# Interaction of cations with SH-modified silica gel: thermochemical study through calorimetric titration and direct extent of reaction determination

**Eunice F. S. Vieira, José de A. Simoni*† and Claudio Airoldi**

*Instituto de Quimica, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970, Campinas, São Paulo, Brasil*

The reaction of silica gel with 3-(trimethoxysilyl)propane-1-thiol, MPTS, produced a thiol-modified silica gel, Sil—SH. This material removes silver, mercury, copper, zinc and nickel ions from aqueous solutions. Enthalpy changes that occur in the interactions between Sil—SH and these cations were obtained by a calorimetric titration technique, in which thermal effects and the quantities of cations that interact at each titration point were determined simultaneously. From this procedure, values of the maximum capacity of interaction ($N^s$), enthalpies of interaction at different coverages of the surface [$\Delta_{\mathrm{int(i)}}H_\mathrm{m}$] and integral enthalpy of interaction for a monolayer ($\Delta_{\mathrm{mon}}H_\mathrm{m}$) have been established. It is shown that this method permits charting the basic sites created upon modification. From $\Delta_{\mathrm{int(i)}}H_\mathrm{m}$ values, the sequence of the interaction strength between the basic sites of the silica-attached MPTS and the cations is $\mathrm{Hg}^{2+} > \mathrm{Ag}^{+} > \mathrm{Cu}^{2+} > \mathrm{Ni}^{2+} > \mathrm{Zn}^{2+}$, in agreement with the concept of hard and soft acids and bases. The influence of some parameters concerning the thermodynamics of solvation of the indicated transition metals has been also taken into account in the investigation of these interaction processes.

The great deal of activity in the synthesis, characterization and application of mechanically stable matrices, such as chemically modified silica gel surfaces, has been important in several areas of science in recent years. These materials 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, finding extensive use in fields as diverse as modern high performance liquid chromatography,[1,2] cation-exchange,[3] catalytic activity,[4] metal ion adsorption,[5] immobilization of biological molecules[6] and separation and preconcentration of trace elements.[7–9] These surfaces enable speciation of trace elements and are useful in solving many problems in nuclear technology, electronics, metallurgy, mining, medicine, agriculture, fisheries and environmental studies.

Taking into account the general formula of an organosilane ($\mathrm{RSiX_3}$), two classes of functional groups are seen: (i) X is a hydrolyzable group, typically a halogen, alkoxy or acyloxy and (ii) R is a non-hydrolyzable organic radical that may possess functional groups with specific characteristics. The quality and durability of silanized materials depends primarily on the nature of the attachment to the surface[10] and the possible technological applicability is strongly related to surface properties.

The main purpose of this work is focused on the determination of the enthalpy change upon interaction of cations with a thiol-modified silica gel surface, in aqueous solution. Calorimetric titration, which is the most appropriate technique for this determination, was used. Such a technique has been widely used to investigate homogeneous solution reactions but its use for heterogeneous medium studies is far less extensive. The interactions of an 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.[11] One aspect of our research is concerned with the direct determination of enthalpy changes for acid–base interactions from the net calorimetric titration curve. An improved calorimetric method is developed here in order to obtain energies evolved at different surface coverages and the corresponding amount of substance which interacts. In following this procedure, the equilibrium conditions are well defined and this method provides a direct means to obtain accurate differential enthalpy values at each increment. As a result, the knowledge of the energy distribution of the adsorption sites on the surface is an essential result of this study of heterogeneous adsorbent.

In this survey, the silica gel surface was modified with 3-(trimethoxysilyl)propane-1-thiol, $\mathrm{(CH_3O)_3Si(CH_2)_3SH}$, to yield a silica-attached organosilane, Sil—SH. This thiol-modified surface has an excellent ability to extract some metal ions from aqueous and non-aqueous solutions.[12] Such properties towards silver, mercury, copper, nickel and zinc have been thermodynamically studied.

## Experimental

### Chemicals

Silica gel (Fluka) with a particle size of 0.063–0.200 mm (70–230 mesh), having a mean pore diameter of 60 Å, was used as support. Reagent grade 3-(trimethoxysilyl)propane-1-thiol (Aldrich) was used without further purification. Acetone (Merck) was stored over an appropriate dehydrating agent and then distilled.[13] Xylene (Merck) was distilled and dried with metallic sodium.

Solutions of cations were prepared from anhydrous silver nitrate (Vetec), mercury (Vetec) and zinc (Ecibra) chlorides and hydrated copper (Carlo Erba) and nickel (Carlo Erba) nitrates, in deionisated water free of $\mathrm{CO_2}$ and $\mathrm{O_2}$ (by an $\mathrm{N_2}$ purge–vacuum cycle).

### Chemical modification of the silica gel surface

In the process of modification, 40.0 g of silica gel were initially degassed under vacuum at 423 K for 8 h in a steam of dry nitrogen, in order to remove physically adsorbed water,[14–17] and subsequently treated with 25.0 $\mathrm{cm^3}$ of 3-(trimethoxysilyl)propane-1-thiol (MPTS) in 250 $\mathrm{cm^3}$ xylene. The mixture was heated under reflux in a dry nitrogen atmosphere for 72 h. The thiol-modified silica, Sil—SH, was washed with acetone and xylene until the washing solvents indicated the absence of free thiol groups, determined by testing with silver nitrate.[18] After filtration, the Sil—SH was dried under vacuum at 323 K for 6 h.

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† E-mail:caja@iqm.unicamp.br

The Sil—SH was characterized by surface area determination using the BET procedure,[19] $^{13}C$ and $^{29}Si$ NMR with cross polarization and magic-angle spinning (CP MAS), FTIR diffuse reflectance spectroscopy and thermogravimetry. 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 $^{29}Si$. IR spectral data were obtained with the use of a Perkin-Elmer 1600 series FTIR spectrophotometer and diffuse reflectance accessory at a resolution of 4 $cm^{-1}$, by using spectro quality KBr powder. Thermogravimetric determinations were performed using a DuPont thermogravimetric analyser in a dynamic atmosphere of argon (0.33 $cm^3$ $min^{-1}$) with a heating rate of 0.16 K $s^{-1}$.

### Calorimetric titration procedure

All experiments were carried out at 298.15 K in the isoperibolic precision calorimetric system LKB 8700-2, whose performance and details have been previously described.[20] Thermostated aqueous solutions of cations were incrementally added, under vigorous stirring (500 rpm), to the calorimeter vessel containing a given amount of Sil—SH suspended in a known volume of bidistilled water. All the experimental conditions for the calorimetric titrations are summarized in Table 1. The added volume of cation solution for each net titration curve is dependent on the saturation of the surface. Each titrant addition yielded a thermal effect, which was corrected by subtracting dilution effects ($Q_d$), for each increment of the cation solution in the same solvent.

The processes of calorimetric titration involving thermal effects of the interactions of suspended Sil—SH, at each equilibrium condition, are outlined as follows:

$$\text{Sil—SH} + M^{n+}(\text{soln}) = \text{Sil—SM}^{(n-1)} + H^+(\text{soln});\ Q_r \qquad (1)$$

$$M^{n+}(\text{soln}) + \text{solvent} = M^{n+}(\text{soln});\ Q_d \qquad (2)$$

Thus, the interaction energies, $Q_{\text{int(i)}}$, were obtained after each titrant addition:

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

The process of interaction [eqn. (1)] involves the effect of swelling of the silica gel upon replacement of $H^+$ with $M^{n+}$. Therefore, $Q_r$ and $Q_{\text{int}}$ values include the corresponding enthalpy change values, $Q_{\text{swel}}$.

Differential interaction enthalpies at different coverage of the surface, $\Delta_{\text{int(i)}}H_m$, were calculated from knowledge of the amount of solute that interacts, $n_{\text{int(i)}}$, required to yield $Q_{\text{int(i)}}$ under each equilibrium condition:

$$\Delta_{\text{int(i)}}H_m = Q_{\text{int(i)}}/n_{\text{int(i)}} \qquad (4)$$

In order to determine $n_{\text{int(i)}}$, it was necessary to devise an appropriate calorimeter vessel connected with an additional capillary tube bearing a 1.0 $cm^3$ pipette at its extremity. The technique consisted of stopping mechanical stirring for five minutes and, through the additional tube, withdrawing 1.0 $cm^3$ of the supernatant solution to determine the cation equilibrium concentration. Each titrant addition was separated by 25 min from the next, during which time the thermal effects due to titrant addition and electrical calibration were recorded. With the exception of mercury, which was determined by complexometric titration with dithizone,[21] all other metal contents were measured by atomic absorption spectrometry on a Perkin-Elmer 5000 atomic absorption spectrophotometer with an air–acetylene flame.

**Table 1** Experimental conditions for the calorimetric titrations performed for cations $M^{n+}$ with initial concentration $[M^{n+}]$, starting from an initial volume $V_0$ to reach the final volume $V_f$ in a suspension with a amount, $m$, of Sil—SH in the calorimetric vessel, to give a number $n_e$ of experiments at 298.15 K

| $M^{n+}$ | $[M^{n+}]$/mol $dm^{-3}$ | $V_0$/$cm^3$ | $m$/g | $V_f$/$cm^3$ | $n_e$ |
|---|---|---|---|---|---|
| $Ag^+$ | 0.125 | 90.0 | 1.0 | 101.5 | 23 |
| $Hg^{2+}$ | 0.125 | 110.0 | 2.0 | 118.5 | 17 |
| $Cu^{2+}$ | 0.100 | 90.0 | 2.0 | 92.0 | 8 |
| $Ni^{2+}$ | 0.250 | 90.0 | 2.0 | 91.5 | 6 |
| $Zn^{2+}$ | 0.100 | 90.0 | 2.0 | 99.0 | 9 |

## Results and Discussion

The determination of surface areas *via* the BET method for unmodified and modified silica gel gave values of 422 and 346 $m^2$ $g^{-1}$, respectively. This 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.

Comparison of the diffuse reflectance spectra of Sil—SH [Fig. 1(a)] with that of unmodified silica gel [Fig. 1(b)] and MPTS [Fig. 1(c), obtained as a film], gives clear evidence of modification as shown by absorption bands at 2578 $cm^{-1}$, attributed to the S—H stretching vibration,[8] and in the region 2900–2850 $cm^{-1}$, due to the aliphatic C—H stretching of the attached propyl groups.[22] The degree of the sulfur content was quantitatively determined by using a recent method established from the thermogravimetric data,[23] which gave 1.37 mmol S per gram of Sil—SH.

CP MAS NMR gives spectra of solids with a quality approaching that obtained routinely with solutions.[24] In the $^{13}C$ CP MAS NMR spectrum of Sil—SH [Fig. 2(a)] the resonance at $\delta$ 49.6 is due to the C atom of the methoxy groups of the attached organosilane [Fig. 2(b)]; a peak at $\delta$ 27.4 is assigned to the $\alpha$ and $\beta$ methylene C atoms and the

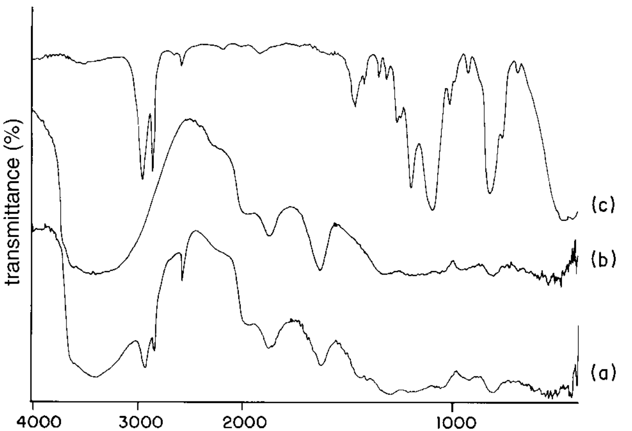

**Fig. 1** FTIR spectra: (a) Sil—SH, (b) unmodified silica gel, (c) MPTS

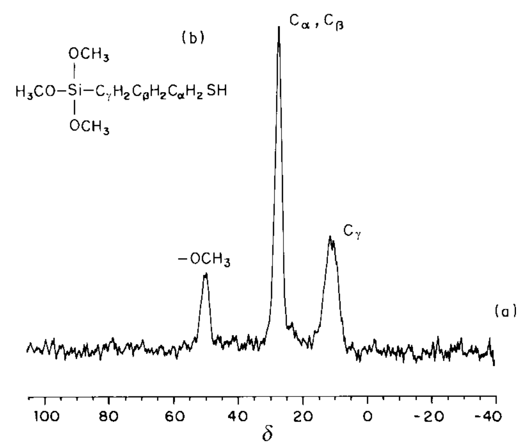

**Fig. 2** (a) $^{13}C$ CPMAS NMR spectrum of Sil—SH, and (b) the silica-attached MPTS structure

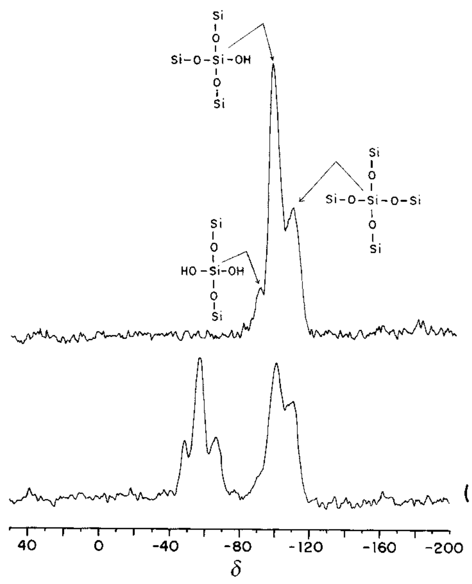

**Fig. 3** $^{29}$Si CP MAS spectra: (a) Sil—SH, (b) unmodified silica gel

peak at δ 11.3 is due to the γ methylene C atom. The $^{29}$Si CP MAS NMR spectrum for the thiol-modified silica [Fig. 3(a)] shows two peaks at δ −110.6 and −100.9. These peaks are attributed to silicon in the siloxane bonding environment without hydroxy groups and to isolated silanol groups, respectively, signals which are also observed for the unmodified silica surface [Fig. 3(b)].[25–27] Three different resonance peaks associated with organosilane molecules in different molecular environments are seen in Fig. 3(a). The signals at δ −48.5, −56.9 and −66.3 are assigned to structures (a), (b) and (c) (Fig. 4), respectively.

In all calorimetric titration processes, the cation solutions were added until the surface was saturated, *i.e*, until no thermal effect was recorded. At this point a monolayer is proposed to be formed.[28] The molar enthalpy of interaction for formation of a monolayer of anchored cations per gram of Sil—SH and per mol of exchanged cation, $\Delta_{mon}H_m$, can be directly obtained by means of the expression:

$$\Delta_{mon}H_m = Q_{mon}/N^s \qquad (5)$$

where $Q_{mon} = \Sigma Q_{int(i)}$ is the integral energy of interaction for a saturated monolayer per gram of Sil—SH, and $N^s = \Sigma n_{int(i)}$ is the maximum amount of solute that interacts for a net calorimetric curve, determined from our method as described in the experimental section. The $N^s$ value corresponds to the maximum capacity of interaction to form a monolayer. The values obtained directly from this method are shown in Table 2.

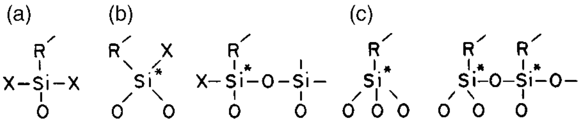

**Fig. 4** Different attachment forms of the MPTS on silica gel surface: (a) monodentate, (b) bidentate, (c) tridentate

**Table 2** Results of maximum capacity of intraction ($N^s$), integral energy of interaction for a saturated monolayer per gram of Sil—SH ($Q_{mon}$) and integral enthalpy of interaction for a monolayer ($\Delta_{mon}H_m$), from calorimetric titration data

| $M^{n+}$ | $N^s/10^{-4}$ mol g$^{-1}$ | $Q_{mon}$/J g$^{-1}$ | $\Delta_{mon}H_m$/kJ mol$^{-1}$ |
|---|---|---|---|
| $Ag^+$ | 11.28±0.11 | −66.56±0.67 | −59.01±0.82 |
| $Hg^{2+}$ | 4.89±0.05 | −25.01±0.25 | −51.14±0.72 |
| $Cu^{2+}$ | 0.81±0.01 | −6.49±0.06 | −80.12±1.09 |
| $Ni^{2+}$ | 0.89±0.01 | −2.85±0.03 | −32.02±0.49 |
| $Zn^{2+}$ | 0.98±0.01 | 2.66±0.03 | 27.14±0.41 |

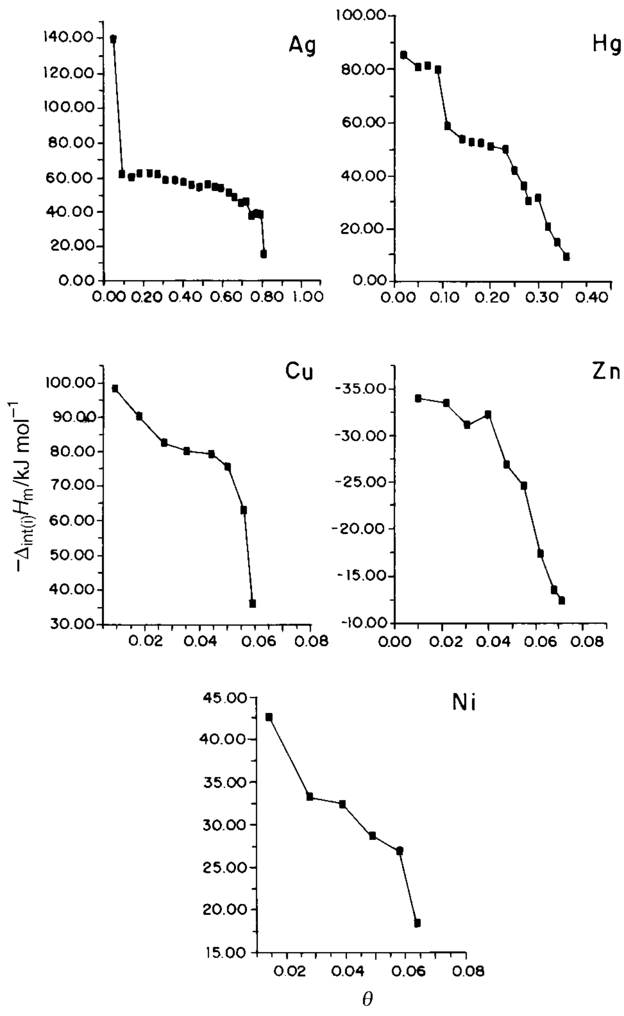

**Fig. 5** Differential interaction enthalpy values ($\Delta_{int(i)}H_m$) *vs.* the covered fraction of the surface (θ)

The surface presented by silica gel is heterogeneous.[1] This heterogeneity arises partly from the processes involved during its preparation (*e.g.*, washing, drying and the presence of metal impurities even at trace levels) and also from the thermal treatment.[29] Adsorption sites on the potentially heterogeneous surface interact with different energies. The differential interaction enthalpies are not constant with the coverage, thus the $\Delta_{mon}H_m$ value is an average value of $\Delta_{int(i)}H_m$. This feature can be observed by examining Fig. 5 which shows the differential interaction enthalpy values, $\Delta_{int(i)}H_m$ as functions of the covered fraction of the surface, $\theta = n_{int(i)}/n^{su}$, where $n^{su}$ is the amount of sulfur per gram of Sil—SH. It is clear that interactions at lower coverage yield higher enthalpy change values, which decrease with increasing coverage.

The interaction capacity, $N^s$, shows the ability of the Sil—SH to remove the metal ions from aqueous solutions. From the results given in Table 2, the $N^s$ values decrease in the order $Ag^+ > Hg^{2+} > Zn^{2+} > Ni^{2+} > Cu^{2+}$, indicating that 36% of the attached organosilanes are available for adsorption with $Hg^{2+}$, whereas only 7.1, 6.5 and 5.9% of the coverage is achieved for interaction of $Zn^{2+}$, $Ni^{2+}$ and $Cu^{2+}$, respectively. Surprisingly, the silver interaction capacity of 1.13 mmol g$^{-1}$ shows that 80% of the attached ligands are available for this metal ion since the surface modification procedure resulted in a product with a sulfur content of 1.37 mmol g$^{-1}$. This result, although not atypical of a modified surface,[8] may also represent the presence of non-specific silver uptake.[30]

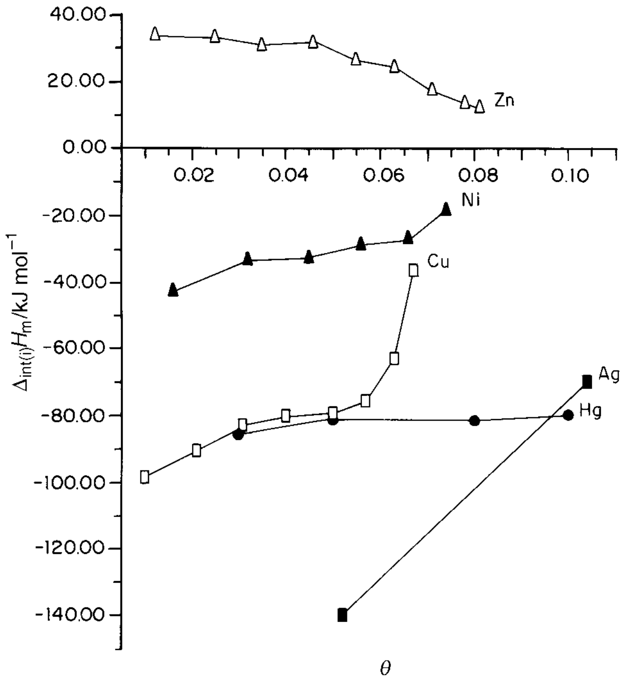

**Fig. 6** Differential interaction enthalpy values ($\Delta_{int(i)}H_m$) *vs.* the covered fraction of the surface (θ) in the same surface coverage range

Previous studies[31,32] concerning thermodynamics of solvation of these metallic ions establish that the experimental values of the molar Gibbs energies of hydration, $-\Delta_{hyd}G°$/kJ mol$^{-1}$ ($Ag^+ = 430$, $Hg^{2+} = 1760$, $Zn^{2+} = 1955$, $Ni^{2+} = 1980$, $Cu^{2+} = 2010$), and the standard molar enthalpy changes of hydration, $-\Delta_{hyd}H°$/kJ mol$^{-1}$ ($Ag^+ = 483$, $Hg^{2+} = 1853$, $Zn^{2+} = 2070$, $Ni^{2+} = 2119$, $Cu^{2+} = 2123$), are in the sequence $Ag^+ < Hg^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+}$. The main contributions to these parameters are electrostatic effects, resulting in solvent interaction, dielectric saturation in a hydration shell of specific thickness and further effects on the water that surrounds this shell. The influence of these parameters has been taken into account in the interaction processes of such ions. The results indicate that on increasing $\Delta_{hyd}G°$ and $\Delta_{hyd}H°$, the interaction capacity of the metal ions with the thiol-modified surface is reduced, from which it is evident that solvation of the metal ions, *i.e.*, their interactions with the solvent molecules, can play a role in these acid–base interaction processes.

A prominent fact upon inspection of Table 2 is that the thiol-modified silica gel may be used for stable bonding of a transition metal. The —SH group is a soft base forming a donor centre which is highly polarizable and capable of interacting with low-lying orbitals of soft acids.[33] Interactions between the Lewis-acidic cations and the sulfur donor atom attached to silica are reflected by $\Delta_{mon}H_m$ values in the sequence $Cu^{2+} > Ag^+ > Hg^{2+} > Ni^{2+} > Zn^{2+}$. However, as $\Delta_{mon}H_m$ is an average value of $\Delta_{int(i)}H_m$, it must be emphasized that this thermodynamic quantity is not the best criterion to evaluate the acid–base interactions in these processes, since the same coverage is not achieved for adsorption of all cations; $Cu^{2+}$, $Zn^{2+}$ and $Ni^{2+}$ ions only interact with the most energetic sites, unlike $Ag^+$ and $Hg^{2+}$. Here, it is more relevant to consider the $\Delta_{int(i)}H_m$ parameter, whose values can be compared in the same surface coverage range. From Fig. 6, derived from Fig. 5, it is clear that the interactions with $Ag^+$ and $Hg^{2+}$ show large enthalpy values in the same coverage range compared to $Cu^{2+}$, $Zn^{2+}$ and $Ni^{2+}$. The $\Delta_{int(i)}H_m$ values, in the sequence $Hg^{2+} > Ag^+ > Cu^{2+} > Ni^{2+} > Zn^{2+}$, confirm the preference of the —SH group for soft acids, supporting the view that Pearson's concept of hard and soft acids and bases[34] is the predominant mechanism in the behavior of the interaction of these transition metals.

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## References

1 J. Nawrocki and B. Buszewski, *J. Chromatogr.*, 1988, **449**, 1.
2 W. Wasiak, *Chromatographia*, 1995, **41**, 107.
3 B. B. Wheals, *J. Chromatogr.*, 1979, **177**, 263.
4 M. Capka, M. Czaksová, E. Hillerová, E. Paetzoldi and G. Oehme, *J. Mol. Catal.* 1995, **104**, L123.
5 A. Aydin, U. Koklu and S. Tascioglu, *Chim. Acta Turc.*, 1987, **15**, 91.
6 E. Nishio, I. Abe, N. Ikuta, J. Koga, H. Okabayashi and K. Nishikida, *Appl. Spectrosc.*, 1991, **45**, 496.
7 K. Terada, *Anal. Sci.*, 1991, **7**, 187.
8 A. G. Howard, M. Volkan and D. Y. Ataman, *Analyst*, 1987, **112**, 159.
9 S. Akman, H. Ince and U. Kokler, *Anal. Sci.*, 1991, **7**, 799.
10 C. P. Tripp and M. L. Hair, *J. Phys. Chem.*, 1993, **97**, 5693.
11 G. K. Dirk and B. Thomas, *Langmuir*, 1993, **9**, 2965.
12 A. R. Cestari and C. Airoldi, *J. Braz. Chem. Soc.*, 1995, **6**, 291.
13 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 2nd edn., 1980.
14 G. Schomburg, A. Deege, J. Kokler and U. Bien-Vogelsang, *J. Chromatogr.*, 1983, **282**, 27.
15 L. C. Sande and S. A. Wise, *J. Chromatogr.*, 1984, **316**, 163.
16 K. D. Lork, K. K. Unger and J. N. Kinkel, *J. Chromatogr.*, 1986, **352**, 199.
17 B. Buszewski, L. Nondek, A. Jurasek and D. Berek, *Chromatographia*, 1987, **23**, 442.
18 R. G. Bowman and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, 1979, **101**, 159.
19 S. Brunauer, P. Emett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
20 C. Airoldi, P. L. O. Volpe and J. M. M. M. Lira, *Polyhedron*, 1983, **2**, 1125.
21 H. Onishi, *Photometric Determination of Traces of Metals, Part II*, John Wiley & Sons, New York, 4th edn., 1986.
22 T. J. Porro and S. C. Pattacini, *Appl. Spectrosc.*, 1990, **44**, 1170.
23 A. R. Cestari and C. Airoldi, *J. Therm. Anal.*, 1995, **44**, 79.
24 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.*, 1973, **59**, 569.
25 C. E. Bronnimann, R. C. Zeigler and C. E. Maciel, *J. Am. Chem. Soc.*, 1988, **110**, 2023.
26 P. Van Der Voort, I. Gillis, D. Hamers, K. C. Vranken and E. J. Vansant, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3899.
27 B. A. Marrow and A. J. MacFarlan, *J. Phys. Chem.*, 1992, **96**, 1395.
28 A. W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York, 5th edn., 1990.
29 E. M. Arnett and T. Ahsan, *J. Am. Chem. Soc.*, 1991, **113**, 6861.
30 J. R. Jerorez, K. H. Faltynski, L. G. Blackburn, P. J. Henderson and H. D. Medina, *Talanta*, 1985, **32**, 763.
31 Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2995.
32 Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1987, **83**, 339.
33 W. Wasiak, *Chromatographia*, 1987, **23**, 423.
34 R. G. Pearson, *J. Chem. Educ.*, 1968, **9**, 581.

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