Journal of Thermal Analysis and Calorimetry, Vol. 97 (2009) 2, 377–382

THERMAL STUDY OF CHELATES OF Co(II), Cu(II), Ni(II), Cr(III), Mo(III), AND Fe(III) WITH *bis*(ACETYLACETONE)ETHYLENEDIIMINE ON ACTIVATED SILICA GEL SURFACE

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The divalent copper, nickel, cobalt and trivalent chromium, molybdenium and iron chelate compounds derived from bis(acetylacetone)ethylenediimine were grafted on activated silica gel using a batch process in methanolic solution. The sequence of the maximum retention capacity was Cr(III)>Mo(III)>Fe(III)>Co(II)>Ni(II)>Cu(II). Calorimetric titration was employed to study the interaction of activated silica gel with these series of metal chelate compounds. Exothermic enthalpic results were obtained throughout all interactions process. The spontaneity of these systems was reflected in negative and positive free Gibbs energy from entropic values.

Keywords: *activated silica gel, bis(acetylacetone)ethylenediimine, calorimetry, metal interactions, thermodynamic data*

Introduction

Grafting an organic molecule on an inorganic matrix displays its ability to coordinate metal complexes, providing an interesting approach in the fields of immobilized catalysts [1–7] and high performance liquid chromatography [8, 9]. Many inorganic oxides, such as silica and alumina, can still offer distinct advantages in a series of applications due to the rigidity, insolubility in a great variety of solvents, with less susceptibility to chemical or thermal degradation [10–12]. Among the different supports, silica gel especially immobilized with various organic compounds with metal chelating ability has received great attention [8, 10–16]. The presence of silanol groups on silica gel surface behave like a weak acid ($pK_a=9.4$); thus they can interact with polar compounds through both strong hydrogen bonds and dipole–dipole interactions as the well known as Brönsted acid [10, 13]. Due to the presence of these groups of acids, silica gel is able to adsorb many of chemical species such as cyclic amines [13], amides [14], protein [15], and also for sorption in the separation process of the platinum metal [16], without previous modification with an organomolecule [13].

In the present work, we investigated the chemisorption and focused the thermodynamic determination upon and interaction of Cr(III), Mo(III), Fe(III), Co(II), Ni(II) and Cu(II) *bis*(acetylacetone)ethylenediimine chelates, M(acac-imine), on activated silica gel surface. Many works related to synthesis of shifts base using acetylacetone molecules could be found in the literature [17–24]. For instance, Darensbourg *et al.* reported Cr(III) derivatives of an alternative N4 dianionic ligand system, tetramethyltetraazannulene, which exhibit real promise as very effective catalysts for CO_2/epoxide coupling reactions [25] and as well reported the (acacen)CrCl complex in the presence of cocatalysts PCy_3 or [PPN][Cl] is an effective catalyst for the production of polycarbonate from cyclohexene oxide and carbon dioxide [26]. Nathan *et al.* synthesized the Schiff bases *bis*(acetylacetone)-*m*-phenylenediimine and *bis*(acetylacetone)-*p*-phenylenediimine and com- plexed Cd in polymeric structures in which the ligands coordinate to Cd only through oxygen atoms and function as bridging bidentate keto-amine tautomers [23], also his group synthesized the structures of six N,N’-polymethylene-*bis*(salicylaldiminato)copper(II) Schiff base complexes with alkyl backbones ranging from two to eight carbons, which have been determined by X-ray crystallography [17, 18]. There are few studies related to modification of silica surface with complex of *bis*(acetylacetone)ethylenediimine [27, 28], and thermodynamic determination [29]. The acetylacetone, acac, ligand was selected because of its large volume and a strong known tendency toward metal cation coordination [6, 7, 23, 28, 30]. This kind of ligand forms stable complexes with a specified composition whose final composition have well-known

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1388–6150/$20.00

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structures with high stability. Thus, these properties provide a substantial evaluation regarding the adsorption of the potential free acidic centers on the complexes formed [31], which available silanol groups from activated silica gel surface can be bonded to it using batch process. Therefore, all experiments were carried out in methanolic medium, since the solute reagents are quite soluble in methanol.

Experimental

Materials

Silica gel (Aldrich) with particle size 70–230 mesh, medium diameter 60 Å and pore volume of 0.75 $m^3\ g^{-1}$, was washed away from surface mineral impurities with H_2SO_4–HNO_3 (2.0 mol dm^{-3}) solutions, in 9:1 proportion. The suspension was left standing for 24 h and the supernatant then decanted. The solid was added to the same acidic solution and the same procedure was repeated. Then, the solid was filtered and extensively washed with twice-distilled water until the filtrate had the same pH as water. After this treatment, the silica was activated by heating at 423 K for 8–10 h in vacuum. The solutions of metallic cations were prepared in methanol from reagent grade materials.

Preparation of the metal chelates

Bisacetylacetone-ethylenediimine chelates was synthesized in agreement with literature [32], but with a light modification. The reagents acethyacetone and ethylenediamine were purchased from Aldrich and used without purification. A mixture of one mole of ethylenediamine and two moles of acetylacetone, both dissolved in methanol, was stirred for 3 h. During the stirring process, was added to the reacting mixture a quantity of diluted solution of NaOH in the molar ratio sodium-ligand of 2:1, until the solid compound started to settle. Then, the liquid was eliminated in rotary evaporators at 380 K, and the solid was washed several time with methanol and filtered. After that, it was dried in vacuum at room temperature for 2 h. The metal chelates were made by the following procedure: a methanolic solution of the M chlorides, (M=Cr(III), Mo(III), Fe(III), Cu(II), Ni(II) and Co(II), with known concentrations, were mechanically stirred with the sodium salt of acetylacetodiimine in the proportion of 1:1 until precipitation of the NaCl, for 2 h at room temperature. The NaCl salt was separated by filtration and the metal chelate in the solution was obtained and dried under vacuum, The obtained solid was recrystallized two times in methanol.

Methods

Adsorption of M(acac-imine) on activated silica

The complex of M(acac-imine) was immobilized on surface of activated silica gel using batch method at 298±1 K. For this process a series of samples of about 50.0 mg of the activated silica, was suspended in 20.0 cm^3 of the metal chloride in methanolic solution of different concentration varying from 0.04 to 0.80 mmol dm^{-3}. The suspension were mechanically stirred for 2 h at room temperature and separated by centrifugation for 10 min operating at 1813 'g'. Aliquots of the supernatant were pipetted and the cations were determined by using a GBC, model 908 AA atomic adsorption spectroscopy apparatus. The adsorption capacity (mmol g^{-1}) was calculated through the expression: $n_f=(n_i-n_s)/m$, where n_f is the number of moles adsorbed on silica surface, n_i and n_s are the initial and supernatant after the equilibrium, and m the mass of modified silica. Adsorption isotherm data were fitted to the modified Langmuir model,

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

where C_s is the concentration of supernatant cations (mol dm^{-3}) at equilibrium, n_f was defined as the number of moles adsorbed on silica surface, n^s is the maximum amount of solute adsorbed per g of the silica surface, which depends on the amount of adsorption sites, and b is a constant. The n^s and b values for each adsorption process were obtained from the slope and intercept, respectively, of the linearized form of the adsorption isotherms, from plots of C_s/n_f related to C_s, by the method of least squares.

Calorimetry

The thermal effect evolved from cation-basic center interaction on anchored pendant groups at the solid/liquid interface was calorimetrically measured in an isoperibolic Hard Scientific calorimeter, model 4285 [12, 33]. A sample of activated silica, varying from 15.0 to 50.0 mg was suspended in 0.025 dm^3 of methanol under stirring at 298.15±0.02 K. The thermostated solutions of the M(acac-imine), in the 0.0004 to 0.008 mol dm^{-3} range, were incrementally added into the calorimetric vessel and the thermal effect of the titration (Q_t) was determined [12, 33]. Under the same experimental conditions, the corresponding thermal effect of the dilution of the Me(acac-imine) solution was obtained in the absence of the support (Q_d). The thermal effect of the activated silica in methanol was determined. Under such experimental condition the net thermal effect of adsorption (ΣQ_r) was obtained through the (Eq. (2)):

$$\Sigma Q_r = \Sigma Q_t - \Sigma Q_d \tag{2}$$

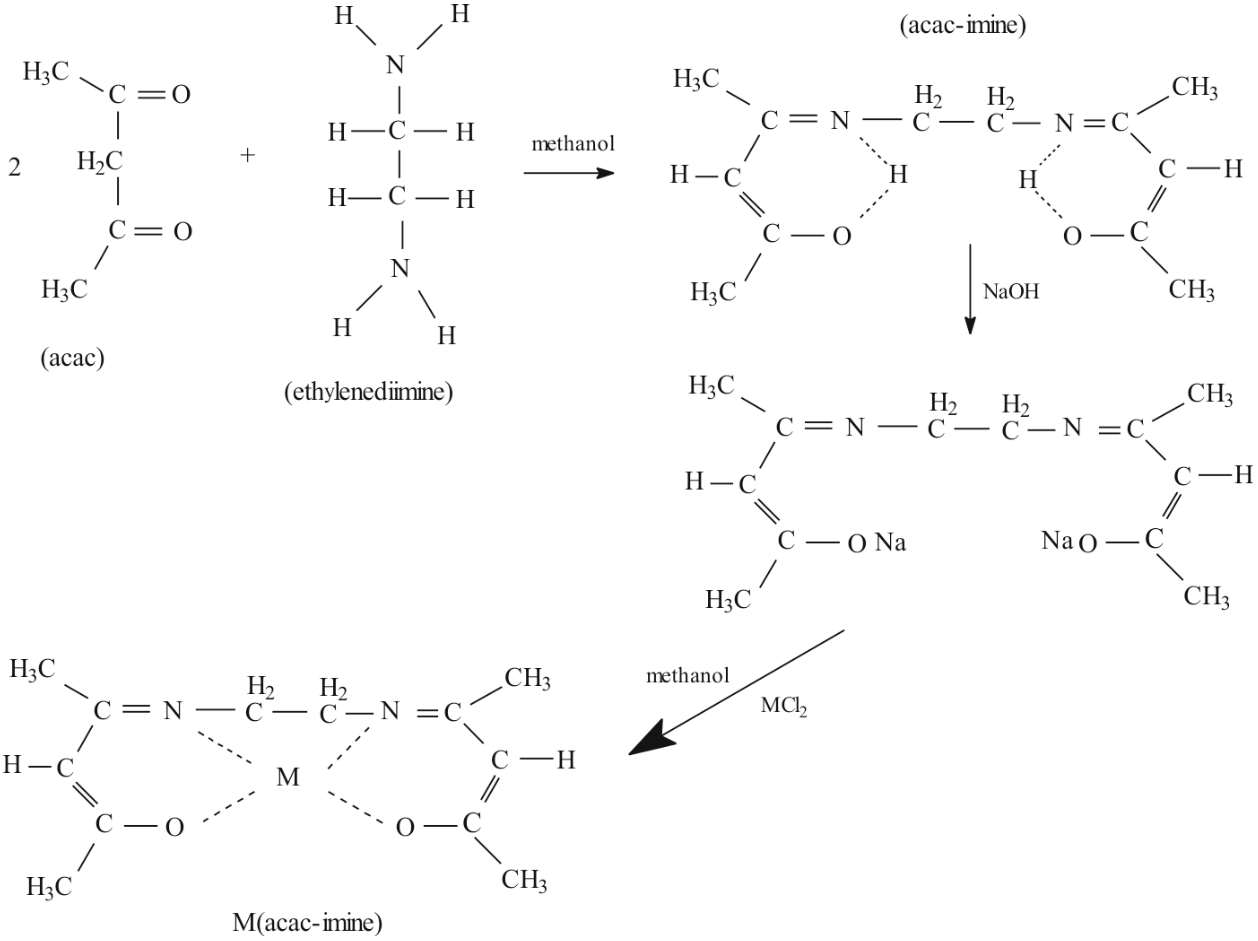
Results and discussion

The reaction of two moles of acetylacetone with one mole of ethylenediimine using ethanol as solvent, yield the bisacetylacetone-ethylenediimine chelates compound, as illustrated in Scheme 1. The elemental analysis of the acac-imine chelates had the amounts of nitrogen, carbon, and hydrogen analyzed in a micro analyzer, generating values of 61.7, 12.3 and 8.5% for carbon, nitrogen, and hydrogen, respectively. The calculated values are: 62.3, 12.5 and 8.9%, respectively for the same sequence of the elements, confirming the success of the synthesis of the product.

The complexation of acac-imine chelate with Cr(III), Mo(III), Fe(III), Ni(II), Co(II) and Cu(II) were made using respectively metallic chlorides in ethanolic solutions, as showed in Scheme 1, and the immobilization of M(acac-imine) on silica gel surface were done using a batch process with these series of cations, as mentioned earlier, in experimental section.

The intensity of the colors acquired by the activated silica gel just after the contact with the M(acac-imine) reveals that the complex extraction from methanolic solutions is due to the metal complex formation on silica gel surface.

Profiles of the adsorption isotherms represented by the number of moles adsorbed (n_f), *vs.* the number of moles at equilibrium per volume of solutions (C_s), are shown in Fig. 1. For the series of isotherms, the data reveal that the adsorption process conforms to the Langmuir model, as proposed for a series of systems [12, 13, 26, 31, 33], through Eq. (1). All these adsorption studies were based on the linearized form of the adsorption isotherm derived from a C_s/n_f as a function of C_s plot, as illustrated in Fig. 2. From this linearization the maximum retention capacity (n^s) for each M(acac-imine)/silica gel interaction can be obtained, by applying the modified Langmuir



Scheme 1

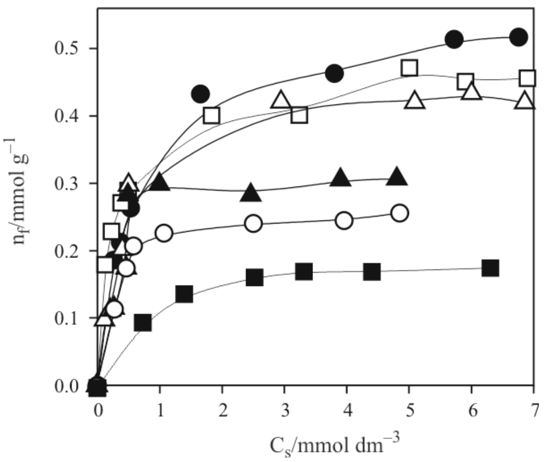


Fig. 1 Isotherm of adsorption of complex of cations on activated silica surface; ● – acac-imineCr(III), □ – acac-imineMo(III), △ – acac-imineFe(III), ▲ – acac-imineNi(II), ○ – acac-imineCo(II) and ■ – acac-imineCu(II) in methanolic solution at room temperature

Table 1 Number of moles adsorbed (n_f), maximum adsorption coefficient (n^s), correlation coefficient (r), and metal (M), for the interactions of acac-imine(M) with activated silica gel surface, at room temperature

acac-imine(M)	n_f/mmol g^{-1}	n^s/mmol g^{-1}	r
Cu(II)	0.17	0.20±0.01	0.997
Ni(II)	0.30	0.33±0.01	0.999
Co(II)	0.25	0.27±0.02	0.999
Fe(III)	0.42	0.46±0.01	0.998
Mo(III)	0.46	0.48±0.02	0.998
Cr(III)	0.51	0.56±0.02	0.999

equation, as listed in Table 1. The adsorption isotherms differed in the capacity for adsorption, and the result showed an excellent fit to the data in the concentration interval studied for the Langmuir model. The number of moles adsorbed (n_f) in this process were 0.51, 0.46, 0.42, 0.30, 0.25 and 0.17 mmol g^{-1} for Cr(III), Mo(III), Fe(III), Ni(II), Co(II) and Cu(II) (acac-imine), respectively.

After the complex M(acac-imine) immobilization on silica surface, the elemental analyses of nitrogen through the Kjeldahl method, the modified materials showed the percentages of nitrogen as 1.58, 1.35, 1.20, 0.85, 0.74 and 0.54%, which correspond to 0.56, 0,48, 0.43, 0.30, 0.26 and 0.19 mmol g^{-1} for Cr(II), Mo(III), Fe(III), Ni(II), Co(II) and Cu(II) complex, respectively. The samples used for nitrogen analyses and TG curves were the major concentration point of the batch process.

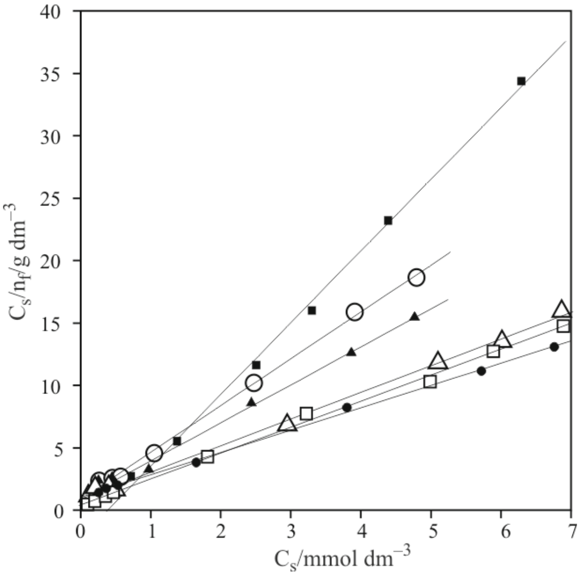


Fig. 2 Linearized isotherm form of adsorption of complex of cations on activated silica surface; ● – acac-imineCr(III), □ – acac-imineMo(III), △ – acac-imineFe(III), ○ – acac-imineCo(II), ▲ – acac-imineNi(II) and ■ – acac-imineCu(II), in methanolic solution at room temperature

The TG curve of complex of M(acac-imine) immobilized on silica surface, are showed in Fig. 3, and are given in Table 2 the mass loss of each curve, by including the interval of temperatures for the thermal decomposition processes. All the experimental results are the accordance with the calculated data.

Table 2 TG data of the activated silica gel (a), and activated silica gel modified with acac-imine(M)

Compound	Mass loss/%	Temp. interval/K
Silica gel (a)	1.00	298–473=W
	2.60	450–1170=S
Sil-acac-imineCu(II) (b)	0.60	310–369=W
	3.30	370–1053=O, S
Sil-acac-imineCo(III) (c)	0.73	305–389=W
	4.99	390–1063=O, S
Sil-acac-imineNi(II) (d)	2.08	330–402=W
	4.90	410–1175=O, S
Sil-acac-imineFe(III) (e)	1.30	305–391=W
	7.29	395–1208=O, S
Sil-acac-imineMo(III) (g)	0.62	302–400=O
	5.72	405–591=O
	2.88	595–1171=S
Sil-acac-imineCr(III) (f)	1.47	297–382=W
	12.61	391–1180=O, S

W – water physically adsorbed; S – condensation of free silanol groups on the surface to form siloxane groups; O – decomposition of the organic groups; T – temperature; K – Kelvin

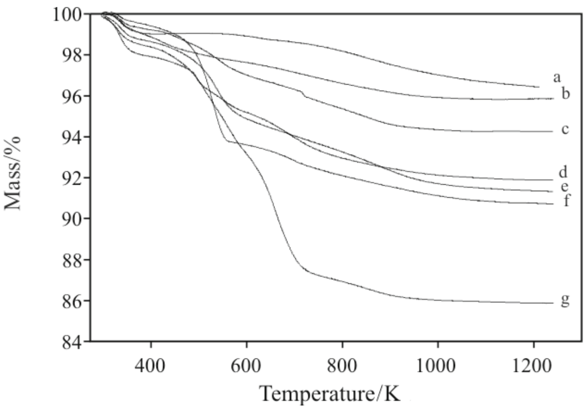


Fig. 3 TG curves of a – activated silica gel, silica gel modified with complex of b – acac-imine Cu(II), c – acac-imine Co(III), d – acac-imine Ni(II), e – acac-imine Fe(III), f – acac-imine Cr(III) and g – acac-imine Mo(III)

Considering the nitrogen elemental analyses, TG curve (Table 2), and results of adsorption process, mainly, the maximum retention capacity (n^s) values, as showed in Table 1, those values are in agreement with the others. In the TG curves, the quantity of mass loss, due to decomposition of the organic groups, followed the sequence: 12.61, 8.60, 7.20, 5.90, 4.98 and 3.29% for Cr(III), Mo(III), Fe(III), Ni(II), Co(II) and Cu(II) (acac-imine), respectively. These sequences of mass loss are in concordance with adsorption capacity of those M(acac-imine) grafted on silica gel surface. Thus, the mass loss of organic groups on silica Cr(acac-imine) and the greatest adsorption of the complex system may be attributed to the expected octahedral geometry of this cation [34], with three ligand or solvent molecules in trans positions with respect to the plane of the complex, containing the acac-imine ligands [25, 26].

The lower selectivity for the Cu(acac-imine) can perhaps be explained if one considers the characteristic of the square planar geometry of these complexes. This geometry proceeding from the pronounced distortion caused due to the John–Teller effect is more significant for cations having a d^9 configuration, such as [Cu(II)]. In these complexes, the fundamental electronic configuration of Cu(II) is given by the d_z^2 orbital with two electrons and it is difficult for the ligand to approximate in the direction of this z axis, unfavoring the bond formation [28].

The activated silica gel surface was calorimetrically titrated with this series of M(acac-imine) in methanolic solutions to elucidate the interactions of these complexes with silica support. During the titration the M(acac-imine) solutions were gradually added to a suspension of the activated silica support until saturation of the surface with a monolayer.

The enthalpic values were obtained by calorimetric titration data by considering the net thermal effect (ΣQ_r) of the titration and dilutions. As the thermal effect of the hydration of the support was null, the thermal effect of the reaction can be calculated by the Eq. (2). The resultant values were adjusted to a Langmuir modified equation, as represented by (Eq. (3)):

$$\frac{\Sigma X}{\Sigma\Delta_r H}=\frac{1}{(k-1)\Delta_{\text{mon}}H}+\frac{\Sigma X}{\Delta_{\text{mon}}H} \tag{3}$$

where ΣX is the mole fractions of each metal complex in solution, and X is obtained for each point of the titration addition by using the modified Langmuir equation (Eq. 3), which previously showed to be a good adjustable model for such heterogeneous system [12], $\Delta_r H$ is the integral enthalpy of adsorption, k is a proportionality factor which includes the equilibrium constant, and $\Delta_{\text{mon}}H$ is the integral heat of adsorption for formation of a monolayer of the unitary mass of immobilized material. The results are listed in Table 3. The molar fraction ΣX of the acidic metal center in each chelate in equilibrium was calculated with aid of the n_s values of the calorimetric titration process, which also included ns values for the solvent used. These values associated with the calorimetric titration data permit one to obtain the enthalpy $\Delta_{\text{mon}}H$ of a monolayer formed on the surface and simultaneously k values, as explained above. The $\Delta_r H$ values representing the enthalpy of adsorption were calculated by considering the number of the cations adsorbed, using the expression: $\Delta_r H=\Delta_{\text{mon}}H/n^s$. From these other thermodynamic data, such as ΔG and ΔS were also calculated based on the expressions $\Delta G=-RT\ln K$, and from $\Delta G=\Delta_r H-T\Delta S$, the variation in entropy can be calculated. All these values are listed in Table 3.

In all determinations the M(acac-imine)/silanol groups interaction on the silica surface showed spontaneity of the proposed reactions, as observed by the negative ΔG values.

Table 3 Thermodynamic data of the interaction of activated silica gel with complex of acac-imine (M), in methanolic solutions at 298.15±0.02 K

acac-imine(M)	$-\Delta H$/ kJ mol^{-1}	$-\Delta G$/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}
Cr(III)	18.62±0.01	38.42±0.06	66±2
Mo(III)	15.24±0.02	38.33±0.07	80±2
Fe(III)	13.89±0.03	37.30±0.03	78±2
Co(II)	12.76±0.02	39.58±0.03	89±2
Ni(II)	14.40±0.02	39.16±0.02	83±2
Cu(II)	17.98±0.03	38.89±0.02	70±2

Conclusions

The chelates compounds of M(acac-imine) [*M*= Cr(III), Mo(III), Fe(III), Ni(II), Co(II) and Cu(II)] have been grafted onto activated silica gel surface using batch process in methanolic solutions. The resulting adsorption isotherms of these series of cations have been characterized by nitrogen elemental analysis which, are in accordance of TG data and also with number of moles adsorbed for each metal. From calorimetric titration, the thermal effect results were obtained for activated silica with these chelates compounds enable the thermochemical data calculations. The Gibbs free energy for all these systems was calculated and the obtained negative values are in agreement with a clear evidence of the spontaneity, in the occurrence of favorable adsorptions for all interactive processes. All systems have an excellent coefficient of correlation values for each linearization. This fact implies that the data obtained with these interactions showed a good adjustment to the Langmuir adsorption model. In this process the interactive effects at these solid/liquid interface is in agreement with the formation of a cation monolayer on the silica surface.

Acknowledgements

The authors are indebted to CAPES and CNPq for fellowships and for financial support.

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ICTAC 2008

DOI: 10.1007/s10973-008-9604-z