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Thermochemical data for interaction of some primary amines with complexed mercury on mercapto-modified silica gel

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Abstract

Mercury chloride was complexed on functional SH groups attached to silica gel to yield the material Sil-S-Hg. Adsorption and thermochemical data for the interaction of some primary amines with the immobilized mercury(II) have been obtained from calorimetric measurements at 298.15 K, with the objective of charting the newly created acidic sites. By using calorimetric titrations with direct determination of reaction extension, values of maximum capacities of interaction (N^s), interaction enthalpies at different coverage of the surface ($\Delta_{\text{int}(i)}H_\text{m}$) and the molar enthalpy of interaction for monolayer formation of the anchoring amines ($\Delta_{\text{mon}}H_\text{m}$) were determined. It is shown that the values of the thermochemical parameters $\Delta_{\text{int}(i)}H_\text{m}$ and $\Delta_{\text{mon}}H_\text{m}$ are in the sequence: Sil-S-Hg/$C_2H_5NH_2$ > Sil-S-Hg/$C_4H_9NH_2$ > Sil-S-Hg/CH_3NH_2 > Sil-S-Hg/$C_3H_7NH_2$, and are correlated with the order of the basicity constants of the amines. The general tendency found earlier for the energy distribution of the adsorption sites on the heterogeneous surface has been confirmed.

Keywords: Organosilanes; Primary amines; Modified silica; Adsorption; Interaction energies

1. Introduction

Mechanically stable matrices, such as chemically modified silica gel surfaces, have awakened growing interest because the knowledge acquired with them permits the transfer of some properties found in homogeneous chemistry to the immobilized state. Among the more promising highly developed surfaces are the silica-attached organosilanes which are widely used in various technologies [1–9]. These materials enable speciation of trace elements and are useful in solving many problems in nuclear technology, electronics, metallurgy, mining, medicine, agriculture, fisheries and environmental studies. Although a large body of data has been reported about anchored silicas, new applications are continuously demanding further information.

Recently [10–12], our group has employed adsorption calorimetry with the purpose of evaluating the nature of the bonds of complexes at the solid–liquid interfaces. The calorimetric titration method has provided quantitative information on both adsorbed amounts and energy data at different surface coverages. In following this procedure, the equilibrium conditions are well defined and this method provides a direct means to obtain accurate differential enthalpy values with the knowledge of the energy distribution of the adsorption sites on the heterogeneous adsorbent. Thus, it is possible to discuss the adsorption processes in an exact thermodynamic way. Calorimetric titration has been widely used to investigate homogeneous solution reactions but its use for heterogeneous medium studies is far less extensive. The interactions of an

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immobilized functional group with a reagent from the ambient can differ from the known reaction in homogeneous medium. The differences can be attributed to transport limitations, solvation effects, charge and dipole effects and steric constraints [13]. Investigations on the thermodynamics of adsorption from solutions have been reported [14–20], however, they are few and scattered because of the complexities of solid–solution interface systems and experimental difficulties.

In this paper, we report the calorimetric results for interactive processes of primary amines with complexed mercury on silica gel modified with 3-(trimethoxysilyl)propane-1-thiol, Sil-S-Hg. An essential feature in the study of this heterogeneous medium is concerned with the direct determination of enthalpy changes for acid–base interactions from a net calorimetric titration curve. Such an investigation demands a knowledge of the amount of amine that interacts at each titration point, which could be satisfactorily determined from our experiment.

2. Experimental

2.1. Chemicals

Reagent grade 3-(trimethoxysilyl)propane-1-thiol (MPTS) from Aldrich and mercury(II) chloride (greater than 98% purity, from Vetec) were used as supplied. The adsorbent was silica gel (Fluka) with a particle size of 0.063–0.200 mm (70–230 mesh), having a mean pore diameter of 60 Å. Xylene (Merck) was distilled and dried with metallic sodium. Methylamine (Aldrich), ethylamine (Riedel-de-Haen), propylamine (Aldrich) and *n*-butylamine (Riedel) were distilled before use. The solutions of these amines (0.3 mol dm^{-3}) were prepared in deionized water, free of CO_2 and O_2 by nitrogen purge-vacuum cycles and standardized against HCl solution by potentiometric titration.

2.2. Chemical modification of the silica gel surface

The inorganic support was modified as follows: a sample of 40 g of activated silica was immersed into 150 cm^3 dry xylene and 25 cm^3 of the silylant agent MPTS was then added with stirring [10]. The stirred suspension was refluxed under dry nitrogen atmosphere for 72 h. The modified silica, Sil-SH, was filtered, washed twice with acetone and xylene and dried under vacuum at 323 K.

The modified silica gel was characterized by specific surface area using the BET method with N_2 at 77 K [21], ^{13}C and ^{29}Si NMR with cross-polarization and magic-angle spinning (CP-MAS), FTIR diffuse reflectance and thermogravimetry. The CP-MAS measurements were made on an AC 300/P Bruker NMR spectrometer operating at 75.47 MHz for ^{13}C and at 59.63 MHz for ^{29}Si. Infrared spectra data for unmodified and modified silica gel were obtained on a Perkin-Elmer 1600 series FTIR spectrophotometer with a diffuse reflectance accessory at a resolution of 4 cm^{-1}, by using spectral quality KBr powder. Thermogravimetric determinations were performed using a DuPont thermogravimetric analyzer with a dynamic atmosphere flow of 0.33 $cm^3\,s^{-1}$ and a heating rate of 0.16 $K\,s^{-1}$.

2.3. Complexation of mercury on Sil-SH

From our previous papers [10–12] it was shown that Sil-SH has the capacity to extract mercury ions from aqueous and ethanolic solutions. In this work, a sample of Sil-SH was added to an aqueous solution of mercury chloride at a sufficient concentration to obtain the maximum quantity of adsorbed cation on the surface [10]. The amount of immobilized mercury was determined by complexometric titration with dithizone and was found to be 0.489 mmol g^{-1}. After stirring for several hours, the solid containing mercury, Sil-S-Hg, was filtered off and washed with water and acetone. After filtration, the Sil-S-Hg was dried under vacuum at 323 K for 6 h.

2.4. Calorimetric titration procedure

The thermochemical data for the interaction processes of RNH_2 ($R = CH_3$, C_3H_7 and C_4H_9) with the Sil-S-Hg were obtained from incremental calorimetric titrations, at 298.15 K, in the isoperibolic precision calorimetric system LKB 8700-2, whose performance and details have been described elsewhere [22]. All results obtained are the averages of two repeated determinations. Thermostated aqueous solutions of the amines were incrementally added, under vigorous stirring (500 rpm), to the calorimeter vessel containing

1.0 g of Sil-S-Hg suspended in 90.0 cm^3 of bidistiled water, until no additional thermal effect, besides the dilution effects, were observed. Thus, the total volume of titrant added for each titration curve was dependent on Sil-S-Hg saturation. Each addition of 0.5 cm^3 of amine solution yielded a thermal effect of interaction, Q_r, which was corrected by subtracting the thermal dilution effect, Q_d, for each increment of amine solution in 90.0 cm^3 of bidistiled water without solid adsorbent.

The processes of calorimetric titration involving thermal effects of Sil-S-Hg/amines interactions, at each equilibrium condition, are outlined as follows:

$$\text{Sil-S-Hg (soln}_1) + \text{RNH}_2 \text{ (soln}_1) = \text{Sil-S-Hg} \cdot \text{RNH}_2 \text{ (soln}_2); \quad Q_r \tag{1}$$

$$\text{RNH}_2 \text{ (soln}_1) + \text{solvent} = \text{RNH}_2 \text{ (soln}_2); \quad Q_d \tag{2}$$

After each Q_r recording, mechanical stirring was interrupted for 5 min in order to withdraw 1 cm^3 of the supernatant solution to determine the amine equilibrium concentration, $C_{eq(i)}$. Thus, the amine amount that interacts with the Sil-S-Hg at each calorimetric titration point, $n_{int(i)}$, could be determined. Each titrant addition was separated by 30 min from the next, during which time the thermal effects due to titrant addition and electrical calibration were recorded.

The corresponding interaction energy, $Q_{int(i)}$, was determined:

$$Q_{int(i)} = Q_{r(i)} - Q_{d(i)} \tag{3}$$

Interaction enthalpies at different coverage of the surface, $\Delta_{int(i)}H_m$, were calculated from knowledge of the amount of amine required to yield $Q_{int(i)}$ under each equilibrium condition:

$$\Delta_{int(i)}H_m = \frac{Q_{int(i)}}{n_{int(i)}} \tag{4}$$

2.5. Quantitative determination of amines

In order to determine the amine amount that interacts with the Sil-S-Hg at each calorimetric titration point, $n_{int(i)}$, experiments were carried out in the LKB 2277 heat-flow microcalorimeter previously described [12]. The titration ampoule of this apparatus has a capacity of 3 cm^3 and was internally covered with Teflon. Aliquots of the supernatant solutions, coming from the Sil-S-Hg/amines titration systems, were neutralized in 2 cm^3 of 0.10 mol dm^{-3} HCl within the titration ampoule.

The areas of the detectable calorimeter signals (power versus time) are dependent on the volumes and concentrations of the amine solutions. When fixed volumes of amine solutions are added, the produced areas are proportional to the concentration of the base. A single analytical curve of concentration versus area, made prior to each experiment, thus allows to determine each unknown equilibrium concentration of amine.

3. Results and discussion

The functional SH group attached on a pendant chain bonded to the surface is a soft base forming a donor center which is highly polarizable and capable of interacting with low-lying orbitals of soft acids [23]. The specific surface area of 346 $m^2 g^{-1}$ for Sil-SH was found to be reduced when compared with the value 422 $m^2 g^{-1}$ for the unmodified silica gel. Such a reduction can be mainly attributed to the coating of the pores of the surface by organofunctional groups, preventing the access of nitrogen molecules into some of the pores. The amount of attached SH groups was quantitatively determined by using a previous method [24] established from thermogravimetric data, which gave 1.37 mmol of sulfur per gram of adsorbent. IR and CP-MAS NMR spectra data gave clear evidence of the modification as previously reported [10].

Calorimetric investigations [10,11] concerning interactions of Hg(II), Ag(I), Cu(II), Ni(II) and Zn(II) ions with mercapto-modified silica gel surface, Sil-SH, have provided a method to chart the basic sites created with the surface modification. The Sil-SH with the complexed cations also has a characteristic related to the presence of acidic sites. With the objective of charting these newly created sites and to study the acid–base interaction effects of solid–solution interfacial processes, interactions of immobilized mercury on thiol ligands with amines have been investigated. The reason to study the Sil-S-Hg/amines interactions is due to these processes to yield more $\Delta_{int(i)}H_m$ values than the Sil-SM/amines (M = Ag, Cu, Ni and Zn) processes. Thus, it is possible an accurate investigation of the energy distribution of the adsorption acidic sites on the potentially heterogeneous surface. One aspect on which we have concentrated our efforts

Table 1
Calorimetric titration of 1 g of Sil-S-Hg suspended in 90 cm^3 of bidistiled water, with 0.30 mol dm^{-3} methylamine solution at 298.15 K

$C_{\mathrm{eq}(i)}$ (10^{-3} mol dm^{-3})		$n_{\mathrm{int}(i)}$ (10^{-4} mol)		$-Q_{\mathrm{int}(i)}$ (J)		$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$ (kJ mol^{-1})	
Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
0.57	0.61	0.98	0.95	3.15	3.41	32.1	35.9
1.43	1.42	0.74	0.78	2.25	2.36	30.4	30.2
2.43	2.40	0.62	0.64	1.67	1.78	26.9	27.8
3.58	3.53	0.51	0.52	1.24	1.37	24.3	26.3
4.94	4.85	0.32	0.36	0.71	0.88	22.2	24.4
6.47	6.34	0.18	0.21	0.34	0.36	18.9	17.2
8.15	7.98	0.06	0.10	0.11	0.16	18.5	16.1

Table 2
Calorimetric titration of 1 g of Sil-S-Hg suspended in 90 cm^3 of bidistiled water, with 0.30 mol dm^{-3} propylamine solution at 298.15 K

$C_{\mathrm{eq}(i)}$ (10^{-3} mol dm^{-3})		$n_{\mathrm{int}(i)}$ (10^{-4} mol)		$-Q_{\mathrm{int}(i)}$ (J)		$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$ (kJ mol^{-1})	
Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
0.67	0.73	0.89	0.84	2.64	2.52	29.6	30.0
1.55	1.71	0.71	0.72	2.11	2.02	29.7	28.1
2.55	2.69	0.62	0.64	1.52	1.44	24.5	22.5
3.75	3.89	0.43	0.47	0.83	0.83	19.3	17.6
5.14	5.24	0.29	0.32	0.49	0.55	16.8	17.1
6.72	6.85	0.14	0.11	0.23	0.18	16.6	16.5

is the simultaneous determination of the thermal effects and the corresponding amounts of amines that interact at each calorimetric titration point. The values directly obtained with this method are shown in Tables 1–3.

Amine solutions were added until the Sil-S-Hg surface was saturated. At this point, it is proposed that a monolayer is formed [25]. The molar enthalpy of interaction for monolayer formation of anchoring amine, per gram of Sil-S-Hg, $\Delta_{\mathrm{mon}}H_{\mathrm{m}}$, can be directly obtained by means of the expression:

$$\Delta_{\mathrm{mon}}H_{\mathrm{m}} = \frac{Q_{\mathrm{mon}}}{N^{\mathrm{s}}} \tag{5}$$

where $Q_{\mathrm{mon}} = \Sigma Q_{\mathrm{int}(i)}$ is the integral energy of interaction for a saturated monolayer per gram of Sil-S-Hg, and $N^{\mathrm{s}} = \Sigma n_{\mathrm{int}(i)}$ is the maximum capacity of interaction to form a monolayer. Table 4 summarizes

Table 3
Calorimetric titration of 1 g of Sil-S-Hg suspended in 90 cm^3 of bidistiled water, with 0.30 mol dm^{-3} butylamine solution at 298.15 K

$C_{\mathrm{eq}(i)}$ (10^{-3} mol dm^{-3})		$n_{\mathrm{int}(i)}$ (10^{-4} mol)		$-Q_{\mathrm{int}(i)}$ (J)		$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$ (kJ mol^{-1})	
Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
0.41	0.43	1.13	1.11	3.85	3.83	34.1	34.8
1.13	1.18	0.85	0.83	2.84	2.86	33.2	34.5
2.08	2.05	0.67	0.74	1.98	2.21	29.5	29.9
3.11	3.17	0.61	0.52	1.73	1.48	28.4	28.5
4.43	4.45	0.35	0.38	0.94	1.05	26.9	27.6
5.84	5.81	0.28	0.33	0.68	0.89	24.3	26.9
7.42	7.34	0.15	0.19	0.35	0.48	23.4	25.3
9.10	8.95	0.07	0.13	0.16	0.30	22.9	23.1

Table 4
Results of maximum capacities of interaction, integral enthalpies of interaction and molar enthalpy of interaction for monolayer formation, from calorimetric titration data at 298.15 K

RNH_2	N^s (10^{-4} mol g^{-1})		$-Q_{mon}$ (J g^{-1})		$-\Delta_{mon}H_m$ (kJ mol^{-1})	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
$R = CH_3$	3.37	3.52	9.38	10.21	27.83	29.00
$R = C_3H_7$	3.09	3.06	7.84	7.45	25.37	24.35
$R = C_4H_9$	4.08	4.21	12.44	13.08	30.49	31.07
$R = C_2H_5$[a]	5.60	–	24.73	–	44.16	–

[a] From [12].

$\Delta_{mon}H_m$, Q_{mon} and N^s values. For comparison, the previous results with the Sil-S-Hg/ethylamine interaction process [12] are also included.

The functionalized silica surface must be a priori regarded as potentially heterogeneous [10]. From Tables 1–3, it can be seen that all experiments yield different interaction enthalpies evolved at different coverages, thus the $\Delta_{int(i)}H_m$ values are not constant with the coverage. This feature can be better observed in Fig. 1, which shows $\Delta_{int(i)}H_m$ values against covered fraction of the Sil-S-Hg, $\theta = \Sigma n_{int(i)}/N^s$. It is clear that interactions at lower coverage yield higher enthalpy change values, which decrease with increasing coverage.

The maximum capacity of interaction to form a monolayer, N^s, shows the ability of the Sil-S-Hg to remove amines from aqueous solutions. From our previous study [10], it was found that 36% of the attached organosilanes on the silica gel, whose sulfur content is 1.37 mmol g^{-1}, are available for adsorption of mercury. The mercury interaction capacity of 0.489 mmol g^{-1} indicates that 86, 72 and 63% of the coverage is achieved for interactions of butylamine, methylamine and propylamine, respectively, as can be seen in Table 4. This finding suggests the formation of complexes of, presumably, 1:1 stoichiometry for the interactions of the amines with the mercury ions, by considering them the only acidic sites present on the surface. It is possible that the amines can be adsorbed by the remaining acidic silanol groups disposed on surface and there may also be interactions between the amino group and residual SH groups on Sil-SH.

Based on previous studies, it was concluded that, when the same coverage is not achieved for adsorption, the thermodynamic quantity $\Delta_{int(i)}H_m$ should be better than $\Delta_{mon}H_m$ to evaluate the acid–base interactions. From Fig. 1, it is possible to compare $\Delta_{int(i)}H_m$ values for the same coverage achieved for adsorption of the four amines. It can be seen that the $\Delta_{int(i)}H_m$ values are in the sequence: Sil-S-Hg/

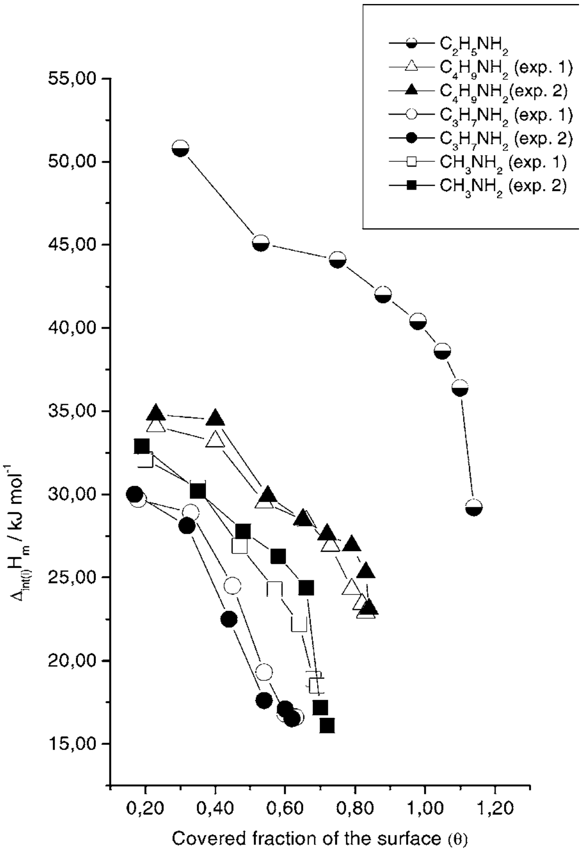

Fig. 1. Interaction enthalpies at different coverage of the surface ($\Delta_{int(i)}H_m$) vs. the covered fraction of the surface (θ), for the interaction of Sil-S-Hg with the primary amines.

$C_2H_5NH_2$ > Sil-S-Hg/$C_4H_9NH_2$ > Sil-S-Hg/CH_3-NH_2 > Sil-S-Hg/$C_3H_7NH_2$. This sequence is in agreement with that observed for $\Delta_{mon}H_m$ values in Table 4, and follows the same order as the basicity constants ($K_b \times 10^{-4}$) of the amines [26]: $C_2H_5NH_2$ (5.1) > $C_4H_9NH_2$ (4.8) > CH_3NH_2 (4.5) > $C_3H_7NH_2$ (4.1). These results, consequently, suggest that the basic character of the primary amines can play an important role in these acid–base interaction processes of amine adsorption from aqueous solutions.

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