

Synthesis of N₂O₂S₂-Schiff base Ligand and Using it to Transport Cu²⁺ Through Bulk Liquid Membrane

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ABSTRACT

New Schiff base (H₂L) containing nitrogen-sulfur-oxygen atoms was synthesized by reaction of α,α' -bis(5-Bromo-2-carboxyaldehyde phenoxy)-1,4-xylene with aminothiophenol. Transport of copper ion across a bulk chloroform membrane containing Schiff base ligand (H₂L) 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 amount of copper transport through the liquid membrane after 48 min., arrived to 100% at temperature 58°C.

Key Words: N₂O₂S₂-type Schiff base ligands, Bulk liquid membrane, Copper (II) ions separation.



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-α. α - - (H₂L)
-4.1(-2- -5)
pH (H₂L)
EDTA
%100 45
58

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. For 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 Ocaik 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 were interested in the design and synthesis of $N_2O_2S_2$ -crown ether extractants for the selected metal ions, which have bigger cavity size. The aim of this investigation is to elucidate the effect of the mixed donors and the structural match between cavity of ligand and metal size on the Transport of copper ion. We report here the transport of copper ions from picrate solution into EDTA solution through a bulk liquid membrane containing $N_2O_2S_2$. The parameters influencing the efficiency of the transport are verified.

Experimental

Reagent

$CuCl_2 \cdot 2H_2O$, EDTA and other reagents were purchased from Merck and Fluka. 2-Aminothiophenol, α, α' -Dibromo-P-xylene, 5-Bromosalicylaldehyde, were obtained from Fluka. Chloroform was used as organic solvent. This solvent was washed three times with distilled water to remove the stabilizers and saturation of them with water. Doubly distilled water was used in Transport experimentals.

The IR spectra of the ligand were recorded with a Midac 1700 instrument in KBr pellets. 1H and ^{13}C -NMR spectra of ligands in $CDCl_3$ 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. The UV-vis spectra of the compound investigated were obtained on a

JASCO model T70 UV-vis spectrophotometer. A pH meter (Metrohm 691 pH Meter) was also used.

Synthesis of α,α' -bis(5-Bromo-2-carboxyaldehyde phenoxy)-1,4-xylene(I)

To a stirred solution of 5-bromosalicylaldehyde (40 g, 0.2 mol) and K_2CO_3 (13.8 g, 0.1 mol) in DMF(100 ml), was added dropwise α,α' -Dibromo-p-xylene. (26.2 g, 0.1 mol) in DMF(40ml). The reaction was continued for 4h at 150-155 °C and then for 4h 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 ligand [N,N'-bis(2-aminothiophenol)- α,α' -bis(5-Bromocarboxylidene phenoxy)-1,4-xylene[H2L](II)

A solution of α,α' -bis(5-Bromo-2-carboxyaldehyde phenoxy)-1,4-xylene (10.0mmol, 5.02g) in 50 ml absolute ethanol was added drop wise over 2h to a stirred solution of 2-aminothiophenol (20.0mmol, 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.

Transport experiments and analysis

The experimental set-up [38,39] was a double jacket cylindrical glass cell (4.5 cm in diameter) holding a glass tube (2.25 cm in 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 1×10^{-2} M metal nitrate solution to 2×10^{-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

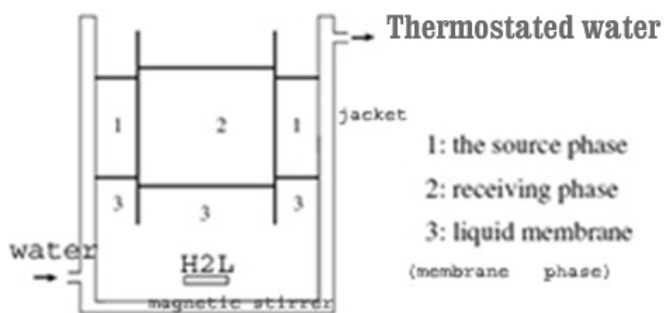
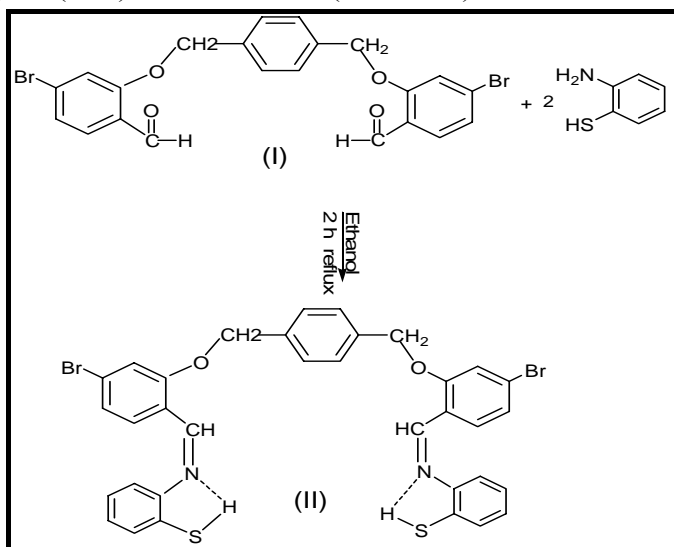


Fig 1. Liquid membrane cell.

Results and discussion

Synthesis of Schiff bases

The new thio Schiff-base [N,N'-bis (2-aminothiophenol) - α,α' -bis (5-Bromocarboxylidene phenoxy) -1,4-xylene [H2L] (II) was synthesized by the condensation of α,α' -bis (5-Bromo-2-carboxyaldehyde phenoxy)-1,4-xylene (I) and 2-aminothiophenol in absolute ethanol. The structure of novel compound was characterized by several techniques as 1H NMR, ^{13}C -NMR, IR and MS spectral data. The condensation reaction of the ligand (H₂L) is illustrated in (Scheme 1).

Scheme 1. Synthesis of ligand [N,N'-bis (2-aminothiophenol) - α,α' -bis (5-Bromocarboxylidene phenoxy) 1,4-xylene [H2L] (II)

IR spectra

The spectrum (Fig. 3) showed a strong band at 1672 cm^{-1} in the spectrum of the Schiff base which is assigned to $\nu(\text{C}=\text{N})$ of azomethine. A broad medium intense band was at 2930 cm^{-1} due to methylene groups.

The IR spectrum of the thio Schiff-base ligand exhibited a strong sharp band at 3400 cm^{-1} . This band was assigned to the stretching frequency of the N^+H group, due to the presence of the intramolecular hydrogen bond ($\text{N}-\text{SH}$) in the molecule [38-40](Scheme 1).

Mass spectrum

The electron impact mass spectrum of the ligand (H_2L)(II) confirm the probable formula by showing a peak at 716 amu, corresponding to the Schiff base.

¹H-NMR spectra

The Schiff base [Fig. 2(a)] 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.

¹³C-NMR spectrum

The ^{13}C NMR spectrum[Fig. 2(b)] 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). CH_2 (70.99). CDCl_3 (77.34, 77.22, 77.02, 76.70).

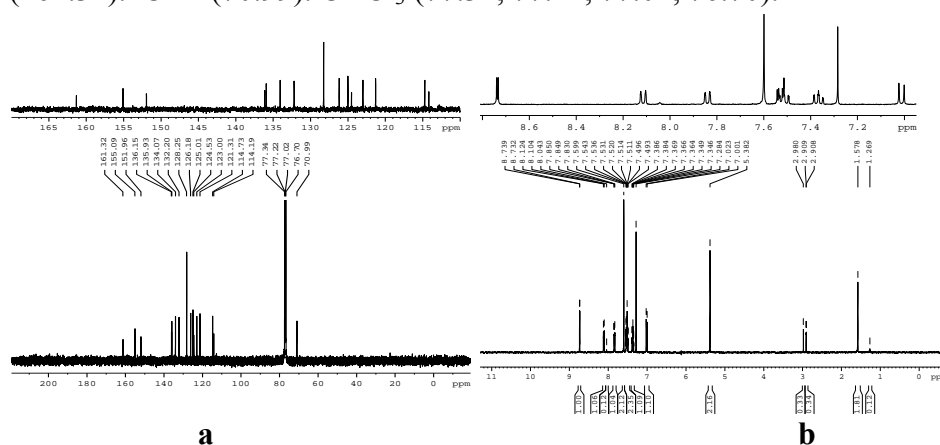


Fig. 2. ^1H NMR(b) and ^{13}C -NMR(a) spectra of ligand (H_2L)(CDCl_3)(II)

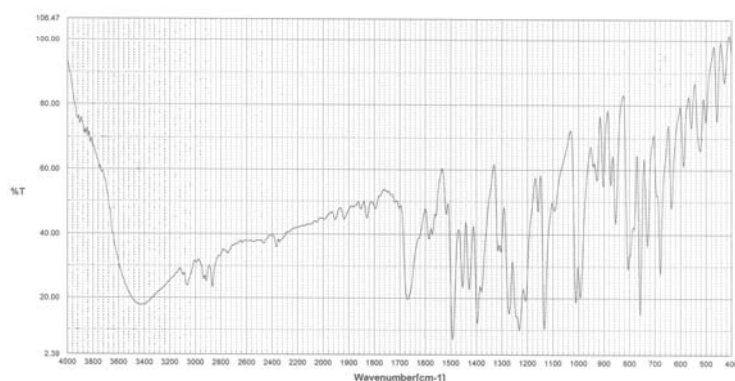


Fig. 3 IR spectra of Ligand(II)

The liquid membrane used in this study is shown schematically in Figure 1. The Cu^{2+} ion is transported from the source phase to the receiving phase via a chloroform membrane. After complexation of the carrier with Cu^{2+} ion on the left side of the membrane, the complex diffuses 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^{2+} 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 $N_2O_2S_2$ 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 the 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 to give it good results in transport of copper). It reveals that the problem is in the

back extraction stage, where the exchange of Cu^{2+} and 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.

We will suggest in the next work that Surfactant systems have been recognized as very useful agents for improving surface properties and development new concepts in analytical chemistry. Surfactants, well known as wetting agents, lower the surface tension of a liquid, allow easier spreading and reduce the interfacial tension between two liquids [40]

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
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 influence of the source phase pH on the transport of copper can be seen from the results given in Figure. 4. The result revealed that the maximum copper transport occurs at pH 2. At lower pH values there was a decrease in the percentage of copper transport, probably due to a decrease in the hydroxide concentration for exchanging protons with Cu^{2+} at the interface of the source/membrane phase or slow partition coefficients of Cu^{2+} at interface between the source/membrane phases. The efficiency of copper transport decreases at higher values, probably due to the complex formation of copper ion with hydroxide. From results, a pH 2 was selected for further studies.

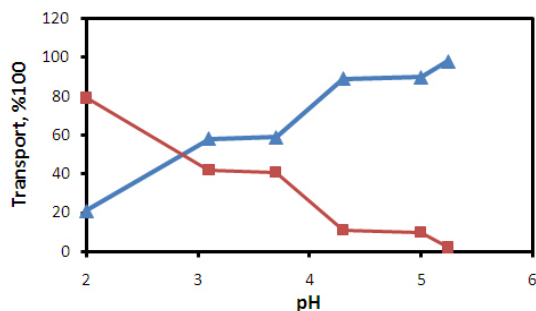


Fig. 4. Effect of pH of the source phase on copper (II) transport. Conditions, (■) source phase, 20 ml of 2.0×10^{-5} M Cu(II) ion at various pH; liquid membrane phase, 20 ml of 4.0×10^{-4} M $N_2O_2S_2$ in chloroform; (▲) receiving phase, 20 ml solution of 0.1 M EDTA, time of transport, 2 h.

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 8.0×10^{-4} M $N_2O_2S_2$. Further excess of the carrier had no considerable effect on the transport efficiency.

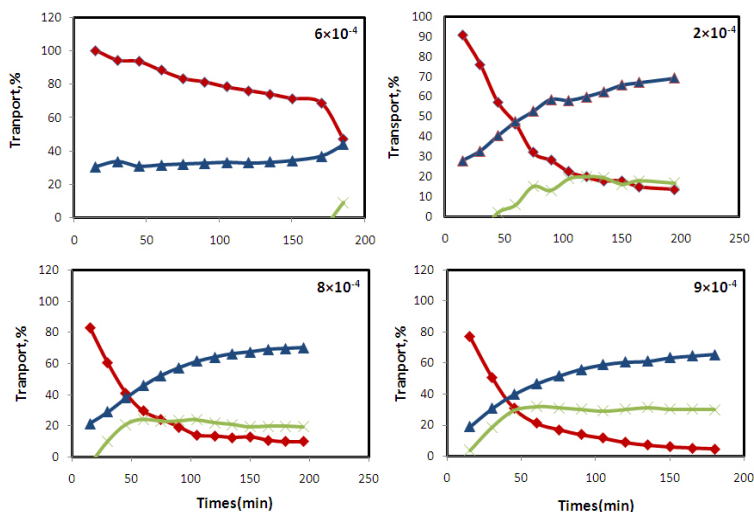


Fig. 5. Effect of $N_2O_2S_2$ concentration in the membrane phase on copper transport. Conditions, (■) source phase, 20 ml of 1×10^{-3} M Cu (II) ion and pH 2; (×) liquid membrane phase, 20 ml of $N_2O_2S_2$ in chloroform at different concentrations; (▲) receiving phase, 20 ml solution of 0.1 M EDTA; time transport, 2h.

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 shows that the transport rate decreases 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.

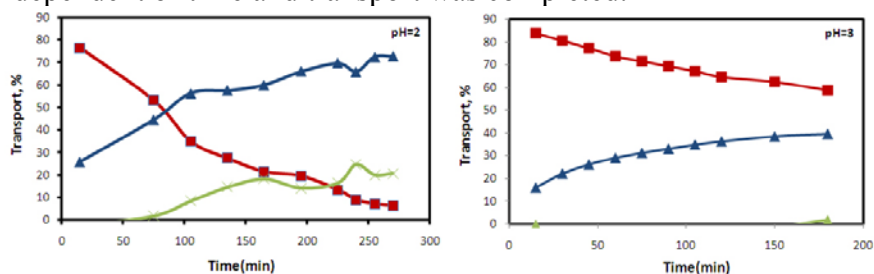


Fig. 6. Percentage of the transported copper ions from feed phase into the receiving phase through the bulk liquid membranes containing $\text{N}_2\text{O}_2\text{S}_2$ ligand as a function of time. Conditions, (■) source phase, 20 ml of 2×10^{-5} M $\text{Cu}(\text{II})$ ion and pH 2 and 3; (×) liquid membrane phase, 50 ml of $\text{N}_2\text{O}_2\text{S}_2$ in chloroform at concentration (4×10^{-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 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.

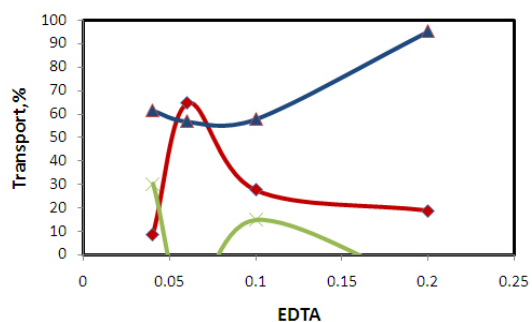


Fig. 7. Effect of EDTA concentration in the membrane phase on copper transport. Conditions, (■) source phase, 20 ml of 2.0×10^{-5} M Cu (II) ion and pH 2; (×) liquid membrane phase, 50 ml of (4×10^{-4} M) H2L in chloroform at different concentration; (▲) receiving phase, 20 ml solution of (0.04- 0.2) M EDTA, time of transport, 2h.

Effect o temperature

The effect of temperature on the transport of the Cu(II) throught the liquid membrane containing [H₂L] in CHCl₃ 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.

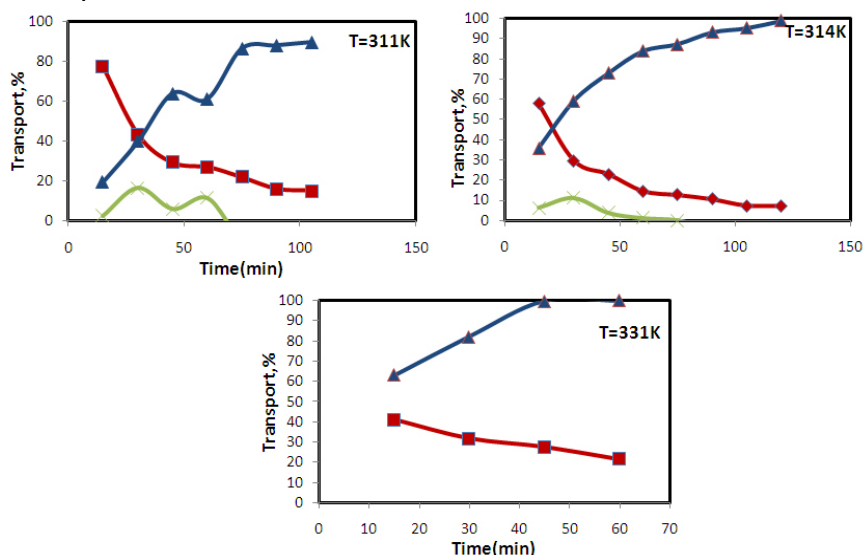


Fig. 8. Effect of temperture on copper transport. Conditions, (■) source phase, 20 ml of 2.0×10^{-5} M Cu(II) ion and pH 2; (×) liquid membrane phase, 50 ml of (4×10^{-4} M) H2L in chloroform at different concentration; (▲) receiving phase, 20 ml solution of 0.1 M EDTA, time of transport, 2h.

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 Cu²⁺ ion into the receiving phase occurs via the decomposition of complex. At this stage, the carrier associates with proton from the receiving phase releasing Cu²⁺ ion into the receiving phase. The free carrier diffuses back across the membrane to the source phase/membrane interface, where the cycle starts again.

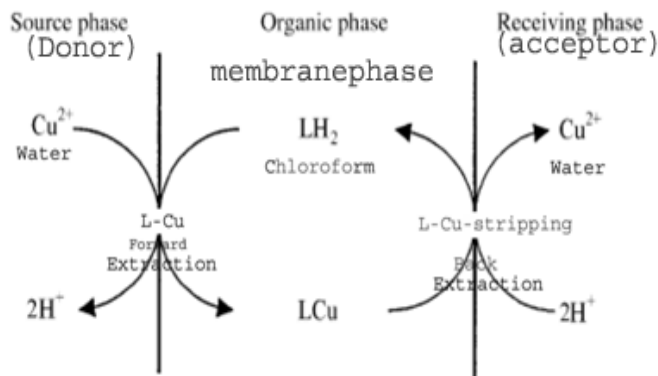


Fig 9. Liquid membrane system for transport of Cu²⁺ ions

Conclusion

In the first stage, substituted Schiff base is obtained from condensation of (I) and 2-aminothiophenol in dry ethanol. The present study demonstrates that the ligand N₂O₂S₂ is an excellent carrier for efficient transport of Cu²⁺.

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 100% at temperature 58 °C after 48 min.

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