesis

**Heterogeneous route.** In the first step, a sample of 10 g of silica gel was suspended in  $100 \text{ cm}^3$  of dry toluene followed by dropwise addition of  $10.0 \text{ cm}^3$  (45.3 mmol) of 3-glycidoxypolytrimethoxysilane (G) and the mixture was allowed to react under continuous stirring and a dry nitrogen atmosphere at 343 K for 72 h. The suspension was filtered off, washed with methanol and dried under vacuum for 24 h, to give a product denoted SiG. In the subsequent step, a suspension of 5.0 g of SiG was reacted with 1.38 g (22.6 mmol) of ethanolamine (E) in  $100 \text{ cm}^3$  of toluene. To complete the incorporation of this molecule into the three-membered epoxide ring, the suspension was kept under reflux and mechanically stirred for 72 h at 343 K.<sup>18</sup> The final product was filtered off, washed with methanol and dried under vacuum, to give the solid denoted SiEB. An identical procedure was used with  $2.17 \text{ cm}^3$  (22.6 mmol) of diethanolamine (D) to give product SiDB.

**Homogeneous route.** To a solution of  $5.0 \text{ cm}^3$  (22.6 mmol) of the precursor 3-glycidoxypolytrimethoxysilane dissolved in  $100 \text{ cm}^3$  of methanol,  $1.38 \text{ cm}^3$  (22.6 mmol) of ethanolamine was added and the mixture was stirred under dry nitrogen atmosphere for 72 h at 343 K. The product formed, denoted GE, was added to a suspension of 5 g of activated silica gel in  $100 \text{ cm}^3$  of dry toluene. This suspension was mechanically stirred under reflux for 72 h at 343 K in a dry nitrogen atmosphere.<sup>19</sup> The final product was filtered off, washed with methanol, dried under vacuum and denoted SiEA. The same procedure was used for diethanolamine by using  $2.17 \text{ cm}^3$  (22.6 mmol) to give solid SiDA.

**Sorption.** For batchwise copper ion sorption, samples of approximately 20 mg of each functionalized silica were suspended in a series of flasks containing aqueous copper

nitrate solutions, varying in concentration from 0.12 to 8.0 mmol dm<sup>-3</sup>, to give a pH 5. These samples were left under stirring for 4 h at 298 ± 1 K, a previously established time. The amount of copper in the supernatant was measured and the obtained data were adjusted to the Langmuir equation.

### Calorimetry

The calorimetric titrations were followed using a differential isothermal LKB 2277 microcalorimetric system. The titration consisted in suspending a sample of approximately 20 mg in 2.0 cm<sup>3</sup> of water inside a steel vessel, which was vigorously stirred at 298.15 ± 0.20 K. After equilibrium, the cation solution was incrementally added through a microsyringe coupled to the calorimetric vessel. For each increment, the thermal effect was recorded and the end of the titration was indicated by a constant thermal effect. The same procedure was employed to monitor the thermal effect of cation dilution without the solid and also of adding water to the chemically modified silica, which gave a null value. By combining these two heat outputs, the net value can be determined. The change in enthalpy associated with the cation–hybrid interaction was obtained by adjusting the batch process data to a modified Langmuir equation.

### Instrumentation

Calculations of the amount of organic pendant chains immobilized onto silica gel surface were based on the nitrogen contents determined through elemental analysis on a Perkin Elmer model 2400 elemental analyzer.

Infrared spectra of the samples in KBr pellets were performed on a Bomem MB-Series FTIR spectrophotometer by accumulating 40 scans, in the 4000 to 400 cm<sup>-1</sup> range with 4 cm<sup>-1</sup> resolution.

Nuclear magnetic resonance spectra in the solid state were obtained with a Bruker AC 300/P spectrometer at room temperature, by assaying approximately one gram of the solid sample compacted into a 7 mm zirconium oxide rotor. The measurements were performed at 75.47 and 59.61 MHz for carbon and silicon, respectively, with the magic angle spinning (MAS) technique at 4 kHz. In order to increase the signal to noise ratio, the cross-polarization (CP) technique was applied. NMR spectra of <sup>13</sup>C and <sup>29</sup>Si were obtained with pulse repetitions of 1 and 3 s and contact times of 1 and 3 ms, respectively.

The thermogravimetric curves were obtained with a TA instrument, coupled to a model 1090 B thermobalance, by using a heating rate of 0.167 K s<sup>-1</sup> in an argon atmosphere under a flow of 30 cm<sup>3</sup> s<sup>-1</sup>, varying from room temperature to 1273 K.

Cation sorption was calculated from the difference between the initial concentration in the aqueous solution and that found in the supernatant at equilibrium by using an inductively coupled plasma optical emission spectrometer (ICP-OES) Perkin Elmer model 3000 DV. For each experimental point the reproducibility was checked by at least one duplicate run.

Thermal effects at the solid–liquid interface were obtained with an isothermal calorimeter, Thermometrics LKB 2277. The calorimetric titration of the copper solution onto the

modified surface was performed by injection of the solution with an auxiliary pumping system, with a series of fixed volumes of 10.0 mm<sup>3</sup> incrementally added. After 2 h the baseline was reached.

### Conclusions

Four new inorganic–organic hybrids synthesized through homogeneous and heterogeneous routes were applied towards copper sorption. The effectiveness of such organofunctionalization depends on the precursor reagents ethanolamine and diethanolamine, which were incorporated into the three-membered ring of the 3-glycidoxypolytrimethoxysilane silylating agent. IR and <sup>13</sup>C and <sup>29</sup>Si NMR clearly supported the attachment of the pendant chains on the polymeric silica surface. Although both employed routes produced identical hybrids, the anchored amounts of the functional molecule from the homogeneous process were greater than from the heterogeneous conditions. However, the low degree of functionalization for the diethanolamine derivatives is expected due to steric hindrance at nitrogen atom of this molecule.

The basic centers attached to the pendant organic chains are more effective to coordinate copper on the hybrid synthesized through diethanolamine incorporated onto the precursor in homogeneous route, due to the greater degree of organofunctionalization and also to the fact that the oxygen basic centers are located at the extremity of the organic chains, which also favor the reactions. The cation removal process, evaluated through calorimetric titration, demonstrated a spontaneous process for basic center/copper interactions with favorable exothermic enthalpies and positive entropies at the solid/liquid interface.

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