

# Synthesis of N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>-Schiff bases and using them to transport Cu<sup>2+</sup> by bulk liquid membrane

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**Abstract:** Two new Schiff bases (I) and (II) containing nitrogen-sulfur-oxygen donor atoms, were designed and synthesized in a multi—step reaction sequence. Transport of copper ion across a bulk chloroform membrane containing Schiff base(I) as carrier has been studied. The parameters influencing the transport efficiency such as composition of receiving phase, pH of the feed phase, carrier concentration in the membrane, EDTA concentration in the receiving phase, effect of temperature and time dependency of the process were studied and discussed. The selectivity of the processes towards copper ions were tested by performing the competitive transport experiments on the mixture containing Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> ions. The amount of copper transport through the liquid membrane after 180 min arrived to 98% at 25°C.

**Key Words :** Schiff base, Bulk liquid membrane, Separation, Transport.

## INTRODUCTION

Usually in many analytical method the performing of a separation step is necessary during the analysis. Among various separation methods (ion exchange, solvent extraction, selective chemical precipitation etc.) one interesting approach is based on the recognition, binding and release of specific solutes carried out by facilitating transport membranes, i.e. organic liquid in contact with two separated aqueous phases working under chemical gradient as the driving force. This technique has been widely used for carrier metal ion separation [1-4] and, to a lesser degree, for organic compounds separation [5,6].

Owing to their coordinating ability with a variety of metal ions, Schiff base ligands have been involved in various analytical investigations for many years. As instance, they are a category of important sensory molecules for fabricating cation- [7,9] and anion- [10,11] selective electrodes. Octadecyl disks modified

by Schiff base ligands have been used for enrichment and separation of trace amount of metal ions [12,13]. Selective separation of a given metal ion from a complex mixture of other ionic species is of increasing importance in industrial and analytical chemistry and separation sciences. In most cases, various interfering species must be removed and/or the species of interest must be enriched before possibility of detection . Carrier mediated transport through liquid membrane is well known as one of the most powerful tools for such concentration, separation and recovery. Also, the selective transport of metal ions across a membrane is known to play an essential role in many biological processes [14-17].

An important advantage for the use of this procedure is that in the liquid membrane technology, the extraction, stripping and regeneration operations are combined in one single step. Proton-driven cation transport through a liquid membrane containing an ion-selective ionophore bearing a proton dissociable

moiety is one of the most effective separation techniques for a particular metal ion [18-22]. In this membrane cation transport system, there is often no need for the counter anion to counterbalance the positive charge because the proton-dissociated ionophore itself can act as the counter anion of the complexing cation. Therefore, cation transport ability is independent of the extent of hydration of a counter anion. The uphill transport against a cation concentration gradient is also feasible since cations are transferred by counter transport of protons.

So far as for transition and heavy metal ions, a number of carriers for Cu(II) that is both vital and toxic for many biological system have been reported [23-29]. These methods for the specific transport of Cu(II) ions across a liquid membrane have the drawbacks of a slow rate of transport or a lack of high selectivity and efficiency.

The Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are known to form very stable complexes with transition metal ions, especially copper [30,31]. In recent years, these ligands have been employed in analytical application, e.g. solid phase extraction [32,33] and ion-selective PVC membrane electrodes [34,35].

Kantekin and Ocak have reported the use of  $N_2O_2S_2$  Schiff base containing aromatic moieties for the transfer of various metal ions from the aqueous phase into the organic phase in liquid-liquid extraction system [36-39].

We have interested in the design and synthesis of  $N_2O_2S_2$ -crown ether extractants for the selected metal ion, which have bigger cavity size. We report here the transport of copper ions from picrate solution into EDTA solution through a bulk liquid membrane containing  $N_2O_2S_2$ . Different experimental conditions, e.g. the effects of  $H_2L$  concentration in the membrane, EDTA concentration in the receiving phase, effect of temperature and time dependency of the process were investigated.

## **EXPERIMENTAL**

### **Reagents and Apparatus**

All the used chemicals were purchased from Aldrich or Merck unless otherwise cited. The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The IR spectra of the ligands were recorded with a Midac 1700 instrument in KBr pellets.  $^1H$  and  $^{13}C$ -NMR spectra of ligands in  $CDCl_3$  and  $C_2D_5OD$  solution were recorded on a Bruker 400MHz spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. Mass spectra were recorded using a KRATOS MS50TC spectrometer. AA 929 Unicam Spectrometer was used for FAAS measurements with an air-acetylene flame. The UV-

vis measurements were recorded on a PerkinElmer  $\lambda$  20 UV-vis Spectrometer. A pH meter (Metrohm 691 pH Meter) was also used.

### **Synthesis of $\alpha,\alpha'$ -bis(5-Bromo-2-carboxyaldehyde phenoxy)-1,4-xylene**

To a stirred solution of 5-bromosalicylaldehyde (40 g, 200 mmol) and  $K_2CO_3$  (13.8 g, 100 mmol) in DMF(100 ml), was added dropwise  $\alpha,\alpha'$ -Dibromo-p-xylene. (26.2 g, 100 mmol) in DMF(40 ml). The reaction was continued for 4 h at 150-155 °C and then for 4 h at room temperature. Then, 200 ml distilled water was added and the mixture kept in refrigerator. After 1 h, the precipitate was filtered and washed with 500 ml water. It was dried in air and recrystallized from EtOH and filtered under vacuum. yield: 80%, Mp 228-230 °C.

### **Synthesis of 1,7-Bis(5-Bromo-2-formylphenyl) - 1,4,7-trioxaheptane**

To a stirred solution of 5-bromosalicylaldehyde (40 g, 200 mmol) and  $K_2CO_3$  (13.8 g, 100 mmol) in DMF(100 ml), was added dropwise 1-chloro-2-(2-chloroethoxy)ethane (14.3 g, 100 mmol) in DMF(40 ml). The reaction was continued for 4 h at 150-155 °C and then for 4 h at room temperature. Then, 200 ml distilled water was added and the mixture kept in refrigerator. After 1 h, the precipitate was filtered and washed with 500 ml water. It was dried in air and recrystallized from EtOH and filtered under vacuum. yield: 85%, mp. 142-144.

### **Synthesis of ligand [N,N'-bis(2-aminothiophenol)- $\alpha,\alpha'$ -bis(5-Bromocarboxylidene phenoxy)-1,4-xylene [ $H_2L$ ](I)**

A solution of  $\alpha,\alpha'$ -bis(5-Bromo-2-carboxyaldehyde phenoxy)-1,4-xylene (10 mmol, 5.02g) in 50 ml absolute ethanol was added drop wise over 2 h to a stirred solution of 2-aminothiophenol (20 mmol, 2.50g) dissolved in 50 ml hot absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. The mixture was then filtered and recrystallized from a mixture of absolute ethanol- DMF, yield 50%, m.p.236-238°C. Anal. Calc. C, 56.98; H, 3.64; N, 3.91; S, 8.93. Found: C, 56.95; H, 3.99; N, 4.1; S, 9.1%.

### **Synthesis of ligand [N,N'-bis(2-aminothiophenol)-1,7-Bis(5-Bromocarboxylidene phenyl)-1,4,7-trioxaheptane] $[H_2L]$ (II)**

A solution of 1,7-Bis(5-Bromo-2-formylphenyl)-1,4,7-trioxaheptane (10.0 mmol, 4.7 g) in 50 ml absolute ethanol was added dropwise over 2 h to a stirred solution of 5-amino-1,3,4-thia-diazole-2-thiol (20 mmol, 2.66 g) dissolved in 50 ml hot absolute

ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered and recrystallized from a mixture of absolute ethanol- DMF, yield 60%, m.p.238-240. Anal. Calc. C, 37.39; H, 3.39; N, 11.89; S, 18.2. Found: C, 37.2; H, 3.32; N, 11.9; S, 18.13%.

### Transport experiments and analysis

The experimental set-up [40,41] was a double jacket cylindrical glass cell (4.5 cm diameter) holding a glass tube (2.25 cm diameter) for separating the two aqueous phases, which is shown schematically in Fig. 1.

Temperature of the solution was kept constant using thermostated water circulating through the jacket of the cell. The source phase (20 mL) contained copper picrates [Copper picrates was prepared by successive addition of a  $1 \times 10^{-2}$  M metal nitrate solution to  $2 \times 10^{-5}$  M aqueous picric acid solution and shaken at 25°C for 1 h]. This metal picrate was measured by UV-vis using maximum wavelength 352 nm. The receiving phase (20 mL) included EDTA solution (0.1 M). The pH of the source was adjusted containing NaOH or HCl solutions. The aqueous phases were bridged by a chloroform solution (50 mL) of the investigated Schiff bases ( $N_2O_2S_2$ ), which is placed below them. The experiment was started by stirring the organic phase (500 rpm) and the concentration of the

metals in the aqueous phases was determined by UV-vis using maximum wavelength 352 nm.

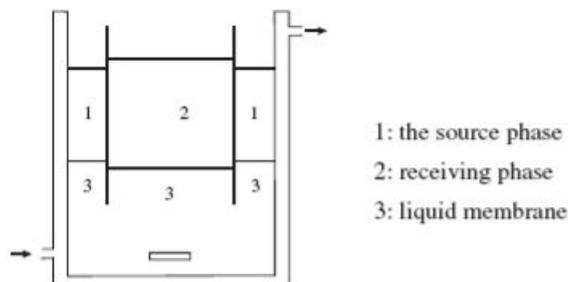


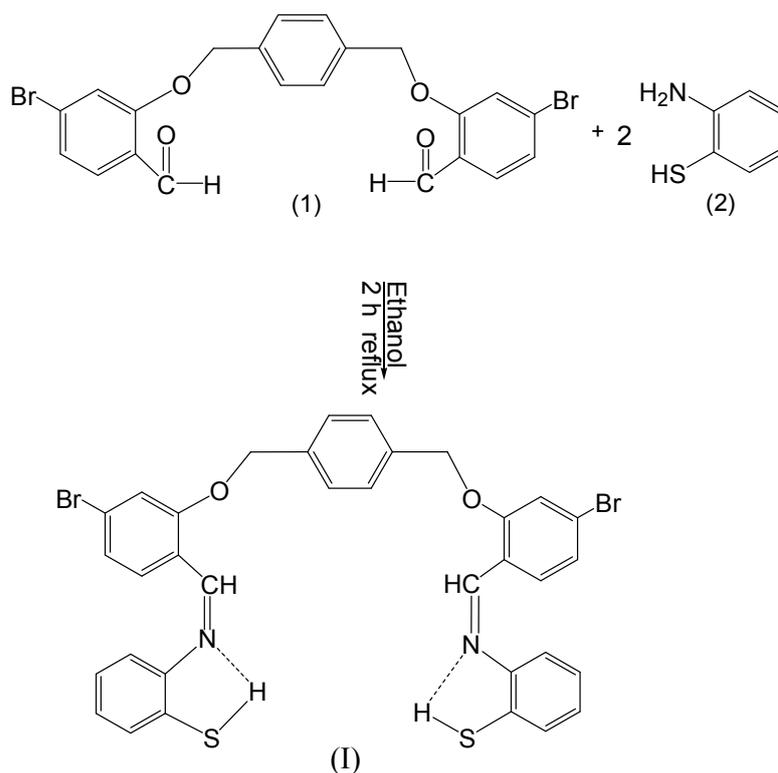
Fig 1. Liquid membrane cell.

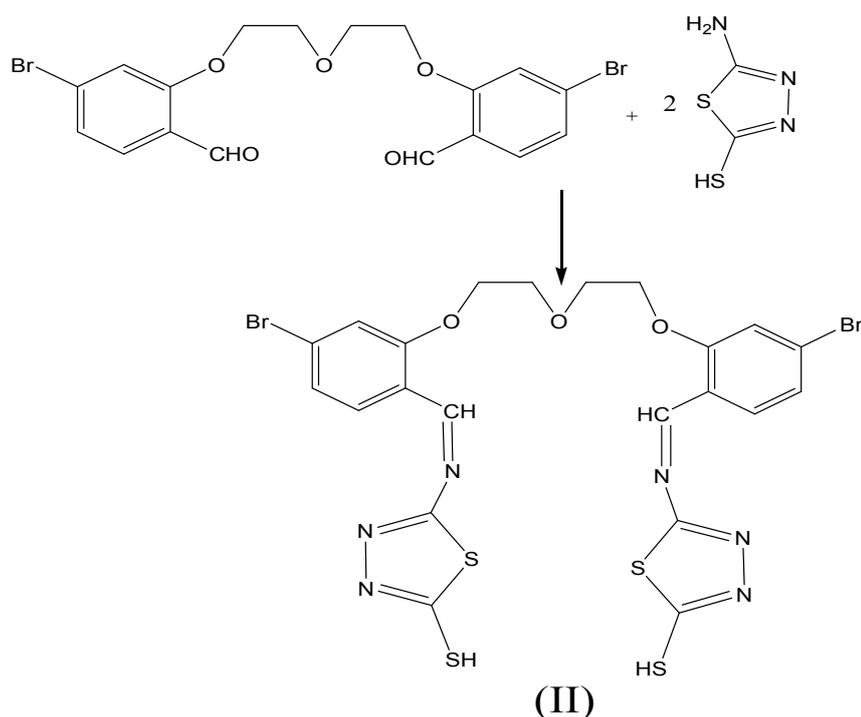
## RESULTS AND DISCUSSION

### Synthesis of Schiff bases

The synthetic experiments of new two Schiff bases (I) and (II) are shown in Scheme 1. The structure of novel compounds were characterized by a combination of elemental, IR, MS,  $^1H$  NMR,  $^{13}C$ -NMR spectral analyses data. The preparation of the Schiff bases illustrated in (Scheme 1).

### Scheme 1. Synthesis of Schiff bases (I) and (II)





### IR spectra

The spectrum showed a strong band at  $1672\text{ cm}^{-1}$  in the spectrum of the Schiff base are assigned to  $\nu(\text{C}=\text{N})$  of azomethine. A broad medium intense band was at  $2930\text{ cm}^{-1}$  due to methylene groups.

The IR spectrum of the thio Schiff-base ligand exhibited a strong sharp band at  $3400\text{ cm}^{-1}$ . This band was assigned to the stretching frequency of the  $\text{N}^+\text{H}$  group, due to the presence of the intramolecular hydrogen bond ( $\text{N}-\text{SH}$ ) in the molecule [42-44](Scheme 1).

In the IR spectrum of Schiff base (II) the absence of band in the region  $3200\text{-}3400\text{ cm}^{-1}$  corresponding to free primary amine and hydroxyl group suggests that complete condensation of amino group with aldehyde. Appearance of a new strong absorption band at  $1607\text{ cm}^{-1}$  attributable to characteristic stretching frequencies of the imino linkage  $\nu(\text{C}=\text{N})$  [32,33] provides strong evidence for the presence of product. The absorption in IR spectrum of Schiff base (II) at  $2728\text{ cm}^{-1}$  is due to the presence of SH. A broad medium intense band was at  $3075\text{ cm}^{-1}$  due to for aromatic protons [42-44].

### Mass spectrum

The electron impact mass spectrum of the Schiff bases (I) and (II) confirm the probable formula by showing a peak at 716 amu, corresponding to the Schiff base(I) and 700 amu, corresponding to the Schiff base(II).

### $^1\text{H-NMR}$ spectra

The Schiff base[Fig. 2(b)] exhibits signal at 1.57 ppm due to SH protons. It also exhibits resonance due to  $-\text{CH}_2-$  protons around 5.38 ppm. The other characteristic resonance due to azomethine proton in Schiff base appears at 8.73 ppm. Signals in the region 7-8.12 ppm due to aromatic protons[29-31].

The Schiff base(II)[Fig. 3(d)] exhibits signal at 5.3 ppm due to SH protons. It also exhibits resonance due to  $-\text{CH}_2-$  protons around 3.8 and 1.1 ppm. The other characteristic resonance due to azomethine proton in Schiff base (II) appears at 8.86 ppm. Signals in the region 6.9-7.9 ppm due to aromatic protons [29-31].

### $^{13}\text{C-NMR}$ spectrum

The  $^{13}\text{C}$  NMR spectrum[Fig. 2(a)] of ligand indicated new resonances are arom. (114.19, 114.73, 121.31, 123, 124.53, 125, 126.18, 128.25, 132.20, 134, 135.93, 136.15, 151.96, 155.09).  $\text{CH}=\text{N}$  (161.32).  $\text{CH}_2$  (70.99).  $\text{CDCl}_3$  (77.34, 77.22, 77.02, 76.70) [29-31].

The  $^{13}\text{C}$  NMR(75 MHz,  $\text{C}_2\text{H}_5\text{OH-d}_6$  75 MHz) d (ppm) spectrum[Fig. 3(C)] of Schiff base (II) indicated new resonances are  $\text{CH}_2$ : 79.92, Arom:110.57, 111.16, 11687.31, 118.90, 120.97, 127.72, 129.28, 131.56, 133.44, 137.55, 154.13, 159.82, 162.58,  $\text{CH}=\text{N}$ : 166.21 [29-31].

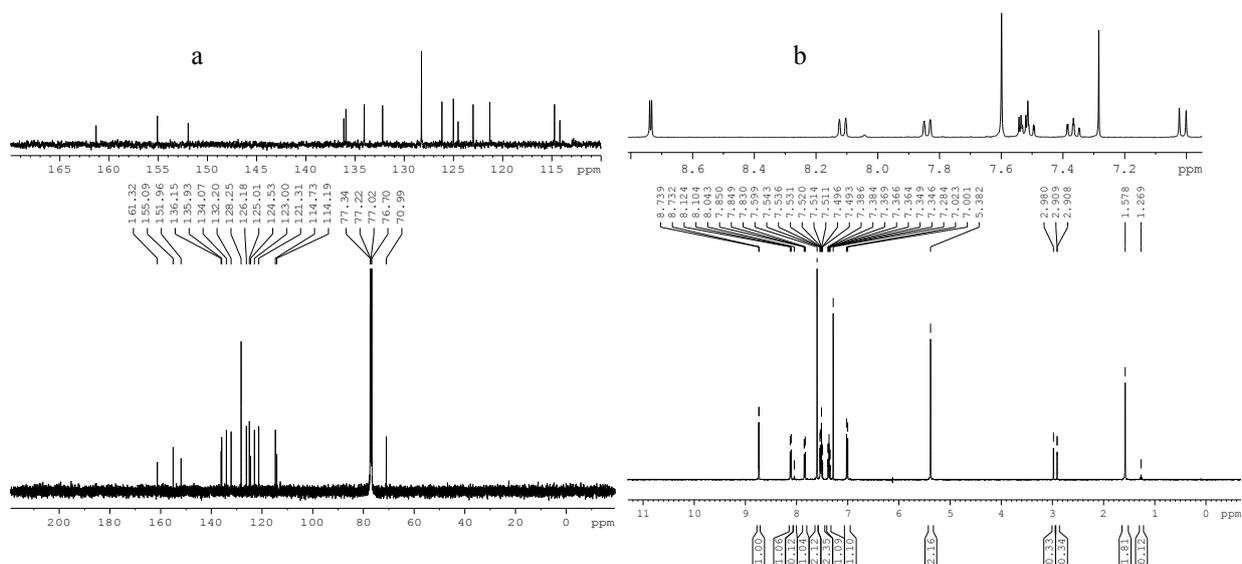


Fig. 2 .  $^1\text{H}$ -NMR(b) and  $^{13}\text{C}$ -NMR(a) spectra of ligand (H<sub>2</sub>L)(CDCl<sub>3</sub>)(I)

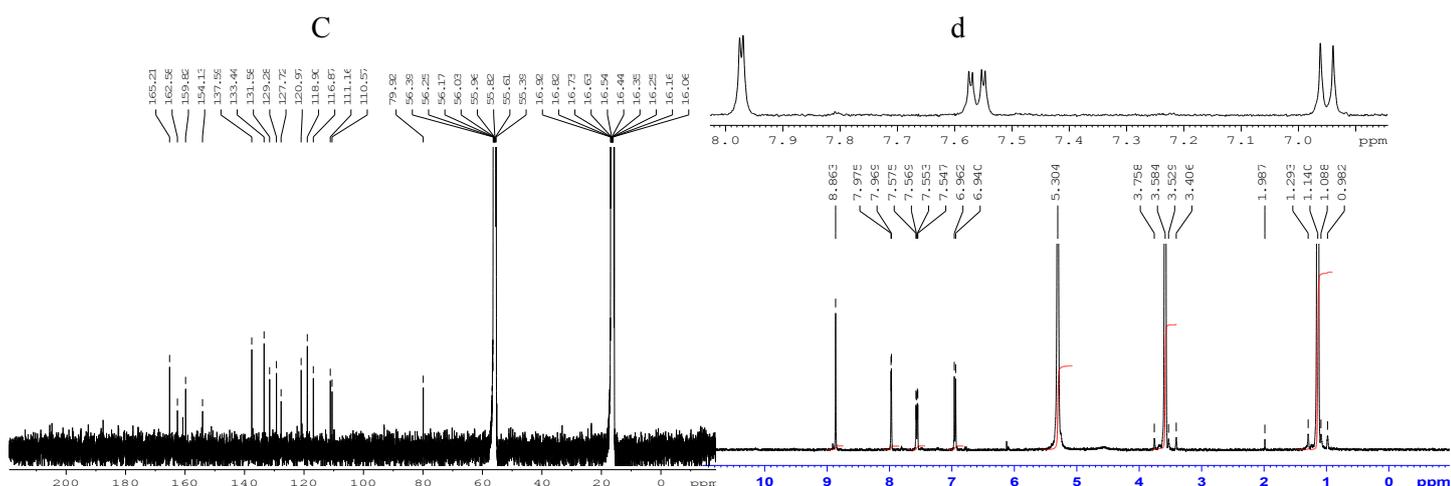


Fig. 3.  $^{13}\text{C}$ -NMR(c) and  $^1\text{H}$ -NMR(d) spectra of Schiff base (C<sub>2</sub>D<sub>5</sub>OD) (II)

The liquid membrane used in this study is shown schematically in **Figure 1**. The Cu<sup>2+</sup> ion is transported from the source phase to the receiving phase via a chloroform membrane. After complexation of the carrier with Cu<sup>2+</sup> ion on the left side of the membrane, the complex diffuse down its concentration gradient. On the right side of the membrane, the metal ion would be released into the receiving phase via formation of a ternary complex (carrier-metal ion-EDTA). At this stage, the free carrier diffuses back across the liquid membrane. The net result is the

transport of Cu<sup>2+</sup> ion from the aqueous source phase to the aqueous receiving phase across the bulk of organic phase (the membrane).

In the preliminary experiment, it was found that N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> had desired ability to the extraction of copper ion from the source phase into the organic membrane. Regarding the fact that this transport is proton-driven, it is expected that the transport of copper to receiving phase to be completed by time the receiving phase acidified. Despite adding different concentrations of various acid solutions, the transport of copper into

receiving phase was quite low. In the next step, the different complexing agents that are well known to form very stable complexes with copper ion were added to the receiving phase at various concentrations and measurements. But in the best state, the maximum percentage of copper transported into the receiving phase was about 60%(Table.1 ). In all experiments, the concentration of copper in source phase decreased to about 20 – 30% after 2 h(beside that we have done all experiments on EDTA because give it good results in transport of copper). It reveals that the problem is in the back extraction stage, where the exchange of  $\text{Cu}^{2+}$  and  $\text{H}^+$  in the membrane/receiving phase interface had some difficulties. We think this problem might have arisen from low surface area of liquid membrane/aqueous receiving phase and/or low interaction of complexed copper ion in the liquid membrane and the receiving phase. This causes high activation energy for the transfer of copper ion from the chloroform to the aqueous receiving phase and a phase transfer process kinetics by lowering its activation energy.

**Table. 1: Effect of composition of receiving phase on the transport of Cu(II) ion**

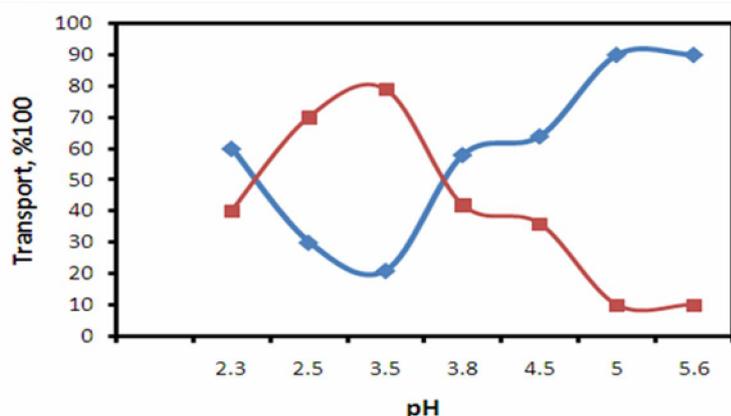
Receiving phase	Percentage transported Into receiving phase
EDTA (0.1)	60
KCl (0.1)	28
$\text{FeCl}_3$ (0.1)	0
$\text{Na}_2\text{S}_2\text{O}_3$ (0.1)	1
DL-Alanin (0.1)	28
Valline (0.1)	59
Lysine (0.1)	50

### Effect of pH of the source phase

The results of transfer of copper ions (initial concentration  $2 \times 10^{-5}$  M) from source phase (20 mL) across a stirred (500 rpm) bulk liquid membrane (50 mL) containing  $\text{H}_2\text{L}$  ( $1 \times 10^{-4}$  M in Chloroform) into a EDTA solution (0.1 M, 20 mL, receiving phase) after 2 h at 25 °C are shown in Fig. 4.

It is seen that for the carrier the transport efficiency increases with pH of the feed phase. This reveals a proton exchange mechanism for the extraction process at the first interface. However at higher pH values, a decrease in transported value of copper ions may be attributed to the depletion of the membrane from ionized carrier, although the formation of copper hydroxide cannot be ignored.

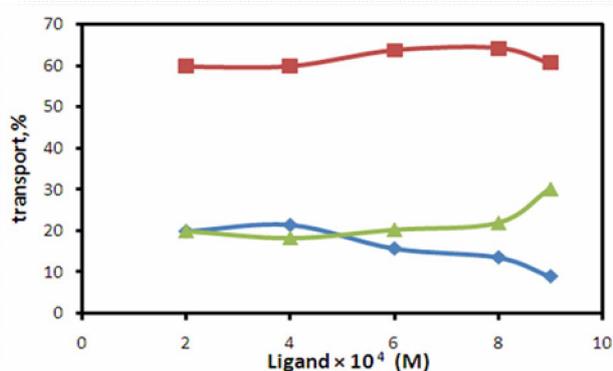
Thus, pH 3.6 was selected for following experiments. At this pH, the amount of transported copper ions was found to be 80 percent. The higher efficiency of the latter can be described by its more complexing ability, due to the presence of more donating atoms in its structure, on the one hand, and the more flexible structure of  $\text{N}_2\text{S}_2\text{O}_2$ , that makes possible a better interaction between the donor atoms of the ligand and the cation, on the other hand.



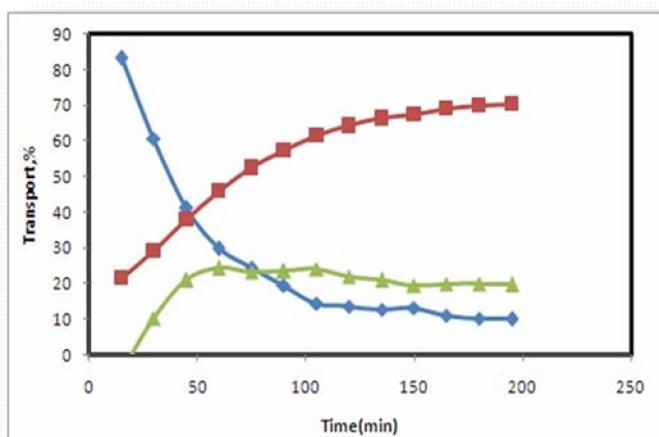
**Fig. 4 .** Effect of pH of the source phase on copper(II) transport. Conditions, (▲)source phase, 20 ml of  $2.0 \times 10^{-5}$  M Cu(II) ion at various pH; liquid membrane phase, 50 ml of ( $4 \times 10^{-4}$  M) $\text{H}_2\text{L}$  in chloroform; (■)receiving phase,20 ml solution of 0.1 M EDTA, time of transport, 2 h.

### Effect of $N_2O_2S_2$ concentration in the organic phase

The influence of  $N_2O_2S_2$  concentration in the organic phase on the transport efficiency of copper was also studied. The Figure 5 shows the percentage of copper transport increase with an increase in  $N_2O_2S_2$  concentration in the organic phase. Maximum transport occurs at a concentration of about  $8.0 \times 10^{-4} M$   $N_2O_2S_2$ . Further excess of the carrier had no considerable effect on the transport efficiency.



**Fig. 5.** Effect of  $H_2L$  concentration in the membrane phase on copper transport. Conditions, (■)source phase, 20 ml of  $1 \times 10^{-3} M$   $Cu(II)$  ion and pH 3.6; (×)liquid membrane phase, 50 ml of ( $4 \times 10^{-4} M$ ) $H_2L$  in chloroform at different concentrations; (▲)receiving phase, 20 ml solution of 0.1 M EDTA; time transport, 2h.



**Fig. 6.** Percentage of the transported copper ions from feed phase into the receiving phase through the bulk liquid membranes containing  $H_2L$  ligand as a function of time. Conditions, (■)source phase, 20 ml of  $2 \times 10^{-5} M$   $Cu(II)$  ion and pH 3.6; (▲)liquid membrane phase, 50 ml of ( $4 \times 10^{-4} M$ ) $H_2L$  in chloroform at concentration ( $8 \times 10^{-4}$ ); (■)receiving phase, 20 ml solution of 0.1 EDTA; time transport, 2h.

It was found that, under the optimum conditions, the transport of copper ion from the aqueous source phase into the receiving phase after 3.5 h is almost quantitative

### Effect of time on transport

Figure. 6 .shows the time dependence of copper transport through the liquid membrane under experimental conditions. It is obvious that the extraction of copper ion from the source phase into the organic membrane occurs almost completely after 200 min. However, the plot shown the transport rate decrease gradually with time and a steady state situation is reached in which the amount of  $cu^{2+}$  ions in MP hardly changes, whereas the decrease in SP and increase in RP are constant and equal. After 3.5 h, the concentrations of  $cu^{2+}$  ions were independent of time and transport was completed.

### Effect of EDTA concentration in the receiving phase

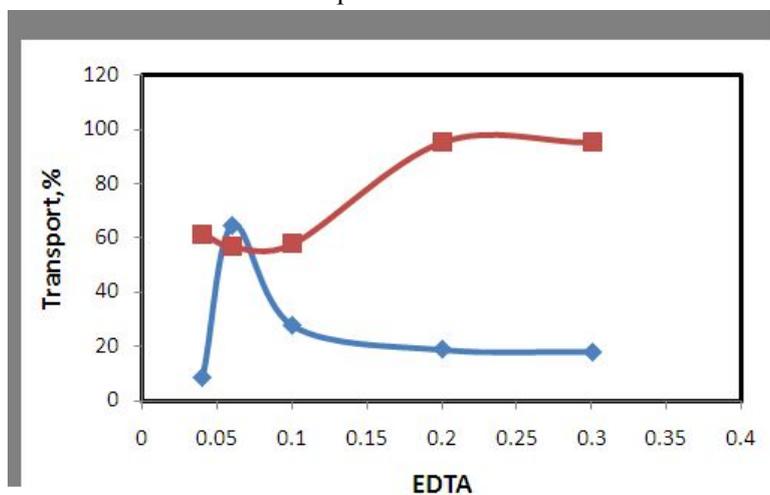
The effect of EDTA concentration in the receiving phase on efficiency of copper transport was also investigated ( Fig. 7), and it was found that maximum copper transport occurs at 0.2M of EDTA.

### Effect o temperature

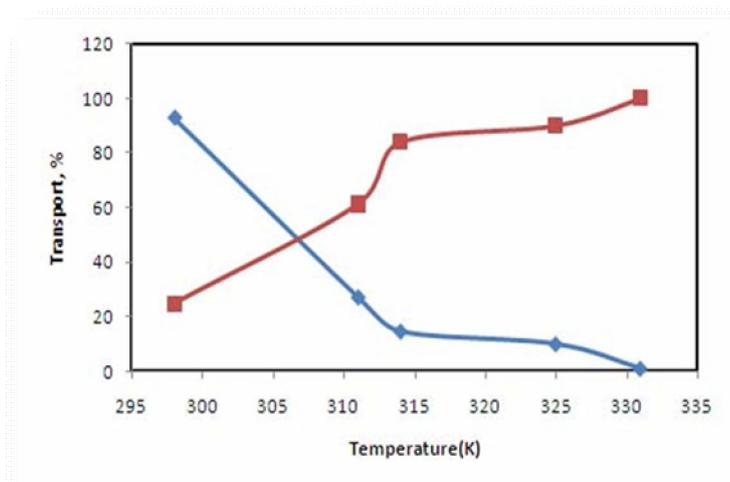
The effect of temperature on the transport of the Cu(II) throught the liquid membrane containing [H<sub>2</sub>L] in CHCl<sub>3</sub> was examined at 311, 314 and 331K, respectively. The experimental results are show in Figure 8. It is quite obvious that transport increases with an increase in the temperature.

### Selectivity of the processes

Selectivity of the transport experiments using N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> carrier under similar experimental conditions towards copper ions over lead, nickel, cobalt, cadmium and zinc ions from binary mixtures was evaluated (Table 2). The results present the suitable selectivity of the studied carriers towards copper ions over the examined ions. It is noteworthy that, the presence of other metal ions in the mixture decreases the percentage of copper transported in comparison with those in the single species experiments. This probably being due to a multi-ion competition or crowding effect[45-47].



**Fig. 7.** Effect of EDTA concentration in the membrane phase on copper transport. Conditions, (■)source phase, 20 ml of  $2.0 \times 10^{-5}$  M Cu(II) ion and pH 3.6; liquid membrane phase, 50 ml of ( $4 \times 10^{-4}$  M)H<sub>2</sub>L in chloroform at different concentration; (▲)receiving phase, 20 ml solution of (0.04- 0.3) M EDTA, time of transport, 2h.



**Fig. 8.** Effect of temperature on copper transport. Conditions, (■)source phase, 20 ml of  $2.0 \times 10^{-5}$  M Cu(II) ion and pH 3.6; liquid membrane phase, 50 ml of ( $4 \times 10^{-4}$  M)H<sub>2</sub>L in chloroform at different concentration; (■) receiving phase, 20 ml solution of 0.1 M EDTA, time of transport, 2h.

**Table 2: Percentage of the transported copper, zinc, cobalt, cadmium, nickel and lead ions from its mixtures by N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>**

Mixture	M <sup>2+</sup>	Transported value(%)
Mix. 1	Cu <sup>2+</sup>	9.2
	Zn <sup>2+</sup>	11
Mix. 2	Cu <sup>2+</sup>	86.7
	Co <sup>2+</sup>	14.6
Mix. 3	Cu <sup>2+</sup>	95.2
	Pb <sup>2+</sup>	22
Mix. 4	Cu <sup>2+</sup>	87.1
	Ni <sup>2+</sup>	7
Mix. 5	Cu <sup>2+</sup>	90.6
	Cd <sup>2+</sup>	3

### Suggested mechanism

The copper ions are transported from source phase to the receiving phase through a chloroform membrane with simultaneous counter-transport of protons. The Cu(II) transport can be explained as follows: At source phase/membrane interface, the carrier complex of copper ion forms uncharged complex LCu. At this stage, the carrier splits off protons into the source phase.

The formed complex diffuses across the membrane and at the membrane/receiving phase interface, the release of the Cu(II) ion into the receiving phase occurs via the decomposition of complex. At this

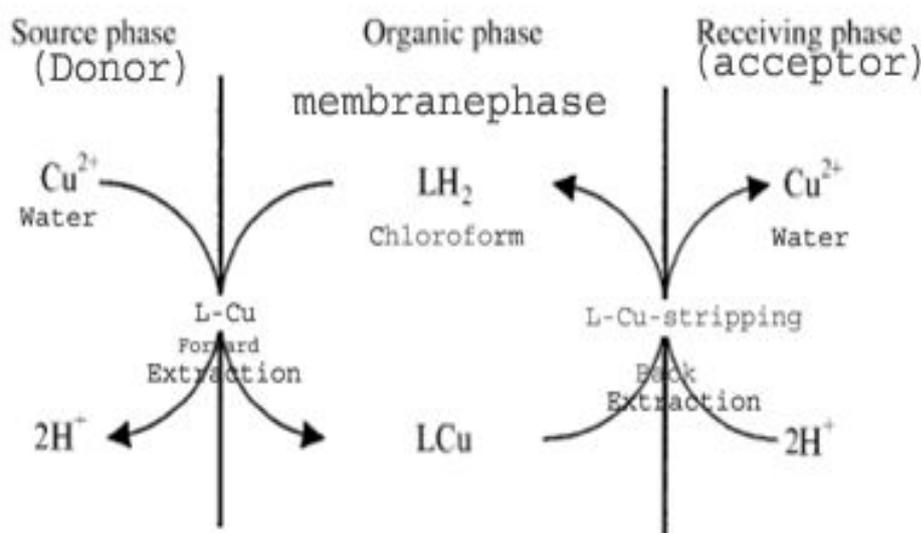
stage, the carrier associates with proton from the receiving phase releasing Cu(II) ion into the receiving phase. The free carrier diffuses back across the membrane to the source phase/membrane interface, where the cycle starts again.

### Conclusion

In the first stage, substituted Schiff Base analogues are obtained from condensation of bis-aldehyde and aminothio in dry Ethno. The present study demonstrates that the ligand N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> is an excellent carrier for efficient transport of Cu(II).

Uphill transport of Cu(II) against its concentration gradient is easily performed with the illustrated system (Figure. 9). Also, this study demonstrates the usefulness of the liquid membrane technique for making it possible to combine extraction and stripping operations in a single process and reducing the solvent inventory requirements. In conclusion, this system has the advantages of high precision, efficiency, simplicity and speed. Also the percentage of copper transport is reached to 99% at temperature 331°C after 48 min.

The simplicity, excellent efficiency and high selectivity for Cu(II) ion transport shown by the membrane system demonstrate its potential applicability to the selective separation, concentration, or purification of Copper from mixtures. Also In conclusion, this system has the advantages of high precision, efficiency, simplicity and speed.

**Fig 9. Liquid membrane system for transport of Cu<sup>2+</sup> ions**

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