Urea Derivatives Anchored on Silica Gel

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Methyl- and 1,3-dimethylurea were covalently bonded to silica gel, giving Sil-mu and Sil-dmu, by reacting these molecules with the (1) silanizing agent previously bonded to the surface (heterogeneous method) or (2) silanized precursor agent with the support (homogeneous method). In this last procedure the silanizing agent was characterized by elemental analyses and infrared, proton and carbon NMR spectra. The basic centers on the immobilizing molecules extract MCl_2 (M = Ni, Co, Zn, Cu, Cd, Hg) from acidic water, ethanol, and acetone solutions at 298 K. The chemisorption isotherms in nonaqueous media conform to a modified Langmuir equation. The retention of cations in aqueous solutions increases with pH for Sil-dmu. The maximum retention capacity followed the sequence Cu > Ni > Hg > Zn > Cd > Co in ethanol and Cu > Zn > Co in acetone for Sil-dmu and Co > Cu > Zn in acetone for Sil-mu. With the exception of Co on both surfaces, and Ni and Cu in ethanol for Sil-dmu, the variation in enthalpy of all solvent–solute interactions on these silicas is exothermic in nature. The free energy values demonstrated the spontaneity of these interactions. Electronic spectra of solid suspended in carbon tetrachloride, collected after batchwise adsorption, indicated a tetrahedral geometry for Ni and Cu complexes. © 1996 Academic Press, Inc.

Key Words: silica gel; immobilization; methylurea; 1,3-dimethylurea; thermodynamic data; chemisorption.

INTRODUCTION

The active hydrogen atom of the silanol groups on silica gel has the ability in reacting with organosilyl groups to give some organic nature to the precursor inorganic carrier. These covalent bonded groups are resistant to removal from the surface by organic solvents or by water (1). The immobilization of the desired reactive atom group causes versatility in this surface in developing various functions (2). Thus, the modified silica gel can be detached as ion exchanger (3), stationary phases in chromatography (4, 5), enzyme catalysts (6, 7), metal ion extractors (8, 9), heterogeneous catalysts (10, 11), or for use in some biotechnology processes (12).

The acquisition of a given modified support depends on the synthetic method, which can be derived to include reac-

tive centers of interest. Thus, basic centers like oxygen (13, 14), nitrogen (15, 16), sulfur (17, 18) and phosphorus (19, 20), disposed in the backbone chains of silica gel, enable the surface to act in many academic or industrial applications (1, 21). Moreover, the majority of these anchored molecules contains nitrogen or oxygen, or a combination of both, which can bind cations in mono- or poydentate fashions (22). Some of these modified silica surfaces have the facility to extract cations from aqueous and nonaqueous solutions (8, 9, 13, 15, 18, 22–25).

The immobilization of a given molecule with active centers can be carried out by two distinct routes. In the homogeneous method the silylant compound is first bound to the inorganic carrier, and in the heterogeneous route the molecule is directly immobilized on a support through a convenient silanizing agent (22). The combination of both routes to organofunctionalize the inorganic carrier has advantages in elucidating the anchoring process. The ability of the new surfaces to perform a given activity can be differentiated, reflecting the degree of the pendant groups attached to the support. This behavior was previously illustrated by urea immobilization, where a considerable increase in the number of groups bonded to the silica was detected in the homogeneous route (22).

The aim of the present study is to report the urea derivatives, methyl- and 1,3-dimethylurea, by using both routes of immobilization. The polydentate molecules anchored have properties in extracting divalent cations from aqueous and nonaqueous solutions, which interactive process was studied thermodynamically in ethanol and acetone.

EXPERIMENTAL

Chemicals

Methyl- and 1,3-dimethylurea (Aldrich) were recrystallized in anhydrous ethanol and dried *in vacuo* for 6 h at 323 K. 3-Chloropropyltrimethoxysilane (Merck) was used without purification. Silica gel (Merck) having a particle size of 70–230 mesh and a pore diameter of 60 Å was activated as before. Its specific area of 411 m^2 g^{-1} was determined by the BET method (13). Acetone and ethanol

for adsorption and calorimetry were previously dehydrated, distilled, and stored. Solutions of all divalent cations for adsorption and calorimetric processes were prepared from anhydrous salts (26). All other chemicals were reagent grade.

Preparation and Analysis

Methylurea (mu) and 1,3-dimethylurea (dmu) were immobilized on silica gel by using two distinct procedures (22):

Heterogeneous method. 3-Choropropyltrimethoxysilane (0.10 mol) was slowly added to a suspension of activated silica gel (50 g) in dry xylene (200 cm^3). After stirring for 72 h at solvent reflux temperature, the solid was washed and dried as before (22). To follow the degree of functionalization, the amount of chloride was titrated (27). The chlorofunctionalized surface was divided into two samples by using the same procedure to immobilize methyl- and 1,3-dimethylurea. Thus, silica surface (25 g) was suspended in *N,N*-dimethylformamide (dmf) and mechanically stirred with the urea derivative (3.0 × 10^{-2} mol) and triethylamine (5.9 × 10^{-2} mol) dissolved in dmf (20 cm^3). This mixture was stirred at solvent reflux under a gaseous nitrogen atmosphere for 10 h. After cooling, the solid was filtered and washed as before, to give Sil-mu and Sil-dmu, respectively. The degree of functionalization was determined by the amount of nitrogen through the Kjeldahl method (22).

Homogeneous method. Methylurea (2.0 g, 2.7 × 10^{-2} mol) or 1,3-dimethylurea (5.0 g, 7.0 × 10^{-2} mol) was allowed to react with 3-chloropropyltrimethoxysilane (25.0 cm^3, 0.14 mol) in dmf (30 cm^3) containing triethylamine (8.0 g, 8.0 × 10^{-2} mol). In each case, the reaction mixture was maintained under solvent reflux with magnetic stirring under dry gaseous nitrogen for 12 h. After cooling, the solvent and the excess silane were evaporated *in vacuo* at 353 K. These final products, having the aspect of solids, were treated with acetone in a dry atmosphere under nitrogen to eliminate the insoluble triethylammonium chloride formed. After solvent evaporation, the compounds, having the consistency of a viscous oil or a nearly solid oil, obtained were methyl- and 1,3-dimethylurea, respectively. Both preceding compounds reacted with activated silica gel (25 g) in xylene with mechanical stirring under conditions identical to those described in the heterogeneous method.

Adsorption of Cations on the Immobilized Surface

A batchwise process was employed in the adsorption of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} cations on both modified surfaces from ethanol and acetone at 298 K. The same procedure was used for Sil-dmu by considering a series of aqueous solutions of controlled pH. In each adsorption, a sample of ca. 0.10 g of the immobilized silica was suspended with mechanical stirring for 3 h in metal chloride solutions (50 cm^3) of different concentrations. The time required to reach equilibrium and the supernatant cations were determined by conventional EDTA complexiometric titration (22). In all cases, less than 2 h was enough to reach equilibrium; however, 3 h was chosen to ensure maximum extraction. The cation adsorption from aqueous solution considered a final volume formed by 25.0 cm^3 of the metal chloride solution plus an identical volume of the desired buffered solution (22). The adsorption procedure was repeated with untreated silica gel for each cation solution, but no adsorption was detected (26).

Physical Measurements

Infrared, electronic, and nuclear magnetic resonance spectra, surface areas, elemental analysis, and thermogravimetric determinations were obtained as before (22). The synthesized silanized compounds were handled in a dry box in an atmosphere of dry nitrogen.

Calorimetry

The heat of the exchange of the species at the solid/liquid interface was followed through a LKB 8700-2 isoperibolic precision calorimeter system. A sample of functionalized silica gel (0.20 g) was suspended in a calorimetric solvent (90.0 cm^3) and titrated with a solution of the cation in the range 10^{-2} to 10^{-3} mol dm^{-3}, to give the heat of reaction (Q_1). An identical titration of the metal solution in the same calorimetric solvent produced the heat of dilution (Q_2). The net heat of reaction (Q_{obs}) is given by $Q_{obs} = Q_1 - Q_2$, because a null heat was observed on addition of immobilized surface in the calorimetric solvent. The variation of the enthalpy of the net reaction (ΔH) can be calculated with the expression $Q = n\Delta H$, where n is the number of moles of solute adsorbed on the functionalized silica (22, 28).

RESULTS AND DISCUSSION

The immobilization of both derivatives of urea is outlined in Scheme 1. Route A summarizes the stages used in the heterogeneous method, where the silylant agent, 3-chloropropyltrimethoxysilane (I), reacts with the activated silica to attach it to the surface, followed by nucleophilic substitution of the urea derivatives. Route B involves the homogeneous method, showing the sequence of reactions to produce the modified silane before attachment to the surface (22, 29).

The amount of immobilized silylant agent attached to the surface was first quantified through chlorine analysis (1.99%); then 0.56 mmol of 3-chloropropyl groups (II) was bonded to each gram of silica (27). These available groups react almost quantitatively with methylurea, but not with 1,3-dimethylurea, as shown by the nitrogen analysis (0.70 and 0.42%) to give 0.50 and 0.30 mmol of the immobilized (III) urea derivative per gram of carrier, respectively. From
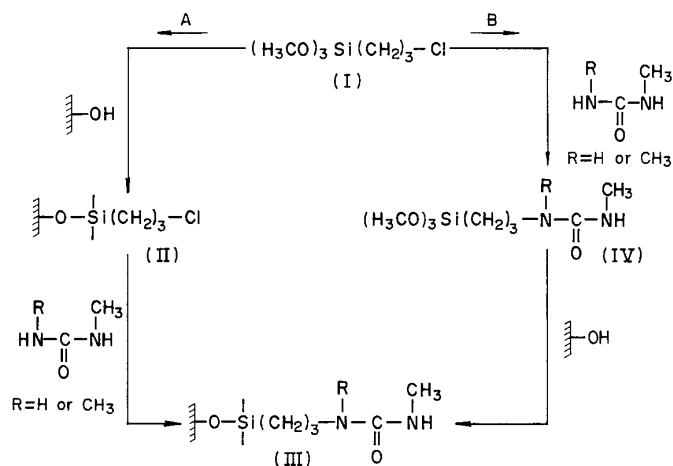
SCHEME 1

the reactions proposed in the homogeneous method the expected compounds (IV) *N*-(3-propyltrimethoxysilane)-methylurea (pmmu) and 1,3-dimethylurea (pmdu) were formulated in Scheme 1. The elemental analyses for both urea derivatives are in good agreement with this proposition, as shown by the percentage values for C, N, and H for pmmu [40.70(39.0), 11.86(11.9), 8.47(8.6)] and for pmdu [43.48(42.5), 6.76(5.9), 8.69(8.8)], with the values found in parentheses.

The infrared spectra of net pmmu as a film and pmdu in fluorolube showed the appearance of new medium and strong bands in comparison to the free molecules. These bands for both compounds are located at 1190 and 1085 cm^{-1} and 1192 and 1082 cm^{-1}, respectively, which are assigned to the Si–C and Si–OC stretching frequencies (30). The characteristic amide I and II bands are assigned at 1660 and 1590 cm^{-1} for mu and dmu, respectively (31). In the synthesized molecules (IV) the correspondent bands are located at 1707 and 1559 cm^{-1} and 1635 and 1590 cm^{-1}, respectively. The C–N stretching frequencies were observed at 1473 and 1463 cm^{-1} for pmmu and pmdu. The strong doublet attributed to NH stretching frequencies at 3420 and 3340 cm^{-1} for the free mu and the single band at 3360 cm^{-1} for the free dmu are presented at 3278 and 3329 cm^{-1} in these modified molecules. Furthermore, these molecules presented well defined bands at 2950 cm^{-1} for pmmu and at 2944 and 2841 cm^{-1} for pmdu attributed to C–H stretching vibrations (30). All these changing in spectra are inequivocal evidence of the success of these homogeneous reactions (30). The infrared spectra of dimethylurea and its silanized form are superposed in Fig. 1.

From the proton NMR spectrum of the product of the alkoxypropylsilation of the methylurea molecule in carbon tetrachloride, a set of peaks can be attributed to three methylenes and the methoxy groups (22). Thus, methylenes 1 and 3, as labeled below, appeared as a triplet centered at 3.45 and 0.65 ppm, respectively, and carbon 2 presented a quintet

centered at 1.80 ppm. The methoxy groups are located as an intense singlet at 3.50 ppm. The integration of these signals (H$_1$ + H$_4$):H$_2$:H$_3$ led to the ratio 6:1:1, which is near the calculated ratio 5.5:1:1. This difference in ratio must be attributed to the facility of the methoxy groups to suffer hydrolysis. In attempting to isolate a purer compound, the product was submitted to sublimation or distillation, but both operations caused the decomposition of the original oil; however, traces of humidity were easily detected from the infrared spectrum due to the hydrolysis and these arguments are supported by a weak broad peak at 4.65 ppm. Two other signals were detected as very weak at 7.83 and weak at 2.90 ppm, which are assigned to the amidic proton and the methyl group bonded to the amide nitrogen.

$$(H_3CO)_3SiCH_2CH_2CH_2-N(R)-CO-N(H)CH_3$$
$$\quad 4 \qquad 3 \quad\; 2 \quad 1$$
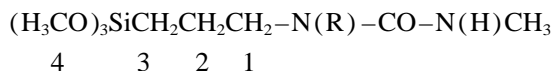
$$(R = H \text{ or } CH_3)$$

The set of peaks found for protons of pmdu of carbons 1 to 4 in the NMR spectrum has the same multiplet of pmmu molecule, with a small shift for carbons 2, 3, and 4 at 1.90, 0.80, and 3.55 ppm, respectively. Integration of these peaks showed a reasonable ratio for these hydrogens; however, peaks associated with the methyl groups were not detected. Nevertheless, for these groups a single peak at 30.11 ppm was observed in the carbon-13 spectrum, indicating the presence of the methyl groups bonded to nitrogen of the pmdu molecule. Also, the isolated signal in the carbonyl region at 159.17 ppm, which is very close to that of the urea derivative, suggests only one substitution on nitrogen during the silanization. Carbon 1 presents a peak at 46.33 ppm, while two peaks of identical intensity were observed for carbons 2, 3, and 4 and for methyl groups at 25.99 and 26.60, 6.57 and 7.84, 49.74 and 49.94, and 36.02 and 35.73 ppm, respectively. The shift for these peaks has been interpreted as due to a partial hydrolysis of methoxy groups. Identically, the same series of peaks (numbering carbons) was observed for the pmmu molecule: 46.44 (C$_1$), 26.12 and 25.72 (C$_2$), 6.74 and 7.99 (C$_3$), 50.02 and 49.83 (C$_4$), and 36.02 and 35.73 ppm (methyl group). In that case, an effect of hydrolysis can be present; however, the shift of the carbonyl peak at 160.66 and 155.58 ppm can also be an indication that a mixture of mono- and disubstituted compounds is present.

Starting from homogeneous or heterogeneous conditions, compound (IV) or surface (II), as indicated in Scheme 1, led to the same final product; however, the procedures anchored different amounts of molecules on surface, which is high in homogeneous medium. In attempting to have a high degree of immobilization with mu only 0.30 mmol g^{-1} was attached. An increase in immobilization was detected for dmu:modified-silane ratio of 1:5 and with large excess ligand in comparison to the silanol groups.
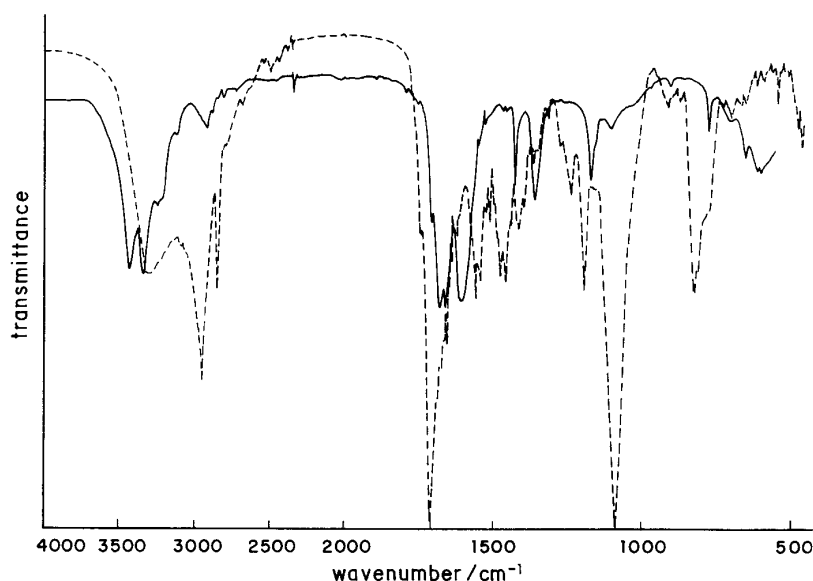
FIG. 1. Infrafed spectra of methylurea (—) and its silanized methylurea (---).

Difference in the degree of functionalization did not alter the spectra in the quantity or intensity of bands (22). The intense and broad band of the matrix in the 3400 to 2600 cm^{-1} range due to the presence of silanol and water species masks completely the possible NH stretching frequencies of both immobilized molecules (15, 26, 32). Some features, however, are associated with this broad band: (1) the sharp band at 3745 cm^{-1}, attributed to the free silanol OH stretching frequency, disappeared completely in the modified surface (32, 33); (2) its regular profile is interrupted near 2900 cm^{-1} due to the presence of small peaks attributed to CH stretching frequencies. Other evidence is in agreement with the immobilization. One of the most characteristic bands for these ligands is the amide I, at 1660 and 1640 cm^{-1} for mu and dmu, respectively. After immobilization these strong bands are located at 1655 and 1660 cm^{-1}. These bands are followed by other equal intense sharp bands at 1460 and 1455 cm^{-1}, which are attributed to the CN stretching frequency (30, 31).

The thermogravimetric curves showed that the immobilized silicas present nearly the same thermal stability. The remaining water presented a first inflection of 3.1% in the 314 to 359 K interval for both supports. The second loss of mass of 8.0 and 10.1% for Sil-mu and Sil-dmu, respectively, corresponds to the loss of organic matter in the range 663 to 884 K. In this interval of temperature, some water is also lost due to the condensation of silanol groups of the original silica surface (34).

These silicas extract cations from a suspension of acidic water solutions and in ethanol and acetone to give the sorption isotherms. Sil-dmu adsorbs all divalent cations from ethanol and acidic water solutions. Co, Cu, and Zn were also adsorbed from acetone solution for both silicas. The acquisition of isotherms is limited by the solubility of a given cation in the solvent or due to the low degree of functionalization of the surface. The solubility in ethanol is largely favorable and the low density of pendant groups on Sil-mu makes adsorption difficult. Profiles of the adsorption isotherms for cations in ethanol (Fig. 2) and acetone (Fig. 3) for the Sil-dmu surface are very similar, but differ in capacity. On the other hand, the pH of buffered solutions influenced the adsorption by the surface differently, as shown in Fig. 3.

Under equilibrium in the exchange process at the solid/liquid interface, the system can be characterized by the number of moles adsorbed (n_f) on the support: $n_f = (n_i - n_s)/m$, n_i and n_s being the initial and equilibrium numbers of moles of cations in solution, respectively, and m the mass of silica used in grams. So, the retention capacity of the cations by the surface in acidic solution (Fig. 4) shows an increase with the pH of solution. Ni changes the retention drastically as the pH is varied from 3.0 to 8.0. Cu has a large increase in retention from pH 6.0. With the exception of Co, all cations have an increase in adsorption from neutral pH to 8.0; however, in this interval of pH the sequence can be given by Co < Zn < Cd < Ni < Cu < Hg.

The adsorption phenomena at the solid–liquid interface demand a competition between the solvent bonded to the anchored surface (AS), which is displaced gradually by the solute in solution until equilibrium is attained to reach a plateau, where a monolayer is assumed to be formed (35), as represented by the equation
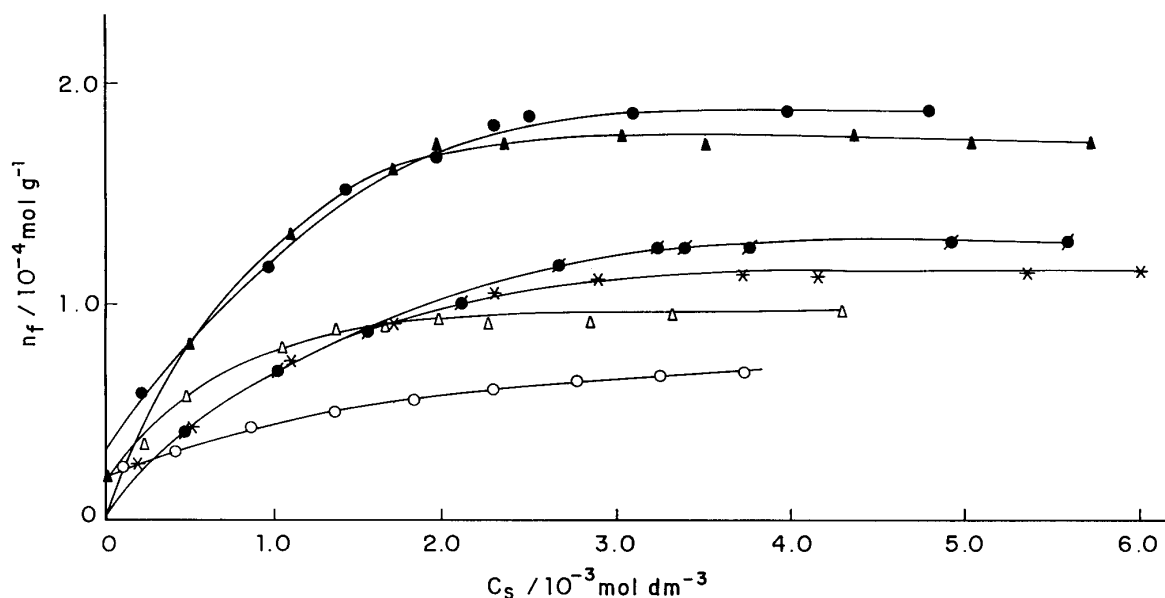
$$AS(solvent) + MCl_2(solvent) = AS(solvent) + solvent.$$
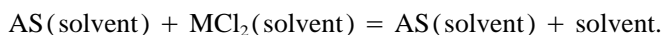
FIG. 2. Chemisorption isotherms of divalent metal chlorides on Sil-dmu silica in ethanol at 298.2 K for Co ($\bigcirc$), Cu (*), Ni ($\bullet$), Zn ($\triangle$), Cd ($\blacktriangle$), and Hg ($\bullet$).

This chemical interaction between cation and surface conforms to the transformed Langmuir adsorption isotherms (22)

$$C_s/n_f = C_s/n^s + 1/n^s b,$$

where C_s is the residual concentration (mol dm^{-3}) of cation in equilibrium with solid and n_f was defined before. A plot of C_s/n_f against C_s permits calculation of b and n^s from linear and angular coefficients of the straight line. This last value is the maximum adsorption capacity. These adsorp-

tions involved dilute solutions and a unity value for the activity of the solvent was assumed. From the linearized form of the adsorption isotherms (22, 32), b and n^s values were calculated and listed in Table 1. The higher adsorption of Co in acetone is illustrated by the linearization of the isotherm with the Sil-dmu surface, as shown in Fig. 5. The maximum retention capacity n^s is always higher in acetone for both silicas. The complete series of adsorption gives the order Cu > Ni > Hg > Zn > Cd > Co in ethanol and Cu > Zn > Co in acetone for Sil-dmu, and Co > Cu > Zn in
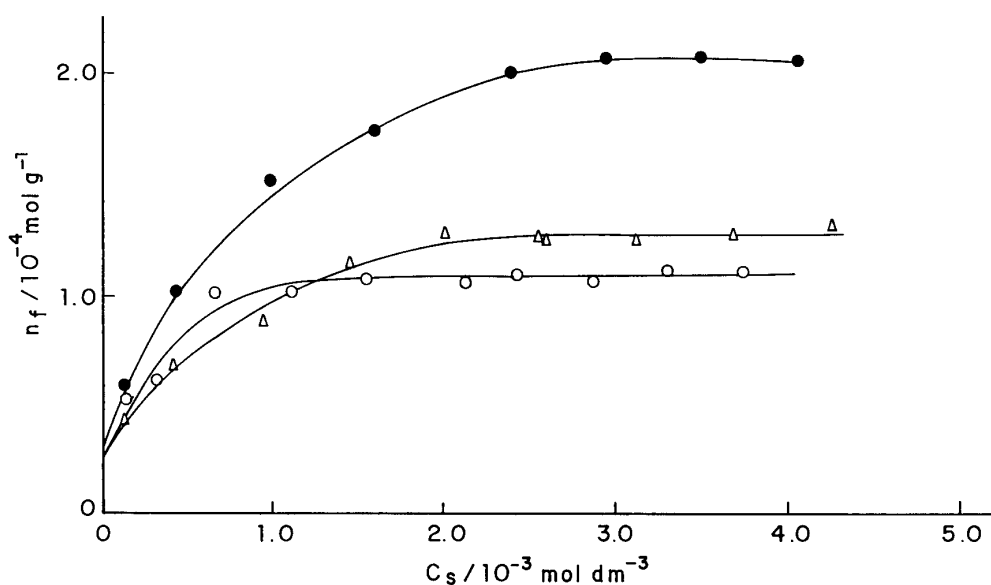
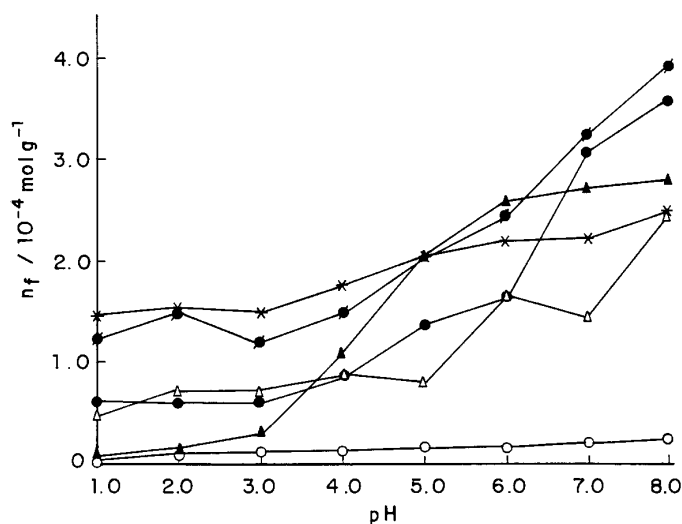**FIG. 3.** Chemisorption isotherms of divalent metal chlorides on Sil-dmu silica in acetone at 298 K for Co ($\bigcirc$), Cu ($\bullet$), and Zn ($\triangle$).

FIG. 4. Chemisorption isotherms of divalent metal chlorides on Sil-dmu silica as a function of pH at 298 K for Co ($\bigcirc$), Cu ($\bullet$), Ni ($\blacktriangle$), Zn ($\triangle$), Cd (*), and Hg ($\bullet$).

acetone for Sil-mu. The high degree of functionalization of Sil-dmu is reflected in the adsorption process. For example, Cu and Zn are nearly twice adsorbed in Sil-dmu than in Sil-mu. On the other hand, the lower polarity of acetone caused a weaker solvation of cations, favoring their complexation with the pendant groups on silica surface (22, 27, 28, 32). The ''bond-term'' values b, listed in Table 1, vary from 0.79 to 2.53 dm^3 mol^{-1} in ethanol and 1.78 to 5.16 dm^3 mol^{-1} in acetone for Sil-dmu, and 0.93 to 2.26 dm^3 mol^{-1} in acetone for Sil-mu. These values are more favorable in acetone, following the same tendency for other bidentate chelates anchored on silicas (32). In the present case, the cations are directly coordinated by the pendant groups immobilized on the support,

TABLE 1

Maximum Adsorption Coefficient, n^S, Constant, b, and Correlation Coefficient, r, for the Adsorption of Divalent Metal by Sil-dmu and Sil-mu at 298 K

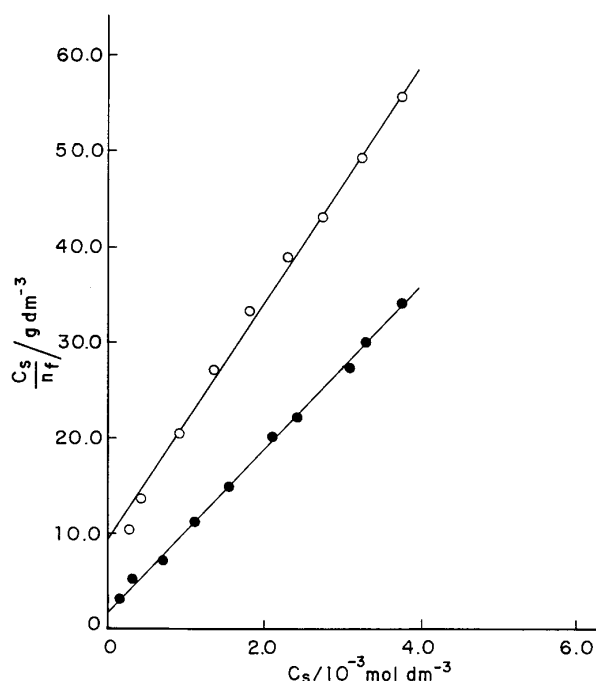| Surface	MCl$_2$	Solvent	$n^S/10^{-4}$ (mol g^{-1})	$b/10^3$ (dm^3 mol^{-1})	r
Sil-dmu	Co	Ethanol	0.79	1.44	0.998
		Acetone	1.16	5.16	0.999
	Cu	Ethanol	2.14	1.71	0.998
		Acetone	2.41	1.78	0.999
	Ni	Ethanol	1.92	1.94	0.994
	Zn	Ethanol	1.34	1.17	0.997
		Acetone	1.42	2.24	0.998
	Cd	Ethanol	1.06	2.53	0.998
	Hg	Ethanol	1.61	0.79	0.993
Sil-mu	Co	Acetone	1.70	2.26	0.998
	Cu	Acetone	1.13	1.98	0.998
	Zn	Acetone	0.78	0.93	0.998

FIG. 5. Linearized form of the chemisorption isotherm of cobalt(II) chloride on Sil-dmu in ethanol ($\bigcirc$) and acetone ($\bullet$) at 298 K.

resulting in stable complexes, by using at the maximum two nitrogens and one oxygen as basic centers to bind cations. Then, the relationship between these basic centers and n^s values could establish a possible stoichiometry. Normally, the n^s values for potentially bidentate basic centres do not demonstrate a clear stoichiometry in solution, when related to the total ligand sites available; however, supposing a bidentate behavior for both anchored ligands, a stoichiometry for cation:basic center of 3:1, 2:1, and 1:1 is found for Co, Cu, and Zn in Sil-mu. For the other surface, Co in both solvents and Cd showed to be 1:1, while Cu in ethanol and Ni gave 1:2 stoichiometries. In considering that Cu in acetone, Zn in both solvents, and Hg have used one pendant group as a bridging ligand, the stoichiometries 2.5:1, 1.5:1, and 1.5:1, respectively, can be obtained.

The effect of complexation of cations on the pendant groups available was detected by titrating calorimetrically a suspension of the immobilized silicas with cations in ethanol and acetone. An illustration is given in Fig. 6, where Sil-mu is titrated with Co in acetone solution. The enthalpy of adsorption as a function of concentration of the cation in equilibrium can be given by the equation

$$N/Q = 1/(K - 1)Q_m + N/Q_m,$$

where N is the mole fraction of the cation in solution, Q is the integral enthalpy of adsorption (J g^{-1}), K is a proportionality factor, which includes the equilibrium constant, and Q_m is
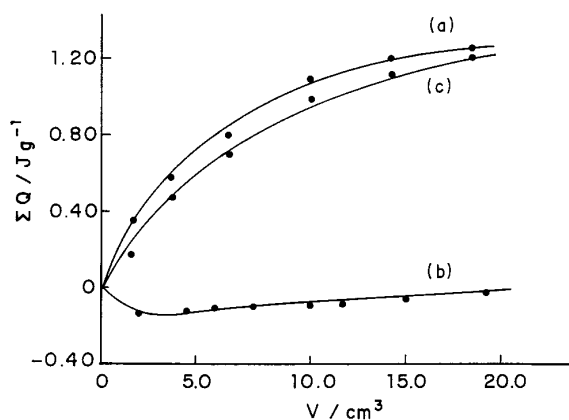
FIG. 6. Calorimetric titration of a volume of 90.0 cm^3 of a suspension of 0.2040 g of Sil-mu silica in acetone with a 8.00×10^{-3} mol dm^{-3} acetone solution of CoCl$_2$ at 298.15 ± 0.02 K. The experimental points in (a) and (b) represent the sum of the thermal effects of surface cation and cation dilution, respectively. The calculated points in (c) represent the sum of the net thermal effect of chemisorption.

the integral heat of adsorption of the saturated monolayer unitary mass of immobilized material. N values can be obtained for each increment of solute on the surface in suspension, the thermodynamic constant is obtained (22), and the values are listed in Table 2.

A plot of N/Q against N provides Q_m from the angular coefficient of the straight line, as shown for the adsorption isotherm of Zn on Sil-dmu in Fig. 7 and the correlation coefficients are listed in the last column of Table 2. From the integral heat of adsorption Q_m and the respective number of moles determined previously, the enthalpy change (ΔH) was calculated. Q_m is always larger in acetone and their values follow the same tendency as the n^s values. The interactions in acetone are always stronger due to the smaller interactive effect with the solute and the surface, reducing the competition between solute and solvent, which is reflected in the enthalpy values, as observed for Zn. With the exception of Co in both silicas, all other enthalpies are exothermic in acetone. Cu and Ni presented endothermic enthalpies values of 1.02 ± 0.01 and 14.13 ± 0.03 kJ mol^{-1} in ethanol, respectively, while exothermic enthalpy values were observed for the other cationic interactions, where Co presented the highest value of -89.60 ± 0.07 kJ mol^{-1}. For all determinations the cation-basic center interactions on the surface demonstrated spontaneity of the proposed reactions, as shown by the exothermic ΔG values. On the other hand, a significant contribution of the entropy should be considered during the formation of these metal–ligand bonds, because the cation desolvation disturbs the structure, causing an entropic enhancement. Table 2 shows unfavorable values for Zn in both silicas and for Co and Hg in ethanol with the Sil-dmu surface.

The electronic spectrum in the visible region of the complexed silica with Co, Ni, and Cu suspended in carbon tetra-

chloride gave a high-quality spectrum for Co with Sil-dmu surface, but a poor spectrum with the Sil-mu surface, due to the low density of the pendant groups. The spectra were nearly the same for partial or saturated surfaces for samples collected during the batchwise adsorption procedures. For Co complexed with Sil-dmu a strong and well-defined band with a maximum near 600 nm was attributed to the $^4A_2 \rightarrow {}^4T_1(P)$ transition for tetrahedral symmetry. The uncomplexed surface did not show any absorption in this visible region; however, in the near-ultraviolet region, strong absorptions are observed due to the charge-transfer bands (36). The electronic spectra of Cu complexes showed an isolated large band from 600 to 950 nm for both silicas, with a maximum near 800 nm. For a bidentate ligand anchored on silica gel an identical band was detected. This band is characteristic of Cu(II) for octahedral symmetry with a strong distortion due to the Jahn-Teller effect (37). As observed before, in the present case, the rigidity of the pendant groups bonded on silica suggests a possible tetrahedral geometry for this complex. The low colouring of the Ni complexes with both silicas cause difficulty in defining the electronic spectra.

CONCLUSION

Urea derivatives were identically immobilized on silica gel from homogeneous or heterogeneous procedures. The active hydrogen atoms on these compounds are substituted due to silanization. The degree of substitution depends on the ligand and the final products present a variable number of pendant groups attached to the support, being always higher in the homogeneous route. These covalently coated silica gels extract cations from aqueous and nonaqueous solvents. Basic nitrogens or oxygen atoms on each anchored
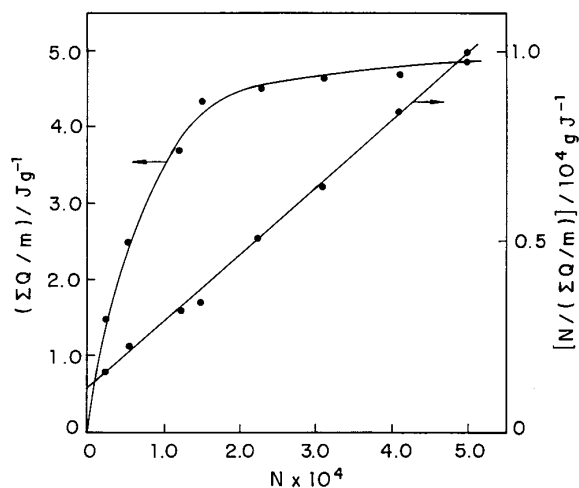

FIG. 7. Isotherm of calorimetric titration of Sil-dmu with ZnCl$_2$ in ethanol at 298.15 ± 0.02 K. The straight line is a linearized form of the isotherm.

TABLE 2
Thermodynamic Data for the Interaction of Divalent Metal Chloride with Sil-dmu and Sil-mu Silicas at 298.15 ± 0.02 K

Surface	MCl_2	Solvent	Qm ($J\ g^{-1}$)	$n^S \times 10^4$ ($mol\ g^{-1}$)	ΔH ($kJ\ mol^{-1}$)	ln K	$-\Delta G$ ($kJ\ mol^{-1}$)
Sil-dmu	Co	Ethanol	−7.08	0.79	−89.60 ± 0.07	10.61	26.30
		Acetone	+8.21	1.16	+70.79 ± 0.11	10.37	25.71
	Cu	Ethanol	+0.22	2.14	+1.02 ± 0.01	12.24	30.34
		Acetone	−1.05	2.41	−4.34 ± 0.01	12.18	30.19
	Ni	Ethanol	+2.71	1.92	+14.13 ± 0.03	10.86	26.92
	Zn	Ethanol	−5.63	1.34	−42.04 ± 0.06	9.69	24.02
		Acetone	−9.39	1.42	−66.16 ± 0.11	9.20	22.81
	Cd	Ethanol	−2.27	1.06	−21.37 ± 0.02	11.04	27.37
	Hg	Ethanol	−7.07	1.61	−43.94 ± 0.05	10.83	26.85
Sil-mu	Co	Acetone	+7.93	1.70	+46.64 ± 0.10	10.61	26.30
	Cu	Acetone	−1.03	1.13	−9.07 ± 0.01	11.70	29.00
	Zn	Acetone	−6.58	0.78	−84.30 ± 0.06	9.33	23.13

molecule are the activity centers to coordinate cations. The low chemisorption in acidic media due to nitrogen protonation changed completely in basic media. The extension of adsorption depends not only on the solubility of the adsorbent, but also on the degree of the pendant groups anchored on surface. The couples Ni–Cd and Cu–Zn are the most adsorbed in ethanol and acetone for Sil-dmu, respectively, whereas Co–Cu is the most adsorbed in acetone for Sil-mu. The coordination involving cation-pendant groups in nonaqueous solutions showed favorable systems with exothermic free energy values. The electronic spectra of the complexes formed on surface, obtained from saturated cationic solutions, suggested a tetrahedral geometry for Co in both surfaces.

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