Selective Transport Of Copper Through Bulk Liquid Membrane Using Neocuproine As A Carrier

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ABSTRACT

Neocuproine was found to be an excellent carrier for uphill transport of copper ions across a chloroform liquid membrane. The initial aqueous phase consisted of hydroxylammonium chloride as a reducing agent and sodium perchlorate as counter ion. The aqueous receiving phase was 1 mol L^{-1} nitric acid solution. It was found that the system is highly efficient and selective for uphill transport of copper. The amount of copper transported through the liquid membrane after 60 min was 98.2 ± 2.5%. The system has high selectivity for copper transport from aqueous solutions containing other ions, such as Mg^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Cr^{3+} and Mn^{2+}. The procedure has been applied to the determination of copper in standard stainless steel alloys.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Copper is one of the most common trace heavy metals and is an essential micronutrient for plants and animals[1-4]. However, due to the great production and industrial use, there are serious water pollution problems due to the fact that high concentration of copper is toxic for most aquatic plants; the inhibition of their growth generally happens larger than 0.1 mg l^{-1}. Copper is highly toxic for drinking water, as well as most spineless marines, and mercury is the only metal more toxic than copper. Therefore, there is considerable interest in the separation and enrichment of copper from different matrices, such as natural waters and biological fluids.

Ion exchange, precipitation, liquid-liquid extraction and solid phase extraction (SPE) are the commonly used techniques for the separation of metal

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ions from complex matrices. The use of liquid membrane, i.e. organic liquids in contact with two separated aqueous phases, is an alternative method for separating of metal ions and is of great importance in chemistry, biology and separation science[5-11]. This technology combines solvent extraction and stripping process in a single step and is especially attractive for the treatment of low metal concentration solutions[12]. Compared to conventional liquid-liquid extraction, it has the advantages of technical simplicity, high efficiency, reduction in solvent inventory and economical use of expensive and highly selective extractants. Various methods have been reported for the selective transport of copper ion across liquid membrane[13-22]. Some of these systems have the drawbacks of slow rate of transport (e.g. 2 days or more is required for a transport)[14,15] or a lack of high selectivity[15] and efficiency[16]. Therefore, the development of an effective and specific methods for the transport of Cu(II) is still a challenging task.

Neocuproine (2,9-dimethyl-1,10-phenanthroline) is a selective ligand for complexation with copper(I). In the presence of reducing agents, it reacts with copper to give a cationic copper(I) complex of composition MA_2^+ with tetrahedral symmetry[23]. However, to the best of our knowledge no works have been reported to date on facilitated transport of copper using bulk liquid membranes with neocuproine as the carrier. In this paper, a selective and efficient liquid membrane containing neocuproine as carrier is reported for the uphill transport of copper.

EXPERIMENTAL

Apparatus

A buckscientific model 210 VGP atomic absorption spectrometer was used for absorbance measurements of metal ion concentration. pH measurements of the aqueous phases were done with a Metrohm model 691 pH meter with a combined glass electrode. A bulk liquid membrane cell[13, 24] was used in this study.

Reagents

All reagents were of analytical reagent grade (Merck, Darmstadt, Germany) and double distilled

water was used throughout.

A stock solution of copper (1.0×10^{-2} mol L^{-1}) was prepared by dissolving 0.2416g of $Cu(NO_3)_2 \cdot 3H_2O$ in a 100 mL calibrated flask and diluting to the mark with distilled water. Extra pure chloroform (Merck) was used as the membrane solvent.

Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 4.0 cm) with a glass tube (inside diameter 2.0 cm), separating two aqueous phases was used. The inner aqueous phase (source phase) contained 5 mL of 1.0×10^{-4} mol L^{-1} of Cu^{+2}, 1.0×10^{-3} mol L^{-1} of $NaClO_4$ and 2% hydroxylammonium chloride. The pH value of the source phase was adjusted to 5 with acetic acid-acetate buffer solution. The outer receiving phase consisted of 10 mL of an aqueous solution containing 1 mol L^{-1} nitric acid. A chloroform membrane phase (25 mL) containing 5×10^{-4} mol L^{-1} neocuproine was laid below these aqueous phases, and bridged the two aqueous phases. The organic layer was stirred by a Teflon-coated magnetic bar (2.0 cm×5 mm diameter). Determination of the metal ion concentration in both aqueous phases was carried out by atomic absorption spectroscopy along with a series of standards made in similar matrix.

RESULTS AND DISCUSSION

Neocuproine is a selective photometric reagent for copper(I). The low solubility of neocuprine, together with its high stability and selectivity for Cu(I) suggest that it may be a promising carrier for highly selective transport of copper ion. Therefore, its capability in transport of copper was investigated.

The liquid membrane performance is shown schematically in figure 1. In this study the driving force for the transport of copper ions across the liquid membrane is concentration gradient. The copper transport can be explained as follows: In the source phase the copper(II) ion is reduced to copper(I) by hydroxylammonium chloride; after complexation of the cation with carrier, it form a neutral ion pair with ClO_4^- and the complex is transferred across the source/organic phase boundary. Within the organic

Figure 1: Bulk liquid membrane for the transport of copper
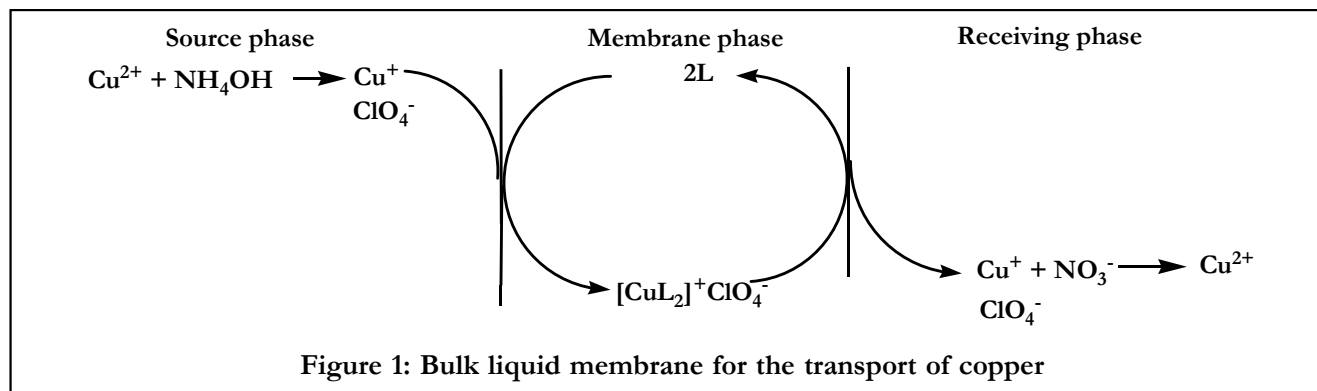
phase the ionic-paired formed diffuse down its concentration gradient. On the right side of the membrane, the copper(I) is oxidize to copper(II) by nitrate ion and is extracted into the receiving phase. Then the carrier is released and transported back across the membrane, where the copper transport cycle start again. The net result is the transport of copper ion from the aqueous source phase into the aqueous receiving phase across the bulk of organic phase (the membrane).

In order to achieve the highest efficiency for the transport of copper across the membrane system, the influences of the experimental variables such as pH of initial phase, concentration of perchlorate and hydroxylamine in source phase, concentration of nitric acid in receiving phase and concentration of neocuproine in organic phase were optimized.

The efficiency of membrane system for copper is considerably dependent on the composition of receiving phase. The data of TABLE 1 indicate that the best results were obtained when nitric acid was used in the receiving phase. Thus, nitric acid was selected for further studies.

The effect of hydroxylammonium chloride in the source phase on efficiency of copper transport was studied. Figure 2 showed that an increase in concentration of hydroxylammonium chloride solution cause a sharp increase in the efficiency of copper transport which leveled off at concentration greater than 1%. Therefore, for subsequent work the source phase was made with a 2% solution of hydroxylammonium chloride.

The effect of pH of the source phase on the copper transport was studied (Figure 3). The results revealed that the maximum transport occurs at pH 4.5

TABLE 1: Effect of composition of receiving phase on the copper transport.
Conditions: Source phase: 5 mL of 1.0×10^{-4} mol L^{-1} Cu^{2+}, 1.0×10^{-3} mol L^{-1} sodium perclorate and 1% hydroxylammonium chloride (pH=5); membrane phase: 25 mL of 5×10^{-4} mol L^{-1} neocuproine in chloroform; receiving phase: 10 mL of each striping agent; time of transport 60 min; rate of stirring, 350 rpm

Stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
Glycine (0.05 mol L^{-1})	8	1
Periodate (0.05 mol L^{-1})	11	2
Thiosolphate (0.05 mol L^{-1})	6	5
Solfosalisilic acid (0.05 mol L^{-1})	2	1
EDTA (0.05 mol L^{-1})	4	1
Hydrochloric acid (1 mol L^{-1})	6	2
Nitric acid (1 mol L^{-1})	98	1

to 5.5. The decrease in percentage of transport at higher pH is due to precipitation of copper as hydroxide, while the decrease in pH<4.5 is due to the competition of the proton with copper ion for extraction into organic phase. An optimum pH of 5 was selected for subsequent work.

TABLE 2 shows that the transport of copper is dependent on the nature of the anion in the source phase. This observation revealed that the transport is carried out via the formation of the ion pair through the organic membrane. As can be seen from the results of TABLE 2, among the anions examined, application of perchlorate as the counter anion resulted
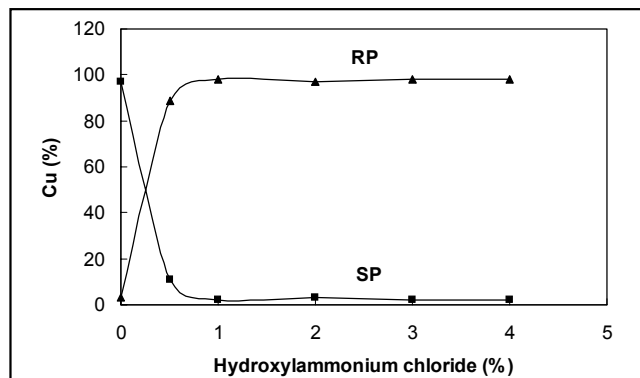
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Figure 2: Effect of hydroxylammonium chloride concentration in the source phase on copper transport. Conditions similar to those mentioned in TABLE 1 except for the parameters changed

Figure 3: Effect of pH in the source phase on copper transport. Conditions similar to those mentioned in TABLE 1 except for the parameters changed

TABLE 2: Effect of various anions in initial phase on transport of copper. Conditions similar to those mentioned in TABLE 1 except for anion in source phase

Anion $(1.0 \times 10^{-3}$ mol $L^{-1})$	% Transported into receiving phase	% Remaining in source phase
Cl⁻	91	0
Br⁻	82	5
SO_4^{2-}	78	2
CH_3COO^-	76	10
ClO_4^-	99	0

with highest enhancement of transport. This result can be related to the formation of stable ion pairs between the anion and large lipophilic cationic complex i.e. CuL_2^+ in the organic phase. Therefore, perchlorate was selected as the counter anion.
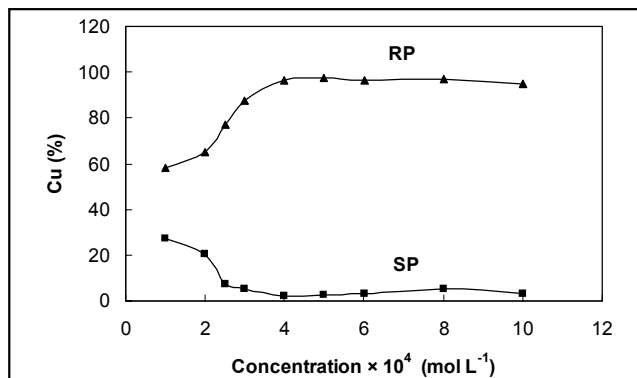

Figure 4: Effect of neocuproine concentration in the membrane phase on copper transport. Conditions similar to those mentioned in TABLE 1 except for the parameters changed
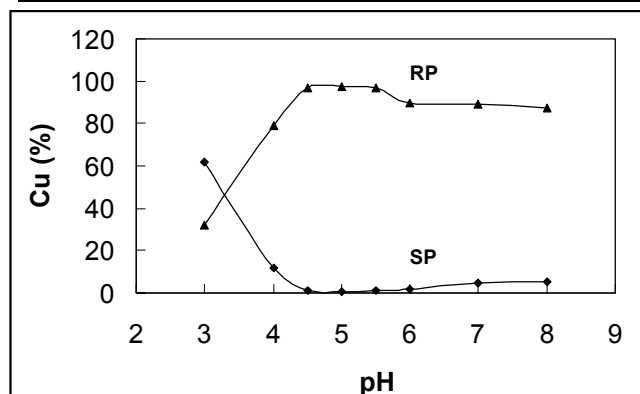
The effect of perchlorate concentration in the source phase on the efficiency of CuL_2^+ transport was studied, and it was found that the efficiency of transport increases with an increase in perchlorate concentration up to 8.0×10^{-4} mol L^{-1}, and then leveled off. A perchlorate concentration of 1.0×10^{-3} mol L^{-1} was selected in further studies.

The influence of neocuproine concentration in the chloroform phase on the copper transport efficiency was also studied and the result of which is presented in figure 4. As can be seen, the amount of copper transport increases with an increase in neocuproine concentration and reaches a maximum at a concentration of 4.0×10^{-4} mol L^{-1}. Further increase in the carrier concentration had no considerable effect on the transport efficiency.

The effect of the nitric acid concentration in the range of 0.25-2.5 mol L^{-1} in the receiving phase was investigated (Figure 5). The results show that maximum copper transport occurs at nitric acid concentration of 1 mol L^{-1}.

The concentration-time profile of copper transport under the optimum experimental conditions was studied and the result is demonstrated in figure 6. It is obvious that the extraction of copper from the source phase into the organic phase is completed approximately in 45 min, while its release into the receiving phase occurs at a slower rate. Thus, it seems reasonable to assume that the release of the Cu^+ ion from the neocuproine is the rate determining step of the membrane transport. Under the optimum condi-
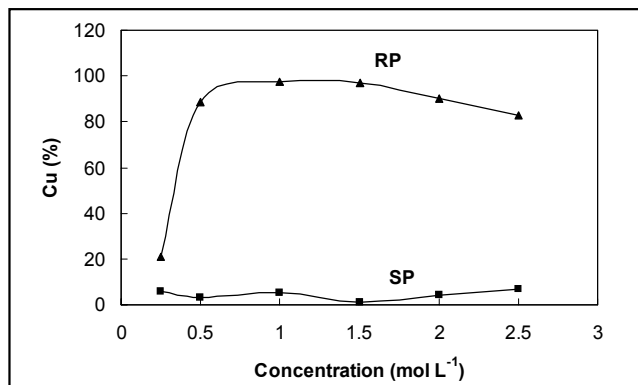
Figure 5: Effect of nitric acid concentration in the receiving phase on copper transport. Conditions similar to those mentioned in TABLE 1 except for the parameters changed
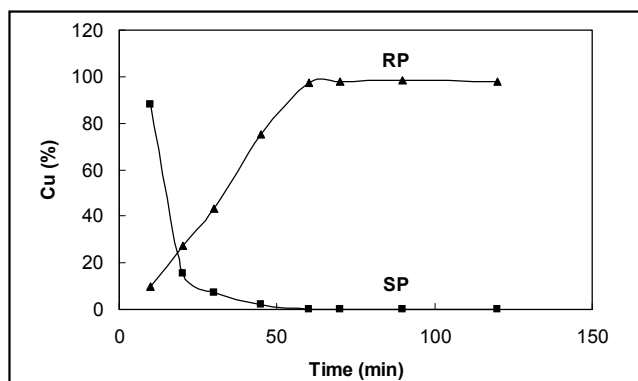

Figure 6: Time dependence of copper transport Conditions similar to those mentioned in TABLE 1

TABLE 3: Amount of cation transport from different various cation mixtures through the membrane at the optimum conditions

Cation	% Transported into receiving phase	% remaining in source phase
Mixture 1		
Cu^{2+}	98	0
Mn^{2+}	0	94
K^+	0	98
Mixture 2		
Cu^{2+}	98	0
Fe^{2+}	0	99
Co^{2+}	0	98
Mixture 3		
Cu^{2+}	98	0
Cd^{2+}	5	90
Mixture 4		
Cu^{2+}	96	0
Ca^{2+}	0	98
Mixture 5		
Cu^{2+}	98	1
Pb^{2+}	3	95
Hg^{2+}	1	96
Mixture 6		
Cu^{2+}	97	0
Cr^{3+}	0	97
Mg^{2+}	3	91

tions, after 60 min, more than 98% of total copper was transported from the aqueous source phase into the receiving phase. The reproducibility of copper transport was investigated, and the percent of copper transported through the membrane during 60 min in eight replicate measurements was found to be 98.2±2.5%.

The selectivity of membrane system for the transport of copper ion over other cations was investigated and at the mol ratio of 1000 of M^{n+}/Cu^{2+} no interference was found (TABLE 3). This surprising high selectivity of copper ion transport over other cations is related to high selectivity of neocuproine for Cu(I) and is an advantage for this method.

The procedure was applied to the determination of copper in two standard steel alloys (MBH Analytical Ltd.). A 0.05 g of alloy was dissolved in 6 mL of aqueous hydrochloric acid (1:1) by heating on the water bath and then 1 mL of 30% hydrogen perox-

ide was added to it. The excess of peroxide was decomposed by further heating. The solution was diluted and 0.5 g hydroxylammonium chloride was added. The pH of solution was adjusted to 5 using buffer and was diluted to 25 mL with distilled water in a standard flask. 5 mL of this sample was taken as the source phase and the procedure was applied. The experimental results with the certified values are given in TABLE 4. As can be seen there is good agreement between the results and certified values, suggesting the suitability of the method for analysis of this type of samples.

CONCLUSION

The present study demonstrates that neocuproine, normally used as a specific chelating agent for the quantitative determination of Cu(I),

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TABLE 4: Determination of copper in alloy samples

Alloy sample	Accepted value (%)	Determined value (%)*
MBH C12×3500	0.150	0.144 ± 0.005
MBH C12×3449	0.200	0.195 ± 0.007

* Average and standard deviation of three determinations

can successfully be used as a carrier for the transport of copper across a bulk liquid membrane of chloroform. This study also shows the potential application of liquid membrane technique for selective removal, concentration and purification of copper ion from mixtures. The system has the advantage of low solvent consumption, high precision and efficiency together with simplicity and speed.

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