

Preparation of Immobilized-Polysiloxane Salicylaldehyde Propylimine and Its Application

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(P-(CH₂)₃NH₂) P (CH₂)₃-C₇H₆NO,
-3
(-3)

ABSTRACT

A porous solid polysiloxane ligand system of the general formula P-(CH₂)₃-C₇H₆NO, (where P represents [Si-O]_n siloxane network) has been prepared by modification of the immobilized 3-aminopropylpolysiloxane, P-(CH₂)₃NH₂ with an excess of salicylaldehyde. The new modified polysiloxane system exhibits good potential for uptake of Co²⁺ and Cu²⁺ metal ions. This ligand system gives more stable complexes with the divalent metal ions than its parent 3-aminopropylpolysiloxane precursor. Characterization was achieved using elemental analysis and FTIR spectroscopy.

Keywords: Metal uptake, salicylaldehyde, imines, polysiloxanes, immobilized-polysiloxane ligand systems

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INTRODUCTION:

There is a growing interest in synthesis of inorganic polysiloxane supports bearing organofunctionalized groups [1-9]. Chemisorbents based on incorporation of chelating ligands at high intensity on to the inorganic polymeric matrix are of particular interest. There are two common methods used to prepare these functionalize ligand systems. The first method is the sol-gel process which involves hydrolysis and condensation of $\text{Si}(\text{OEt})_4$ with the appropriate silane coupling agent $(\text{RO})_3\text{SiX}$ where X represents an organofunctionalized ligand [1-9]. The second approach is the chemical modification of the pre-prepared functionalized polysiloxane. The second method appears as an interesting alternative mainly on account of substitution of organofunctionalized groups when appropriate chelating silane agents are difficult to prepare [10-14]. The main advantages of these functionalized inorganic supports are their high thermal, hydrolytic and mechanical stability in addition to lack of swelling in solvents [15,16]. These functionalized systems have been used in many important applications such as; chemisorption, recovery and separation of metal cations from organic solvents [17,18] and aqueous solutions [1-14]. In addition they were used widely as stationary phases in chromatography [7,19] and as heterogeneous catalysts [8,20,21]. A variety of spectroscopic techniques such as solid state nuclear magnetic resonance (NMR), thermal analysis and photoelectron spectroscopy (XPS) have been employed to study the ligand-modified polysiloxane systems [22-30]. This report describes synthesis and characterization of a new functionalized polysiloxane ligand system. The immobilized ligand system was used for extraction of Co^{2+} and Cu^{2+} metal ions from aqueous solutions.

2. EXPERIMENTAL:

2.1. Reagents and Materials.

Tetraethylorthosilicate, 3-aminopropyltrimethoxysilane, and salicylaldehyde were purchased from (Merk) and used as received. Diethyl ether and methanol (spectroscopic grade) were also used as received. Metal ion solutions of appropriate concentration were prepared by dissolving the metal chloride (analytical grade) in distilled water. Various buffer solutions with pH values in the range of 3.5-6.0, were controlled using acetic acid and sodium acetate buffer solutions.

2.2. General Techniques:

Analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer Analyst-100 spectrophotometer. The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR, spectrophotometer using KBr disk in the range 4000 to 400 cm^{-1} . All pH measurements were obtained using HM-40V pH Meter.

2.3. Preparations:

2.3.1. Preparation of 3-aminopropylpolysiloxane (P-A).

Aminopropylpolysiloxane was prepared as reported previously [1] by adding 3-aminopropyltrimethoxysilane (9.86 g, 50 mmol) to a stirred solution of tetraethylorthosilicate (20.83 g, 100 mmol) in 15 mL methanol and HCl (9.95 mL, 0.42 M). Gelation occurred within a few seconds. The product was left to stand for 12 hours then dried in vacuum oven at 90 °C. The material was crushed, sieved, washed successively with 50 mL portions of 0.025 M NaOH, water, methanol and diethyl ether and then dried in vacuum oven at 90 °C at 0.1 torr for 10 hours. The elemental analysis for the aminopropylpolysiloxane is given in Table 1.

Table 1. Elemental Analysis Data for P-A and P-G.

Polysiloxane		%C	%H	%N	C/N
P-A	Expected	15.7	3.9	6.1	3.0
	Found	13.1	4.6	4.9	3.1
P-S	Expected	30.9	3.1	3.6	10.0
	Found	24.68	3.8	4.3	6.69

2.3.2. Preparation of salicylaldehydepropylimine ligand system (P-S).

3-aminopropylpolysiloxane (P-A) (5.0 g, 17.5 mmol) was refluxed for 12 hours with an excess (5 g, 41 mmol) of salicylaldehyde in 50 mL ethanol. The solid product was filtered off, washed successively with 50 mL portions of 0.025 M NaOH, methanol and diethyl ether and then dried in vacuum

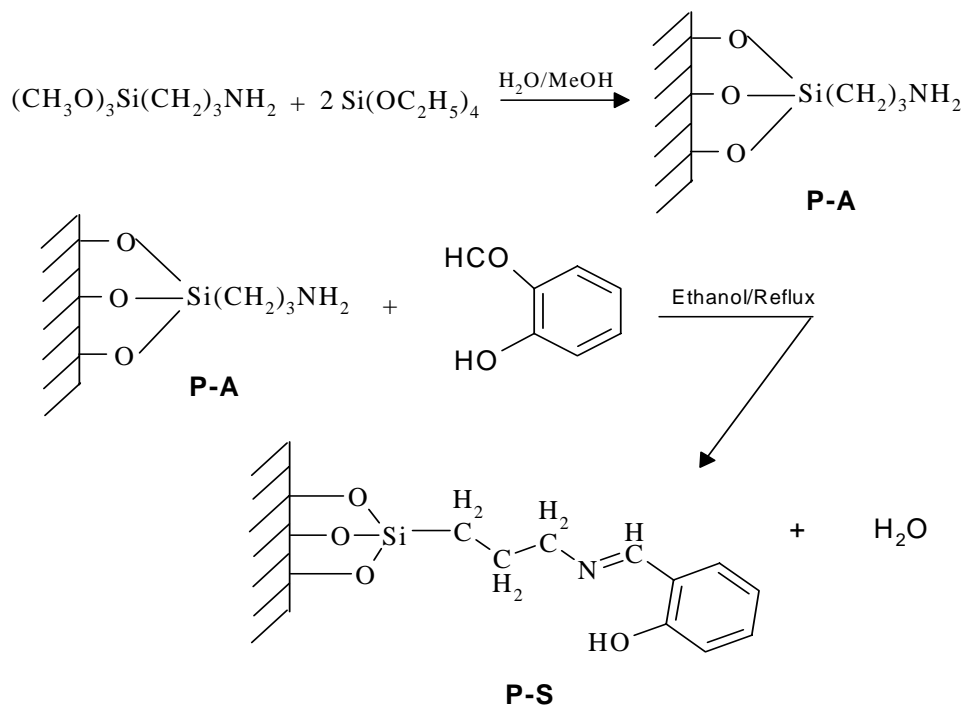
oven at 90°C for 12 hours. Elemental analysis for salicylaldehydepropylimine polysiloxane (P-S) is given in Table 1.

3. RESULTS AND DISCUSSION

3.1. Preparation of Salicylaldehydepropylimine Ligand System (P-S).

The salicylaldehydepropylimine ligand system (P-S) was prepared by two steps (Scheme 1):

- 1- Preparation of 3-aminopropylpolysiloxane was prepared as previously reported[1], by hydrolytic polycondensation of 3-aminopropyltrimethoxysilane and tetraethylorthosilicate (TEOS) in the ratio of 1:2 (Scheme 1).
- 3- The new functionalized ligand system (P-S) was achieved by direct reaction of P-A ligand system with salicylaldehyde.



Scheme 1

From elemental analysis, given in Table 1, it is obvious that the reaction between 3-aminopropylpolysiloxane and salicylaldehyde occurred. The

percentage of carbon increases and the percentage of nitrogen decreases in case of P-S compared with the starting material (P-A). The lower carbon and higher nitrogen values are probably due to incomplete reaction of the amino groups with salicylaldehyde and the surface amino groups only were involved in the reaction.

3.2. Ftir Spectra:

The FTIR spectra of the immobilized 3-aminopropylpolysiloxane P-A and the modified form P-S ligand systems are given in Fig's. 1a-b. The spectra show three characteristic absorption regions at 3500-3000 cm^{-1} due to $\nu(\text{OH})$ and/or $\nu(\text{NH}_2)$, 1645-1560 cm^{-1} due to $\delta(\text{OH})$ and/or $\delta(\text{NH}_2)$ and 1200-900 cm^{-1} due to $\nu(\text{Si-O})$. The spectrum of the immobilized ligand P-S (Fig. 1b) shows a strong band at 1647 cm^{-1} due to $\nu(\text{C}=\text{N})$ stretching vibration. This confirms that the salicylaldehyde functionalized group is chemically bonded to the surface of the polysiloxane.

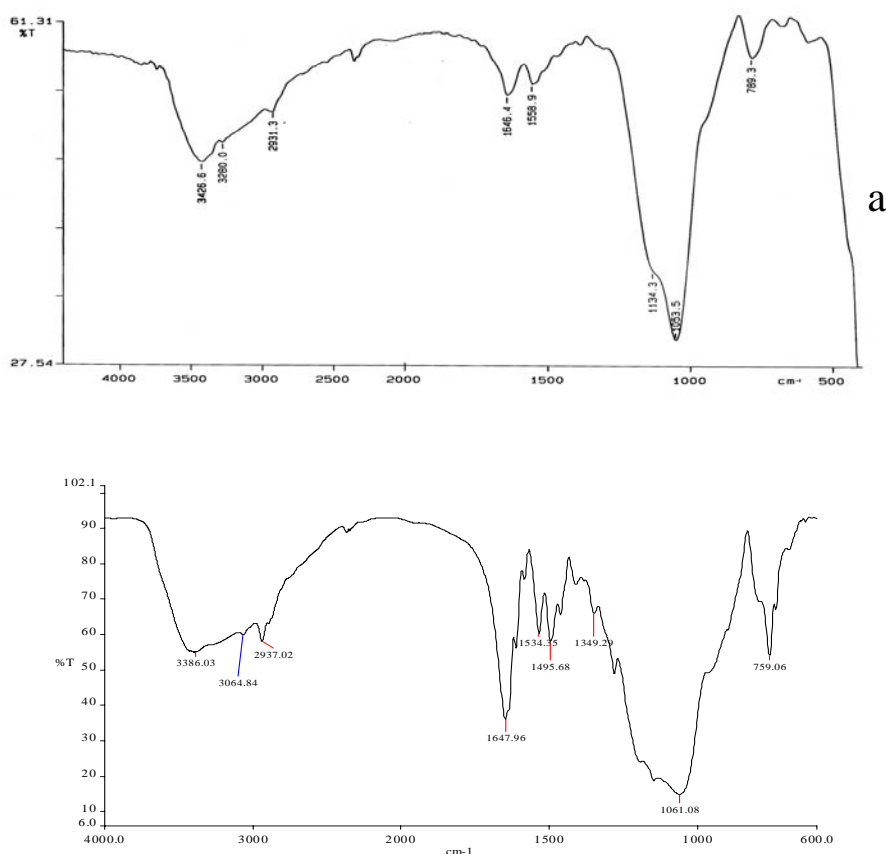


Figure 1. FTIR Spectra of a) P-A, b) P-S.

3.3 Metal uptake capacity.

The metal ion uptake capacity of Co^{2+} and Cu^{2+} metal ions by P-S was determined by shaking the functionalized ligand system P-S with buffered solutions of the divalent metal ions. Measurements were studied versus time. The maximum metal uptake capacities by P-S system as mg metal ion per gram ligand at the optimum conditions are given in Table 2

Table 2. Metal ion uptake capacity of P-S system

Metal ion	Co^{2+}	Cu^{2+}
Maximum Uptake (mg M^{2+} /g Ligand)	27.5	52.4

The Table shows that copper(II) ion uptake was higher than cobalt(II) ion, which can be attributed to the higher stability of copper(II) complex than cobalt(II) complex when bonded by the ligand system.

3.3.1. Effect of pH:

The effect of the pH value on the uptake of Co^{2+} and Cu^{2+} ions by P-S is shown in Fig. 2. The results show an increase of metal ion uptake as the pH value is raised. The uptake reached its maximum at pH 5.5. Low uptake capacity occurs at lower pH values. This is probably due to protonation of amine nitrogens [31].

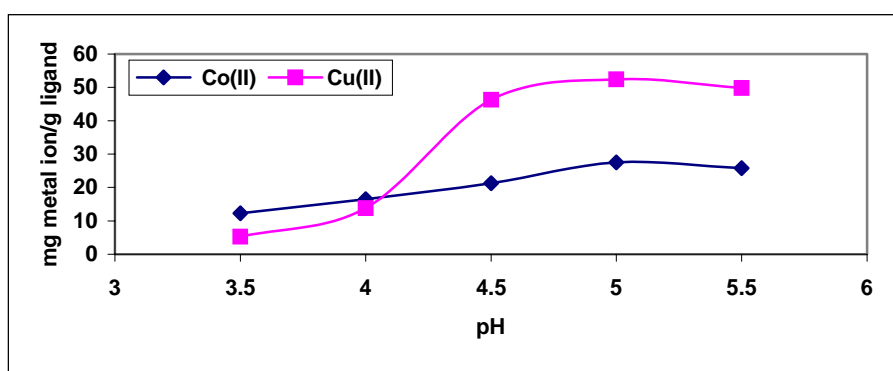


Figure 2. Uptake of Cu^{2+} and Co^{2+} metal ions by P-S versus pH values (72 hrs shaking time).

CONCLUSION:

The immobilized P-S salicylaldehydepropylimine ligand system was prepared by treatment the 3-aminopropylpolysiloxane with salicylaldehyde. This immobilized ligand system exhibits high potential for extraction of Co^{2+} and Cu^{2+} metal ions. Measurements of metal ion uptake by the chelating ligand system were carried out at various pH values using buffer solutions. The optimum pH value was 5.

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