

## Thiol-Anchored Silica and its Oxidized Form - Some Divalent Cations Chemisorbed in Aqueous and Non-Aqueous Solvents

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O agente sililante 3-trimetoxisilil-1-propanotiol foi imobilizado sobre sílica gel em xileno, e essa sílica modificada foi também oxidada com solução aquosa de permanganato. Ambas as sílicas foram caracterizadas por análise elementar, infravermelho, termogravimetria e ressonância de carbono no estado sólido. Através da análise de enxofre foram encontrados 0,98 mmol de grupos tióis e um quarto desses grupos na forma oxidada por grama do suporte, respectivamente. Esses grupos são sensíveis à adsorção pelo método de batelada dos seguintes cátions divalentes: níquel, cobalto, cobre e mercúrio tanto em meio aquoso como não aquoso. Dentre esses cátions, o mercúrio é o mais fortemente adsorvido tanto em etanol como em água, quer na sílica de forma tiol ( $7,46$  e  $8,55 \times 10^{-4} \text{ mol g}^{-1}$ ), quer na sílica oxidada ( $4,15$  e  $5,21 \times 10^{-4} \text{ mol g}^{-1}$ ).

The silylating agent 3-trimethoxysilyl-1-propanethiol was immobilized on silica gel in xylene and this modified silica surface was also oxidized in water with a permanganate solution. Both silicas were characterized by elemental analysis, infrared spectroscopy, thermogravimetry and carbon NMR in solid state. Sulphur analysis showed 0.98 mmol of thiol groups and one fourth of these as oxidized groups per gram of support. These groups chemisorb in batches according to the following divalent cations: nickel, cobalt, copper and mercury from both aqueous and non-aqueous solvents. Mercury is the most adsorbed cation for thiol ( $7.46$  and  $8.55 \times 10^{-4} \text{ mol g}^{-1}$ ) and the oxidized ( $4.15$  and  $5.21 \times 10^{-4} \text{ mol g}^{-1}$ ) silicas in ethanol and water solutions, respectively.

**Keywords:** silica gel, immobilization, 3-trimethoxysilyl-1-propanethiol, chemisorption, thiol-modified silica

### Introduction

In recent years there has been a pronounced tendency to utilize mechanically stable synthetic<sup>1</sup> or natural<sup>2</sup> matrices in many applications. One of the properties explored is related to the adsorption of trace elements onto acidic surfaces, taking into account pre-concentration or separation operations. From a complex mixture, a single element or a series of similar elements can be separated and quantitatively determined. Among the different adsorbents, activated carbon<sup>3</sup> and various materials with chelating agents supported on the surface<sup>4,5</sup> have received great attention. The advancement in this field is associated with the silylation process, which is employed to generate products of coupling agents, to permit the fixation of a reagent that is able to fulfill predetermined specific applications<sup>6,7</sup>. Silane coupling agents are a group of chemicals which facilitate the bonding of otherwise nonbonding surfaces. Silica gel is

one of the most favorable inorganic supports which serves for this kind of reaction<sup>7</sup>. This fact is related to the existence of silanol groups on the surface, which interact with the alkoxide groups of the agent to form a covalent bond with the surface<sup>8</sup>. Thus, the ligand-silica formed gives a set of properties to the surface, which differs considerably from the original matrix<sup>9</sup>.

The immobilization of chelating groups on siliceous surfaces has been successfully employed to produce a variety of modified silicas<sup>6,7</sup>. However, in this process a simple chelating agent can be attached to the support, or the original chain bonded to it suffers a sequence of reactions to increase the main chain, where other basic centers can be added to ensure the enhancement of a specific adsorption<sup>10</sup>. In this sense, various simple or complex molecules have been anchored on silica surfaces with the purpose of applying them, for example, in many chromatographic

operations<sup>11,12</sup>, ion exchanges<sup>13</sup>, determinations of metals from dilute solutions<sup>14</sup>, and so on.

After immobilization of the silylating agent, 3-trimethoxysilyl-1-propanethiol on silica gel, the new silica surface has the ability to: i) chemisorb some cations from acidic solutions<sup>15</sup>, ii) separate and concentrate traces of copper and cadmium<sup>16</sup>, iii) concentrate silver and to remove arsenite from a series of arsenates<sup>17</sup>, and iv) be used as a column packing containing a stable copper complex to separate a set of unsaturated linear and branched or cyclic and aromatic hydrocarbons<sup>18</sup>.

The present study is focused on the above mentioned thiol groups immobilized on silica gel and their oxidized form. After characterization of these silicas, the adsorption capacity of some divalent cations, determined by means of a batch process in aqueous and non-aqueous media, is explored.

## Experimental

### Reagents

All chemicals used were reagent grade. Silica gel ( $\equiv\text{Si-OH}$ ) used in all preparations was a commercial product (Merck), having a particle size of 0.063-0.200 mm (70-230 mesh) with a surface area of 321 m<sup>2</sup> g<sup>-1</sup>, determined through the BET method. The silica had its surface activated by heating in vacuo for 8 h at 443 K<sup>19</sup>. Anhydrous salts were used to prepare solutions for the adsorption process. Thus, divalent chlorides of cobalt (Merck), nickel (Nuclear) and copper (Merck) were dried in vacuo for 8 h at 443 K before use<sup>20</sup>. Mercury chloride (Riedel) was dried in vacuo at room temperature. All prepared cation solutions were stored in polyethylene flasks. The solvents were stored over dehydrating agents overnight, distilled through an efficient column and kept over molecular sieves. The silanizing agent 3-trimethoxysilyl-1-propanethiol (Aldrich) was used without purification, and stored at low temperature.

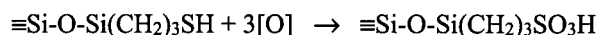
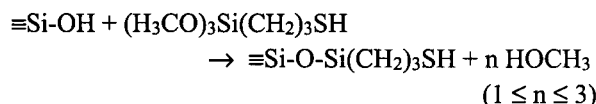
### Preparations

3-trimethoxysilyl-1-propanethiol (15.0 cm<sup>3</sup>) (83.6 mmol) was slowly added to a stirred suspension of activated silica gel (45 g) in dry xylene (100 cm<sup>3</sup>). The suspension was mechanically stirred for 72 h in an atmosphere of dry nitrogen at xylene reflux temperature. After cooling, the material was filtered and washed with xylene and acetone. This process continued until a negative test for sulphide in the washing liquid by silver nitrate solution was obtained. The resulting new silica with thiol groups anchored in the surface  $\equiv\text{Si}(\text{CH}_2)_3\text{SH}$  ( $\equiv\text{Si-SH}$ ) was then dried in vacuo for 6 h at 323 K. Identical immobilization was obtained when the reaction solvent was changed to a 1:1 mixture of aqueous acetic acid and methanol. However, the first preparation was shown to be more efficient in adsorbing cations, and was therefore chosen for this study.

A sample of this selected silica (20 g) was suspended through mechanical stirring in 300 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup>

sulphuric acid solution. A saturated permanganate solution in 1.0 mol dm<sup>-3</sup> sulphuric acid was added by drops to the suspension. The addition of the oxidant solution was stopped when the suspension was slightly brown. Successive drops of a saturated solution of oxalic acid in 1.0 mol dm<sup>-3</sup> sulphuric acid was then added until the supernatant was colorless. The resulting oxidized silica  $\equiv\text{Si}(\text{CH}_2)_3\text{SO}_3\text{H}$  ( $\equiv\text{Si-SO}_3\text{H}$ ) was filtered, washed with 250 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> nitric acid solution, water until pH 5 to 6, and acetone, and dried in vacuo for 6 h at 323 K.

Both general reactions can be illustrated by the following scheme:



### Instruments

The infrared spectra were obtained using a Perkin-Elmer model 1600 FTIR spectrophotometer. Each sample was ground to obtain disks comprised of the pulverized material. The nuclear magnetic resonance spectra for solid samples were obtained on an AC 300/P Bruker spectrometer. Mass loss was determined on a DuPont model 1090 B thermogravimetric apparatus coupled with a thermobalance 951, with samples weighing 10.0 to 20.0 mg and a heating rate of 0.16 K s<sup>-1</sup> in a dry nitrogen atmosphere. The surface area was obtained by using a Flowsorb II 2300 Micromeritics instrument. Sulphur elemental analyses were determined by using a Perkin-Elmer microelemental analyzer.

### Adsorption of cations

The batch method was used to adsorb cations onto organo-functionalized silicas in water, acetone and ethanol. For these adsorption measurements<sup>21</sup>, samples of about 0.10 g of the functionalized materials were suspended in 50 cm<sup>3</sup> of the divalent cation solution, the concentration of which varied between 5.0 x 10<sup>-3</sup> and 2.5 x 10<sup>-5</sup> mol dm<sup>-3</sup>, in the respective solvent. The suspension was mechanically stirred at 298 K. To establish the time, aliquots were periodically analyzed, and one hour was sufficient to define the isotherm. For each determination, aliquots of supernatant were removed with a pipet and the metals were analyzed by conventional EDTA complexometric titration<sup>21</sup>. In the same procedure with untreated silica gel with cations no adsorption was detected. For each experimental point, the reproducibility was checked by at least one duplicate run. The surfaces showed high stability over time, and no noticeable loss of adsorption capacity was detected<sup>20,21</sup>.

## Results and Discussion

Some general properties of silica and functionalized silicas are listed in Table 1. The sulphur elemental analysis

for  $\equiv\text{Si-SH}$  was 3.13%. Based on the percentage found, 0.98 mmol of thiol groups were immobilized per each gram of support. These thiol groups are prone to adsorb cations from dilute aqueous or non-aqueous solutions by using the ability of sulphur to chelate cations. On the other hand, the sulphonic groups of the oxidized silica  $\equiv\text{Si-SO}_3\text{H}$  have facilities for exchanging their protons with cation solutions. The capacity of this latter 0.25 mmol  $\text{g}^{-1}$  of silica was determined by immersing a sample in 0.10 mol  $\text{dm}^{-3}$  of sodium chloride solution for 24 h. After filtration and washing the solid several times with deionized water, the exchanged proton was potentiometrically titrated with standard sodium hydroxide solution.

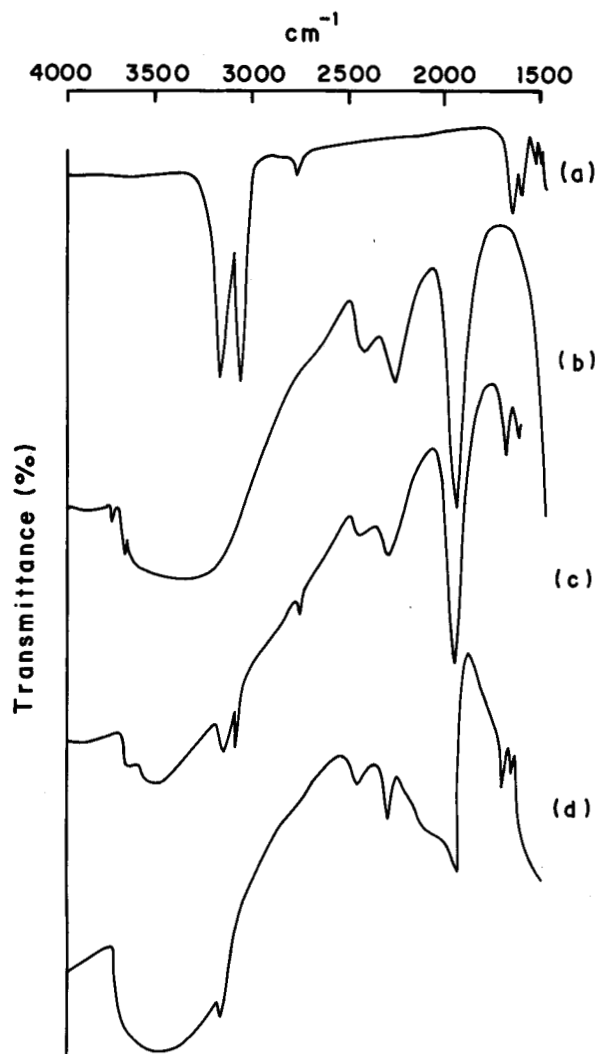
After functionalization a decrease in area in relation to the original surface is expected for silica gel. In this case, the area of 321  $\text{m}^2 \text{g}^{-1}$  changed to 256 and 294  $\text{m}^2 \text{g}^{-1}$  for  $\equiv\text{Si-SH}$  and  $\equiv\text{Si-SO}_3\text{H}$ , respectively, as shown in Table 1. The decrease of 65 and 27  $\text{m}^2 \text{g}^{-1}$  can be related to the difficulty of the gaseous nitrogen to reach the pores of the functionalized silica. This fact can be explained by considering the obstructing effect of the anchored groups, due to a certain degree of surface coverage<sup>20,21</sup>. In considering the number of groups that occupy the effective area<sup>20</sup>, the mean distances between them on the surface were estimated to be 0.66 and 0.68 nm for thiol and oxidized silicas, respectively.

Both silicas were characterized by infrared spectra. These spectra, together with those of the original silica and the silylating agent, are shown in Fig. 1. The main vibration bands of the silylating agent are also observed as weak bands in both functionalized silicas. However, the great difficulty in examining these spectra is related to the original activated matrix, which shows absorption in the high frequency range, mainly masking the CH stretching frequency<sup>19-22</sup>. The sharp band presented by the activated silica gel at 3745  $\text{cm}^{-1}$  is attributed to the free silanol

**Table 1.** Some general properties of original silica ( $\equiv\text{Si-OH}$ ), thiol-silica ( $\equiv\text{Si-SH}$ ) and its oxidized form ( $\equiv\text{Si-SO}_3\text{H}$ ).

Property	$\equiv\text{Si-OH}$	$\equiv\text{Si-SH}$	$\equiv\text{Si-SO}_3\text{H}$
Area/ $\text{m}^2 \text{g}^{-1}$	321	256	294
Sulphur analysis/%		3.13	3.40
$\nu_{\text{OH}}/\text{cm}^{-1}$	3745	3740	3740
$\nu_{\text{CH}}/\text{cm}^{-1}$		2848/2948	2950
$\nu_{\text{SH}}/\text{cm}^{-1}$		2560	
water loss/%	1.88	0.97	4.74
organic matter loss/ %		9.10	6.66
C <sub>3</sub> /ppm		9.9	10.2
C <sub>1</sub> + C <sub>2</sub> /ppm		26.7	26.8
C-O-R/ppm		49.0	54.0

stretching frequency band<sup>22,23</sup> (Table 1). The absence of this band in the anchored material indicates that the silanol groups reacted with the silylating agent<sup>19-22</sup>. In the regular profile of the broad matrix absorption an interruption is observed by the presence of weak peaks at 2848 and 2948  $\text{cm}^{-1}$ , for both anchored silicas, which are attributed to CH stretching frequencies<sup>24</sup>. The SH stretching frequency<sup>17,25</sup> appeared at 2560  $\text{cm}^{-1}$  for the  $\equiv\text{Si-SH}$  surface with weak intensity, as observed in the free silylating agent. However, this band is absent in the oxidized surface. This fact is an excellent indication that the thiol groups reacted in the oxidation with the permanganate solution. An explanation for the disappearance of this weak band after oxidation may be due to the irregularities of the silica surface, which presents inaccessible crevices and varying pore diameters<sup>26</sup>. As such, during the first stage of immobilization some silylating agents can enter small pores, which become unreactive in subsequent reactions<sup>20-22</sup>. The partial oxi-



**Figure 1.** Infrared spectra of (A) 3-trimethoxysilyl-1-propanethiol, (B)  $\equiv\text{Si-OH}$ , (C)  $\equiv\text{Si-SH}$  (C) and (D)  $\equiv\text{Si-SO}_3\text{H}$ .

dized form of the thiol group is enough to suppress the infrared signal of the original thiol band.

The thermogravimetric curves for untreated silica and the thiol and oxidized thiol-silicas are shown in Fig. 2. For all silicas, the first loss of mass is attributed to physically adsorbed water<sup>8</sup>, (see Table 1). Another water is lost from the original silica due to the condensation of the silanol groups on the surface. For the anchored surfaces, this loss is less pronounced because the great majority of these groups was used in the immobilization with the alkoxyisilyl groups<sup>27</sup>. Table 1 lists these losses and the respective temperature ranges for the anchored and original silicas. In comparing both anchored silicas, the lowest percentage of mass lost by the  $\equiv\text{Si-SH}$  surface is in agreement with the non-aqueous preparative method. In this case, the polarity of the thiol groups on the carbon chain is insufficient to maintain strong hydrogen bonds with water<sup>28</sup>. Both anchored silicas differ in the beginning of the second loss of mass, being 523 and 596 K for the thiol and oxidized form, respectively. This difference in temperature indicates that the oxidized silica is a little more thermally stable. However, in this process, the 6.66% of organic moiety containing sulphonic groups attached to the silica surface is lower than in the preceding thiol silica, which is 9.10%. On the other hand, based on a direct comparison involving the overall loss of mass of anchored and original silicas, the application of a proposed method<sup>29</sup> gave results which are in complete agreement with the 0.98 mmol g<sup>-1</sup> of anchored thiol groups on silica found from the analytical procedure.

The carbon-13 NMR spectra of 3-trimethoxysilyl-1-propanethiol obtained in carbon tetrachloride, with tetramethylsilane as an internal standard, presented the methylene group peaks at 27.5, 27.3 and 8.3 ppm, which were attributed as indicated for carbons 1, 2, 3 and a peak at 50.1 ppm, assigned to methoxy groups, indicated as carbon 4<sup>30</sup>, (see these numbered carbons below in the mentioned molecule). These results are listed in Table 1. The same sequence of peaks for this silica and the respective assignment has been previously observed<sup>24</sup>.

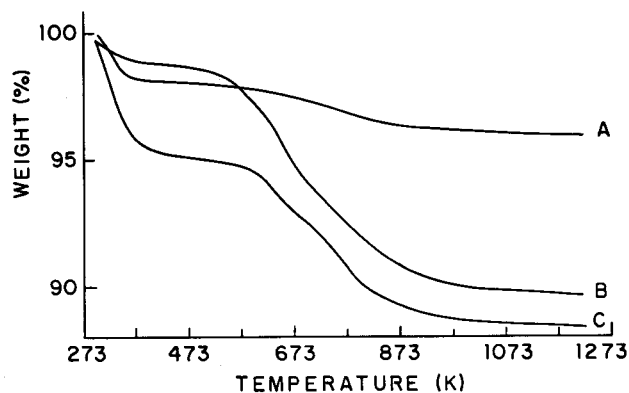
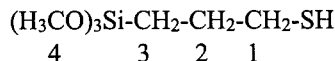


Figure 2. Thermogravimetric curves of (A)  $\equiv\text{Si-OH}$ , (B)  $\equiv\text{Si-SH}$  and (C)  $\equiv\text{Si-SO}_3\text{H}$ .



The carbon NMR spectra of the immobilized alkoxyisilanes presented, for methylenes 1 and 2, unshifted peaks for both surfaces. Figure 3 illustrates the set of peaks displayed by the thiol silica. These peaks appear in the same region as those observed for the free molecule. For  $\equiv\text{Si-SH}$  and  $\equiv\text{Si-SO}_3\text{H}$  the peaks were observed at 26.7 and 26.8 ppm, respectively. The methylene 3 shifted to a high field in comparison to the free molecule, for both surfaces, at 9.9 and 10.2 ppm, respectively. The thiol-silica was prepared in a non-aqueous solvent and a signal attributed to the methoxy group was centered at 49.0 ppm. The appearance of this peak confirms that the silylating agent can retain an unreacted methoxy group, as proposed in other functionalizations<sup>24</sup>. The peak found at 15.9 ppm is attributed to the methylene of carbon 3 in a different environment. This fact may occur due to the alkoxyisilane groups bonded to the surface. However, this signal vanished completely in the oxidized surface as a consequence of the use of a water medium in the oxidation process. On the other hand, in the oxidized surface a peak at 54.0 ppm is detected and might be attributed to carbon bonded to the oxygen of the  $\text{SO}_3\text{H}$  group<sup>24,31</sup>.

The amount of pendant groups attached to the structure of silica gel may extract cations from dilute solutions of water, acetone and ethanol. In equilibrium, the adsorption process at the solid/liquid interface can be characterized by

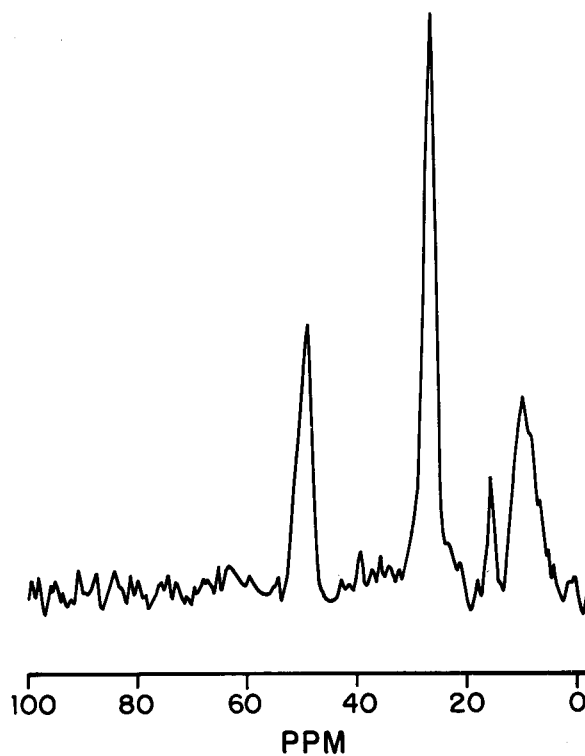
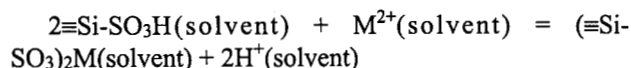
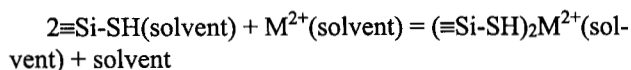


Figure 3. Carbon-13 NMR spectrum of  $\equiv\text{Si-SH}$  in solid state.

the number of moles adsorbed ( $nf$ ) on the support, which can be calculated by applying the expression:  $nf = (n_i - n^s)/m$ , where  $n_i$  and  $n^s$  are the initial and the equilibrium number of moles of cations in solution, respectively, and  $m$  is the mass of support in grams. The suspended anchored silica ( $\equiv\text{Si-SH}$ ) has the solvent gradually replaced by the cations from the solution to reach the state of equilibrium<sup>19-22</sup>. The same behavior is observed with the oxidized surface according to the cation-exchange process<sup>32</sup>:



Profiles of adsorption isotherms for cations in the three solvents are similar in shape, but vary in capacity. However, the acquisition of the isotherm is limited to the solubility of the salts. For example, only cobalt and copper in acetone enabled the attainment of the isotherms with both surfaces, the former cation being the most adsorbed. On the other hand, adsorption in ethanol and water showed a set of very similar isotherms for both surfaces.

In all cases, mercury was the most adsorbed. However, for the oxidized surface, the maximum of the isotherm with mercury in both solvents was about half of the value obtained with the thiol-silica.

When the adsorption reaches a plateau, a monolayer is supposed to be established<sup>33</sup>. For the system involving a metallic ion surface interaction, a modified Langmuir equation can be applied to the adsorption isotherm,<sup>19-22,34</sup> as follows:

$$\frac{C_s}{nf} = \frac{C_s}{n^s} + \frac{1}{n^s b}$$

where  $C_s$  is the residual concentration ( $\text{mol dm}^{-3}$ ) of a given cation in equilibrium with the solid. A plot of  $C_s/nf$  against  $C_s$  permits the calculation of the constants  $b$  and  $n^s$ . This last parameter is the maximum adsorption capacity, given as mole of solute per gram of adsorbent<sup>22</sup>.

A normal isotherm giving  $nf$  against  $C_s$  and the linearization of the results for mercury chloride in water for the  $\equiv\text{Si-SH}$  surface is shown in Fig. 4. From the linear plot the coefficient  $n^s$  was obtained and, consequently, the relation of  $n^s$  per number of ligands ( $L$ ) present in each gram of silica can be calculated. Nevertheless, these attached groups are distributed in a given area of the organofunctionalized silica and the calculated values relating to the specific area are listed in Table 2. The  $n^s/L$  values indicate a low density of cations bonded per suspended group attached to the surface. However, this general behavior differed for mercury, where the quotient is near one. Similar levels of adsorption were previously found for this

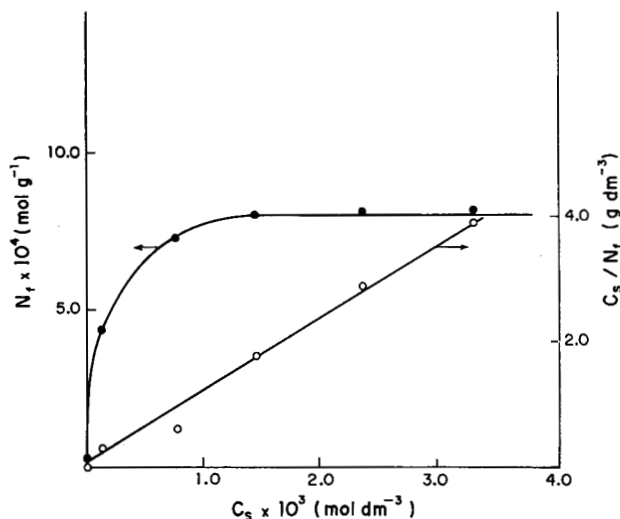


Figure 4. Isotherm of chemisorption of Hg in water for thiol-silica at 298 K and the respective linearization.

Table 2. Chemisorption data of divalent cations onto  $\equiv\text{Si-SH}$  and  $\equiv\text{Si-SO}_3\text{H}$  silicas at 298 K.

Silica	M(II)	Solvent	$N^s \times 10^4$ ( $\text{mol g}^{-1}$ )	$N^s/L$ ( $\text{mol m}^{-2}$ )
$\equiv\text{Si-SH}$	Co	ethanol	0.23	0.023
		acetone	0.24	0.024
		water	0.66	0.067
	Cu	ethanol	0.40	0.041
		acetone	0.41	0.041
		water	0.30	0.031
Ni	ethanol	0.51	0.052	
	water	0.49	0.050	
$\equiv\text{Si-SO}_3\text{H}$	Hg	ethanol	7.46	0.76
		water	8.55	0.87
		Co	ethanol	1.30
	Cu	acetone	1.38	0.13
		water	1.65	0.16
		ethanol	0.30	0.028
Ni	acetone	0.31	0.029	
	water	1.65	0.15	
	ethanol	0.12	0.011	
Hg	water	1.62	0.15	
	ethanol	4.15	0.39	
	water	5.21	0.49	

cation<sup>16</sup>. For copper adsorption in water<sup>15</sup> the  $n^s$  value of  $0.022 \text{ mmol g}^{-1}$  is comparable to  $0.030 \text{ mol g}^{-1}$  for the same thiol silica found in this work. The high adsorption values obtained for mercury show that this cation has a great affinity for extraction in ethanol or water with thiol-silica,

with similar affinities for the oxidized surface. For this latter surface, a higher adsorption in water is observed for the other cations. The adsorption process with  $\equiv\text{Si-SO}_3\text{H}$  is higher in aqueous media than that found for the same cation for the thiol-silica surface. This fact seems to be reasonable because the ionic exchange process becomes easier due to the ionization of the sulphonic acid in this solvent.

## Conclusions

The immobilized  $\equiv\text{Si-SH}$  and its oxidized form have the ability to adsorb cations from aqueous and non-aqueous solutions. The intensity of the adsorption is related to the properties associated with the acid and base couples involved in the process. Thus, the higher affinity of mercury for the thiol-silica surface is easily interpreted as being due to the soft-soft acid-base interactions<sup>35</sup>. This behavior is supported by the contrast observed with the divalent borderline acid in the same adsorption procedure. On the other hand, the increasing cation adsorption in water involving sulphonic groups is favorable due to the dissociation of the acid groups, and consequently, the ionic exchange process is enhanced.

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