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Thermochemical investigation on the adsorption of some divalent cations on modified silicas obtained from sol–gel process

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Abstract

Silicas with one or two immobilised ethylenediamine molecules, presenting electron donor Lewis bases, have been prepared through sol–gel method. Characterisation by various techniques indicated equivalent quantities of nitrogenated groups on both kinds of silicas. The adsorption enthalpy changes obtained from the interaction between basic sites on pendant groups and M(II) {Hg(II), Cu(II) and Co(II)} and were determined from calorimetry, carried out at 298.15 K in aqueous solution. From these determinations, the maximum capacity of adsorption (N^s), the adsorption enthalpy at different coverages of the surface ($\Delta_{ads}H_m$) and the integral enthalpy for the maximum adsorption ($\Delta_{sat}H_m$) were obtained. The determined energy of distribution of the adsorption sites indicates the heterogeneous adsorbentes. It is shown that N^s values are very similar for both silicas, despite the differences of the total number of immobilised groups. All reactions have favourable enthalpic contributions. Other thermodynamic quantities are discussed in terms of stability of the complexes at the solid/solution interfaces. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Silica gel; Sol–gel process; Immobilisation; Adsorption; Thermochemical data

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1. Introduction

Silica gel modified by inorganic and, in several cases, by organic functional groups has been a subject of considerable interest due to the many possibilities of applications [1–11]. The applicability of such material is strongly dependent on its surface properties. Surface chemical modifications are usually achieved by bonding appropriate organosilane agents, which embrace desirable terminal functional groups. Silica gel has been an attractive substrate for organosilanisation because its surface is covered by hydroxyl groups that promptly react with organosilane agents. The Si-O-Si-C moiety so formed has a bifunctional nature and a high chemical stability. The quality and durability of the organosilanised materials depend primarily on the nature of the attachment to the surface. From the large amount of data collected on silica gel modification and the subsequent reactivity of this material, new applications are continuously demanding further information.

Diamine modified silica gel was easily prepared through unconventional sol–gel process to form a rigid and stable support, as reported before [12]. In this publication, in essence, an investigation on the energetics of the interactions of these matrices with some

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divalent cations is reported. Thus, to achieve this objective, adsorption calorimetry was employed due to the fact that this method is the most appropriate for direct measurement of the interaction energy between the adsorbent and adsorbate species. From these values, the adsorption energies and the corresponding amount of cations, which are involved in these kinds of interactions, have been obtained in aqueous solution. The results fit a simple Langmuir isotherm, which successfully describes the adsorption equilibrium behaviour in the entire concentration range studied. The energetic results for these typical acid–base reactions have also been determined, in order to acquire more information about the phenomena at the solid/solution interface. Thus, the energetic interaction between the aminated pendant groups, covalently bonded to the inorganic support, with divalent cobalt, copper and mercury cations dissolved in aqueous solution was investigated.

2. Experimental

2.1. Chemicals

Unless otherwise stated, all reagents were of analytical grade. Ethylenediamine was purchased from Merck. Tetraethoxysilane obtained from Fluka was distilled before use. The ligand 3-ethylenediamine-propyltrimethoxysilane (EPTS), glutaraldehyde solution (50%) and sodium borohydrate were obtained from Aldrich and were used as received. The copper, cobalt and mercury chlorides (Aldrich) were used without further purification, although they were vacuum dried before use. Solutions were prepared in CO_2 and O_2 free deionised water. To avoid any participation of water in the system, anhydrous metal chlorides were handled in a dry nitrogen atmosphere.

2.2. Preparations of the diamine-modified silica gels

Diamine-modified silica gels were obtained from the sol–gel method which has been described recently [12], thus only a brief description is here reported. A volume of 40.0 cm^3 of concentrated HCl was slowly added to a mixture containing 50.0 cm^3 of tetraethoxysilane and 25.0 cm^3 of EPTS. This proportion produces the best results in terms of the quantity of the immobilised organic groups [13]. The solution was stirred for 10 min in an ice bath; ethanol and 5% sodium bicarbonate solution were added. The isolated silica, named Si-et-1, was filtered off, rinsed with bidistilled water and dried under vacuum at room temperature for 6 h. This silica reacted with 1.5% glutaraldehyde aqueous solution to yield a new Si-glut silica, which was treated with ethylenediamine and $NaBH_4$ to yield a final Si-et-2 silica. The synthesis reactions are outlined in Fig. 1.

Both Si-et-1 and Si-et-2 silicas were characterised by nitrogen and carbon analysis, thermogravimetry, ^{13}C and ^{29}Si solid state NMR with cross polarisation and magic angle spinning (CP/MAS) [12]. The nitrogen contents were determined by the Kjeldhal method and the carbon contents using a Perkin–Elmer model 2400 instrument. Thermogravimetric determinations were performed using a DuPont thermogravimetric

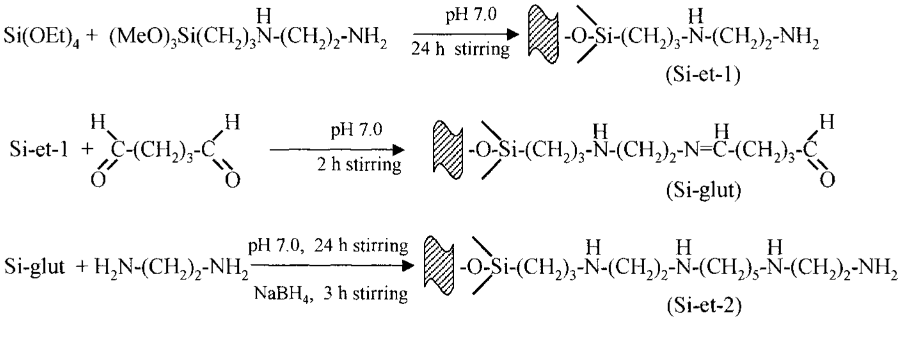

Fig. 1. Scheme of immobilisation of Si-et-1 by using sol–gel method, the increase in organic chain from the glutaraldehyde reaction to give Si-glut and the subsequent reaction with aliphatic amine to produce Si-et-2.

analyser where a heating rate of $0.16\ \mathrm{K\ s^{-1}}$ was employed under a dynamic flow of argon of $120\ \mathrm{cm^3\ min^{-1}}$. The CP/MAS NMR measurements were made on an AC 300/P Bruker spectrometer, operating at 75.47 MHz for ^{13}C and 59.63 MHz for ^{29}Si.

2.3. Calorimetry

All calorimetric determinations were performed at 298.15 ± 0.02 K in an LKB 8700-1 isoperibolic precision system, whose performance and details of operation were described elsewhere [14]. Samples of Si-et-1 or Si-et-2 silicas, weighing approximately 110.0 mg were put into $90.0\ \mathrm{cm^3}$ of cation aqueous solutions in the concentration range of 5.0×10^{-5} to $5.0 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$. The thermal effects and the corresponding amount of adsorbed cations were simultaneously determined. The total data were treated as presented in Section 3.

3. Calculations

The present investigation is focused on thermochemical data involving the adsorption of cations Hg(II), Cu(II) and Co(II) for both diamine modified silica gels, Si-et-1 and Si-et-2.

The involved thermal effects, at equilibrium conditions, can be stated as following:

$$\begin{aligned}&\text{Adsorbent} + \text{M(II)(soln)}\\ &\quad = \text{Adsorbent}\cdot\text{M(II)(solvent)};\ Q_r \qquad (1)\end{aligned}$$

$$\text{Adsorbent} + \text{Solvent} = \text{Adsorbent(solvent)};\ Q_w \qquad (2)$$

Each individual experiment yield a thermal effect, Q_r, which is corrected by subtracting the corresponding wetting effect, Q_w, of the silicas in the pure solvent, i.e., bidistilled water. The thermal effect of empty ampoule breaking was found to be negligible compared to Q_r and Q_w values.

The thermal effect originating from the adsorption, Q_{ads}, can be calculated by means of the relationship:

$$Q_{ads} = Q_r - Q_w \qquad (3)$$

with both Q_r and Q_w normalised for 1 g of adsorbent.

The cation equilibrium concentrations were determined after each ampoule breaking, in order to determine the amount of adsorbed cation, n_{ads}, which is required to yield Q_{ads} under each equilibrium condition:

$$n_{ads} = \frac{(n_i - n_s)}{m} \qquad (4)$$

where n_i is the initial amount of cation in the solution of a given concentration into the calorimeter vessel, n_s is the amount of cation in the supernatant solution after equilibrium. The cation concentrations in the supernatant were determined by complexometric back-titration with EDTA and standard Zn(II) solutions [15].

From the determined Q_{ads} and n_{ads} values, the enthalpies of adsorption, $\Delta_{ads}H_m$, at different surface coverages of the adsorbent surface can be calculated (Table 1) through the expression:

$$\Delta_{ads}H_m = \frac{Q_{ads}}{n_{ads}} \qquad (5)$$

On the other hand, the quantitative data to perform a Langmuir isotherm requires the use of an ideal solution, which implies that the adsorbate forms an ideal monolayer to give a localised adsorption. In this condition, it remains a satisfactory empirical model to fit the adsorption data at low to moderate concentrations [16]. This model is applied to the adsorption processes where the adsorbate/surface interactions are independent of coverage [17–19]. Here we used a similar equation of this model to fit the data and found it worked well:

$$\frac{C_{eq}}{n_{ads}} = \frac{C_{eq}}{N^s} + \frac{1}{bN^s} \qquad (6)$$

The C_{eq} term is the cation equilibrium concentration, n_{ads} is the corresponding amount of adsorbed cation per mass of adsorbent and N^s corresponds to the maximum capacity of adsorption per mass of adsorbent. In this case, the b values can be related to the equilibrium tendencies. From the plot of C_{eq}/n_{ads} against C_{eq}, the N^s and b values for the interaction processes can be calculated by considering the slope and intercept of the straight line obtained in all cases. Although the Langmuir model is not applicable to the process of cation adsorption, since the $\Delta_{ads}H_m$ values change with the surface coverage, Eq. (6) was applied to the present data, showing a good fit. The resulting N^s and b values are presented in Table 2.

Table 1
Thermochemical data for the adsorption of divalent cations [Hg(II), Cu(II), Co(II)] by Si-et-1 and (Si-et-2) silicas in aqueous solutions at 298.15 K

M	Experiment	$(-Q_{\mathrm{ads}})^{\mathrm{a}}$ (J g^{-1})	$(-\Delta_{\mathrm{ads}}H_{\mathrm{m}})^{\mathrm{b}}$ (kJ mol^{-1})	$(-Q_{\mathrm{sat}})^{\mathrm{a}}$ (J g^{-1})	$(-\Delta_{\mathrm{sat}}H_{\mathrm{m}})^{\mathrm{b}}$ (kJ mol^{-1})
Hg	1	21.8 (11.6)	218 (149)	30.0 (12.5)	167 (71.0)
	2	24.6 (11.8)	205 (114)		
	3	27.3 (12.0)	202 (111)		
	4	29.4 (12.4)	196 (90.5)		
	5	30.2 (12.4)	177 (80.1)		
	6	30.0 (12.5)	175 (78.3)		
Cu	1	31.8 (9.9)	137 (44.0)	41.7 (10.3)	116 (30.3)
	2	34.0 (10.0)	136 (40.1)		
	3	37.7 (10.1)	135 (38.2)		
	4	40.0 (10.3)	132 (37.0)		
	5	41.5 (10.3)	120 (31.0)		
	6	41.7 (10.3)	121 (31.2)		
Co	1	8.91 (7.70)	203 (222)	9.75 (7.90)	127 (127)
	2	9.25 (7.80)	210 (177)		
	3	9.55 (7.85)	191 (167)		
	4	9.87 (7.90)	179 (165)		
	5	9.80 (7.90)	140 (144)		
	6	9.75 (7.90)	135 (127)		

[a] Estimated uncertainty of 0.5%.
[b] Estimated uncertainty of 2.0%.

Table 2
Quantitative data for the adsorption of divalent cations Hg(II), Cu(II), Co(II) on Si-et-1 and (Si-et-2) silicas in aqueous solutions at 298.15 K

M	Experiment	$C_{\mathrm{eq}} \times 10^3$ (mol dm^{-3})	$(n_{\mathrm{ads}})^{\mathrm{a}}$ (10^{-4} mol g^{-1})	$(N^{s})^{\mathrm{a}}$ (10^{-4} mol g^{-1})	b (dm^3 mol^{-1})
Hg	1	0.35 (0.37)	1.00 (0.78)	1.80 (1.77)	2323 (1486)
	2	0.70 (0.73)	1.20 (1.04)		
	3	1.65 (1.70)	1.35 (1.08)		
	4	2.68 (2.73)	1.50 (1.37)		
	5	3.75 (3.84)	1.70 (1.55)		
	6	4.65 (4.76)	1.71 (1.59)		
Cu	1	0.35 (0.42)	2.32 (2.25)	3.60 (3.40)	3289 (2768)
	2	0.50 (0.67)	2.50 (2.50)		
	3	1.52 (1.60)	2.78 (2.65)		
	4	2.58 (2.73)	3.03 (2.77)		
	5	3.47 (3.60)	3.45 (3.32)		
	6	4.49 (4.60)	3.44 (3.30)		
Co	1	0.25 (0.26)	0.44 (0.45)	0.77 (0.62)	1731 (2638)
	2	0.70 (0.71)	0.44 (0.44)		
	3	1.78 (1.80)	0.50 (0.47)		
	4	2.70 (2.74)	0.55 (0.48)		
	5	3.65 (3.70)	0.70 (0.55)		
	6	4.80 (4.86)	0.72 (0.62)		

[a] Estimated uncertainty of 1.5%.

4. Results and discussion

The surface modifications resulted in solids that contain available nitrogen basic sites on pendant organic groups, that interact with cations from aqueous solution. From the elemental analysis, the carbon/nitrogen ratio was 2.50 and 2.75 for Si-et-1 and Si-et-2, respectively. The remaining techniques used to characterise these surfaces confirmed the success of immobilisation. A full characterisation has been previously explored in detail [12].

The maximum adsorption capacities represented by N^s values, as given in Table 2, correspond to the abilities of both Si-et-1 and Si-et-2 silicas in removing cations from aqueous solution. These values decrease in the sequence Cu(II) > Hg(II) > Co(II). It is worthwhile to emphasise that the adsorbed amount reflects only the amount of adsorbate on the surface of the adsorbent and cannot directly reveal the strength of interaction between the adsorbate and adsorbent. The above mentioned sequence of cation preferences is coherent with the stability of the complexes formed as proposed by the Irving–Williams series [20] and is also in agreement with adsorption of cations as a function of pH, when ethylenediaminepropyl are the pendant groups attached to the silica matrix [21].

An important feature related to the degree of adsorption comes from the similarity in the N^s values as listed in Table 2, in spite of the differences in the amount of basic adsorption sites on Si-et-1 and Si-et-2 silicas. It is possible to attribute this fact to the steric effects occurring in Si-et-2, which impedes the accessibility to nitrogen atoms nearest to the surface. Thus, only the terminal nitrogen atom is accessible for coordination.

The thermal effect of wetting, Q_w, of the silicas which is -9.29 and -0.90 J g^{-1}, for Si-et-1 and Si-et-2, respectively [12], is supposed to be affected by the presence of silanol groups, which are hydrophilic in character. The lower value for Si-et-2 can be assigned to its lower hydrophilic character caused by, for instance, the length of the aliphatic chain of the attached organic group on the surface.

Both diamine-modified silicas must be regarded as having potentially energetically different types of sites, which can coexist on the surface. Consequently, the adsorption enthalpies, $\Delta_{ads}H_m$, evolved at different adsorption coverages in going from higher sites to those of lower energy. Fig. 2 outlines the variation of the enthalpy of adsorption values, $\Delta_{ads}H_m$, as a function of the covered fraction of the surface, $\theta = n_{ads}/\beta$, where β is the amount of nitrogen per gram of silica, which is 2.70 and 2.56 mmol g^{-1} for Si-et-1 and Si-et-2, respectively. Site energy distribution, here being understood as the variation of the $\Delta_{ads}H_m$ values as a function of the covered fraction of the surface, clearly demonstrates a high degree of heterogeneity of these surfaces in the present adsorption processes. Thus, at greater coverages of pendant groups, lower enthalpic values are found, as was previously observed [22].

The last $\Delta_{ads}H_m$ values, which can be correlated to the mean interaction strengths, since more basic sites are occupied in this row, show that the interaction between the basic sites of the adsorbents and the cations decrease in the sequence Hg(II) > Co(II) > Cu(II) and Co(II) > Hg(II)> Cu(II) for Si-et-1 and Si-et-2 silicas, respectively. Another important feature, comes from the comparison between these $\Delta_{sat}H_m$ values and indicates a greater interaction between Si-et-1 and Hg(II) and Cu(II) in comparison with Si-et-2. This finding suggested that steric effects apparently limit the interaction strength as the length of the attached organic groups increased on a surface. Besides relatively high values of $\Delta_{sat}H_m$ for Co(II), the low adsorbed quantities, i.e. N^s, makes difficult a secure overall comparison.

The relatively high values of the constant b (Table 2) obtained from application of a similar equation to the Langmuir model, suggest a reasonable thermodynamic stability of the complexes formed on both Si-et-1 and Si-et-2 silicas.

During the adsorption, as represented by Eq. (1), the interaction can be seen as a simple transfer process, where solvent molecules, initially bonded to the solid surface, are displaced by solute molecules dispersed into the solution. The solute molecules leave the bulk liquid and enter the surface layer in the solid, and solvent molecules leave the surface layer to enter in the bulk liquid. Additionally, solute solvation is modified with the adsorption process. These exchange effects occurring in the adsorption processes are included in the adsorption enthalpy change values. If the entirely process represents a competition between cation and water molecules for the surface, the high enthalpic values could indicate that the dessolvation of surface is not an important process in this adsorption. In spite of the large difference between values of thermal effect of wetting, Q_{wet},

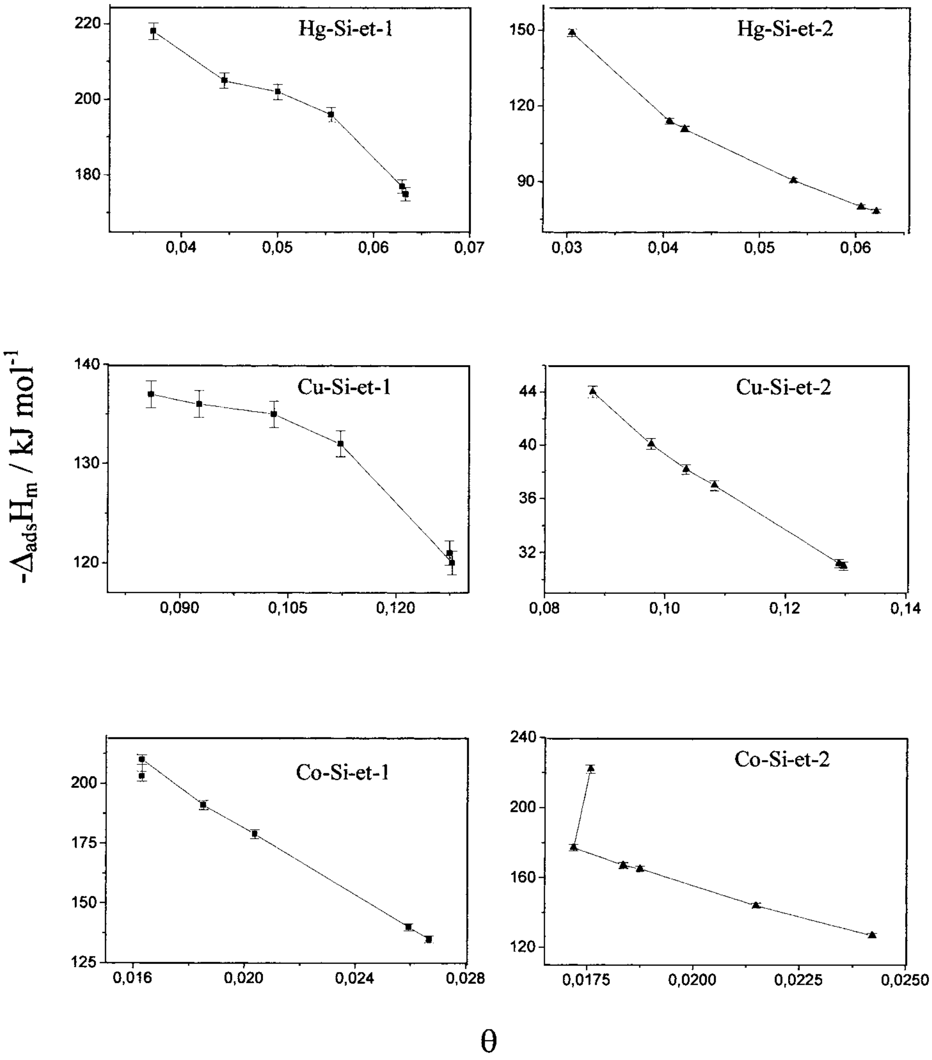

Fig. 2. The variation of the enthalpy of adsorption, $\Delta_{\mathrm{ads}}H_{\mathrm{m}}$, as a function of the covered fraction of the surface, θ, for Hg(II), Cu(II) and (Co(II)) adsorption on Si-et-1 and Si-et-2 silicas.

-9.29 for Sil-et-1 and $-0.90\ \mathrm{J\ g^{-1}}$ for Sli-et-2, all $\Delta_{\mathrm{ads}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{sat}}H_{\mathrm{m}}$ values were higher for Sil-et-1. At least it is possible to think of differences in surface wetting after cation adsorptions, but is very difficult to quantify and discuss these differences. The same argument is valid for the differences between solute solvations, before and after adsorption.

Finally, calorimetric measurements alone cannot clarify all the effects which follow the adsorption mechanism. One of the most important factors that have an influence on the adsorption enthalpies is, possibly, a conformational change. It is also difficult to say, from the present experiments, whether rearrangements occur as the surface coverage increases. Detailed investigations in these aspects should therefore be encouraged.

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