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Use of calorimetric titration to determine thermochemical data for interaction of cations with mercapto-modified silica gel

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Abstract

Interactions occurring between mercapto-modified silica gel and silver, mercury, copper and zinc ions in ethanolic solutions have been investigated by using calorimetric titrations with direct determination of the reaction extension. A calorimetric technique is described for the simultaneous determination of thermal effects and quantities of cations that interact at each titration point. From this procedure, values of maximum capacity of interaction (N^s), differential interaction enthalpies at different coverages of the surface ($\Delta_{\text{int(i)}}H_{\text{m}}$), integral energy of interaction (Q_{mon}) and molar integral enthalpy of interaction for a monolayer ($\Delta_{\text{mon}}H_{\text{m}}$) have been obtained. The maximum capacity of interaction values are compared with those previously published for analogous interaction processes in aqueous solutions. Thermochemical quantities are discussed in terms of evaluation criterion of the acid–base interactions, and generally support the conclusion that the Pearson's hypothesis of hard and soft acids and bases is appropriated to describe the behavior of the interaction of the above-mentioned cations. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Enthalpy; Silica gel; Adsorption; Immobilization

1. Introduction

The chemical modification of the silica gel surface is a well-known and convenient method for combining silica gel with an organic molecule [1–7]. Silica gel is of particular interest because it does not swell and has good mechanical strength and thermal stability. Among the more promising highly developed surfaces are the silica-attached organosilanes which are widely used in various technologies [8–16].

Fairly recently, we have investigated interactions of mercury, silver, copper, nickel and zinc ions with mercapto-modified silica gel surface (Sil-SH) in aqueous solutions [17]. One motivation was to provide a calorimetric titration method that could yield energies involved at different surface coverages and the corresponding amount of cation that interacts at each titrant increment. The developed method has provided quantitative information on the energetic effects of solid/solution interfacial displacement processes and it was possible to discuss the adsorption processes in an exact thermodynamic way. Investigations on the thermodynamics of adsorption from the solutions have been reported [18–24]; 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 the interactive processes of mercury, silver, zinc and

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copper ions with the silica gel modified with 3-(trimethoxysilyl)propane-1-thiol (3-mpts) in ethanolic solution. The determination of the energy distribution of the adsorption sites on the Sil–SH is an essential feature in the study of this heterogeneous medium.

2. Experimental

Unless stated otherwise, all reagents were of analytical reagent grade. The organosilane used in this study, 3-mpts, was supplied by Aldrich and used without further purification. The silica used as the support is a porous sample supplied by Fluka with a nitrogen BET surface area of 422 $m^2 g^{-1}$, and a mean pore diameter of 60 Å. Particle size ranges between 0.063 and 0.200 mm (70–230 mesh). Xylene from Merck was distilled and dried with sodium metal before use. Acetone and ethanol (Merck) were purified following procedures available in the literature [25] and kept dry under nitrogen atmosphere.

Ethanolic solutions of the anhydrous salts $AgNO_3$ (Vetec), $CuCl_2$ (Merck), $ZnCl_2$ (Ecibra) and $HgCl_2$ (Vetec) were used. The $CuCl_2$ was obtained from $CuCl_2{\cdot}3H_2O$ which was dehydrated by heating for 8 h in vacuum at 383 K [26]. Zinc chloride was vacuum-dried for 6 h before use and handled in a dry nitrogen atmosphere using a glove-box.

The surface modification procedure with 3-mpts has been detailed in our previous paper [17]. Assuming a non-polymerised mercapto layer, the idealised reaction can be considered to be as shown in Fig. 1.

The specific surface area (by BET method using N_2 at 77 K [27]) of Sil–SH was found to be 346 $m^2 g^{-1}$, but reduced when compared with the value for the unmodified silica gel (422 $m^2 g^{-1}$). Such a reduction can be mainly attributed to the coating of the pores of the surface by organofunctional groups which prevents the access of nitrogen molecules into some of the pores. ^{13}C and ^{29}Si NMR with cross polarisation and magic-angle spinning(CP-MAS), FTIR diffuse reflectance and thermogravimetry have been used to characterise the Sil–SH. The CP-MAS measurements were made on a AC 300/P Bruker NMR spectrometer operating at 75.47 MHz for ^{13}C and at 59.63 MHz for ^{29}Si. Infrared spectral data for unmodified and modified silica gel were obtained on a Perkin–Elmer 1600 series FTIR spectrophotometer and diffuse reflectance accessory at a resolution of 4 cm^{-1}, by using spectral quality KBr powder. Thermogravimetric determinations were performed using a Dupont thermogravimetric analyser with a dynamic atmosphere flow (0.33 $cm^3 s^{-1}$) and a heating rate of 0.16 $K s^{-1}$.

The thermochemical data for the interaction processes of Ag(I), Hg(II), Zn(II) and Cu(II) with the silica-attached 3-mpts were obtained from incremental calorimetric titrations, at 298.15 K, performed in an isoperibolic precision calorimetric system LKB 8700-2. The performance of the calorimeter has been described elsewhere [28] and details of the operation involving the calorimetric measurements have been outlined in our previous paper [17].

Thermostated ethanolic solutions containing 0.040 mol dm^{-3} ($AgNO_3$) or 0.050 mol dm^{-3} ($HgCl_2$) were added to the calorimeter vessel containing $\approx$0.3 g of Sil–SH suspended in 110.0 cm^3 of ethanol, under vigorous stirring. Thermostated ethanolic solutions containing 0.008 mol dm^{-3} ($CuCl_2$) or 0.050 mol dm^{-3} ($ZnCl_2$) were added to a suspension of $\approx$2.0 g of Sil–SH in 90.0 cm^3 of the same solvent. Each cation solution addition (0.50 cm^3 for $AgNO_3$, $HgCl_2$, $CuCl_2$ and 1.00 cm^3 for $ZnCl_2$) yielded a thermal effect, $Q_{r(i)}$. The total volume of titrant added for each titration curve was dependent on the Sil–SH saturation, i.e. the cation solutions were added until no further thermal effect was recorded. The $\sum Q_{r(i)}$ thermal effects were corrected by subtracting the thermal dilution effects, $\sum Q_{d(i)}$. Interactions energies, $Q_{int(i)}$, were calculated at each calorimetric titration point (i)

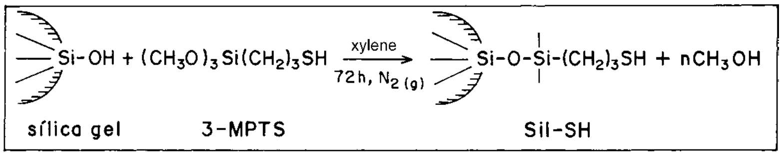

Fig. 1. Reaction for the modification of silica gel with 3-(trimethoxysilyl)propane-1-thiol.

by using the equation:

$$Q_{\mathrm{int}(i)} = Q_{\mathrm{res}(i)} - Q_{\mathrm{res}(i-1)} \tag{1}$$

where $Q_{\mathrm{res}(i)} = \sum Q_{\mathrm{r}(i)} - \sum Q_{\mathrm{d}(i)}$ is the resulting thermal effect.

After each $Q_{\mathrm{r}(i)}$ recording, mechanical stirring was stopped in order to withdraw 1.0 cm^3 of the supernatant solution for determination of the cation equilibrium concentration, $n_{\mathrm{eq}(i)}$, and thus the amount of solute that interacts with the Sil–SH at each calorimetric titration point, $n_{\mathrm{int}(i)}$.

$$n_{\mathrm{int}(i)} = n_{\mathrm{add}(i)} - \left(n_{\mathrm{eq}(i)} - n_{\mathrm{eq}(i-1)}\right) \tag{2}$$

where $n_{\mathrm{add}(i)}$ is the added solute amount. Mercury content was determined by complexometric titration with dithizone [29], while silver, copper and zinc contents were obtained by atomic absorption spectrometry on a Perkin–Elmer 5000 atomic absorption spectrophotometer with an air-acetylene flame.

From a knowledge of $n_{\mathrm{int}(i)}$ together with Q_{int} under each equilibrium condition, differential interaction enthalpies at different coverage of the surface, $\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$, have been calculated:

$$\Delta_{\mathrm{int}(i)}H_m = Q_{\mathrm{int}(i)}/n_{\mathrm{int}(i)} \tag{3}$$

3. Result and discussion

All the results used to provide quantitative and qualitative information about Sil–SH, based on Refs. [30–32], were somewhat emphasised on Ref. [17].

One potential strategy in which we have concentrated our efforts, is the simultaneous determination of the thermal effects and the corresponding quantities of cations that interact at each calorimetric titration point. The cation solutions were added in order to saturate the surface where a monolayer is assumed to be formed [33]. In essence, values of integral energy of interaction for a saturated monolayer per gram of Sil–SH, $Q_{\mathrm{mon}} = \sum Q_{\mathrm{int}(i\mathrm{th})}$, and the maximum amount of solute that interacts for a net calorimetric curve, $N^{\mathrm{s}} = \sum n_{\mathrm{int}(i\mathrm{th})}$, have been determined. From this procedure, the molar enthalpy of interaction for formation of a monolayer of anchored cations per gram of Sil–SH and per mol of exchanged cation, $\Delta_{\mathrm{mon}}H_{\mathrm{m}}$, can be directly obtained:

$$\Delta_{\mathrm{mon}}H_{\mathrm{m}} = Q_{\mathrm{mon}}/N^{\mathrm{s}} \tag{4}$$

The values of Q_{mon}, N^{s} and $\Delta_{\mathrm{mon}}H_{\mathrm{m}}$, presented in Tables 1–4, clearly characterise the energy of distribution of the adsorption sites on the Sil–SH. The Q_{mon} and N^{s} values, shown in the last rows, are normalised for 1.0 g of Sil–SH. From the tabulated values, it can be seen that all measurements yield different interaction energies evolved at different coverages; thus, the differential interaction enthalpy values, $\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$, are not constant with the coverage, but yield an average value of $\Delta_{\mathrm{mon}}H_{\mathrm{m}}$. It is clear that interactions at lower coverage yield higher enthalpy values, which decrease at increasing coverage. Whence the surface in question must be regarded as potentially heterogeneous.

Table 1
Calorimetric titration of 0.301 g of Sil–SH suspended in 110.0 cm^3 of ethanol, with 0.049 mol dm^{-3} AgNO$_3$ solution

$n_{\mathrm{int}(i)}/(10^{-4}$ mol)	$-Q_{\mathrm{int}(i)}$/J	$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$/(kJ mol^{-1})
0.245	1.64	66.9
0.241	1.14	47.3
0.244	0.84	34.4
0.238	0.80	33.6
0.250	0.57	22.8
0.223	0.47	21.1
0.232	0.46	19.8
0.225	0.30	13.3
0.156	0.21	13.5
0.224	0.21	9.4
0.210	0.18	8.6
0.161	0.12	7.5
$\sum n_{\mathrm{int}(i)}/\mathrm{m} \equiv \mathrm{N^s} \times 10^4$/mol g^{-1} $= 8.84 \pm 0.09$	$\sum \mathrm{Q}_{\mathrm{int}(i)}/\mathrm{m} \equiv Q_{\mathrm{mon}}$/J g^{-1} $= -23.1 \pm 0.3$	$\sum Q_{\mathrm{int}(i)}/\sum n_{\mathrm{int}(i)} \equiv \Delta_{\mathrm{mon}}H_{\mathrm{m}}$/kJ mol^{-1} $= -26.2 \pm 0.4$

Table 2
Calorimetric titration of 0.299 g of Sil–SH suspended in 110.0 cm^3 of ethanol, with 0.050 mol dm^{-3} $HgCl_2$ solution

$n_{\mathrm{int}(i)}/(10^{-4}$ mol)	$-Q_{\mathrm{int}(i)}$/J	$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$/(kJ mol^{-1})
0.250	2.51	100.4
0.250	1.50	60.0
0.250	1.28	51.2
0.250	1.12	44.8
0.250	1.00	40.1
0.250	0.98	39.2
0.250	0.81	32.4
0.250	0.72	28.8
0.243	0.55	22.6
0.250	0.49	19.6
0.247	0.41	16.6
0.249	0.39	15.7
$\sum n_{\mathrm{int}(i)}/\mathrm{m} \equiv \mathrm{N}^{\mathrm{s}} \times 10^4/\mathrm{mol\ g}^{-1} = 9.96 \pm 0.10$	$\sum Q_{\mathrm{int}(i)}/\mathrm{m} \equiv Q_{\mathrm{mon}}/\mathrm{J\ g}^{-1} = -39.3 \pm 0.4$	$\sum Q_{\mathrm{int}(i)}/\sum n_{\mathrm{int}(i)} \equiv \Delta_{\mathrm{mon}}H_{\mathrm{m}}/\mathrm{kJ\ mol}^{-1} = -39.4 \pm 0.5$

Table 3
Calorimetric titration of 1.992 g of Sil–SH suspended in 90.0 cm^3 of ethanol, with 0.050 mol dm^{-3} $ZnCl_2$ solution

$n_{\mathrm{int}(i)}/(10^{-4}$ mol)	$-Q_{\mathrm{int}(i)}$/J	$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$/(kJ mol^{-1})
0.462	1.40	30.3
0.417	1.09	26.1
0.358	0.75	20.9
0.235	0.34	14.5
0.208	0.29	13.9
0.179	0.21	11.7
$\sum n_{\mathrm{int}(i)}/\mathrm{m} \equiv \mathrm{N}^{\mathrm{s}} \times 10^4/\mathrm{mol\ g}^{-1} = 0.93 \pm 0.01$	$\sum Q_{\mathrm{int}(i)}/\mathrm{m} \equiv Q_{\mathrm{mon}}/\mathrm{J\ g}^{-1} = -2.04 \pm 0.02$	$\sum Q_{\mathrm{int}(i)}/\sum n_{\mathrm{int}(i)} \equiv \Delta_{\mathrm{mon}}H_{\mathrm{m}}/\mathrm{kJ\ mol}^{-1} = -21.9 \pm 0.3$

Table 4
Calorimetric titration of 2.005 g of Sil–SH suspended in 90.0 cm^3 of ethanol, with 0.008 mol dm^{-3} $CuCl_2$ solution

$n_{\mathrm{int}(i)}/(10^{-5}$ mol)	$-Q_{\mathrm{int}(i)}$/J	$-\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$/(kJ mol^{-1})
0.400	0.53	132
0.400	0.52	130
0.400	0.48	120
0.342	0.42	122
0.386	0.40	103
0.373	0.38	102
0.359	0.35	97
0.332	0.31	93
0.306	0.23	75
$\sum n_{\mathrm{int}(i)}/\mathrm{m} \equiv \mathrm{N}^{\mathrm{s}} \times 10^{-5}/\mathrm{mol\ g}^{-1} = 1.66 \pm 0.10$	$\sum Q_{\mathrm{int}(i)}/\mathrm{m} \equiv Q_{\mathrm{mon}}/\mathrm{J\ g}^{-1} = -1.81 \pm 0.02$	$\sum Q_{\mathrm{int}(i)}/\sum n_{\mathrm{int}(i)} \equiv \Delta_{\mathrm{mon}}H_{\mathrm{m}}/\mathrm{kJ\ mol}^{-1} = -108 \pm 2$

The maximum capacity of interaction values (N^{s}) indicates that the coverages achieved for adsorption of Hg^{2+}, Ag^{+}, Zn^{2+} and Cu^{2+} are 73%, 64%, 6.8% and 1.2%, respectively, by assuming an Sil–SH with a sulphur content of 1.37 mmol g^{-1}. The surface coverage by the bivalent copper is smaller than the others,

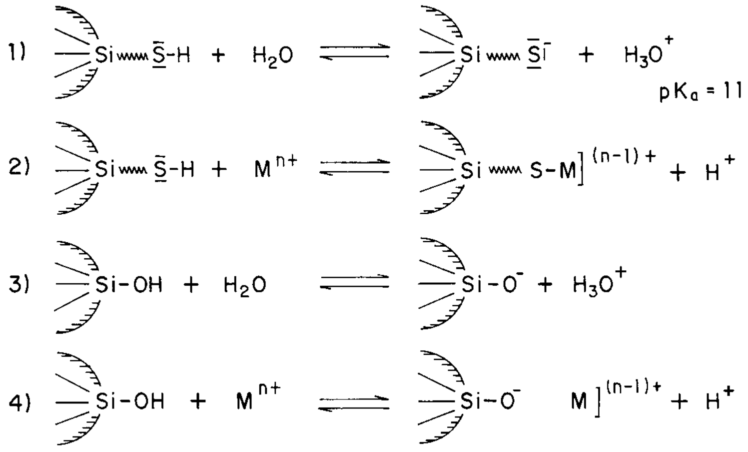

Fig. 2. Equilibria involved in the interaction of the cations with mercapto-modified silica gel.

but has the highest $\Delta_{\mathrm{mon}}H_{\mathrm{m}}$ value for its interaction with Sil–SH, which indicates that Cu^{2+} only interacts with the most energetic sites.

Based on our previous study, which deals with determination of enthalpy change of cations interacting with Sil–SH in aqueous solutions [17], we conclude that, when the same coverage is not achieved for adsorption of all cations, the thermodynamic quantity $\Delta_{\mathrm{int(i)}}H_{\mathrm{m}}$ should be better than $\Delta_{\mathrm{mon}}H_{\mathrm{m}}$ to evaluate the acid–base interactions, since the former values can be compared for the same surface coverage range. To support this view, we took the results of silver, mercury and zinc and neglected those of copper. From Tables 1–3, we can compare the $\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$ values for the same coverage achieved for adsorption of the three cations. It can be seen that, at the first point of the titration of Sil–SH, silver and mercury adsorptions are $n_{\mathrm{int}(i)}/m = 0.814$ and 0.836×10^{-4} mol g^{-1}, respectively, and this value is nearly achieved for zinc at the fifth point of the titration. At this surface coverage, the $\Delta_{\mathrm{int}(i)}H_{\mathrm{m}}$ (kJ mol^{-1}) values present the sequence $Hg^{2+}(-100.4) > Ag^{+}(-66.9) > Zn^{2+}(-23.0)$, which indicates the preference of the soft –SH group for the soft acids, according to Pearson's hypothesis [34].

Our previous study [17], found the following order for the N^{s} values (mol g^{-1}) for the interaction of cations with mercapto-modified silica gel in aqueous solutions: Ag^{+} $(11.28 \times 10^{-4}) > Hg^{2+}(4.89 \times 10^{-4}) > Zn^{2+}(0.98 \times 10^{-4}) > Cu^{2+}(0.81 \times 10^{-4})$. This clearly shows that, with the exception of mercury, more attached –SH groups are available for adsorption of the metal ion in aqueous solutions. According to Aydin [12], the proton of the thiol group on the surface is dissociated and the metal ions are adsorbed via complexation with the thiol and silanol groups on the surface. Four equilibria are involved in the interaction processes, as viewed by the equations in Fig. 2. Although this is not a sufficient argument to determine the mechanism involved in these reactions, it is evident that the –SH group of the mercapto-modified silica gel is more easily dissociated in aqueous solutions, and this enhances the interaction capacity of the cations with sulphur atom. Such considerations, consequently, suggest that the process of ion exchange is involved in the adsorption of metal cations but more sophisticated measurements are necessary to understand all the effects.

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