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# INTERACTION OF DIVALENT CATIONS Zn, Cd AND Hg ON SURFACE OF SILICA GEL WITH AMINOETHANETHIOL AS EVALUATED BY CALORIMETRIC TITRATION

*Vera Lucia da S. Augusto Filha, Oberto G. da Silva, J. R. da Costa, Albaneide F. Wanderley, Maria G. da Fonseca and Luiza N. H. Arakaki**

Departamento de Química, CCEN, Universidade Federal da Paraíba, 58059-900 João Pessoa, Paraíba, Brazil

Calorimetric titration was applied to study the interaction of zinc, cadmium and mercury on surface of silica gel modified with 2-aminoethanethiol, using 3-chloropropyltrimetoxysilane as precursor silylating agent. The anchored Sil–SN$H_2$ surface gave 0.70 mmol $g^{-1}$ of molecules covalently bonded per gram of silica. This surface displayed a chelating moiety containing sulfur and nitrogen basic centers, which are potentially capable of extracting cations from aqueous solutions, such as $MCl_2$ ($M$=Zn, Cd, Hg). This process of extraction was carried out by the batch method when similar chemisorption isotherms were observed for all cations.

The data were adjusted to modified Langmuir equation. The sequence of the maximum retention capacity was Hg>Cd>Zn. The processes of cation interactions showed exothermic enthalpies. The calculated $\Delta G$ values are in agreement with the spontaneity of the proposed reactions and conformed to the values found by using Langmuir model applied to these systems. The endothermic entropic values, as expected, indicated that the reactions are favorable.

***Keywords:*** *2-aminoethanethiol, calorimetry, divalent metal of group 12, silica gel, thermochemical data*

## Introduction

Pollution of drinking water and foods by heavy metals, particularly mercury, cadmium, chromium, and lead, has deleterious effects on the health of living organisms, even if their concentration is very low. Heavy metals are not biodegradable like biologically organic pollutants [1–3]. Therefore, the removal of heavy metals is very important in environmental remediation and cleanup efforts. Treatment process for contaminating metals include chemical precipitation, membrane filtration, ion exchange, and coprecipitation/adsorption, which have been applied for many years. Several adsorptive compounds can capture metal ions from solutions, including activated charcoal, zeolites, and clays. An inherent disadvantage of these materials is their low loading capacities and relatively small metal ion binding constants. Nevertheless, to improve the removal efficiency and adsorption capacity of these naturally occurring adsorbents, modification of surfaces has been necessary [4] by coupling chelating ligands to support matrices consisting of inorganic oxides, like silica, alumina, clay, or organic polymers [5]. Such functionalized materials have relatively high metal ions loading capacities and strong binding affinities for selected metal ions. Composites based on inorganic silica matrix and chelating organic pendant groups are one of the most used to remove metal ions from water and other solvents [1, 6–8] due to the abundance, high thermal and chemical stabilities and specific bonding abilities of desired functional organic groups attached on silica surface [1, 9, 10]. After the modification, the surface properties of silica are changed to interact with metal ions and/or organic molecules, in order to be used as chemical sensor, ion exchange coating, for high-performance liquid chromatography and gas chromatography in many different investigations [11, 12] in catalysis [13, 14], for treatment of waste and toxic effluents produced by a variety of chemical processes [13] and other applications.

Our earlier publications reported the immobilization of 2-aminoethanethiol and the cation adsorbing abilities for divalent Cu, Ni and Co [15]. The main objective of this publication is to report the structure of the modified silica gel and the energetics of the basic center/cation interaction with grafted 2-aminoethanethiol on silica for divalent mercury, cadmium and zinc in aqueous solution.

## Experimental

### *Materials*

All solvents used were reagent grade and purified by distillation. Silica gel (Aldrich) with a particle size in the range 70–230 mesh, a median pore diameter of

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* Author for correspondence: luiza_arakaki@yahoo.com.br

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*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

60 Å, and a pore volume of 0.75 $cm^3$ $g^{-1}$ was activated as described elsewhere [8, 10, 15]. The silylating agent 3-chloropropyltrimethoxysilane (Aldrich) was used without purification. Solutions of all divalent cations in form of chlorides were prepared from reagent grade salts.

### Immobilization of 2-aminoethanethiol onto the silica surface

In this procedure, 30.0 g of the activated silica was suspended in 100.0 $cm^3$ of dry toluene. To this suspension 15.0 $cm^3$ of 3-chloropropyl trimethoxysilane (75.0 mmol) was dropwise added. The mixture was mechanically stirred under reflux of the solvent under an inert dry atmosphere of nitrogen for 72 h [15]. The resulting modified silica, 3-chloropropylsilica gel (Sil–Cl) was filtered and washed with toluene, double distilled water, and ethanol. The product (Sil–Cl) was dried under vacuum for 8 h at 393 K. In the next step, 10.0 g of this modified silica was suspended in 50.0 $cm^3$ of dry toluene. This suspension was maintained under solvent reflux with mechanical stirring, while 9.09 g of 2-aminoethanethiol hydrochloride (0.080 mol) and 15.0 $cm^3$ of triethylamine were added, under a dry atmosphere of nitrogen. The mixture was allowed to stand for another 24 h. After cooling the solid ($Sil–SNH_2$) was filtered, washed with toluene, double distilled water, and ethanol, and dried under vacuum at 0.10 mm Hg (13.3 Pa) for 8 h at 350 K.

### *Methods*

The degree of 2-aminoethanethiol attached to the silica surface was estimated by analyzing the corresponding nitrogen content by Kjeldhal method. Infrared spectra of the compounds were obtained in an MB-Bomem FTIR spectrophotometer, using KBr pellets in the range of 4000 to 400 $cm^{-3}$, with a resolution of 4 $cm^{-1}$. $^{13}C$ NMR spectra for solid samples were obtained on an AC/300P Bruker spectrometer with cross-polarization and magic angle spinning at a frequency of 75.47 MHz.

Mass loss measurements were performed on a DuPont 951 thermobalance, using 5 to 15 mg of sample under argon atmosphere, with a programmed heating rate of 10 K $s^{-1}$.

### Adsorption isotherms

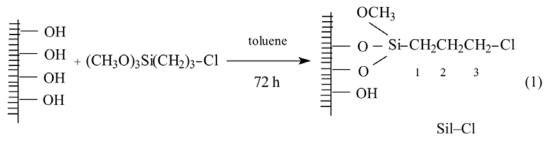
The adsorption isotherms were obtained through batch method, by suspending of 50.0 mg of modified silica samples in 20.0 $cm^3$ of an aqueous solution, containing one of the cations at several different concentrations, being mechanically stirred for 3 h at 298±1 K. The adsorbed amount was estimated by the difference between the initial concentration in aqueous solution and that was found in the supernatant, by using a GBC, model 908 AA atomic absorption spectroscopy apparatus. Only Hg(II) was estimated by EDTA complexometric titration. In every case, all samples were analysed in triplicate.

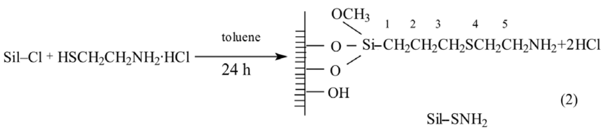
### Calorimetry

The thermal effect evolved from cation-basic center interaction on anchored pendant groups at the solid/liquid interface was measured in an isoperibol Hard Scientific calorimeter, Model 4285 [8, 16]. A sample of functionalized silica, varying in mass from 15.0 to 50.0 mg was suspended in 25.0 $cm^3$ of water under stirring at 298.15±0.02 K. Thermostated solutions of the cations, in the 1.05 to 1.20 mmol $dm^{-3}$ range, were incrementally added into the calorimetric vessel and the thermal effect ($Q_t$) was then measured [8, 16]. Under the same experimental conditions, the corresponding thermal effect of dilution of the cation was obtained in the absence of the support ($Q_d$). The thermal effect of the hydration of the immobilized silica in water was evaluated as before [8, 16]. The net thermal effect of adsorption ($\Sigma Q_r$) was obtained from equation: $\Sigma Q_r = \Sigma Q_t - \Sigma Q_d$.

## Results and discussion

The first stage when anchoring the designed molecule, consisted in reacting the activated silica to obtain the Sil–Cl precursor, as represented by Eq. (1). Onto this immobilized surface a subsequent reaction of 2-aminoethanethiol hydrochloride yielded the final silanized silica represented in Eq. (2):





Immobilization of 2-aminoethanethiol was confirmed by elemental analysis of nitrogen, $^{13}C$ solid-state NMR spectra, infrared and thermogravimetric curves.

The elemental analysis of modified silica, $Sil–SNH_2$, obtained with nitrogen basic atoms on the pendant groups, gave 0.98% of nitrogen through the Kjeldhal method, which corresponds to 0.70 mmol of these groups per gram of silica [15].

The thermogravimetric curve of the activated silica gel shows in Fig. 1 an initial 1.0% mass loss at 298 and up to 473 K, which resulted from the release of surface adsorbed water. It was followed by a 2.60% of mass loss at 1170 K connected to condensation of free silanol groups on the surface, yielding siloxane groups [8, 10, 15]. For the Sil–Cl compound three mass loss stages occurred. The first stage occurred between 323 and 438 K, with a 0.6% of mass loss resultted from the release of the physically adsorbed water. The second one, which occurred in the 506–670 K range, had a 3% mass loss due to the decomposition of the organic groups covalently bonded on the silica surface. The last stage which began at 670 and lasted up to 1170 K was due to the condensation of the remaining silanol groups to produce siloxane groups. The immobilized compound Sil–$SNH_2$ showed the first mass loss of 0.60% between 320 and 423 K, which was also related to water adsorption, as happened with the untreated silica gel. The second and third mass losses were 7.2 and 4.9% in 433–733 K range and from this temperature to 962 K, respectively, were related to the anchored organic groups on silica surface. The condensation of silanol groups started from 953 K to give siloxane groups in the inorganic structure.

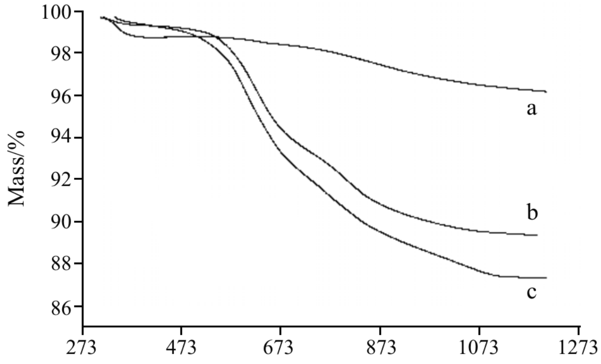


**Fig. 1** TG curves for a – silica gel, b – modified with 3-chloropropyltrimetoxysilane (Sil–Cl) and c – immobilized with 2-aminoethanethiol

The solid-state carbon NMR spectra of the final immobilized surface, Sil–$SNH_2$, gave a series of peaks, the methoxy carbon groups at 58.0 ppm and those attributed to carbons 1 and 2 at 11.2 and 23.3 ppm, respectively. The equivalent carbons 3 and 4 presented a peak at 33.6 ppm and finally, the peak at 40.0 ppm was assigned to carbon 5 [8, 10, 15], as it is shown in Fig. 2.

In the infrared spectra for the modified surfaces Sil–Cl and Sil–$SNH_2$, obtained from Eqs (1) and (2), the characteristic CH stretching vibration modes at 2846 and 2955 $cm^{-1}$ were observed. Other vibrations, related to NH bands, which are normally weak, are obscured by the presence of the remaining water molecules or silanol groups bonded to silica surface. However, a CN stretching band occurred at 1600 $cm^{-1}$. The second unequivocal feature in favor of the proposed mechanism described in Eq. (2) is the absence of a band related to the SH stretching frequency, which should be detected near 2550 $cm^{-1}$ [8, 15–17].

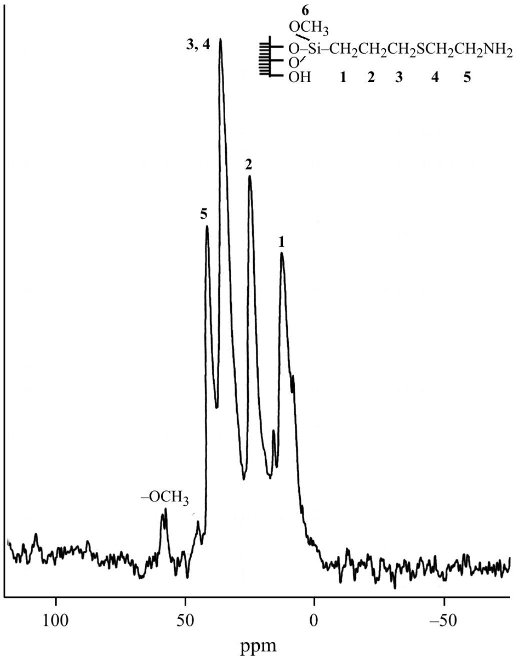


**Fig. 2** $^{13}C$ NMR-CPMAS spectrum of silica modified with 2-aminoethanethiol

The immobilized surface, Sil–$SNH_2$, acts also as a chelating agent for divalent zinc, cadmium, mercury, dissolved in aqueous solutions [10, 16, 17] as shown in Table 1. Adsorption of Cu(II), Ni(II), Co(II) and their ($n_f$) values, previously reported [15] were 0.69±0.03, 0.35±0.02 and 0.62±0.04, respectively. The number of adsorbed moles ($n_f$) was calculated by: $n_f=(n_i-n_s)/m$, where, $n_i$ and $n_s$ are the beginning of the reaction and the supernatant after equilibrium, respectively, and $m$ is the mass of the modified silica. The ($n_f$) values found were 1.25±0.02, 0.96±0.01 and 0.74±0.02 mmol $g^{-1}$ for Hg(II), Cd(II) and Zn(II), respectively. The adsorption isotherms are very similar to the three metals (Fig. 3) and are well-fitted by a modified Langmuir model. The *b* listed in Table 1 suggests that direct adsorption occurs between the cations and the pendant groups containing the basic centers immobilized on surface [8]. These values are larger for zinc, suggesting a high thermodynamic stability.

The modified matrix, Sil–$SNH_2$, containing two basic centers, is made up of one characteristically soft base of sulfur and another one of nitrogen that behaves as a hard base [18, 19], which interacts with divalent metals such as Zn, Cd and Hg. The Hg(II) cation being softer than the other two cations, generates

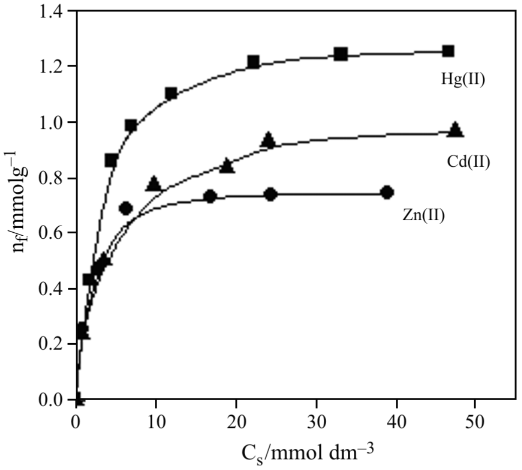


**Fig. 3** Adsorption isotherms of divalent cations on anchored silica gel surfaces containing the 2-aminoethanethiol, in aqueous solutions, at 298±1 K

a pronounced adsorption capacity. The Zn(II) cation is less soft than the two other cations so, the number of adsorbed moles for zinc was smaller than for mercury and cadmium. Zn(II) belongs to the first row of transition metals together with Cu(II), Co(II) and Ni(II). Zn(II) and Cu(II) are classified as 'intermediate' [18, 19]. Ni(II) and Co(II) are classified as hard cations, according to the softness of parameters of ions ($\sigma_M$) suggested by Marcus [19].

In early study of adsorption of divalent Cu, Ni and Co [15] on the same Sil–SNH$_2$ surface, demonstrated that these series of cations adsorbs less than Zn(II), Cd(II) and Hg(II), which are in agreement with $\sigma_M$ [19]. Soft cations have a positive softness parameter $\sigma_M$ and the hard ones, a negative $\sigma_M$ [19]. Thus, the $\sigma_M$ for divalents Hg, Cd, Cu, Zn, Ni and Co are +1.28, +0.59, +0.39, +0.37, –0.11 and –0.18, respectively [19]. The adsorption capacity followed the sequence Hg>Cd>Zn>Cu>Ni>Co for Sil–SNH$_2$ surface [15]. So, the interactive effect of mercury on the Sil–SNH$_2$ matrix is much more effective than for other cations. This feature was also observed in other modified surfaces containing thiol groups [7, 10, 20, 21].

**Table 1** Amount of adsorbed cations ($n_f$), maximum adsorption ($n^s$), constant ($b$) and correlation coefficient ($r$) for the adsorption of MX$_2$, by immobilized 2-aminethanethiol on silica at 298±1 K

| MXl$_2$ | $n_f$/ mmol g$^{-1}$ | $n^s$/ mmol g$^{-1}$ | $b$/ dm$^3$ mol$^{-1}$ | $r$ |
|---|---|---|---|---|
| ZnCl$_2$ | 0.74±0.02 | 0.77±0.02 | 1286 | 0.9995 |
| CdCl$_2$ | 0.96±0.01 | 1.03±0.01 | 0971 | 0.9991 |
| HgCl$_2$ | 1.25±0.02 | 1.33±0.02 | 0747 | 0.9995 |

$\Sigma Q_r$ values were fitted with a modified Langmuir equation [8, 10, 17] to calculate the integral per unit mass of adsorbate $\Delta_{mon}H$.

$$\frac{\Sigma X}{\Sigma \Delta_r H} = \frac{1}{(K-1)\Delta_{mon} H} + \frac{\Sigma X}{\Delta_{mon} H} \tag{3}$$

where $\Sigma X$ is the sum of the mole fraction of the cation in solution after adsorption, and $X$ is obtained for each point of the titration by the modified Langmuir equation (Eq. (3)); $\Delta_r H$ is the integral enthalpy of adsorption (kJ mol$^{-1}$) obtained by dividing the thermal effect resulting from adsorption ($Q_r$) by the number of moles of the adsorbate; and $K$ is a proportionality constant that also includes the equilibrium constant. By using the slope and intercept values from $\Sigma X/\Delta_r H$ *vs.* $\Sigma X$ plot, it was possible to obtain the $\Delta_{mon}H$ value. The enthalpy of adsorption $\Delta_{ads}H$ could be calculated by means of the expression $\Delta_{ads}H=\Delta_{mon}H/n^s$. From these $K$ values, $\Delta G=-RT\ln K$, and from $\Delta G=\Delta_{ads}H-T\Delta S$, the entropy change can be calculated. These values are listed in Table 2.

**Table 2** Thermodynamic data for the interaction of divalent metal with Sil–SNH$_2$, at 298.15±0.02 K

| MXl$_2$ | $-\Delta H$/ kJ mol$^{-1}$ | $-\Delta G$/ kJ mol$^{-1}$ | $\Delta S$/ J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| HgCl$_2$ | 1.03±0.01 | 28.86±0.01 | 93.00±1.0 |
| ZnCl$_2$ | 0.20±0.01 | 29.83±0.02 | 99.39±1.0 |
| CdCl$_2$ | 0.09±0.02 | 27.44±0.01 | 92.00±1.0 |

The thermodynamic data in Table 2 demonstrate that organofunctionalized silica form stable complexes with these divalent cations. The cation-basic center interaction with 2-aminoethanethiol pendant group showed negative enthalpic values for mercury, cadmium and zinc. The cation-basic center interaction was spontaneous, i.e. it had negative $\Delta G$ values. The entropy change makes a significant contribution to the formation of these complexes.

## Conclusions

Silica gel modified with 2-aminoethanethiol presents the ability to bond through the basic sulfur and nitrogen atoms to give a good sorption capacity for the divalent cations mercury, cadmium and zinc in the extraction process, simulating the extraction of toxic cations from aqueous solutions.

The negative values obtained from the Gibbs free energy for all of these systems are in agreement with a clearly evident spontaneity, in the occurrence of favorable adsorptions for all interactive processes.

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