Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hamidi, Akram Sadat , Kazemi, Sayed Yahya and Zolgharnein, Javad(2010) 'Highly Efficient and Selective Transport of Cu(II) with a Cooperative Carrier Composed of Tetraaza-14-Crown-4 and Oleic Acid through a Bulk Liquid Membrane', Separation Science and Technology, 45: 1, 58 — 65
To link to this Article: DOI: 10.1080/01496390903256117
URL: http://dx.doi.org/10.1080/01496390903256117

Separation Science and Technology, 45: 58–65, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903256117

Highly Efficient and Selective Transport of Cu(II) with a Cooperative Carrier Composed of Tetraaza-14-Crown-4 and Oleic Acid through a Bulk Liquid Membrane

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Tetraaza-14-crown-4 and oleic acid was successfully applied for transport of Cu(II) in chloroform bulk liquid membrane. The uphill moving of Cu(II) during the liquid membrane transport process has occurred. The main effective variable such as the type of the metal ion acceptor in the receiving phase and its concentration, tetraaza-14-crown-4 and oleic acid concentration in the organic phase on the efficiency of the ion-transport system were examined. By using L-cysteine as a metal ion acceptor in the receiving phase, the maximum amount of copper (II) transported across the liquid membrane was achieved to 96 ± 1.5% after 140 minutes. The selectivity of copper ion transport from the aqueous solutions containing Pb^{2+}, Tl^{+}, Ag^{+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+} and Ca^{2+} ions were investigated. In the presence of CH_3COONH_4 and $Na_4P_2O_7$ as suitable masking agents in the source phase, the interfering effects of Pb^{+2} and Cd^{2+} were diminished drastically.

Keywords bulk liquid membrane; copper (II); crown ether; L-cysteine; oleic acid

INTRODUCTION

The complexing ability of ordinary crown ethers toward soft heavy metal ion is quite low (1). This problem has been overcome by the substitution of some oxygen atoms of crown ethers by nitrogen or sulphur atoms, which results in a considerable increase in the stability of cations such as Ag^{+}, Tl^{+} and Hg^{2+} in solution, while diminishing the stability constants of their alkali and alkaline earth complexes (1,2). Thus, in recent years, some nitrogen and sulphur-containing crown ethers have been used as neutral carriers in solvent extraction (3–7) and also as ionophore for some heavy metal ions in designing PVC- membrane electrode (8–12).

Copper is one of a relatively small group of metallic elements which are essential to human health and toxic for many biological systems (13–15). It plays a vital part in the development and performance of the human nervous and cardiovascular system as well as the skin, bone, immune and reproductive systems, including gene transcriptions (13). Copper also inhibits the growth of microbe, thus it serves as a measure of protection against harmful germs and bacteria in many environments (16). These points make the ion-transport process of copper as a vitally important phenomenon in the preservation of life. Moreover, due to increasing industrial use of copper (15), the development of new transport systems for the selective removal, concentration and purification of Cu(II) ion from its mixtures is also of special importance.

During the past decades, there have been some studies made toward developing methods for its application to the separation of various metal ions using neutral ionophores (17–23), while a few protons driven copper (II) transport have also been reported (24–27). Liquid-membrane transport in which the extraction and stripping operations are combined in a single process reduces the solvent inventory requirement, where the volume ratio of the aqueous phases to the membrane phase is 2:1, while the volume ratio for SLM can be >1000:1 and also allows the use of expensive and highly selective extractions, which otherwise would be uneconomic in solvent extraction. For these reasons, liquid-membrane transport has attracted worldwide attention and much work has been directed toward developing methods for its application to the separation of various metal ions (18–21,28).

In this work, tetraaza-14-crown-4 (A_414C4) and oleic acid (OA) used as a suitable carrier for efficient and selective transport of copper (II) across a chloroform bulk liquid membrane.

EXPERIMENTAL

Reagents and Chemicals

The tetraaza-14-crown-4 (A_414C4, I) and other used macrocyclic ligands were purchased from either Fluka or Merck Chemical Companies. Extra pure chloroform

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Received 1 January 2009; accepted 16 July 2009.
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(Merck) was used as the membrane organic solvent. All other chemicals used in this study were of the highest purity available from either Merck or Fluka and they were used without further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

Apparatus and Procedure

A bulk type liquid membrane cell was used in this study. The pH measurements were made with a Metrohm 744 pH meter using a combined glass electrode. The atomic absorption spectrophotometer used for the measurement of metal ion concentration in the aqueous phases was a Varian Specter AA10 instrument. The measurement of atomic absorption was made according to the recommended conditions for each ion.

All transport experiments were done as reported earlier using a bulk liquid membrane apparatus at ambient temperature about 23°C (19). A cylindrical glass cell (inside diameter of 4.0 cm) which held a glass tube (inside diameter of 2.0 cm) and then separated the two aqueous phases was used. The source phase contained copper nitrate (5 ml, 1.0×10^{-4} M) and sodium perchlorate (5.0×10^{-2} M). The receiving phase included L-cysteine pH 2.9 (as metal ion receptor), (10 ml, 0.08 M). A chloroform phase (20 ml) containing $A_4$14C4 (9.0×10^{-4} M) and OA (0.03 M) lay below these aqueous phases and bridged them.

The organic layer was magnetically stirred by a teflon-coated magnetic bar (2 cm × 5 mm diameter). The source and receiving phases were sampled and analyzed for the corresponding metal ion concentration by atomic absorption spectroscopy. Each experiment was repeated at least three times. Reproducibility was confirmed as ±1.2% or better. A similar transport experiment was carried out in the absence of the cooperative carriers for reference. The detailed conditions are included in the tables of the text.

RESULT AND DISCUSSION

Effect of the Membrane Composition on Copper Ion Transport

Our preliminary experiments revealed that $A_4$14C4 (9×10^{-4} M) alone was not an effective carrier for the transport of copper (II) ion through the bulk liquid membrane (i.e., amount of copper transport was less than 60% after 140 min). This is mainly due to the considerable solubility of the ligand, especially its copper complex in the aqueous phases. It has been shown that this difficulty can be overcome by the addition of a long chain fatty acid to the organic phases (19,20,29). Thus, a given mixture of $A_4$14C4 and OA was found to mediate the transport with surprisingly high efficiency (i.e., some 96% transport after 140 min). It is interesting to note that, in the presence of OA (9×10^{-2} M) as the only carrier, the copper transport after 140 mins is only 18%. This confirms the cooperative behavior of the two components as carrier. As earlier Guyon et al. reported on the basis of ^{1}HMR studies in chloroform, the interaction between azacrown ether and lauric acid is mainly caused by the presence of a basic nitrogen atom in the former and the acidic proton in the latter molecule (30). The proton shared by the azacrown ethers and fatty acid delocalizes its positive charge between the amine part of the azacrown ether and the carboxylic part of the fatty acid. Thus the interactions between OA and $A_4$14C4 which can impart a greater degree of lipophilicity to the carrier system, facilitating the cation transport through the liquid membrane. In addition, a synergistic effects of the mixture of the azacrown ether and fatty acid on the selectivity of Cu(II) transport has been observed (31,32). As could be expected the carboxylate group tend to dimerize in the presence of Cu(II) ions and form stable complexes as:

$$2\mathrm{Cu(LA)_2(LAH)_2} \longleftrightarrow \mathrm{(CuLA_2.LAH)_2} + \mathrm{(LAH)_2} \quad (1)$$

where LA and LAH are lauric anion and lauric acid respectively.

Therefore both the azacrown ether and the fatty acid could serve as carrier, since both are known to complex Cu(II) in bulk and that both are expected to have surfactant properties (32). Thus the fatty acid would form an inverse micelle (33), inside which the crown ether molecules may be trapped. The crown ether may then be easily transported across the membrane inside the inverse micelle formed (19,20).

Optimization of the Membrane Composition

The membrane system was optimized with respect to the relative concentrations of $A_4$14C4/OA by making the amount of one of the constituent constant and varying the concentration of the other. The results are shown in Fig. 1. It was found that, while neither $A_4$14C4 nor OA alone can transport Cu(II) in a considerable amount through the liquid membrane, a mixture of the two components mediates the transport very effectively. As can be seen, maximum copper transport is achieved with $A_4$14C4 in the concentration range of 8.0×10^{-4}–9.0×10^{-4} M and 3.0×10^{-2} M of OA.

pH Effect of Source Phase

Figure 2 shows the effect of pH of the source phase on the efficiency of copper(II) transport. It is quite clear that the transport of Cu(II) is influenced by the pH of the source phase. The pH values were adjusted by using 0.1 M of either nitric acid or sodium hydroxide. The source phase on the transport efficiency of Cu(II) was studied in the pH range 3.0–9.0, and the results revealed that the maximum copper transport occurs at pH 3.5–4.5. At lower

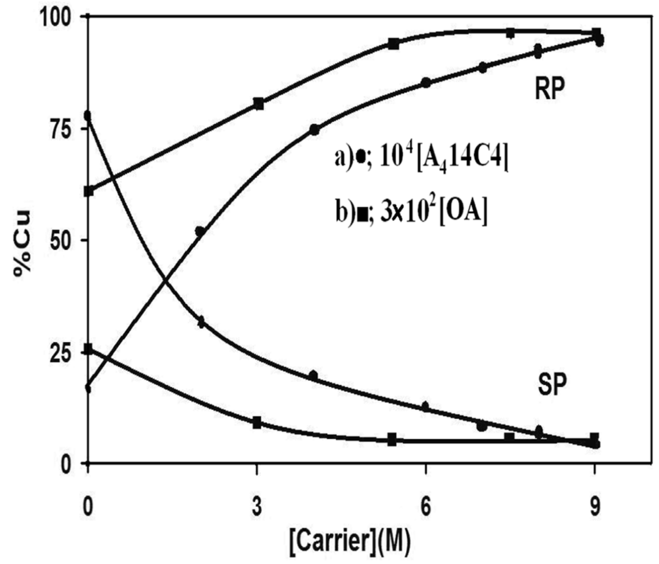

FIG. 1. Effect of $A_4$14C4 and OA concentration on copper(II) transport. Conditions: source phase at pH = 4; copper nitrate (5 ml, 1.0×10^{-4} M) and sodium perchlorate (5.0×10^{-2} M); receiving phase, 10 ml of 0.08 M L-cysteine; time of transport, 140 min, membrane phase, a (●); 20 ml of 0.03 M OA and varying concentration of $A_4$14C4; and b (■); 20 ml of 9.0×10^{-4} M $A_4$14C4 and varying concentration of OA in chloroform.

pH, there is a decrease in the percentage transport of copper (II) probably due to the protonation of the azacrown ether in the membrane interface of the source phase. By increasing the pH the efficiency of the transport decreases because of the formation of copper hydroxide and hydroxo complexes of Cu(II).

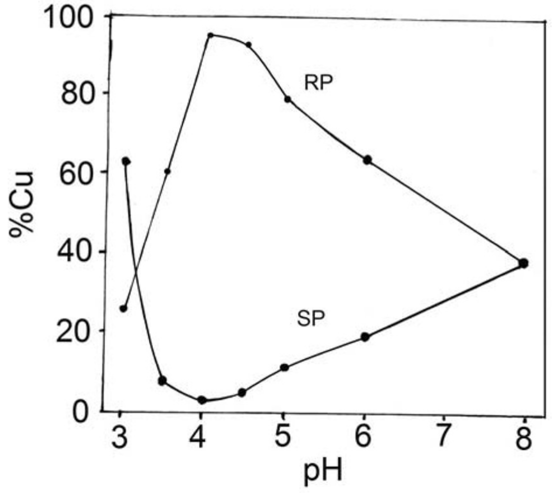

FIG. 2. Effect of pH of source phase on the transport of Cu^{2+}. Conditions: source phase; 5 ml of 1.0×10^{-4} M Cu^{2+} and 5.0×10^{-2} M ClO_4^-, membrane phase; 20 ml of 9.0×10^{-4} M $A_4$14C4 and 0.03 M OA in chloroform; receiving phase, 10 ml of 0.08 M L-cysteine ; time of transport, 140 min.

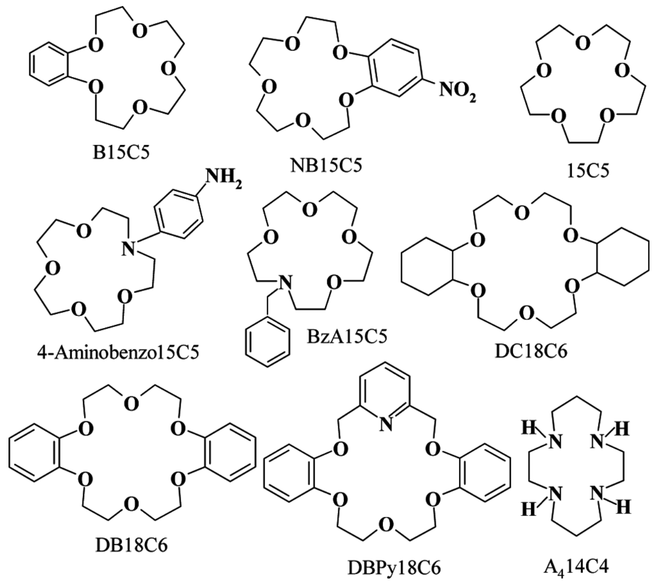

FIG. 3. Structures of ligands.

Effect of Carrier Structure

The transport efficiency of the Cu(II) ion was found to be significantly dependent on the nature of the macrocyclic ligand which were used as a binary carrier. In other experiments (under the same experimental condition) we have examined eight macrocyclic ligands as well as $A_4$14C4 as carriers (Fig. 3) to transport the copper ion. The results are given in Table 1. As can be seen, the transport efficiency for the entire carriers used (except for $A_4$14C4) is low, which is mainly due to incomplete extraction of

TABLE 1
Effect of carrier structure on copper transport[a]

Carrier	Percentage transported into receiving phase	Percentage remaining in source phase
B15C5	7	93
NB 15C5	3	93
15C5	2	95
4′-Aminobenzo A15C5	3	95
BzA15C5	5	91
DB18C6	0	100
DBPy18C6	1	99
DC18C6	2	90
$A_4$14C4	95	4

[a] *Conditions*: Source phase; copper nitrate (5 ml, 1.0×10^{-4} mol · L^{-1}) and sodium perchlorate (5.0×10^{-2} mol L^{-1}) pH 4, membrane phase; 20 ml of 0.03 mol L^{-1} OA and $A_4$14C4 (9.0×10^{-4} mol L^{-1}) in chloroform; receiving phase, 10 ml of 0.08 mol L^{-1} L-cysteine; time of transport, 140 min.

copper (II) from the source phase into the organic membrane. Copper transport efficiency A$_4$14C4 is the most, due to copper ion radii with 0.77 A fits the ring hole size of A$_4$14C4. On the other hand, according to the HSAB theory, A$_4$14C4 with four nitrogen atoms will give a strong complex with Cu(II) (1,34). Therefore in the case of A$_4$14C4, the extraction of copper ion from the source phase into the membrane is almost quantitative, emphasizing the cooperative achievement of the macrocycles in the presence of OA.

Effect of Perchlorate Anion Concentration in the Source Phase on Transport Efficiency

In preliminary experiments, it was found that nitrate ion is not a suitable counter ion to accompany with the Cu(II)-A$_4$14C4 complex into the membrane phase; only 73% of Cu(II) was transported into the receiving phase after 140 minutes in the presence of nitrate. As shown earlier, the efficiency of metal ion transfer from the aqueous solution into the organic phase not only depends on the type of cation and properties of the ionophore, but also may be influenced strongly by the properties of the anion (17,35). However, adding of sodium perchlorate to the source phase increased the extent of the copper transport significantly. A similar influence of perchlorate ion on the solvent extraction of the Ag$^+$-HT18C6 complex has been reported in the literature (4,36). It has been suggested that the crown ether places Cu(II) in its cavity and the counter anion is coordinated in the axial position forming a lipophilic neutral complex. This complex is suitable for the transfering of Cu(II) to the organic phase. Thus, the degree of extraction increases with increasing hydrophobicity of the anion.

The influence of the concentration of perchlorate ion in the source phase on the copper ion transport was investigated and the results are shown in Fig. 4. As seen, the percentage of copper ion transported in the receiving phase increases with an increasing in perchlorate ion concentration in source phase. Maximum transport occurs when the sodium perchlorate transport concentration is 0.05 M (i.e., [ClO$_4^-$]/ [Cu(II)] ratio of 200).

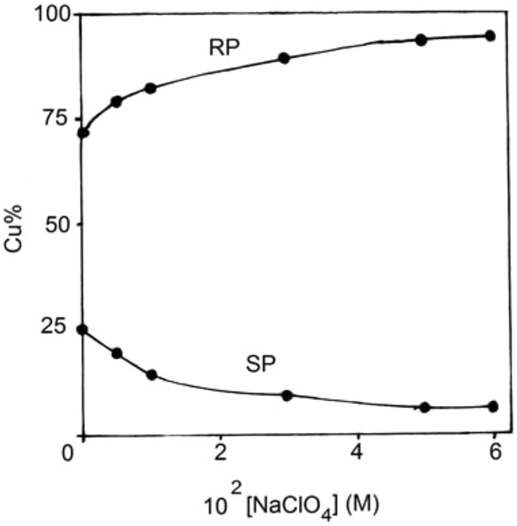

FIG. 4. Effect of percholorate concentration on copper (II) transport. Conditions: source phase; 5 ml of 1.0×10^{-4} M Cu^{2+} and varying amount of ClO$_4^-$ at pH 4, the membrane phase, 20 ml of 9.0×10^{-4} M A$_4$14C4 and 0.03 M OA in chloroform; receiving phase, 10 ml of 0.08 M L-cysteine; time of transport, 140 min.

Effect of the Nature of Stripping Agent on Copper (II) Transport

As expected, the permeability of the membrane system for copper(II) ion transport was found to be largely dependent on the nature and concentration of the receiving ligand used in the receiving phase. Thus, eight potential candidates for the stripping of copper(II) ions from the organic membrane phase into the aqueous receiving phase were examined and the results are given in Table 2. Among different receiving agents used, L-cysteine with increased complexing ability towards copper (II) acts as the most suitable receiver for the release of the cation from the membrane phase into the receiving phase. The log β for Cu(II)-L-cysteine is equal 16 (37). L-cysteine as a nitrogen containing amino acid represents high complexing ability towards Cu(II) due to the Irving-Williams series.

The optimum concentration of L-cysteine in the receiving phase was investigated and the results are shown in Fig. 5. As seen, maximum copper transport occurs in the presence of 0.08–0.09 M L-cysteine in the receiving phase.

TABLE 2
Effect of the nature of stripping agent in the receiving phase on copper transport^a

Stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
Thiosulfate	30	7
EDTA	75	5
Thioacetamide	19	21
Thiocyanate	11	16
Nitrite	18	14
Thiourea	20	3
Hydrochloric acid	70	20
L-Cysteine	80	2

[a] *Conditions*: Source phase; copper nitrate (5 ml, 1.0×10^{-4} mol L^{-1}) and sodium perchlorate (5.0×10^{-2} mol L^{-1}) at pH = 4, membrane phase; 20 ml of 0.03 mol L^{-1} OA and A$_4$14C4 (9.0×10^{-4} mol L^{-1}) in chloroform; receiving phase, 10 ml of stripping agent; time of transport, 140 min.

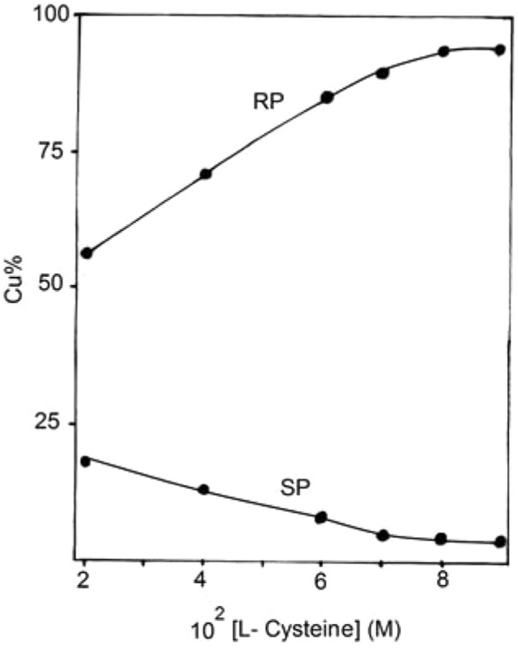

FIG. 5. Effect of L-cysteine concentration on copper(II) transport. Conditions: source phase; 5 ml of 1.0×10^{-4} M Cu^{2+} and 5.0×10^{-2} M ClO_4^- at pH 4; the membrane phase, 20 ml of 9.0×10^{-4} M $A_4$14C4 and 0.03 M of OA in chloroform; receiving phase, 10 ml of 0.08 M L-cysteine; time of transport, 140 min.

It is interesting to note that in the absence of a metal ion acceptor in the receiving phase resulted in no promising copper transport, even at much longer periods of time.

Time Dependence of Membrane Transport on Copper (II) Transport

The time dependence of copper(II) transport through the liquid membrane under optimal experimental conditions were investigated. It showed that the extraction of copper from the source phase into the organic membrane occurs very quickly, so that the extraction is almost completed after approximately 60 min. However, the release of copper(II) ion from the crown ether-OA complex is the rate determining step of the membrane transport (38). It was found that under the optimum conditions, more than 96% of total copper(II) was transported from the source phase into the receiving phase after 140 min.

Kinetics Study of copper (II) Transport

The kinetics parameters that affect the transport efficiency are usually rate constant values (k), permeability coefficient (*P*) and distribution coefficients (D_s & D_r). The kinetics of copper(II) transport can be described by a first-order reaction in metal ion concentration:

$$\ln(C/C_i) = -kt \qquad (2)$$

Where C is the copper (II) concentration in the source aqueous phase at some given time, C_i the initial copper (II) concentration in the source phase, *k* the rate constant and *t* is the time of transport. To calculate the *k* value, a plot of $\ln(C/C_i)$ versus time was prepared. In 2005, the rate constant values for the copper (II) transport through a liquid membrane containing a Dithiophosphonate Derivative as carrier by Alpoguz et al. reported, $k_1 = 1.08 \times 10^{-3}$ min^{-1} & $k_2 = 3.55 \times 10^{-3}\, min^{-1}$ (39). In this work, the rate constant value for the copper (II) transport process was calculated ($k_1 = -1.45 \times 10^{-2}\, min^{-1}$) & $k_2 = 6.9 \times 10^{-3}$ min^{-1}. The relationship of $\ln(C/C_i)$ versus time was linear, which was confirmed by a reasonable high value coefficient of determination ($r^2 = 0.993$) (40).

To determine the influences of the chemical variables which have been studied on the efficiency of the designed transport system, the permeability coefficient (*P*) was calculated as:

$$P = -(V/A)k \qquad (3)$$

Where V is the volume of the aqueous source phase and A is the effective area of the membrane. The P value was evaluated ($P = 2.3 \times 10^{-2}$ cm.min^{-1}). The initial flux (J_i) was also determined from the following equation:

$$J_i = PC_i \qquad (4)$$

The initial flux (J_i) value was found to be $J_i = 2.3 \times 10^{-10}\, mol \cdot cm^{-2}\, min^{-1}$.

To describe the efficiency of metal removal from the source phase, the recovery factor (RF) was calculated as follows:

$$\%RF = [(C_i - C)/C]100\% \qquad (5)$$

$RF = [[(1 \times 10^{-4})\text{–}(3.8 \times 10^{-6})]/1 \times 10^{-4}] \times 100 = \%96.2$

Considering the earlier reports copper transport, such as %90 and %70 transport of Cu(II) with hydroxamic acid presented by Kubo et al. in 1998 (24), 63% transport of Cu(II) with N,N-Bis(8-quinolyl)glutaramide after 48 hours done by Hiratani and Taguchi in 1990 (41) and %90.2 transport of copper ion Using K -Dicyclohexyl-18-crown-6 as carrier in by Akhond and Shamsipur in 1995 (42). As can be seen, our present system is more efficient. This high efficiency can be explained by the cooperative effect of fatty acid and azacrown ether on exerting negligible disturbances on transport of Cu(II).

The distribution coefficients into the membrane from source (D_s) and into the membrane from receiving (D_r) were obtained:

$$D_s = C_m/C_s = (2.0 \times 10^{-7})/(3.8 \times 10^{-6}) = 0.052 \qquad (6)$$

$$D_r = C_r/C_m = (9.6 \times 10^{-5})/(2.0 \times 10^{-7}) = 480 \qquad (7)$$

Assuming that the distribution coefficient of copper (II) between the membrane phase and the source phase is much lower than that between the receiving phase and the membrane, the concentration of the copper-extracted complex in the membrane phase on the source solution side may be negligible compared with that on the receiving solution side (43,44).

Precision of Measurement

In order to find the relative standard error in the measurements, the transport was operated eight times under the optimum conditions. A relative standard error of 1.2% was obtained from the results for an average 96.2%.

Effects of Interfering Ions on Copper (II) Transport

The percentage transport of copper (II) and M^{n+} cations, which were present with copper ion in equimolar concentrations, into the receiving phase are listed in Table 3. As can be seen, among the different cations tried, Pb^{2+} and Cd^{2+} ions seriously interfere in the transport of copper ion. It is noteworthy that the negligible interfering effect of other cations could be related to different parameters, including improper ionic size, high hydration energy and especially the decreased tendency for binding with L-cysteine (45). The interfering effect of Pb^{2+} and Cd^{2+} ions on the copper transport were, however, significantly decreased by the addition of CH_3COONH_4 and $Na_4P_2O_7$ respectively as suitable masking agents in the source phase. It should be noted that cadmium and lead ions form complexes with the masking agents that are much more stable than that with copper ion (35,45). The influence of increasing of acetate and pyrophosphate ions on the interfering effects of Pb^{2+} and Cd^{2+} ions are shown orderly in Table 3. It is clear that in the presence of CH_3COONH_4 and $Na_4P_2O_7$ effects of these cations have been reduced drastically.

TABLE 3

Amount of cation transported from various cation mixtures through the membrane[a]

Cations	Percentage transported into receiving phase	Percentage remaining in source phase
Cu^{2+a}	90	8
Ni^{2+}	2	97
Cu^{2+a}	95	4
Co^{2+}	0	69
Cu^{2+a}	95	4
Ag^{+}	1	98
Cu^{2+a}	95	3
K^{+}	0	100
Tl^{+}	1	85
Cu^{2+a}	89	10
Cr^{+3}	4	40
Ca^{+2}	7	90
Cu^{2+a}	90	10
Cd^{2+}	87	11
Cu^{2+a}	83	16
Pb^{2+}	82	1
Cu^{2+b}	88	9
Pb^{2+}	7	84
Cu^{2+c}	91	9
Cd^{2+}	4	88

[a] *Conditions*: Similar to those mentioned in Table 2.

[b] The presence of 0.2 mol L^{-1} NH_4CH_3COO in the source phase as masking agent.

[c] The presence of 0.001 mol L^{-1} $Na_4P_2O_7$ in the source phase as masking agent.

Recommended Transport Mechanism

The guest Cu(II) is transported from the source phase to the receiving phase via a chloroform membrane. The movement of the charged species through the hydrophobic liquid membrane is accomplished by the presence of a host cooperative carrier composed of $A_4$14C4 and OA. After complexation of the Cu(II) with a carrier host on the left side of the membrane, the complex formed diffuses down its concentration gradient. On the right side of the membrane, the metal ion is released into the receiving phase via the formation of a ternary complex (carrier ($A_4$14C4 + OA)-Cu(II)-L-cysteine). At this stage, the free carrier diffuses back across the liquid membrane. The net result is the transport of copper ion from the aqueous source phase to the receiving phase across the bulk liquid membrane.

CONCLUSIONS

A highly selective and efficient transport of copper (II) through a chloroform bulk liquid membrane was designed. In this system, tetraaza-14-crown- 4 accompanied with oleic acid was used as a suitable carrier for ion-transport of copper (II). L-cysteine shows good affinity for extracting of copper (II) from the membrane phase. All the influences parameters on transport efficiency were optimized. The interferences of some metal ions such as Pb^{2+} and Cd^{2+} by using CH_3COONH_4 and $Na_4P_2O_7$ as masking agents drastically decreased. The maximum copper (II) could be selectively transported after 140 minutes.

REFERENCES

1. Izatt, R.M.; Bradshaw, J.S.; Nielsen, S.A.; Lamb, J.D.; Christensen, J.J.; Sen, D. (1985) Thermodynamic and kinetic data for cation-macrocycle interaction. *Chem. Rev.*, *4* (85): 271.
2. Izatt, R.M.; Pawlak, K.; Bradshaw, R.S.; Bruening, R.L. (1991) Thermodynamic and kinetic data for macrocycle interactions with cations and anions. *Chem. Rev.*, *8* (91): 1721.

3. Saito, K.; Murakami, S.; Muromatsu, A.; Sekido, E. (1993) Extraction behavior of silver(I) with some cyclic thioethers. *Polyhedron*, *12*: 1587.
4. Ishikawa, J.; Sakamoto, H.; Mizuno, T.; Doi, K.; Otomo, M. (1998) Acyclic and cyclic polythiamonoaza-and polythiadiaza-alkane hydrazone derivatives as chromogenic extractants for silver ion. *Analyst*, *123*: 201.
5. Masuda, Y.; Zhang, Y.; Yan, C.; Li, B. (1998) Studies on extraction and separation of lanthanide ions with a synergistic exteraction system combined with 1,4,10,13-tetrathia-7,16-diazacyclooctadecane and lauric acid. *Talanta*, *46*: 203.
6. Villamo, O.; Barboiu, C.; Barboiu, M.; Yau-Chun-Wan, W.; Hovnanian, N. (2002) Hybrid organic–inorganic membranes containing a fixed thio ether complexing agent for the facilitated transport of silver versus copper ions. *J. Memb. Sci.*, *204*: 97.
7. Lachowicz, E.; Różańska, B.; Teixidor, F.; Meliani, H.; Barboiu, M.; Hovnanian, N. (2002) Comparison of sulphur and sulphur–oxygen ligands as ionophores for liquid–liquid extraction and facilitated transport of silver and palladium. *J. Memb. Sci.*, *210*: 279.
8. Jeong, T.; Jeong, D-C.; Kyoung, L.; Jeon, S. (2005) Lead (II)-selective polymeric electrode using a schiff base complex of N,N′- bis-thiophene-2- ylmethylene-1,2-diamine as ion carrier. *Bull. Korean Chem. Soc.*, *8* (26): 1219.
9. Khayatian, G.; Shariati, S.; Salimii, A. (2003) Thallium(I)- selective membrane potentiometric sensor based on dibenzodiaza-18-crown-6. *Bull. Korean Chem. Soc.*, *4* (24): 421.
10. Shamsipur, M.; Ganjali, M.R.; Rouhollahi, A. (2001) Lead-selective membrane potentiometric sensor based on an 18-membered thiacrown derivative. *Anal. Sci. Jpn*, *17*: 935.
11. Zielinska, D.; Radecka, H.; Radecki, J. (1998) A liquid/liquid type heteropolyanion reference electrode for ion-transfer voltammetry. *Anal. Sci. Jpn*, *14*: 151.
12. Shamsipur, M.; Kazemi, S.Y.; Niknam, K.; Sharghi, H. (2002) A new PVC membrane electrode based on a thia-substituted macrocyclic diamide for selective potentiometric determination of silver ion. *Bull. Korean. Chem. Soc.*, *1* (23): 53.
13. Danzeisen, R.; Araya, M.; Harrison, B.; Keen, C., Solioz, M.; Thiele, D.; McArdle, H.J. (2007) How reliable and robust are current biomarkers for copper status? *British Journal of Nutrition*, *98*: 676.
14. Scheinberg, I.H.; Morell, A.G.; in Eichhorn, G.L. (Ed.) (1973) *Inorganic Biochemistry*, Vol. 1; Elsevier: New York.
15. Greenwood, N.N.; Earnshaw, A. (1984) *Chemistry of Elements*; Perganion Press: New York.
16. Simeon, C.P.; Wegrowski, Y.; Bontemps, P.; Marquart, F.X. (2000) Expression of glycosaminoglycans and small proteoglycans in wounds: modulation by the tripeptide-copper complex glycyl-L-histidyl-L-lysine-Cu(II). *J. Invest. Dematol*, *115*: 962.
17. Shamsipur, M.; Kazemi, S.Y.; Azimi, G.; Madaemi, S.S.; Lippolis, V.; Garau, A.; Isaia, F. (2003) Selective transport of silver ion through a supported liquid membrane using some mixed aza-thioether crowns containing a 1,10- Phenantroline sub-unit as specification carrier. *J. Membr. Sci.*, *215*: 87.
18. Shamsipur, M.; Kazemi, S.Y. (2007) Highly efficient and selective membrane transport of silver(I) using dibenzodiaza-15-crown-4 as a specific ion carrier. *J. Chin. Chem. Soc.*, *54*: 963.
19. Kazemi, S.Y.; Shamsipur, M. (1999) Membrane transport of Cu(II) with a cooperative carrier composed of dibenzodiaza-15-crown-4 and oleic acid. *Sep. Purif. Technol.*, *17*: 181.
20. Kazemi, S.Y.; Shamsipur, M. (2005) Selective transport of lead(II) through a bulk liquid membrane using a cooperative carrier composed of benzylaza-12-crown-4 and oleic acid. *Bull. Korean. Chem. Soc.*, *6* (26): 930.
21. Chaudry, M.A.; Amin, S.; Malik, M.T. (1996) Tri-n-octylamine-xylene-based supported liquid membranes and transport of Ce(IV) ions. *Sep. Sci. Technol.*, *31*: 1309.
22. Guizard, Ch.; Bac, A.; Barboiu, M.; Hovnanian, N. (2001) Hybrid organic-inorganic membranes with specific transport properties: Applications in separation and sensors technologies. *Sep. Pur. Tech.*, *25*: 167.
23. Barboiu, M.; Guizard, C.; Hovnanian, N.; Cot, L. (2001) New molecular receptors for organics of biological interest for the facilitated transport in liquid and solid membranes. *Sep. Pur. Tech.*, *25*: 211.
24. Kubo, K.; Kubo, J.; Kaminaga, C.; Sakurai, T. (1998) Transport of Cu(II) with hydroxamic acid through a liquid membrane. *Talanta*, *45*: 963.
25. Maruyama, K.; Tsukube, K.; Araki, T. (1981) Highly selective membrane transport of copper(II) ion by synthetic linear oligomer carrier. *J. Chem. Soc. Dalton Trans.*, 1486.
26. Schiffer, D.K.; Hackhauser, A.; Euans, D.F.; Cassler, E.L. (1974) Concentrating solutes with membranes containing carriers. *Nature*, *250*: 484.
27. Dicasa, M.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Renato, R. (1986) Ligand field effects on the transport of 3d metal ions across a bulk liquid membrane by lipophilic tetraamine carriers. *Inorg. Chem.*, *22* (25): 3984.
28. Granado-Castro, M.-D.; Galindo-Riano, M.-D.; Garcia-Vargas, M. (2004) Separation and preconcentration of cadmium ions in natural water using a liquid membrane system with 2-acetylpyridine benzoylhydrazone as carrier by flame atomic absorption spectrometry. *Spect. Chim. Acta. Part B.*, *59*: 577.
29. Lindoy, L.F.; Baldwin, D.S. (1989) Ligand design for selective metal-ion transport through liquid membranes. *Pure. Appl. Chem.*, *5* (61): 909.
30. Guyon, F.; Parthasarathy, N.; Buffle, J. (2000) Permeation liquid membrane metal transport: studies of complex stoichiometries and reactions in Cu(II) extraction with the mixture 22DD–laurate in toluene/phenylhexane. *Anal. Chem.*, *72*: 1328.
31. Parthasarathy, N.; Buffle, J. (1994) Capabilities of supported liquid membranes for metal speciation in natural waters application to copper speciation. *Anal. Chim. Acta*, *284*: 649.
32. Wojciechowski, K.; Buffle, J. (2004) The intraction of azacrown ether with fatty acid in nonpolar solvents and at the organic-aqueous interface. *Biosensors Bioelectronics.*, *20*: 1051.
33. Myers, D. (1988) *Surfactant Science and Technology*; VCH Publishers: Weinheim.
34. Pearson, R.G. (1963) Hard and soft acids and bases. *J. Am. Chem. Soc.*, *85* (22): 3533.
35. Olsher, U.; Hankins, M.G.; Kim, Y.D.; Bartsch, R.A. (1993) Anion effect on selectivity in crown ether extraction of alkali metal cations. *J. Am. Chem. Soc.*, *8* (115): 3370.
36. Shamsipur, M.; Khayatian, G. (2001) A liquid membrane system containing dibenzyldiaza-18-crown-6 for selective and efficient transport of silver ions. *Indian J. Chem., Sec. A*, *40*: 594.
37. Eichhorn, G.L. (Ed.), (1973) *Inorganic Biochemistry*; Elsevier: New York.
38. Akhond, M.; Shamsipur, M. (1996) Specific uphill transport of Cd^{2+} ion by a cooperative carrier composed of aza-18-crown-6 and palmitic acid. *J. Membr. Sci.*, *117*: 221.
39. Alpoguz, H.K.; Kaya, A.; Karakus, M. (2005) Mechanism and kinetics of Copper(II) transport through a liquid membrane containing a dithiophosphonate derivative as carrier. *Turk J Chem.*, *29*: 345.
40. Ulewicz, M.; Lesinska, U.; Bochenska, M.; Walkowiak, W. (2007) Facilated transport of Zn(II), Cd(II) and Pb(II) across polymer inclusion membranes doped with calyx[4]-crown-6 derivatives. *Sep. and Purf. Technol.*, *54*: 299.

41. Hiratani, K.; Taguchi, K. (1990) N,N-Bis(8-quinolyl)glutaramide as a highly selective and effective Cu(II) carrier for the uphill transport through liquid membranes. *Chem. Lett.*, *20*: 725.
42. Akhond, M.; Shamsipur, M. (1995) Highly selective and efficient membrane transport of copper as $Cu(SCN)_4^{2-}$ ion using K-Dicyclohexyl-18-crown-6 as carrier. *Sep. Sci. and Technol.*, *30*: 3061.
43. Gumi, T.; Oleinikova, M.; Palet, C.; Valiente, M.; Munoz, M. (2000) Facilated transport of lead(II) and cadmium(II) through novel activated composite membrane containing di-(2-ethyl-hexyl) phosphoric acid as carrier. *Anal. Chem. ACTA*, *408*: 65.
44. Ulewicz, M.; Sadowska, K.; Biernat, J.F. (2007) Facilated transport of Zn(II), Cd(II) and Pb(II) across polymer inclusion membranes doped with imidazole azacrown ethers. *Desalination*, *214*: 352.
45. Larie, Ju. (1978) *Handbook of Analytical Chemistry*; Mir Publishers: Moscow.