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Thiol-Acetate Polysiloxane-Immobilized Ligand System and its Applications

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Thiol-acetate polysiloxane ligand systems of formula P-$(CH_2)_3$-SCH_2CO_2H, where P represents the polysiloxane silica like framework, have been made from the reaction of thiol polysiloxane ligand system P-$(CH_2)_3SH$ with ethylchloroacetate. An indirect method is used through modification of the mercaptopropyltrimethoxysilane by ethylchloroacetate, followed by copolymerization with tetraethylorthosilicate. The thiol-acetate immobilized ligand system exhibits high potential towards extraction of copper ions from aqueous solutions.

INTRODUCTION

In the last two decades, a great deal of research concerning the preparation of porous polysiloxane ligand systems and their applications has been carried out. The polysiloxane-immobilized ligand systems were prepared either by polycondensation of tetraethylorthosilicate (TEOS) and the appropriate silane coupling agent[1–5] R_3OSiX (where X = ligand group) or by modification of already prepared polysiloxane with an organoligand containing groups[6–10]. Several immobilized ligand systems were prepared, including amines,[1, 2, 10] thiol,[1] phosphines'[3] glycinate,[5] iminodiacetate[4] and others[8]. These ligand systems have various applications, such as metal ion extraction[1, 2], separation and catalysis[3]. In this work we have attempt to prepare polysiloxane ligand systems with selective properties (*e.g.*, removal of heavy metals). In the previous work the analogous glycinate ligand system and its metal ion uptake was reported[10]. Two synthesized routes were used to prepare the thiol-acetate polysiloxane ligand system and its metal uptake capacity was examined.

High resolution solid state NMR techniques have recently been used to investigate their structural properties[11–15]. The synthesis and the chemistry of metal uptake for this ligand system have been examined and discussed in this work.

EXPERIMENTAL

The starting materials which include tetraethylorthosilicate, 3-mercaptopropyltrimethoxysilane and ethylchloroacetate were purchased from Merck and used as received. Cu(II) solution of the appropriate concentration was prepared by dissolving the Cu(II) chloride (Analar Grade) in deionized water. Acetate buffer was prepared using hydrochloric acid/sodium acetate for pH 1–4 and acetic acid/sodium acetate for pH 4–6.

Analysis for carbon, hydrogen, nitrogen, chlorine and iodine were carried out by the Elemental Analyzer EA 1110–CHNS CE Instrument. Infrared spectra of the materials using KBr disk were recorded from 4000 to 400 cm^{-1} using a Shimadzu FTIR-8201 PC. The concentrations of Cu^{2+} ions in aqueous solutions were obtained using a Shimadzu AA-6601 PC atomic absorption spectrometer. All pH measurements were made using HM-40 V pH meter for adjustment. Shaking of ligand samples with aqueous metal ion solutions was carried out using ELEIA MMS-Multi Shaker.

Preparation of Polysiloxane Immobilized Thiol Ligand System (SH)

This functionalized polysiloxane was made as previously described[1] by adding tetraethylorthosilicate (20.83 g, 0.10 mol) in 15 cm^3 dry methanol and HCl (4.95 cm^3, 0.42 M) to a stirred solution of 3-mercaptopropyltrimethoxysilane (8.96 g, 0.05 mol). Gelation occurred within 24 h. The product was left to stand for 12 h, then dried in vacuum oven at 90°C. The material was crushed, sieved, washed with successive portions 30 cm^3 of 0.025 M NaOH, water, methanol and diethyl ether. The material was then dried in vacuum oven (0.10 torr) at 90°C for 10 h.

Preparation of Polysiloxane-Immobilized Thiol-acetate Ligand System (PS_1)

5.0 g of polysiloxane thiol ligand system (SH) was refluxed for 12 h with an excess of ethylchloroacetate (20 cm^3) in a round bottom flask, in the presence of few portions of triethylamine. The solid product was filtered off, washed with successive portions 50 cm^3 of 0.025 M NaOH, water, methanol and diethyl ether. The material was dried in vacuum oven (0.10 torr) at 90°C for 12 h.

Preparation of Polysiloxane-Immobilized Thiol-acetate Ligand System (PS_2)

The preparation of this polysiloxane-immobilized ligand system includes a two-step process:

Preparation of Thiol-acetatepropyltrimethoxysilane

Ethylchloroacetate (6.13 g, 0.05 mole) was added dropwise to 3-mercaptopropyltrimethoxysilane (9.80 g, 0.05 mole) with stirring. The mixture was refluxed at 120°C for 12 h, then cooled to room temperature.

Polymerization Step

Tetraethylorthosilicate (20.8 g, 0.10 mole) in 25 cm^3 of absolute methanol and (4.95 g of 0.42 M HCl) was stirred with 3-ethylthiolacetatepropyltrimethoxysilane (0.05 mole). Polymerization occurred within 3 days. The product was dried in vacuum (0.10 torr) at 85°C. The material was crushed, sieved and washed with successive portions 50 cm^3 of 0.025 M NaOH, water, methanol and diethyl ether.

The solid material was dried in vacuum (0.10 torr) at 85°C in vacuum oven for 12 h.

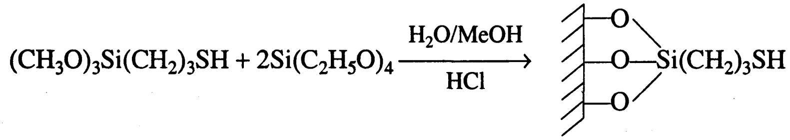
Hydrolysis of the Thiol-acetate Polysiloxane (PS_1h and PS_2h)

The thiol-acetate polysiloxane ligand systems (PS_1 and PS_2) was hydrolyzed by refluxing the ligand system (5.0 g) with 150 cm^3 of 2.0 M HCl for 6 h. The solid material was then filtered, washed with successive portions 30 cm^3 of 0.025 M NaOH aqueous solution, water, methanol and diethyl ether. The material was dried in vacuum (0.10 torr) at 100°C for 10 h.

RESULTS AND DISCUSSION

Preparation of Polysiloxane-Immobilized Thiol Ligand System (SH)

The polysiloxane-immobilized thiol ligand system was prepared as described before[1] (Scheme-1).



Scheme-1

The molar ratio of tetraethylorthosilicate (TEOS) to 3-mercaptopropyltriethoxysilane used in this reaction was 2 : 1 respectively, which is the optimum ratio of these reactants as predicted by Khatib.[1] The microanalysis data of thiol polysiloxane (SH) are given in Table-1. The lower percentage of C and S compared with the expected values is obviously due to the formation of small oligomers which leached during the washing process. The formation of these small oligomers is due to the different rates of hydrolysis of different alkoxy groups of silane agents. This is in consistent with reported results of similar systems.[1]

The C/N ratio for the thiol polysiloxane is 2.5 which closely resembles the expected value. This suggests that the fraction lost during the washing process has always a ratio of 1 sulfur to 3 carbons.

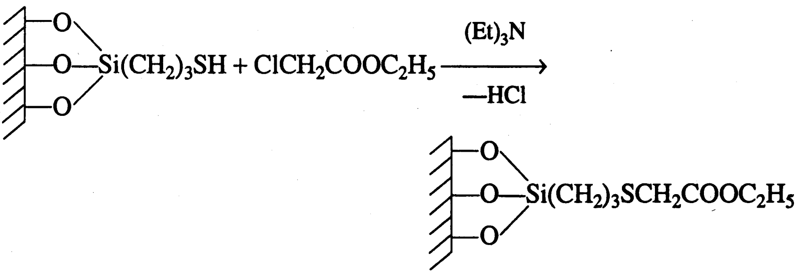
Preparation of Thiol-acetate Immobilized Ligand Systems (PS_1 and PS_2)

Two methods were used to incorporate thiol-acetate chelating ligands, in a similar procedure as used for the glycinate ligand system.[10]

1. Chemical modification of already prepared polymer.
2. Direct polymerization of monomers which contain the desired functional groups.

Preparation of PS_1

The thiol-ethylacetate immobilized ligand system (PS_1) was prepared by the reaction of polysiloxane-immobilized thiol ligand system with an excess of ethylchloroacetate in the presence of triethylamine to facilitate the removal of generated HCl (Scheme-2). The microanalysis results are given in Table-1.



Scheme-2

The reaction between thiol polysiloxane and ethylchloroacetate is evident from the increase of carbon and decrease of sulfur percentages in the resulting polysiloxane, compared with the thiol polysiloxane system (SH, Table 1). The lower carbon and sulphur percentage than the expected values is probably due to incomplete reaction between the thiol groups and ethylchloroacetate. This may be explained that some thiol groups (—SH) are not accessible and may be carried into the bulk and only the surface thiol groups are involved in the reaction with ethylchloroacetate.

The thiol-acetate polysiloxane ligand system (PS_1) was hydrolyzed using aqueous HCl (2 M). The microanalysis data for the resulting product (PS_1h) along with the expected values are summarized in Table-1. The hydrolysis of the ethoxy groups was evident from the decrease of C% and increase of S% compared with that of the unhydrolysed material (PS_1). The higher C and H percentages than the expected values are due to the presence of some unhydrolyzed ethoxy groups. Further evidence for the presence of unhydrolyzed ethoxy groups was confirmed from the IR spectra discussed later.

Preparation of PS_2: The thiol-acetate polysiloxane ligand system (PS_2) was prepared through two steps reaction:

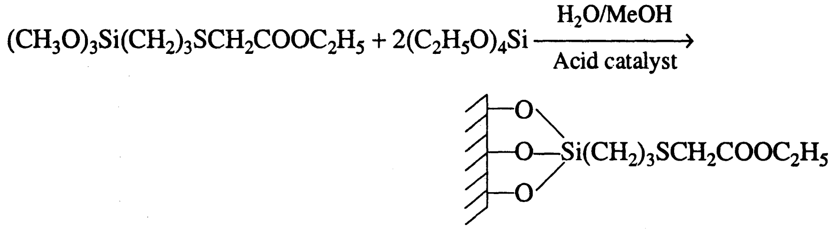
Step 1: Functionalization of 3-mercaptopropyltrimethoxysilane with ethylchloroacetate.

Step 2: Co-polymerization of the previously prepared thiol-acetate silane coupling agent with tetraethylorthosilicate.

The reaction was carried out by stirring 3-mercaptopropyltrimethoxysilane with ethylchloroacetate in presence of triethylamine to produce thiolethylacetatepropyltrimethoxysilane. This was then copolymerized with tetraethylorthosilicate in a 1 : 2 molar ratio, respectively (Scheme-3).

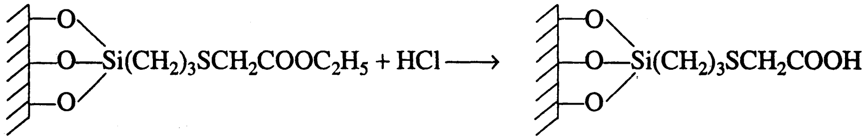
The microanalysis of thiol-acetatepolysiloxane ligand system PS_2 along with the expected values is given in Table-1.

$$(CH_3O)_3Si(CH_2)_3SH + ClCH_2COOC_2H_5 \xrightarrow[\text{—HCl}]{(Et)_3N} (CH_3O)_3Si(CH_2)_3\,SCH_2COOC_2H_5$$



Scheme-3

Although the found values are not consistent with the expected values for the thiol-acetate immobilized ligand system (PS_2), there is not an unequivocal interpretation about the exact structure formed. But there are some notifications based on the found elemental analysis data which may give some interpretations about the formed structure. There is a considerable difference between the found and the percentage of carbon (Table-1) which can be explained due to incomplete reaction of 3-mercaptopropyltrimethoxysilane with ethylchloroacetate leading to the presence of unreacted sites of the thiol groups. This also was obvious from the lower C/S ratio (4.9) than the expected value (7.0) (Table-1). This ligand system was hydrolyzed by an aqueous solution of HCl (Scheme-4).



Scheme-4

The elemental analysis data for the resulting compound (PS_2h) along with the expected values are given in Table-1. The hydrolysis reaction was evident from the decrease of carbon percentage from 15.6 to 12.5 (Table-1).

TABLE-1
ELEMENTAL ANALYSIS DATA FOR DIFFERENT PREPARED POLYSILOXANES

Type	Element	% Analysis				mmol S/g
		C	H	S	C/S	
P-SH	Expected	14.6	2.8	13.0	3.0	4.0
	Found	9.9	3.4	11.2	2.5	3.5
PS_1	Expected	22.6	3.5	8.6	7.0	2.7
	Found	15.7	3.7	6.7	6.2	2.1
PS_1h	Expected*	11.5	2.8	7.0	4.4	2.1
	Found	13.0	3.5	7.2	4.9	2.3
PS_2	Expected	25.2	3.9	9.6	7.0	3.0
	Found	15.6	3.7	8.5	4.9	2.7
PS_2h	Expected*	11.8	2.7	9.0	3.5	2.8
	Found	12.5	3.5	8.4	4.0	2.6

*The expected values were calculated based on the found values of the unhydrolyzed ligand system.

Infrared Spectra: The FTIR spectrum for the thiol polysiloxane system shows two characteristic regions at 3500–3000 cm^{-1} and 1200–900 cm^{-1} due to (OH) and (SiO) vibrations. The IR spectrum of the unhydrolyzed thiol-acetate shows the presence of new peak at 1750 cm^{-1} characteristic to ν(CO). After the acid hydrolysis of PS_1 two absorption bands are obtained at 1650 and 1750 cm^{-1} due to ν(CO) stretching and (OH) bending vibrations respectively. These assignments were based upon the literature spectral data reported for similar systems[16, 17].

Metal Uptake: Copper ion uptake capacity of the polysiloxane-immobilized thiol-acetate PS_1 and PS_2 was examined by shaking the immobilized ligand system in aqueous solution of copper ions at different time intervals. The results are given in Figures 1 and 2. It is obvious that uptake of copper ions increases as a function of shaking time. Saturation of Cu^{2+} ions is found to be pH dependent. It is clear that rapid uptake occurred at the first 10 h (60%). The slow uptake after 10 h is probably due to blocking of the initial binding metal ions, therefore preventing further contact with copper ions.

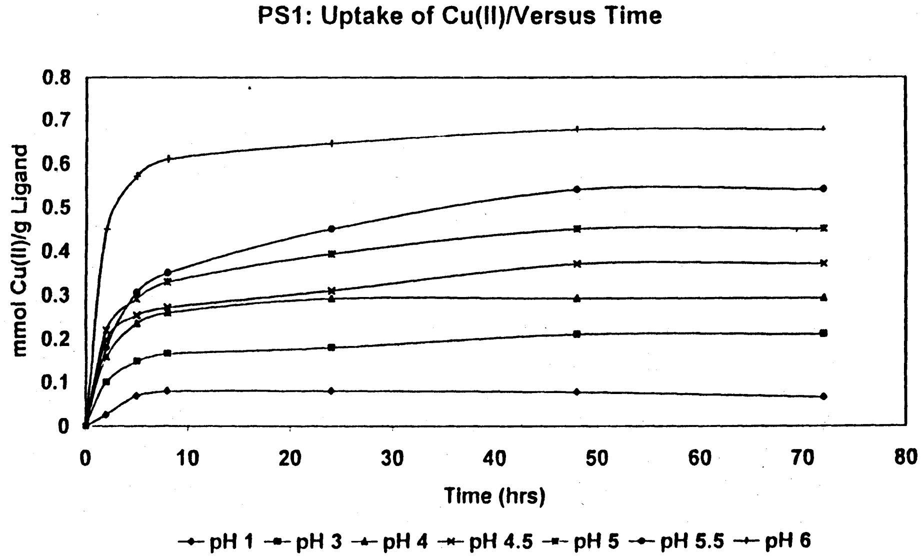


Fig. 1. Uptake of Cu^{2+} ions by polysiloxane-immobilized thiol-acetate (PS_1) ligand system versus time, acetate buffer, pH values 1–6.

pH Dependence: The uptake of copper ions was examined at different pH values (1–7). The results are given in figures 3 and 4. There is an increase of copper uptake as the pH increase. In contrast to the polysiloxane amines and glycinate ligand systems it show no maximum uptake with increasing pH and nearly linear relationship is obtained (Figure 3 and 4).

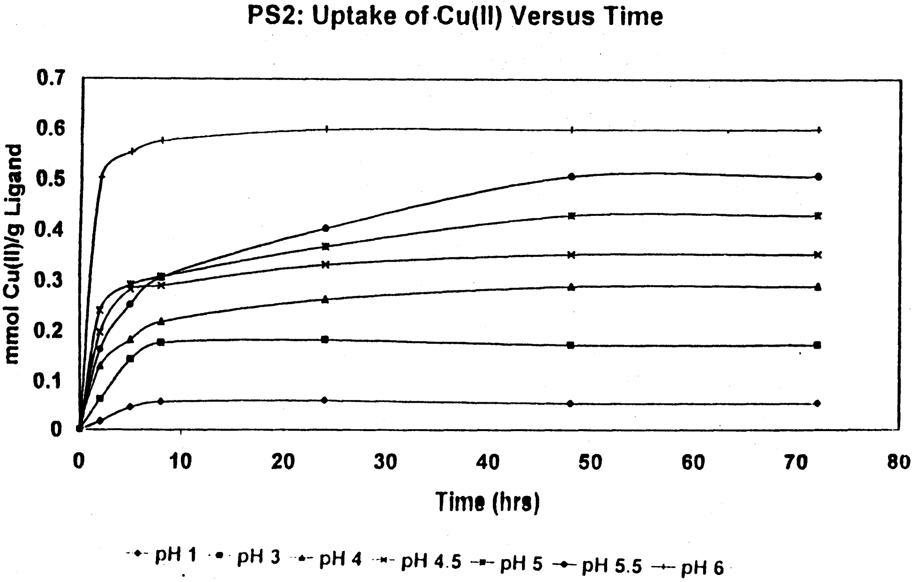


Fig. 2. Uptake of Cu^{2+} ions by polysiloxane-immobilized thiol-acetate ligand system (PS_2) versus time, acetate buffer, pH values 1–6.

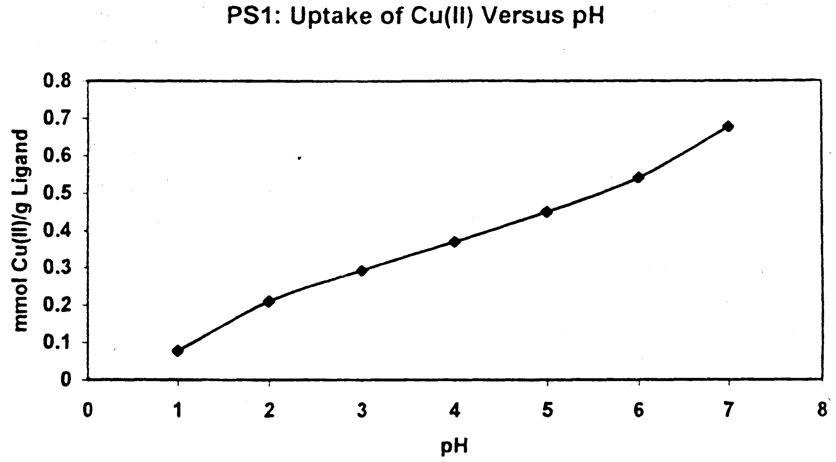


Fig. 3. Uptake of Cu^{2+} ions by polysiloxane-immobilized thiol-acetate ligand system (PS_1) versus pH, acetate buffer.

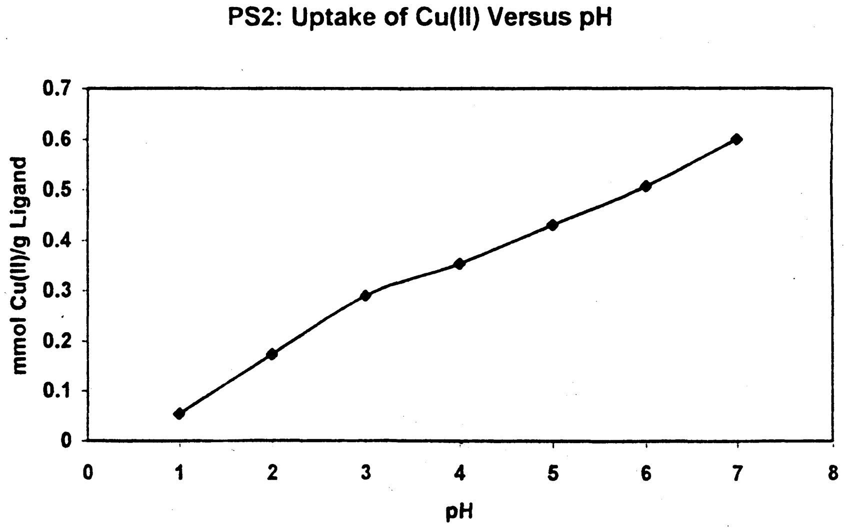


Fig. 4. Uptake of Cu^{2+} ions by polysiloxane-immobilized thiol-acetate ligand system (PS_2) versus pH, acetate buffer.

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