

SEPARATIONS

**UPTAKE OF DIVALENT METAL IONS
(Cu²⁺, Zn²⁺, AND Cd²⁺) BY POLYSILOXANE
IMMOBILIZED DIAMINE
LIGAND SYSTEM**

**Farid R. Zaggout,* Issa M. El-Nahhal,
and Nizam M. El-Ashgar**

Department of Chemistry, Al-Azhar University of Gaza,
P.O. Box 1277, Gaza, via Israel

ABSTRACT

Porous solid siloxane polymers carrying diamine functional group of formula P-(CH₂)₃NH-CH₂CH₂NH₂ (where P—represents a silica-like siloxane framework) have been prepared by replacement of the iodine in iodopolysiloxane with ethylenediamine. The iodofunctionalized polysiloxane was prepared by polycondensation of Si(OEt)₄ and (MeO)₃Si(CH₂)I. The polysiloxane diamine ligand system exhibits high potential for preconcentration of divalent metal ions (Cu²⁺, Zn²⁺, and Cd²⁺). The tendency to chemisorb these divalent metal ions by the diamine ligand system at the optimum conditions was found in the order: Cu²⁺ > Zn²⁺ > Cd²⁺. Diamine ligand system suffers from leaching of ligand containing groups upon treatment with acidic solutions.

Key Words: Metal uptake; Diamine ligands; Polysiloxanes; Immobilized polysiloxane ligand systems

*Address correspondence to Farid R. Zaggout.

INTRODUCTION

Polysiloxane bound complexing agents including amines (1,2), phosphines (3), glycinate (4), iminodiacetate (5), and macrocyclic derivatives (6) have been prepared. These polysiloxane ligand systems exhibit great potential in the extraction, recovery, and separation of metal ions from aqueous solution (1,2,7) and as supported ligands for catalysis (3). Recently high resolution solid-state nuclear magnetic resonance (NMR) techniques (8–11) and other chemical tools (12–16) have been used to examine their structural properties. Although the diamine ligand system is known for some time and its structure is now well established (8), there is a need for studying its metal binding chemistry in some detail. In this study, several factors were investigated to optimize its metal uptake capacities from aqueous solutions. These factors include exposure time, pH, shaking, solution nature, competing ions, and the particle size. The chemical stability of the diamine ligand system is also investigated.

EXPERIMENTAL

Reagents and Materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane and ethylenediamine were purchased from MERCK and used as received. Solvents were dried before used. Acetone and diethyl ether were dried using anhydrous sodium sulfate for 3 days and filtered, then distilled. Absolute ethanol and methanol were used as received. Metal(II) solutions of the appropriate concentration were prepared by dissolving the metal(II) chloride (analar grade) in deionized water. Different pH ranges were prepared. Acetate solutions were prepared using hydrochloric acid/sodium acetate for pH (1–3), acetic acid/sodium acetate (buffer for pH 4–6), and acetic acid/NaOH for pH 6.5–8. Ammonium solutions were prepared using HCl/ammonia for pH 4–8. The glycinate solutions were prepared from glycine/sodium hydroxide for pH 4–8. Citrate solutions were prepared from citric acid/sodium hydroxide for pH 4–8.

General Techniques

Analysis for carbon, hydrogen, nitrogen, chlorine, and iodine were carried out by the Microanalytical Service Laboratories, in the Department of Chemistry (UMIST), UK. The concentrations of metal ions in aqueous solutions were obtained using a SHIMADZU AA—6601PC atomic absorption spectrometer. All

Table 1. Elemental Analysis Data for 3-Iodopropyltrimethoxysilane

Polysiloxane	Element	C%	H%	Cl%	I%	C/X
SI	Expected	24.8	5.3	0.0	43.8	6.0
	Found	23.2	4.6	1.5	40.5	5.4
PI	Expected	10.5	1.8	0.0	37.2	3.0
	Found	9.0	2.2	0.0	32.3	3.0

X = I + Cl.

pH measurements were made using HM-40 V pH Meter for adjustment. Shaking of ligand samples with aqueous metal ion solutions were carried out using ELEIA MMS-Multi Shaker.

Preparation of 3-Iodopropyltrimethoxysilane (SI)

The 3-iodopropyltrimethoxysilane was prepared as previously reported (6), where a solution of sodium iodide (15 g, 0.10 mole) in 100 cm³ of dry acetone, and 3-chloropropyltrimethoxysilane (19.87 g, 0.10 mole) was added dropwise with stirring at room temperature. The mixture was refluxed at 70°C for 48 h. White solid of NaCl was filtered off and the solvent was removed under reduced pressure (40 cm Hg), at 60°C. The residue was extracted four times using 100 cm³ of diethyl ether using a separatory funnel. The diethyl ether was removed at 35°C under reduced pressure (40 cm Hg), producing a light yellow oily product. The elemental analysis for the product are given in Table 1.

Preparation of 3-Iodopropylpolysiloxane (PI)

Iodopropylpolysiloxane was prepared as previously reported (4,6) by adding 3-iodopropyltrimethoxysilane (14.5 g, 0.05 mol) to stirred solution of tetraethylorthosilicate (20.8 g, 0.1 mol) in 20 cm³ methanol, followed by 4.95 cm³ of 0.42 M HCl as a catalyst. The mixture was stirred at room temperature for several hours. Gelation occurred after 24 h, the gel was left for 12 h then dried at 100°C overnight. The material was crushed, sieved, washed with successive portions, 50 cm³ of water, methanol, and diethyl ether. Finally the product was dried for 12 h at 100°C. The elemental analysis for the iodopolysiloxane are given in Table 1.

Table 2. Elemental Analysis Data for Polysiloxane-Immobilized Diamine Ligand Systems

Type	Element	C%	H%	I%	N%	C/N	mmol N/g
PDA	Expected	18.3	4.2	0.0	8.7	2.5	6.2
	Found	15.3	4.6	0.0	6.7	2.7	4.8

Preparation of Polysiloxane-Immobilized Diamine Ligand System (PDA)

10.0 g of the previously prepared 3-iodopropylpolysiloxane (PI) was refluxed with an excess of 50 cm³ of ethylenediamine, at 120°C for 48 h under nitrogen. The mixture was cooled to room temperature. The solid product was filtered, washed with successive portions 50 cm³ of 0.025 M NaOH, water, methanol, and diethyl ether. The final product was dried at 90°C in vacuum oven (0.1 torr) for 10 h. The elemental analysis are given in Table 2.

Metal Uptake Experiments

A 250 mg of functionalized polysiloxane-immobilized diamine ligand system was shaken with 50 cm³, 0.1 M of aqueous solution of the appropriate metal(II) ions (Cu²⁺, Zn²⁺, and Cd²⁺), using 250-cm³ polyethylene bottles. Measurement of the metal ion concentration was carried out by allowing the insoluble complex to settle down and appropriate volume of the supernatant was withdrawn using a micropipette then diluted to the linear range of the calibration curve for each metal. The metal ion uptake was calculated as mmole of M²⁺/g ligand. Each study was performed at least in triplicate. The effect of various factors on metal ion uptake including the pH, concentration of metal ions, solution types, shaking, competing ions, particle size, shaking time were examined.

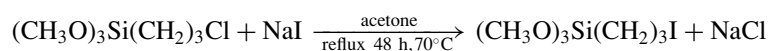
RESULTS AND DISCUSSION

Preparation

Replacement of Cl with I on 3-Chloropropyltrimethoxysilane (SI)

3-Iodopropyltrimethoxysilane (6) was prepared by the reaction of 3-chloropropyltrimethoxysilane with an excess amount of sodium iodide, using dry acetone as a solvent. The mixture was refluxed at 70°C and the product was extracted using

diethyl ether (Scheme 1). The elemental analysis data of the product are given in Table 1.

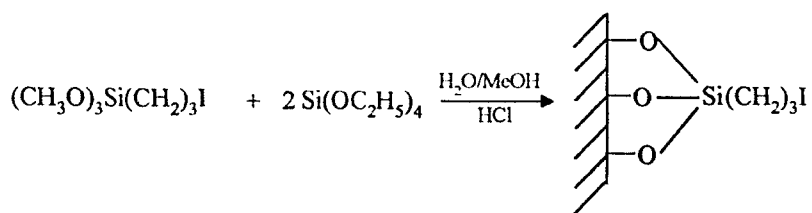


Scheme 1

From the elemental analysis given in Table 1, it is clear that most of chlorine atoms have been replaced by iodine. The slight decrease of the percentages of C, H, and I from the expected values is obviously due to incomplete replacement of Cl with I (Tab. 1).

Preparation of 3-Iodopropylpolysiloxane (PI)

This polysiloxane was obtained by hydrolytic condensation of tetraethylorthosilicate with the previously prepared 3-iodopropyltrimethoxysilane in the ratio of 2:1 (Scheme 2). The elemental analysis results are given in Table 1.



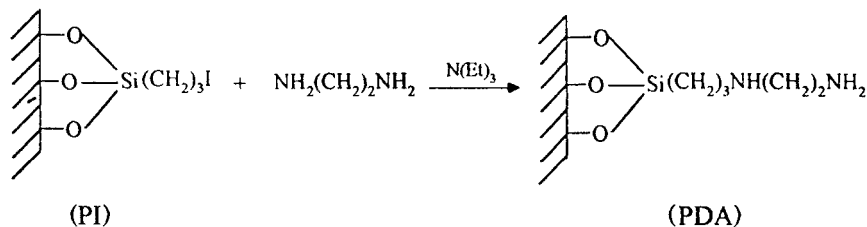
Scheme 2

From the results given in Table 1, it is obvious that the found carbon and iodine percentages are lower than the expected ones. This can be explained by the formation of small oligomers of low molecular weight as a result of self condensation of 3-iodopropyltrimethoxysilane, which were washed away. On the other hand, the increase of H% compared with the expected value, may be explained due to the presence of uncondensed hydroxyl groups. The found results are consistent with the results obtained by Ahmed (6) and El-Nasser (17).

Preparation of Polysiloxane-Immobilized Diamine Ligand System (PDA)

This polysiloxane was prepared by direct reaction of 3-iodopropylpolysiloxane with an excess of ethylenediamine in the presence of $\text{N}(\text{Et})_3$ (Scheme 3). The triethylamine was used to combine with the generated HCl . The microanalytical

data are given in Table 2. Different approach was reported (2) for the preparation of diamine ligand system.



Scheme 3

Table 2 indicates that the reaction of diamine with iodofunctionalized polysiloxane was complete and all iodine were completely replaced by ethylenediamine molecules. The replacement of all iodine by ethylenediamine is obviously explained; firstly because iodide groups are good leaving groups and secondly the large size make them accessible for replacement (18). The lower percentages of C and N than the expected values is obviously due to some degradation of the polymer as the reaction proceeded.

Metal Uptake: Effect of Exposure Time

The metal ion uptake capacity (Cu^{2+} , Zn^{2+} , and Cd^{2+}) as $\text{mmol M}^{2+}/\text{g}$ ligand, was determined by shaking the diamine ligand in aqueous solution of the divalent metal ion at different time intervals. The results are given in Figures 1–3. It is shown that the metal ion uptake is increased as a function of exposure time in a nonlinear fashion. The increase of the metal ion uptake with time is attributed to diffusion factors. The slow uptake is due to the blocking of the pores by already complexed amino groups, therefore, preventing more metal ions to contact the unreacted amine ligand groups. This is consistent with the suggestions of El-Nahhal and coworkers (8). Saturation of a given metal ion is found to be pH dependent; in case of copper saturation occurred at 24 h, whereas in case of zinc and cadmium saturation occurred at 48 h.

Effect of pH

The effect of changing the solution pH of on the uptake of copper, zinc, and cadmium ions is shown in Figure 4. The results show an increase of metal ion uptake with increasing pH value and reached its maximum at pH 5.5 in case of copper and at pH 6.5–7 in the case of zinc and cadmium. Only minor uptake

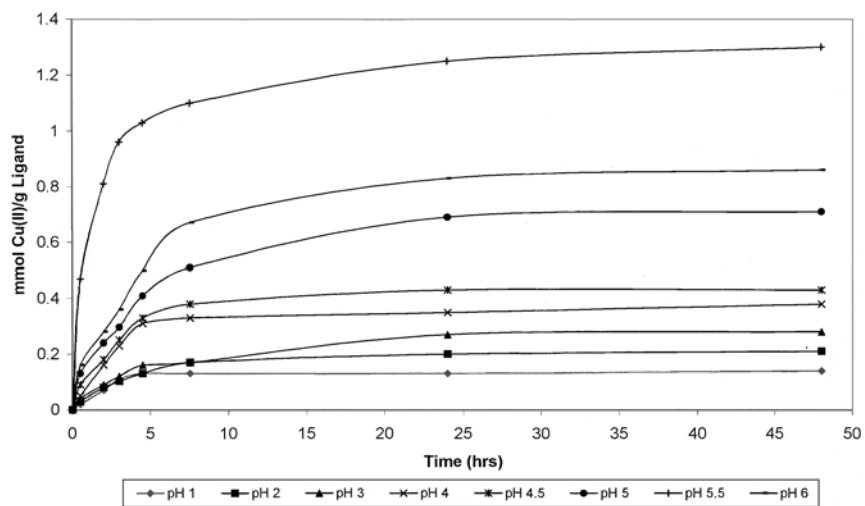


Figure 1. The uptake of Cu²⁺ ions by polysiloxane immobilized diamine ligand system versus time at different pH (pH 1–6, HCl/acetate solutions).

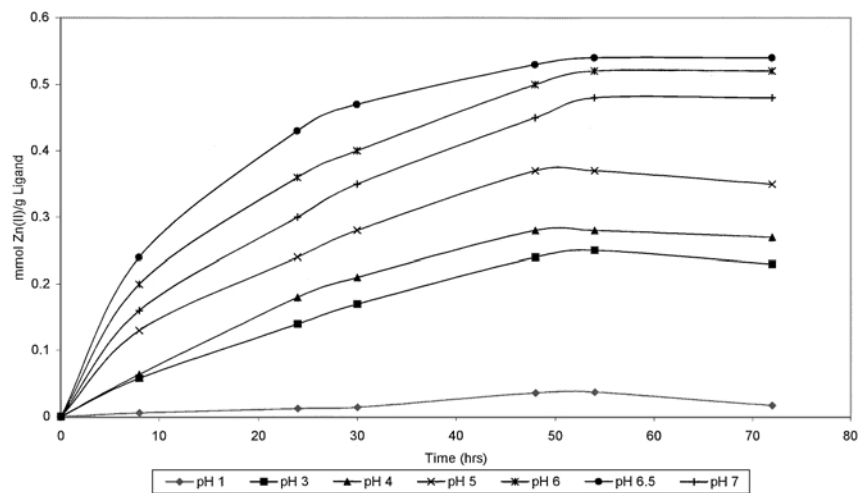


Figure 2. The uptake of Zn²⁺ ions by polysiloxane immobilized diamine ligand system versus time at different pH (pH 1–6.5, HCl/acetate solutions).

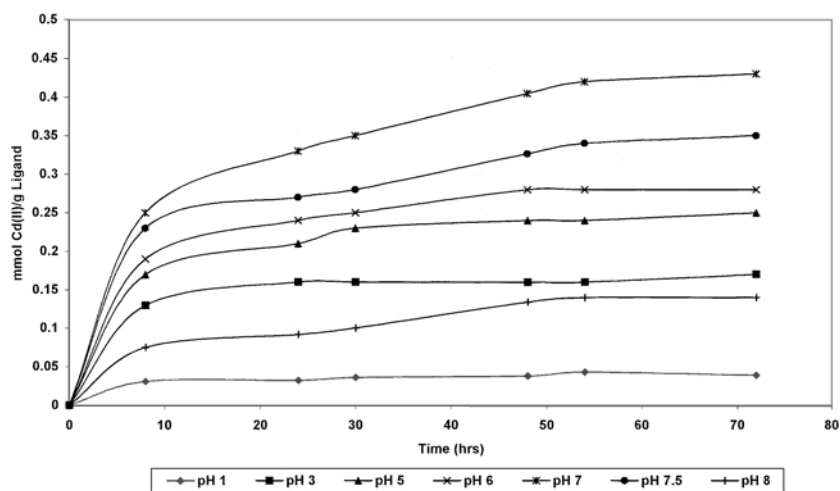


Figure 3. The uptake of Cd²⁺ ions by polysiloxane immobilized diamine ligand system versus time at different pH (pH values 1–7, HCl/acetate solution).

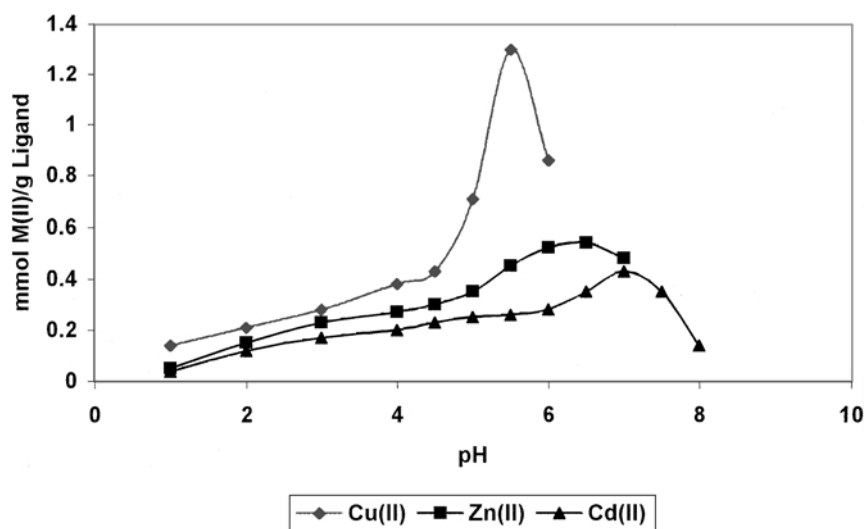


Figure 4. Metal uptake versus pH (pH 1–8, HCl/acetate solution, 48 h shaking time).

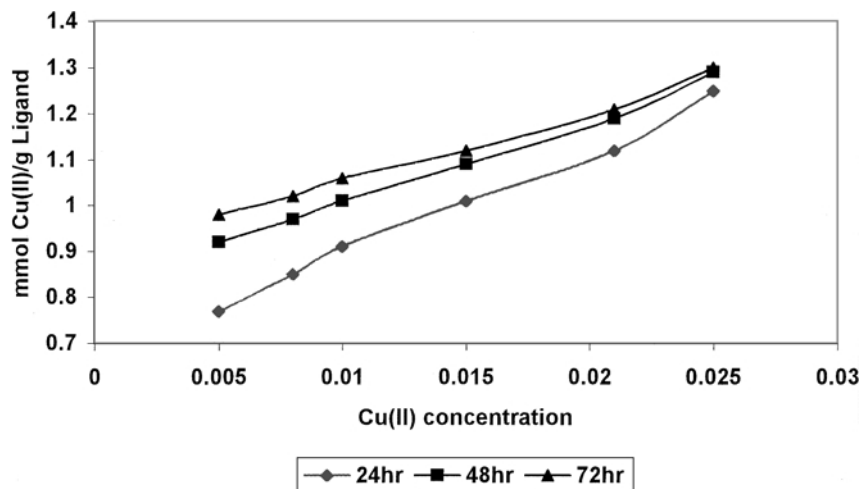


Figure 5. The uptake of Cu^{2+} ions versus concentration of Cu^{2+} ions (pH 5.5, acetate buffer).

capacity occurs at lower pH values (1–3) due to the protonation of the amine moieties. (19,20)

Effect of Concentration of Cu^{2+} Ions

The uptake capacity of polysiloxane immobilized diamine ligand system (PDA) was investigated using different concentrations of copper ions (0.005–0.025 M) at pH 5.5 buffer solutions. The results are shown in Figure 5. It is shown that copper uptake increased with concentration of Cu^{2+} ions at different time intervals. Maximum uptake occurs at high concentration (0.025 M). This can be explained due to the formation of 1:1 complex (metal to ligand) at high concentration of Cu^{2+} ions while at low concentration of Cu^{2+} ions there was low uptake due to formation of 1:2 complex (metal to ligand) (18,20).

Effect of Type of Solution

The uptake capacity was investigated as a function of solution type. The results are shown in Figures 6–8. The HCl/ammonia solutions were found to exhibit the highest uptake for all metal ions followed by acetate solutions. In case

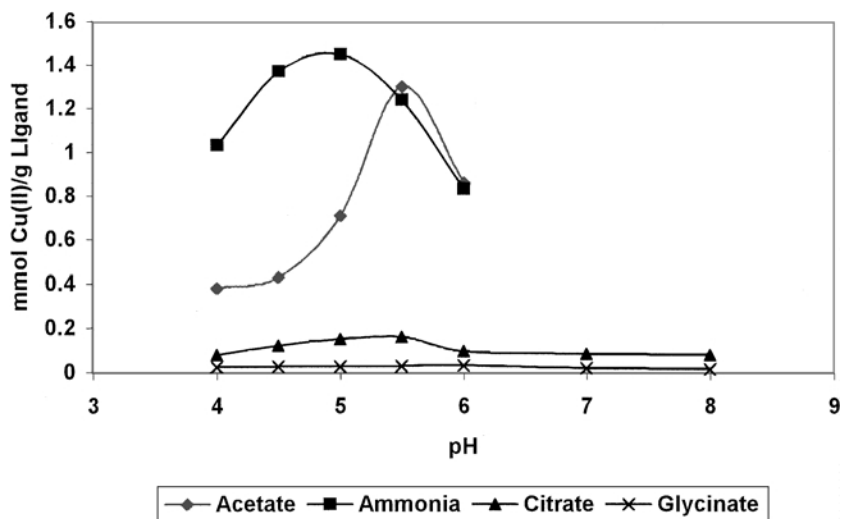


Figure 6. The uptake of Cu^{2+} ions using different solutions, 48 h shaking time. Acetate solutions (pH 4–6), HCl-Ammonia solutions (pH 4–6), Citrate solutions (pH 4–8), Glycinate solutions (pH 4–8).

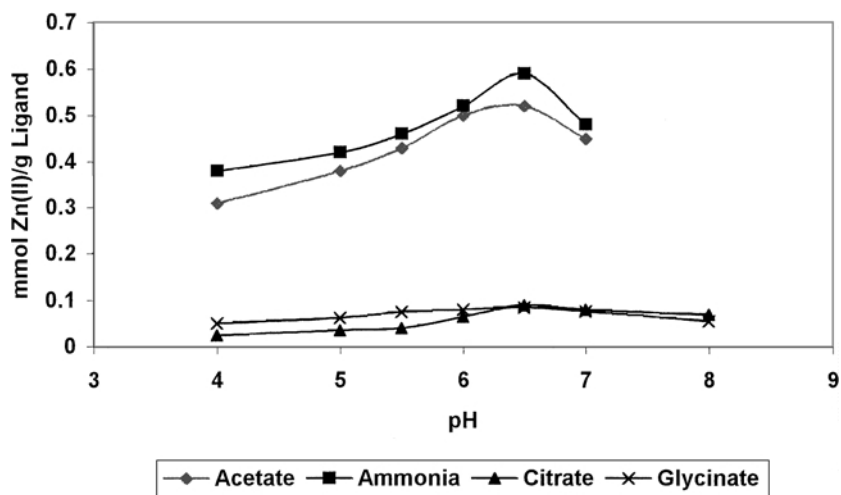


Figure 7. The uptake of Zn^{2+} ions using different solutions, 48 h shaking time. Acetate solutions (pH 4–7), HCl-Ammonia solutions (pH 4–7), Citrate solutions (pH 4–8), Glycinate solutions (pH 4–8).

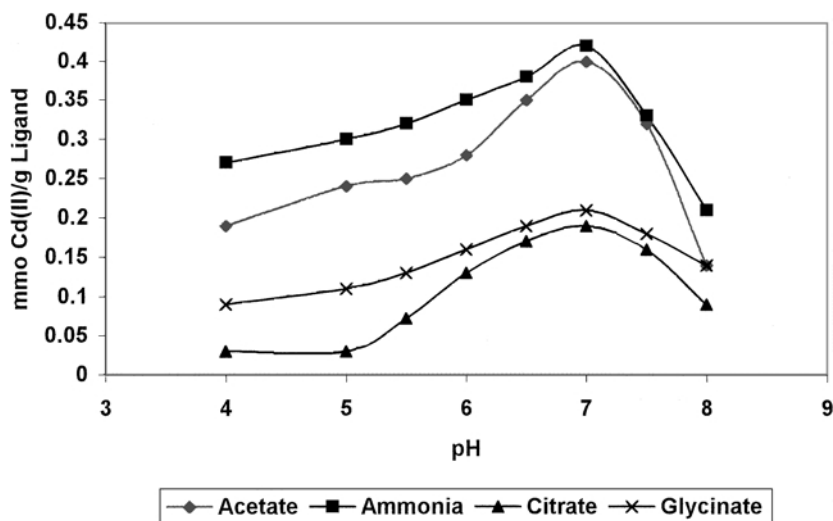


Figure 8. The uptake of Cd²⁺ ions using different buffers (48 h shaking time). Acetate solutions (pH 4–8), HCl-Ammonia solutions (pH 4–8), Citrate solutions (pH 4–8), Glycinate solutions (pH 4–8).

of citrate and glycinate solutions; low metal ion uptake was observed. This could be due to the formation of soluble complexes with citrate and glycinate (20,21).

Effect of Particle Size

The effect of the particle size of polysiloxane on the metal uptake was investigated. The results are shown in Figures 9–11. It is found that the metal uptake capacities are inversely proportional to the particle size, which is expected as the surface area exposed to the metal ion increases by decreasing the particle size. Therefore ligand groups are readily accessible for complexation when contact with the metal ion solution and maximum uptake was found for the powdered material in the range of <60 μm.

Effect of Shaking

A comparison between the metal ion uptake using shaking and unshaking samples was performed. The results are given in Table 3. In general, shaking samples exhibit higher metal ion uptake than unshaken samples. This could be due to better diffusion of the metal ion with shaking, so the ligand groups becomes

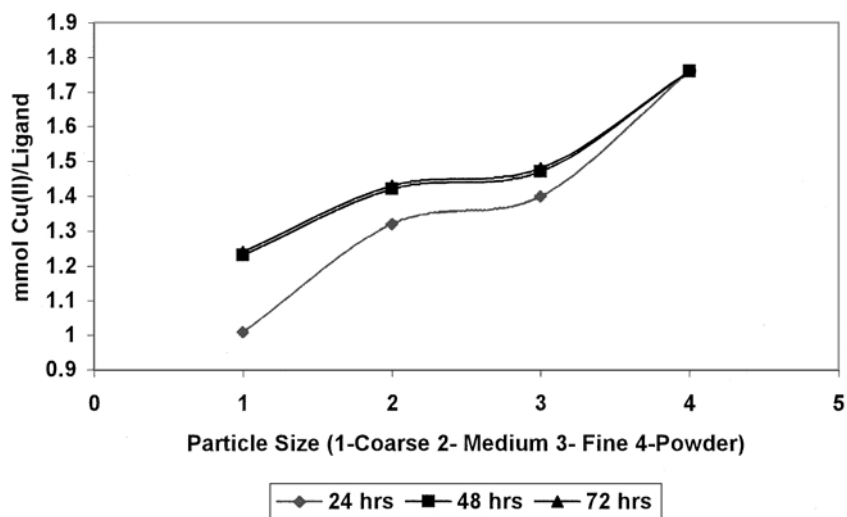


Figure 9. The uptake of Cu^{2+} ions as a function of particle size (pH 5). 1-Coarse (250–500 μm), 2-Medium (25–125 μm), 3-Fine (60–125 μm), 4-Powder (<60 μm).

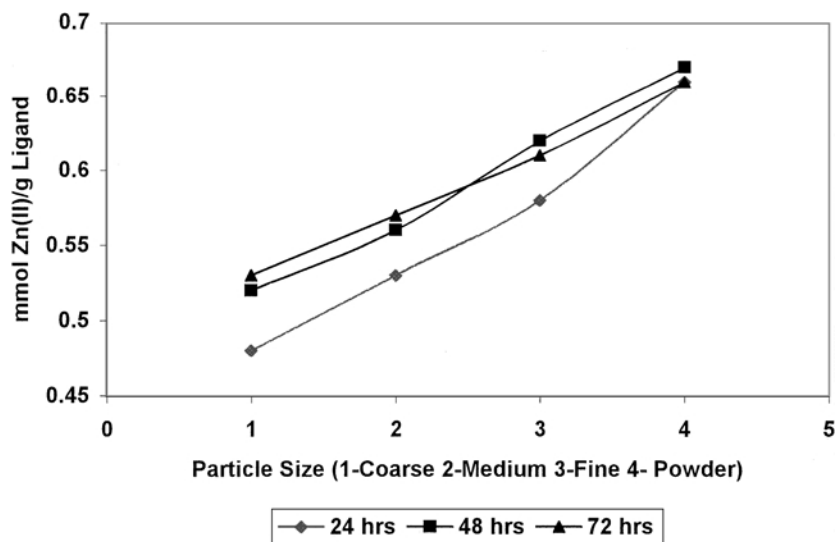


Figure 10. The uptake of Zn^{2+} ions as a function of particle size (pH 6.5). 1-Coarse (250–500 μm), 2-Medium (25–125 μm), 3-Fine (60–125 μm), 4-Powder (<60 μm).

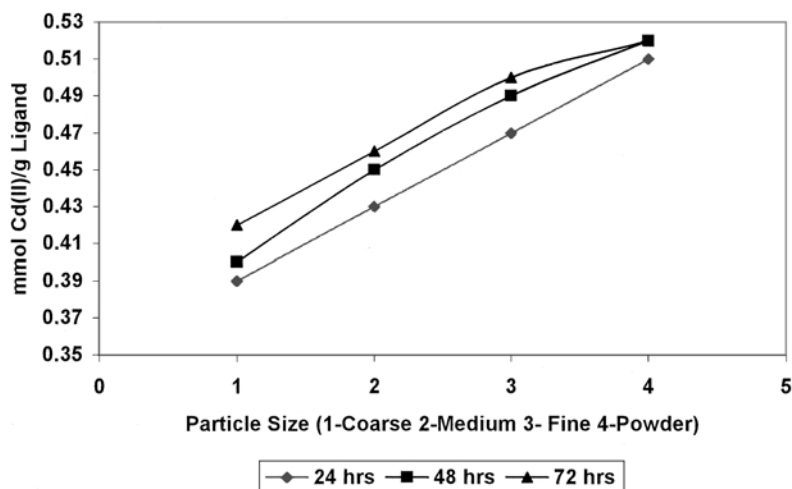


Figure 11. The uptake of Cd²⁺ ions as a function of particle size (pH 7). 1-Coarse (250–500 μm), 2-Medium (25–125 μm), 3-Fine (60–125 μm), 4-Powder (<60 μm).

more accessible for the metal ions and therefore higher uptake were observed. Similar trends are reported for monoamine ligand systems (20).

Effect of Competing Ions

The uptake of a mixture of copper, zinc, and cadmium (0.05 mmol each) by 150 mg of the polysiloxane immobilized diamine ligand system was studied at different pH values. Maximum uptakes for copper, zinc, and cadmium ions were achieved at their optimum pH values (Tab. 4). For example, at pH 5, the uptake capacity is in the order: copper > zinc > cadmium, whereas at pH 5.5–6, the uptake is in the order of zinc > copper > cadmium and at pH 7 the order of uptake is zinc > cadmium > copper (Tab. 4). Therefore the presence of competing ions do not affect considerably the maximum uptake that might achieved at the optimum pH except for cadmium. Cadmium affected significantly by the presence of the other competing ions. This may be due to lack stability of the cadmium complex formed in the presence of other metal ions.

Comparison Between the Different Metal Uptake Capacity by Polysiloxane Immobilized Diamine Ligand System PDA

The uptake of the different metal ions, (Cu²⁺, Zn²⁺, and Cd²⁺) by the polysiloxane-immobilized diamine ligand is shown in Figure 12 at the optimum

Table 3. Metal Uptake by Polysiloxane Immobilized Diamine Ligand System With and Without Shaking

Particle Size (μm)	mmol Cu^{2+}/g Ligand (pH 5) ^a						mmol Zn^{2+}/g Ligand (pH 6.5) ^a						mmol Cd^{2+}/g Ligand (pH 7) ^a					
	After 24 h		After 48 h		After 72 h		After 24 h		After 48 h		After 72 h		After 24 h		After 48 h		After 72 h	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Coarse (250–500)	1.01	0.61	1.23	0.88	1.25	1.02	0.48	0.26	0.52	0.34	0.52	0.35	0.37	0.28	0.40	0.32	0.42	0.35
	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
	2	3	1	2	3	3	3	2	4	3	4	2	3	2	4	6	3	4
Medium (125–250)	1.32	0.89	1.42	1.13	1.42	1.17	0.53	0.37	0.56	0.46	0.56	0.49	0.43	0.32	0.45	0.36	0.46	0.39
	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
	1	2	5	5	4	6	4	2	3	2	2	4	4	3	4	4	2	2
Fine (60–125)	1.40	1.01	1.47	1.25	1.47	1.31	0.58	0.41	0.62	0.54	0.62	0.58	0.47	0.40	0.49	0.43	0.50	0.47
	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
	3	3	4	4	5	1	3	5	3	5	3	3	2	4	5	3	3	2
Powder (<60)	1.76	1.35	1.76	1.47	1.76	1.56	0.65	0.55	0.66	0.57	0.66	0.65	0.51	0.48	0.52	0.50	0.52	0.50
	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	0.02	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
	2	2	3	1	3	4	4	4	3	1	3	5	4	3	2	4	2	3

a: with shaking; b: without shaking.

^a Mean and standard deviation for three determinations.

Table 4. Metal Uptake (Per 150 mg Ligand^a) of Polysiloxane-Immobilized Diamine for a Mixture of Metal Ions^b

pH	mmol Cu ²⁺			mmol Zn ²⁺			mmol Cd ²⁺			mmol Cu ²⁺ + Zn ²⁺ + Cd ²⁺
	a	b	c	a	b	c	a	b	c	
5	0.050	0.043	43.0	0.036	0.035	35.0	0.027	0.022	22.0	0.100
5.5	0.048	0.036	37.1	0.042	0.037	38.1	0.030	0.024	24.7	0.097
6	0.045	0.034	34.3	0.049	0.040	40.4	0.036	0.025	25.3	0.099
6.5	0.035	0.022	23.9	0.050	0.044	47.8	0.045	0.026	28.3	0.092
7	0.030	0.020	23.0	0.048	0.040	46.0	0.050	0.027	31.0	0.087

a: The uptake of metal ion when exist alone; b: The uptake of metal ion from mixture of competing ions; c: Calculated percentage of each metal uptake based on the total amount of metal uptake.

^aMean for three determinations, with maximum standard deviation of 0.05.

^b0.05 mmol of each metal ion was used.

conditions. Figure 12 shows the highest uptake capacity for Cu²⁺ ions towards PDA followed by zinc and cadmium ions. These differences are presumably related to the different stereochemistries and coordination numbers preferentially adopted by these metal ions (22) Zn(II) and Cd(II) are likely to be tetrahedrally co-ordinated and the uptake data suggest that this involves two amine ligands (1). The lower uptake than for copper may be connected with the smaller bond angle required, or with the presumed irregularity of distribution of amine groups

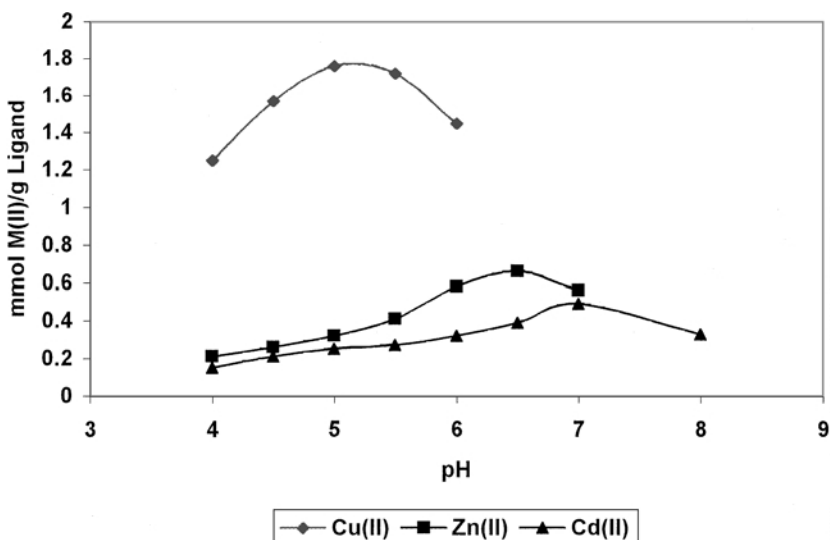


Figure 12. Optimum Cu²⁺, Zn²⁺, and Cd²⁺ metal ion uptake by diamine ligand system, 48 h shaking time, fine particle size and HCl/Ammonia solution.

throughout immobilized diamine matrix or it may indicate that initial binding of metal ion effectively blocks the access to deeper sites (1).

Estimation of Metal Complexes and Stoichiometry of the Diamine Ligand System (PDA)

According to the elemental analysis of diamine ligand system (PDA), it contains (4.8 mmol N/g ligand). The maximum uptake capacity of Cu^{2+} by this ligand system at the optimum conditions is equal to 1.76 mmole Cu^{2+} /g ligand. Therefore the ratio of the metal to nitrogen is approximately 2:6. This simply can be calculated to be 2:3 as the metal to ligand complex. The expected structure might be a mixture of structures: 1:1 and 2:1, combination of ligand to metal ion, forming metal complex, which was reported $\text{Cu}(\text{en})_2\text{X}_2$ previously (1,2).

Stability Studies of Polysiloxane-Immobilized Diamine Ligand System PDA

The stability of the polysiloxane-immobilized diamine ligand system PDA was also investigated upon treatment with solutions at different pH values and metal ion aqueous solutions. The results are shown in Figure 13 (a and b).

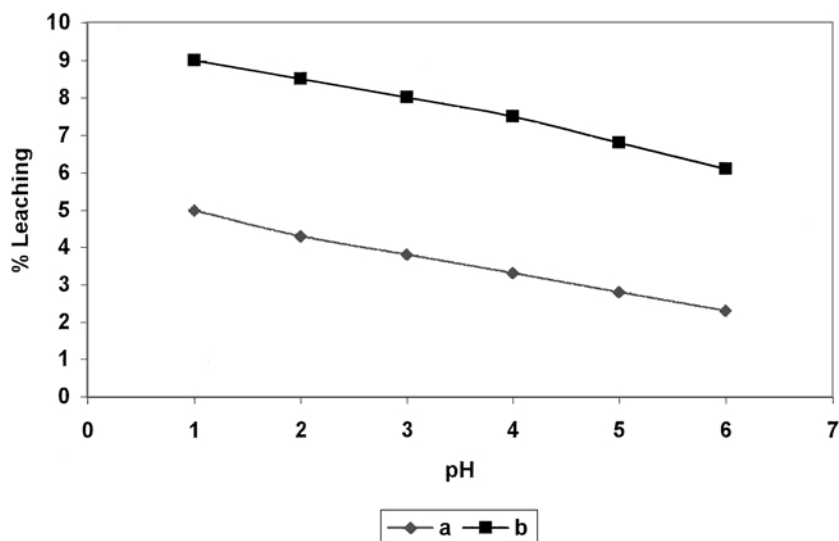


Figure 13. Leaching percentage of diamine ligand system versus pH (1–6), 120 h shaking time: a) treatment with aqueous solutions; b) treatment with Cu^{2+} aqueous solutions.

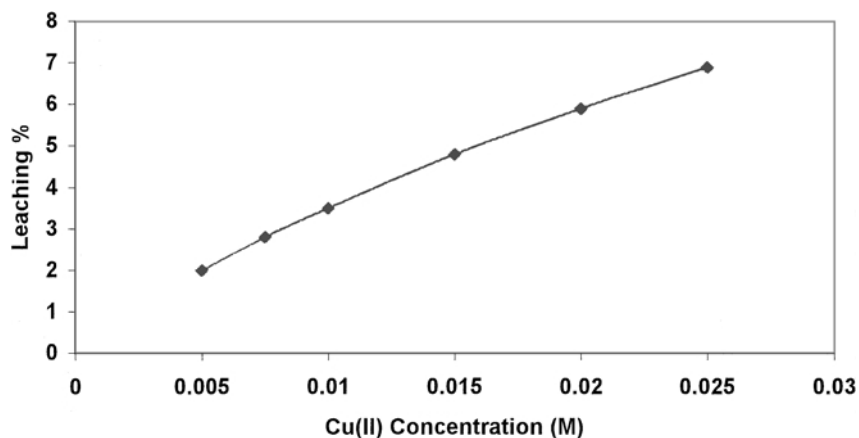


Figure 14. Leaching percentage of diamine ligand system versus concentration of Cu^{2+} ions at pH 5.5, 120 h shaking time.

Treatment with Acetate Solutions and Cu^{2+} Solutions

Gravimetric analysis for the diamine ligand system upon treatment with both the acetate solution and Cu^{2+} ion solutions that the leaching percent of PDA ligand in copper(II) solution are higher than those of the acetate solution only. The high degradation is probably due to the presence of copper ions that may facilitate the hydrolysis of Si–O–Si linkages (20).

Treatment with Different Concentrations of Cu^{2+}

The stability of the diamine ligand system (PDA) was examined in different concentrations of Cu^{2+} ions. The gravimetric results, calculated as leaching percentage, are shown in Figure 14. It is clear that the amount of species leached from the polymeric matrix is directly proportional with the concentration of Cu^{2+} ions. This is probably due to the presence of more copper ions attacking the polymeric matrix that facilitates degradation and hydrolysis of Si–O–Si links (8). Similar observations are also reported for monoamine ligand systems (8,20).

FTIR and ^{13}C Spectra

The FTIR spectra for the immobilized diamine ligand was recorded at RT in the range $4000\text{--}400\text{ cm}^{-1}$. There were three major regions of absorption at

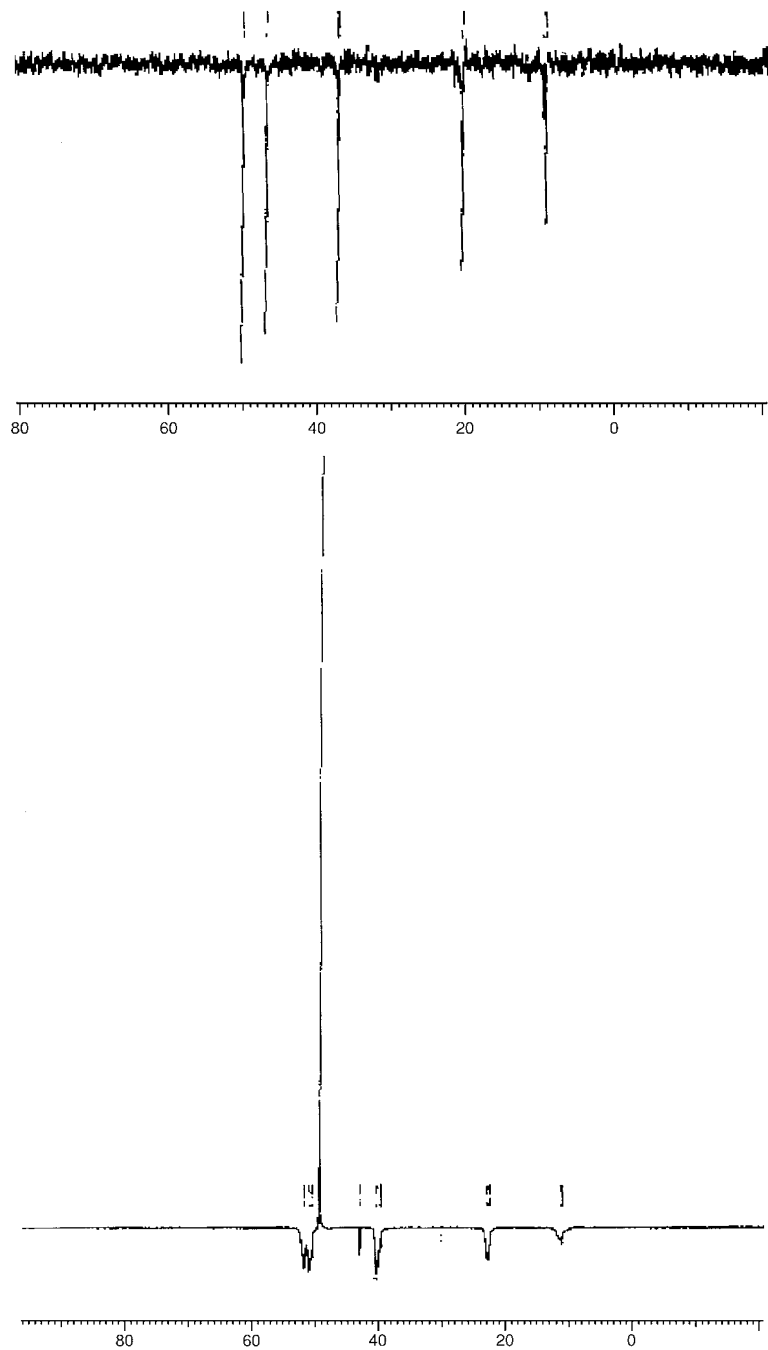


Figure 15. ^{13}C NMR spectra a) Leached material, b) 3-diaminepropyltrimethoxysilane.

3500–3000 cm^{-1} , 1600–1500 cm^{-1} , and 1200–900 cm^{-1} due to $\nu(\text{OH})$ stretching, $\delta(\text{NH}_2)$ deformations, and $\nu(\text{SiO})$ stretching vibrations (20). Upon treatment with acidic solutions, there was an increasing of intensity of $\nu(\text{OH})$ band and a decreasing of the $\nu(\text{SiO})$ band. This reflects the hydrolysis of the Si–O–Si linkages.

Further evidence for the hydrolysis of siloxane network was confirmed by ^{13}C NMR spectra of the leached material in which small oligomer species of diamine containing groups were identified. The spectrum of the leached material shows the methylene carbon signals similar to those of the corresponding material 3-(2-aminoethylimino)propyltri-methoxysilans (Fig. 15). The slight shift of the signals from the starting material is probably due to loss of (OMe) signal. This provide strong evidence that diamine groups are leached out into solution upon treatment with acidic solution. Similar behaviour was confirmed for the immobilized monoamine ligand system (16).

REFERENCES

1. Khatib, I.S.; Parish, R.V. J. Organomet. Chem. **1989**, 369, 9.
2. El-Nahhal, I.M.; Parish, R.V. J. Organomet. Chem. **1993**, 452, 19.
3. Parish, R.V.; Habibi, D.; Mohammadi, V. Organomet. Chem. **1989**, 369, 17.
4. Parish, R.V.; El Nahhal, I.M.; El-Kurd, H.M.; Baraka, R.M. Asian J. Chem. **1999**, 11 (3), 790.
5. El Nahhal, I.M.; R. V. Parish; El-Kurd, H.M. Asian J. Chem. **1999**, 11 (4), 1217.
6. Ahmed, I.; Parish, R.V. J. Organomet. Chem. **1993**, 452, 23.
7. El-Nahhal, I.M. Bull. Fac. Sci., Alex. **1991**, 31B, 12.
8. Yang, J.J.; El-Nahhal, I.M.; Chung, I.S.; Maciel, G.E. J. Non-Cryst. Solids **1997**, 209, 19.
9. El-Nahhal, I.M.; Yang, J.J.; Chuang, I.S.; Maciel, G.E. J. Non-Cryst. Solids **1996**, 208, 105.
10. Yang, J.J.; El-Nahhal, I.M.; Chuang, I.S.; Maciel, G.E. J. Non-Cryst. Solids **1997**, 212, 281.
11. Yang, J.J.; El-Nahhal, I.M.; Maciel, G.E.; J. Non-Cryst. Solids **1996**, 204, 105.
12. Stephen Caravajal, G.; Leyden, D.E.; Quinting, G.R.; Maciel, G.E. Anal. Chem. **1988**, 60, 1776.
13. Chiang, C.H.; Ishida, H.; Koenig, J.L. J. Colloid Interface Sci. **1980**, 74, 396.
14. Ishida, H.; Chiang, C.H.; Koenig, J.L. Polymer **1982**, 23, 251.
15. Taylor, I.; Howard, A.G. Anal. Chimica. Acta **1993**, 27, 77.
16. El-Nahhal, I.M.; Chehimi, M.M.; Cordier, C.; Dodin, G. J. Non-Cryst. Solids 2000, *in press*.

17. El-Nasser, A.A. Ph. D. Thesis, UMIST, UK, 1992.
18. Ahmed, I. Ph. D. Thesis, UMIST, UK, 1991.
19. Mahmoud, M.E. *Anal. Lett.* **1996**, *29*, 1791.
20. El-Nahhal, I.M.; Zaggout, F.R.; El-Ashgar, N.M. *Anal. Lett.* **2000**, *33* (10).
21. Ince, H.; Akman, S.; Koklu Fresenius, U. J. *Anal. Chem.* **1992**, *342*, 560.
22. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed., Wiley-Interscience Publications: New York, 1980.

Received August 21, 2000

Accepted September 28, 2000

Copyright of Analytical Letters is the property of Taylor & Francis Ltd and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.