Available online at www.sciencedirect.com
SCIENCE DIRECT

Thermochimica Acta 440 (2006) 176–180

thermochimica acta

www.elsevier.com/locate/tca

Silica gel ethyleneimine and its adsorption capacity for divalent Pb, Cd, and Hg

Luiza N.H. Arakaki [*], Vera Lucia S. Augusto Filha, Kaline S. de Sousa,
Franklin P. Aguiar, Maria G. da Fonseca, Jose G.P. Espínola

Departamento de Química, CCEN, Universidade Federal da Paraíba,
58059-900 João Pessoa, PB, Brazil

Received 12 September 2005; received in revised form 28 October 2005; accepted 3 November 2005
Available online 7 December 2005

Abstract

Activated silica gel was directly modified with a cyclic molecule, ethyleneimine, yielding a surface with various nitrogen basic centers, $\equiv$Sil–O(CH_2CH_2NH)$_n$$CH_2CH_2NH_2$. Infrared spectroscopy, ^{13}C NMR, thermal, and elemental analyses confirmed the covalent attachment of the organic species onto the silica matrix. The purpose of this paper is to describe the interaction involving the grafted species on silica surface with the divalent heavy cations, Pb(II), Cd(II), and Hg(II), from aqueous solutions at room temperature. The process of metal extraction was followed by the batch method and the order of the maximum extraction capacities found was: 1.27 ± 0.04, 1.02 ± 0.02, and $0.98 \pm 0.01\,\mathrm{mmol\,g^{-1}}$ for Pb(II), Cd(II), and Hg(II) chlorides, respectively. These interactions were followed by calorimetric titration. The enthalpies of these processes are: -3.05 ± 0.02, -1.09 ± 0.01, and $-9.88 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$ for Pb(II), Cd(II), and Hg(II), respectively. The standard molar Gibbs free energies are in agreement with the spontaneity of the proposed reactions between cation and basic center.

Keywords: Silica gel; Adsorption of heavy metal; Thermodynamic; Calorimetry

1. Introduction

The use of materials derived from grafting organic compounds onto the surface of inorganic oxides has been studied for the last half century. These supports offer pronounced advantages over polymeric resins. Some of the advantages of inorganic supports are: (i) good selectivity, (ii) no swelling, (iii) rapid sorption of metal ions, and (iv) good mechanical stability. Silica gel is the most popular substrate because it was the first commercially available high specific surface area substrate with constant composition, enabling analysis, and interpretation of results, and particularly, having high thermal resistance [1]. The surface of silica has silanol (SI–OH) groups. The presence of silanol groups on the surface creates Brønsted acidity [2–4] and makes this surface capable of adsorbing an enormous variety of chemical species, such as cyclic amines [5], amides [6], proteins [7], and biologically active phosphates [8]. It also used for adsorptive separation of platinum metals [9] and for grafting metal by using $AlCl_3$ or $TiCl_4$ [10], without previous modification of the silica surface with an organosilane.

Modification of the surface is mostly done with a silylating agent. Thus, a covalent bond can be formed between the silica surface and the silylating agent to give a new modified silica surface with an anchored functionality. After that, it is possible to immobilize new molecules, to increase the chain of the silylating agent with a variety of other organic functions even more active as chelating agents. Organofunctionalized silica is widely used as the stationary phase in chromatography [11–14], catalysts or supports for catalyts [15–19], as well as medium for attaching biologically active components used in sensors [20].

Our earlier publications reported the direct immobilization of ethyleneimine (etn) onto the silica gel surface [5]. The main objective of this publication is to report the structure of the modified silica gel and the energetics of the basic center/cation interaction with grafted ethyleneimine on silica for divalent lead, cadmium, and mercury in aqueous solutions.

---

[*] Corresponding author. Tel.: +55 83 32167591; fax: +55 83 32167437.
E-mail address: luiza_arakaki@yahoo.com.br (L.N.H. Arakaki).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.004

2. Experimental

2.1. Materials

Silica gel (Aldrich) with particle size 70–230 mesh, medium diameter 60 Å and pore volume of 0.75 $cm^3\,g^{-1}$, was stirred with H_2SO_4–HNO_3 (2.0 mol dm^{-3}) 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 bidistilled 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. Ethyleneimine was synthesized by reacting 2-aminoethyl-hydrogen sulfate (Aldrich) in hot alkali medium [21]. Toluene was firstly treated with metallic sodium and distilled just before use. The solutions of divalent metals were prepared in bidistilled water from reagent grade materials.

Five grams of silica were suspended in 50.0 cm^3 of dry toluene and 10.0 cm^3 (193.5 mmol) of ethyleneimine in a sealed tube closed under low pressure. The mixture was heated at 353 K for 48 h and was periodically shaken at least three times a day. The solid was filtered and washed with toluene, water, and finally ethanol and dried in vacuum for 8 h at room temperature, as shown in Scheme 1 [5].

2.2. Physical measurements

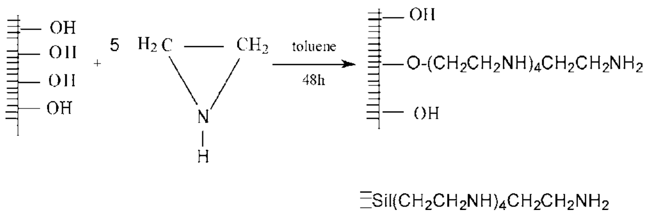
The amount of attached ethyleneimine was determined by determining the nitrogen content by the Kjeldhal method.

Activated silica gel and functionalized silica were characterized by determining the surface area through the BET method [22] in a Flowsorb II 2300 Micrometrics apparatus.

Thermogravimetric curves were produced with a DuPont model 1090 B apparatus coupled with a thermobalance 951, by heating the samples from room temperature to 1273 K at a heating rate of 0.17 K s^{-1}, with the sample varying in weight from 15.0 to 30.0 mg.

IR spectra for all compounds were obtained with a Fourier transform IR spectrophotometer (MB-Bomem). Liquid sample spectra were obtained with the thin film technique between windows of sodium chloride; solid sample spectra were obtained from KBr pellets.

For solid samples, ^{13}C NMR spectra were obtained on a AC/300P Bruker spectrometer with cross-polarization and magic-angle spinning (CPMAS) at a frequency of 75.47 MHz with acquisition time 0.156 s, pulse delay at 4 s, contact time 1 ms and number of scans in the range of 13,663–25,600.



Scheme 1.

2.3. Adsorption isotherms

The capacity of the modified silica to extract metal ions from aqueous solution was determined in duplicate using a batch process with divalent Pb, Cd, and Hg chlorides, as follows: about 50.0 mg of the modified silica was suspended in 20.0 cm^3 of an aqueous solution of metals with concentration varying from 1.0 to 8.0 mmol dm^{-3}. The suspensions were mechanically stirred for 3 h at room temperature and separated by centrifugation for 10 min at 1813 × g. Aliquots of the supernatant were pipetted and the cations were determined by EDTA complexometric titration. From these values the adsorption capacities were calculated.

The adsorption at solid/liquid interface is a competition between the solvent (solv) on the anchored surface (AS), which is gradually displaced by the solute to reach equilibrium (Eq. (1)):

$$AS_{(solv)} + MCl_{2\,(solv)} \rightleftarrows AS\cdot MCl_{2\,(solv)} + solv\,(solv = solvent) \quad (1)$$

The ratio between the number of moles of metal in solution at equilibrium and the number of moles of metal adsorbed on the surface is used to obtain the modified Langmuir isotherm (Eq. (2)):

$$\frac{C_s}{n_f} = \frac{C_s}{n^s} + \frac{1}{n^s b} \quad (2)$$

where C_s is the concentration of solute in the supernatant (mol dm^{-1}) at equilibrium, n_f the number of moles adsorbed, n^s the maximum number of moles of solute adsorbed per gram of the silica, which depends on the number 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 isotherm, from plots of C_s/n_f versus C_s, by the method of least squares.

2.4. Calorimetry

The thermal effect from cation-basic center interaction was measured in an isoperibol Hart Scientific calorimeter, model 4285 [23–25]. A sample of functionalized silica, varying in mass from 15.0 to 50.0 mg was suspended in 2.0 cm^3 of water under stirring at 298.15 ± 0.02 K. Thermostated solutions of the cations, in the 0.74–1.26 mmol dm^{-3} range, were incrementally added into the calorimetric vessel and the thermal effect (Q_t) determined [24–26]. Under the same experimental conditions, the corresponding thermal effect of dilution of the titrant was obtained in the absence of the support (Q_d). The thermal effect of the hydration of the immobilized silica in water was determined as before [24–26]. The net thermal effect of adsorption ($\sum Q_r$) was obtained from Eq. (3):

$$\sum Q_r = \sum Q_t - \sum Q_d. \quad (3)$$

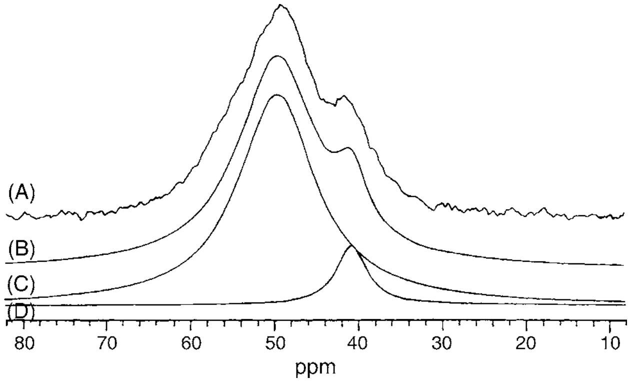


Fig. 1. ^{13}C NMR–CPMAS spectra for $\equiv$Sil(CH$_2$CH$_2$NH)$_4$CH$_2$CH$_2$NH$_2$ (A), computer simulation (B) and the deconvoluted signals (C and D).

3. Results and discussion

Nitrogen elemental analysis indicated 3.40 mmol etn g^{-1} of support [26,27]. The number of etn molecules interacting with the surface is evaluated from the number of free silanol groups, 4–5 mmol g^{-1} [2,28]. Based on results in the literature [5], each new pendant group on the surface of silica has, on average, five nitrogen atoms in the organic chain, giving approximately 0.70 mmol g^{-1} of grafted molecules. By using Eq. (4), it is possible to evaluate the number of the silanol groups per gram of silica [2,29,30].

$$T_{\mathrm{OH}} = S_{\mathrm{BET}} \times \beta_{\mathrm{OH}} \qquad (4)$$

where T_{OH} is the number of silanol groups available per gram of the silica before reaction with etn, β_{OH} the number of silanol groups per nm^2 of silica, and S_{BET} is the specific surface area (after activation 484 m^2 g^{-1}). Thus, T_{OH} = (484 m^2 g^{-1}) (1.0 × 10^{18} nm^2 m^{-2}) (5 OH nm^{-2}) = 2.42 × 10^{21} g^{-1} (OH groups per gram of silica) or 2.42 × 10^{21} g^{-1}/6.02 × 10^{23} = 4.0 mmol OH groups g^{-1} silica. The 0.70 mmol grafted molecules g^{-1} silica, considering the length of this molecule, could explain the low surface area of 121 m^2 g^{-1} after immobilization of etn. This decrease in surface area is due to the pendant groups which block access of gaseous nitrogen to the silica gel [22,26].

Knowledge of the distribution of these pendant groups on the silica surface was obtained through solid state ^{13}C NMR. The spectrum showed an intense peak at 49.2 ppm and a small one at 41.5 ppm, as illustrated in Fig. 1. These peaks were deconvoluted with the Varian VNMR program simulation. The relative areas of the peaks are 9:1. Peak C was assigned to a set of nine non-resolved carbon atoms and peak D to the methylene group bonded to the amine function [5,31].

The thermogravimetric curve of the activated silica gel is shown in Fig. 2A. An initial 1.0% weight loss in the range 298–473 K is attributed to the release of water physically adsorbed on the surface. The following loss of mass of 2.60% with maximum at 1170 K, is related to the condensation of free silanol groups on the surface to form siloxane groups [32]. The thermogravimetric curve of the $\equiv$Sil–O(CH$_2$CH$_2$NH)$_n$CH$_2$CH$_2$NH$_2$ anchored surface, as represented in Fig. 2B, showed a second loss of mass of 23.40% between 475 and 660 K, due to the decomposition of the organic groups. The last decomposition of 4.21% in the range 621–1040 K is related to the condensation of remaining silanol groups to produce siloxane. The mass loss agrees with the amount of organic molecules anchored on the silica gel.

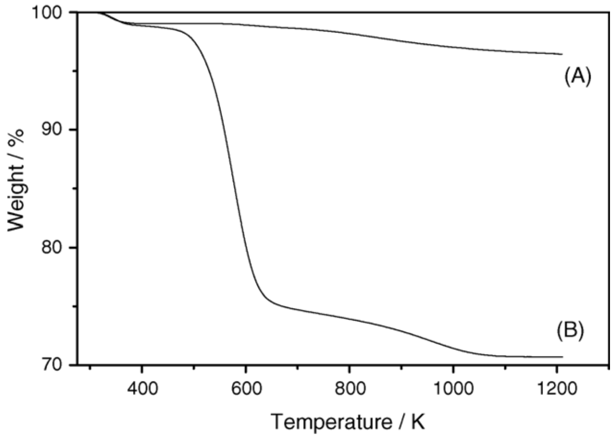


Fig. 2. Thermogravimetric curve for silica gel (A), and for matrix $\equiv$Sil(CH$_2$CH$_2$NH)$_4$CH$_2$CH$_2$NH$_2$ (B).

The IR spectrum in Fig. 3 showed a large and broad band near 3600 cm^{-1} for the activated silica (A), which corresponds to O–H stretching vibration. Some additional bands appear after anchoring the etn molecule on the surface, as illustrated in

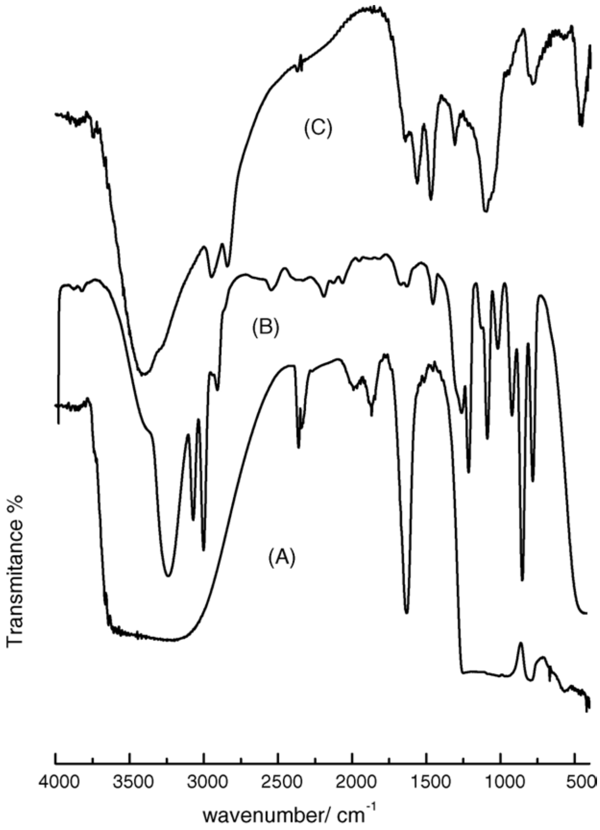


Fig. 3. IR spectra of silica gel (A), free ethyleneimine (B), and modified silica with ethyleneimine $\equiv$Sil(CH$_2$CH$_2$NH)$_4$CH$_2$CH$_2$NH$_2$ (C).

Table 1
Amount of adsorbed cations (n_f), maximum adsorption (n^s), constant (b), and correlation coefficient (r), for the adsorption of MX_2, by immobilized ethylenimine on silica at 298 ± 1 K

MX_2	n_f (mmol g^{-1})	n^s (mmol g^{-1})	b (dm^3 mol^{-1})	r
$PbCl_2$	1.27	1.39 ± 0.04	980	0.9997
$CdCl_2$	1.02	1.31 ± 0.02	285	0.9991
$HgCl_2$	0.98	1.06 ± 0.01	1925	0.9987

Fig. 3C, The material presented a strong and large band at 3397 cm^{-1} related to O–H stretching vibration mode due to water in the KBr and the silica surface, also showed two bands in the range 2949–2838 cm^{-1}, characteristic of CH stretching vibration mode [5,33]. It is common to observe a shoulder on the low frequency side (3290 cm^{-1}) of the symmetric $-NH_2$ stretching band [33]. This shoulder is attributed to the first overtone of $-NH_2$ scissoring enhanced by Fermi resonance interaction with the NH_2 symmetric stretching [33] The $-NH_2$ scissors frequencies occurs at 1568 cm^{-1} [33]. The large band located at 3327 cm^{-1} for the free etn molecule (Fig. 3B) was attributed to NH strechting vibrational modes of the secondary amine [33,34]. The two medium bands at 3068 and 2995 cm^{-1} are related to CH_2 stretch vibration modes [33,34]. The 1457 cm^{-1} weak band could be assigned to CH_2 deformation mode of etn [34]. Bands observed at 1269 and 1215 cm^{-1} in the free etn molecule are assigned to the antisymmetric ring and ring breathe vibration, respectively [34]. The N–H bending vibration occur at 1093 and 866 cm^{-1} [34].

The results of the adsorption of lead, cadmium, and mercury are presented in Table 1. The number of moles adsorbed (n_f) was calculated by: $n_f = (n_i - n_s)m$, where, n_i and n_s are the beginning of the reaction and the supernatant after equilibrium, respectively, and m is the mass of the modified silica. The values found were 1.27 ± 0.04, 1.02 ± 0.02, and 0.98 ± 0.01 mmol g^{-1} for Pb(II), Cd(II), and Hg(II), respectively.

The adsorption isotherms are very similar for the three metals, Fig. 4. The isotherms are L2 type by Giles' classification [35,36]. However, they are well-fitted by a modified Langmuir model, Eq. (2). Fig. 5 shows the cations adsorption illustrated by the linearization of the isotherm.

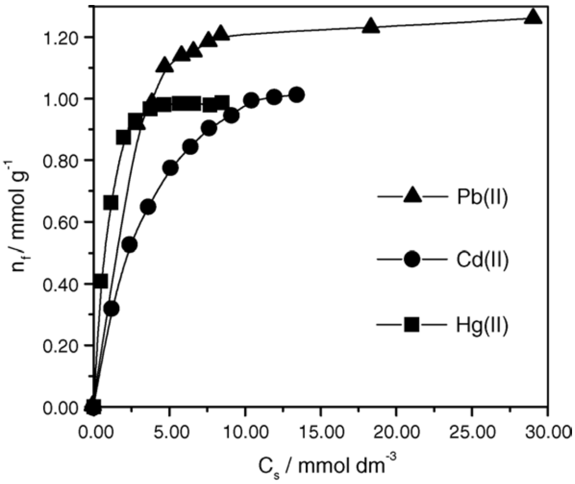


Fig. 4. Adsorption isotherms of divalent cations on surface $\equiv Sil(CH_2CH_2NH)_4CH_2CH_2NH_2$, at 298 ± 1 K.

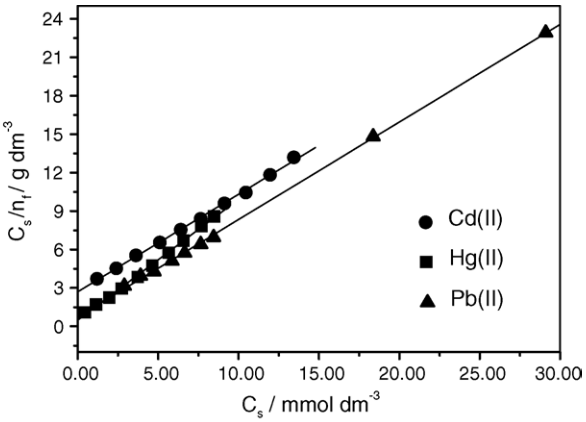


Fig. 5. The linearized forms of the isotherms of adsorption on matrix $\equiv Sil(CH_2CH_2NH)_4CH_2CH_2NH_2$.

The constant b, listed in Table 1, suggests that direct adsorption occurs between the cations and the pendant groups containing the basic centers immobilized on surface [24]. These values are larger for mercury, suggesting a high thermodynamic stability. However, the number of moles adsorbed for mercury was smaller than of cadmium and lead.

$\sum Q_r$ values were fitted with a modified Langmuir equation [5,24,26] to calculate the integral per unit mass of adsorbate $\Delta_{mon}H$:

$$\frac{\sum X}{\sum \Delta_r H} = \frac{1}{(k-1)\Delta_{mon}H} + \frac{\sum X}{\sum \Delta_{mon}H} \qquad (5)$$

where $\sum X$ is the sum of the mole fraction of the cation in solution after adsorption, and X is obtained for each point of the titration by the modified Langmuir equation (Eq. (5)), $\Delta_r H$ is the integral enthalpy of adsorption (kJ mol^{-1}) obtained by dividing the thermal effect resulting from adsorption (Q_r) by the number of moles of the adsorbate, and k is a proportionality constant that also includes the equilibrium constant. By using the slop and intercept values from the $\sum X/\Delta_r H$ versus $\sum X$ plot, it was possible to obtain the $\Delta_{mon}H$ value. The enthalpy of adsorption $\Delta_{ads}H$ could be calculated by means of the expression $\Delta_{ads}H = \Delta_{mon}H/n^s$. From these K values, $\Delta G = -RT \ln K$, and from $\Delta G = \Delta_{ads}H - T\Delta S$, the entropy change can be calculated. These values are listed in Table 2.

The enthalpy changes are −3.05 ± 0.02, −1.09 ± 0.01, and −9.88 ± 0.03 kJ mol^{-1} for, Pb(II), Cd(II), and Hg(II), respectively.

Table 2
Thermodynamic data for the interaction of divalent metals with $\equiv Sil(CH_2CH_2NH)_4CH_2CH_2NH_2$, at 298.15 ± 0.02 K

MX_2	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$PbCl_2$	3.05 ± 0.02	23.35 ± 0.001	68 ± 1
$CdCl_2$	1.09 ± 0.01	23.79 ± 0.003	76 ± 2
$HgCl_2$	9.88 ± 0.03	22.18 ± 0.002	41 ± 1

The cation-basic center interaction was spontaneous, i.e. had negative ΔG values. The entropy change makes a significant contribution to the formation of these complexes.

4. Conclusions

The results demonstrate that the direct synthesis of etn onto the silica gel surface was successful in forming a new stable support. This kind of synthesis is an economical method for covering the activated silica gel surface without using silylating agent. The new material contains many nitrogen basic centers, has great ability to adsorb soft divalent cations from aqueous solutions. This material has good adsorption capacity for heavy cations, and may be used for extraction of toxic metal ions from wastewater.

Acknowledgments

The authors are indebted to CNPq (M.G. da Fonseca, V.L.S. Augusto Filha, F.P. Aguiar), and CAPES (L.N.H. Arakaki, K.S. de Sousa) for fellowships.

References

[1] V.I. Lygin, Kinet. Katal. 35 (1994) 480.
[2] R.K. Iler, The Chemistry of Silica, John Wiley & Sons, New York, 1979.
[3] H.M. Iamail, S.A.A. Monsour, M.I. Zaki, Thermochim. Acta 202 (1992) 269.
[4] T. Takei, E. Eriguchi, M. Fuji, T. Watanabe, M. Chikazawa, Thermochim. Acta 308 (1998) 139.
[5] L.N.H. Arakaki, C. Airoldi, Polyhedron 19 (2000) 367.
[6] C. Airoldi, L.S. Santos Jr., Thermochim. Acta 104 (1986) 111.
[7] M. Ito, K. Yamauchi, K. Matsuzawa, Colloids Surf. A 74 (1993) 107.
[8] K. Hamdani, K.L. Cheng, Colloids Surf. A 63 (1992) 11.
[9] A. Trujillo, H. Fryi, Chem. Anal. 56 (1997) 90.
[10] L.T. Kubota, Y. Gushiken, S. Castro, J.C. Moreira, Colloids Surf. 57 (1991) 11.
[11] M. Björklund, M.T.W. Hearn, J. Chromatogr. A 728 (1996) 149.
[12] C.-E. Lin, F.-K. Li, C.-H. Lin, J. Chromatogr. A 722 (1996) 211.
[13] M. Mifune, Y. Shimomura, Y. Saito, Y. Mori, M. Onoda, A. Iwado, N. Motohashi, J. Haginaka, Bull. Chem. Soc. Jpn. 71 (1998) 1825.
[14] K.K. Unger, Packing and Stationary Phases in Chromatographic Techniques, Marcel Dekkar, New York, 1990.
[15] S.F. Oliveira, J.G.E. Espínola, W.E.S. Lemus, A.G. Souza, C. Airoldi, Colloids Surf. A 136 (1998) 151.
[16] A.J. Butterworth, J.H. Clark, P.H. Walton, S.J. Barlow, Chem. Commun. (1996) 1859.
[17] J.P. Collman, J.A. Belmont, J.I. Brauman, J. Am. Chem. Soc. 105 (1983) 7288.
[18] K. Wilson, J.H. Clark, Chem. Commun. (1998) 2135.
[19] P.M. Price, J.H. Clark, D.J. Macquarrie, J. Chem. Soc. Dalton Trans. (2002) 101.
[20] T. Weiss, K.D. Scheirbaum, V. Thoden Van Velzen, D.N. Reinhoudt, W. Gopel, Sens. Actuators B26–B27 (1995) 203.
[21] C.F. Allen, F.W. Spnagler, E.R. Webster, Org. Synth. Coll. 4 (1963) 433.
[22] S. Brunauer, P. Emett, E. Teller, J. Am. Chem. Soc. 60 (1938) 308.
[23] C. Airoldi, M.R.M.C. Santos, J. Mater. Chem. 9 (4) (1994) 1479.
[24] L.N.H. Arakaki, J.G.P. Espínola, M.G. da Fonseca, S.F. de Oliveira, A.N. de Sousa, T. Arakaki, C. Airoldi, J. Colloid Interface Sci. 273 (2004) 211.
[25] S. Roca, C. Airoldi, Thermochim. Acta 284 (1996) 289.
[26] L.N.H. Arakaki, L.M. Nunes, J.A. Simoni, C. Airoldi, J. Colloid Interface Sci. 228 (2000) 46.
[27] C. Airoldi, E.F.C. Alcântara, J. Chem. Thermodyn. 27 (1995) 623.
[28] K.K. Unger, Angew. Chem. Int. Ed. Engl. 11 (1972) 267.
[29] L.T. Zhuravlev, Langmuir 3 (1987) 316.
[30] E. Gruska, L.J. Kikta, Anal. Chem. 49 (1977) 1004.
[31] D.E. Leyden, D.S. Kendall, T.G. Waddell, Anal. Chim. Acta 126 (1981) 207.
[32] S. Kutahara, K. Takata, T. Sakata, H. Murashi, J. Colloid Interface Sci. 84 (1981) 519.
[33] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, London, 1991.
[34] R.W. Mitchell, J.C. Burr Jr., J.A. Merritt, Spectrochim. Acta 23A (1967) 195.
[35] C.H. Gilles, D. Smith, A. Huistson, J. Colloid Interface Sci. 47 (1974) 755.
[36] C.H. Gilles, J.A. Baston, J. Colloid Interface Sci. 47 (1974) 766.