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Highly Selective and Efficient Membrane Transport of Copper as $Cu(SCN)_4^{2-}$ Ion Using K^+-Dicyclohexyl-18-crown-6 as Carrier

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ABSTRACT

Potassium-dicyclohexyl-18-crown-6 complex was used as a highly efficient carrier for the uphill transport of copper as $Cu(SCN)_4^{2-}$ complex ion through a chloroform bulk liquid membrane. By using histidine as a metal ion acceptor in the receiving phase at the optimum pH of 7.4, the amount of copper transported across the liquid membrane after 2 hours was 90.2 ± 1.0%. The selectivity and efficiency of copper transport from aqueous solutions containing equimolar mixtures of Ag^+, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Fe^{3+}, Bi^{3+}, and Cr^{3+} ions were investigated. In the presence of pyrophosphate as a suitable masking agent in the source phase, the interfering effects of Co^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions were completely eliminated.

Key Words. Liquid membrane; Copper transport; K^+-Dicyclohexyl-18-crown-6 carrier; $Cu(SCN)_4^{2-}$ anion; Histidine; Pyrophosphate

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INTRODUCTION

There has been a rather increasing interest over the past two decades in the transport of metal ions across artificial membranes (1–3). The recognition and transportation of different cations by membrane carriers are of fundamental importance in chemistry, biology, and separation science (1, 4, 5). Among several types of carriers used in liquid membranes, macrocyclic crown ethers (6) have been extensively used as suitable cation carriers in liquid membranes for the selective and uphill transport of alkali and alkaline earth cations (2, 3, 7–9). However, much less attention has been devoted to the transport of transition and heavy metal ions (10–14).

Recently, the transport of such metal ions as silver, palladium, gold, aluminum, and mercury in the form of anionic complexes by M^{n+}-crown ether carriers has been reported (15–18). In this case, M^{n+} is usually an alkali or alkaline earth cation which is strongly complexed by crown ethers. Because of low hydration of the complexed anion containing the metal ion of interest, it can form a suitable ion pair with M^{n+}-crown carrier which can distribute preferentially into the organic membrane. Finally, the presence of a proper metal ion acceptor in the receiving phase would complete the transport process by removing the metal ion from its complex anion.

In this paper we describe a highly selective and efficient liquid membrane system containing potassium-DC18C6 for the transport of the copper ion as $Cu(SCN)_4^{2-}$ counteranion. The receiving phase contains histidine as a copper ion acceptor, which was found to play an important role in the transport process.

EXPERIMENTAL

Reagents

Dicyclohexyl-8-crown-6 (DC18C6) and other macrocyclic ligands used were purchased from Merck Chemical Company and used as received. Reagent-grade chloroform (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 Chemical Companies and used without further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

Apparatus

The atomic absorption spectrophotometer used for the measurement of metal ion concentrations was a Philips Pye Unicam SP9 instrument. pH measurements were made with a Corning 125 pH-meter using a combined glass electrode. A bulk-type liquid membrane cell (8, 19) was used.

Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter of 4.0 cm) containing a glass tube (inside diameter of 2.0 cm), thus separating the two aqueous phases, was used. The inner aqueous phase (source phase) contained copper nitrate, potassium nitrate, and sodium thiocyanate (5 mL). The outer aqueous phase (receiving phase) contained histidine (10 mL). The chloroform solution (30 mL) containing DC18C6 lay below these aqueous phases, and bridged the two phases. The organic layer was slowly stirred by a Teflon-coated magnetic bar (3 cm × 5 mm diameter). Determination of metal ion concentration in both aqueous phases was carried out by AAS. A similar experiment was carried out in the absence of the carrier for reference. The detailed experimental conditions are included in the tables.

RESULTS AND DISCUSSION

In preliminary experiments it was found that, due to the relatively high hydration energy of Cu^{2+} ion (20) and its too small size for the cavily of DC18C6 (21), DC18C6-mediated copper transport in liquid membrane systems is very low. However, in the presence of excess thiocyanate ion, Cu^{2+} exists as a stable complex anion $Cu(SCN)_4^{2-}$ (22) and, hence, it can easily accompany the K^+-DC18C6 cation into the chloroform membrane. In the next steps, such experimental variables as concentration of potassium and thiocyanate ions in the source phase, nature and concentration of the stripping agent, pH of the receiving phase, and nature and concentration of the macrocyclic polyether in the membrane phase were optimized in order to achieve the highest efficiency and selectivity of a 1.26×10^{-4} M solution of Cu^{2+} across the membrane system used.

The effect of the concentrations of SCN^- and K^+ ions in the source phase on the transport of copper was studied, and the results are shown in Tables 1 and 2, respectively. It is seen that the percentage of copper ion transported increases with increasing concentration of both thiocyanate and potassium ions in the source phase. Maximum transport occurs when the concentration of SCN^- is about 0.75 M and that of K^+ is about 0.01 M. It should be noted that about 50% of Cu^{2+} will be transported in the absence of potassium ion, most probably via Na^+-DC18C6 as carrier (Na^+ ion present as the counterion of thiocyanate).

TABLE 1
Effect of Thiocyanate Concentration in the Source Phase on Copper Transport[a]

Concentration of SCN^- (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.25	70	28
0.30	74	25
0.50	82	17
0.60	85	14
0.70	89	9
0.75	92	8
0.85	91	6
1.0	84	15

[a] Conditions: Source phase, 5 mL of 1.26×10^{-4} mol/L Cu^{2+}, 0.01 mol/L K^+, and varying concentration of SCN^-; membrane phase, 30 mL of 5×10^{-3} mol/L of DC18C6 in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L histidine at pH 7.4; time of transport, 2 hours.

Permeability of the membrane system for $Cu(SCN)_4^{2-}$ ion was found to be strongly dependent on the nature of the amino acid used as the stripping agent for Cu^{2+} ion in the receiving phase (Table 3). As seen from Table 3, 90% of copper ion transports through the liquid membrane during 2

TABLE 2
Effect of Potassium Concentration in the Source Phase on Copper Transport[a]

Concentration of $K^+ \times 10^2$ (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.50	85	14
0.75	89	10
1.0	91	8
1.5	91	8
2.5	91	7
3.2	91	7

[a] Conditions: Source phase, 5 mL of 1.26×10^{-4} mol/L Cu^{2+}, 0.75 mol/L SCN^-, and varying concentration of K^+; membrane phase, 30 mL of 5×10^{-3} mol/L DC18C6 in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L histidine at pH 7.4; time of transport, 2 hours.

TABLE 3
Effect of Amino Acid Present in Receiving Phase on Copper Transport[a]

Amino acid	Percentage transported into receiving phase	Percentage remaining in source phase
Asp	47	29
Ala	15	27
Arg	48	29
Glu	38	25
Gly	20	31
His	90	10

[a] Conditions: Source phase, 5 mL of 1.25×10^{-4} mol/L Cu^{2+}, 0.01 mol/L K^+, and 0.75 mol/L SCN^-; membrane phase, 30 mL of 5×10^{-3} mol/L of DC18C6 in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L of different amino acids at pH 7.4; time of transport, 2 hours.

hours in the presence of histidine in the receiving phase, while the use of other amino acids results in no promising uphill transport of Cu^{2+} ion. It should be noted that the amino acids are hardly soluble in the membrane phase, and hence they are found to scarcely move into the aqueous source phase.

The optimum concentration of histidine in the receiving phase was investigated (Table 4) and found to be 0.01 mol/L. It should be noted that the absence of a metal ion acceptor in the receiving phase resulted in no promising transport of copper even in much longer time periods.

The influence of the pH of the receiving phase on the transport efficiency of Cu^{2+} was studied in the pH 5.0–10 range. The results revealed that maximum copper transport occurs at pH ≥ 7.0. At lower pH values there was a decrease in the transport efficiency of copper due to the diminished complexing ability of the amino acid at such pH values.

The transport efficiency of Cu^{2+} was also found to be critically dependent on the nature of the macrocycle used as the carrier in the organic phase. In other experiments (and under similar experimental conditions) we tried several crown ethers as well as cryptand C222 as carrier for the transport of $Cu(SCN)_4^{2-}$ in the presence of K^+ ion, and the results are given in Table 5. As seen among different K^+–macrocycle systems tried, K^+-DC18C6 exhibits the highest transport efficiency for the transport of copper as $Cu(SCN)_4^{2-}$. This could be mainly due to the relatively high

TABLE 4
Effect of Histidine Concentration in the Receiving Phase on Copper Transport[a]

Concentration of histidine × 10^2 (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.1	25	23
0.5	90	7
0.7	90	7
1.0	91	7
2.0	91	7
5.0	90	8
7.0	88	12
10.0	86	12
12.0	85	13

[a] Conditions: Source phase, 5 mL of 1.26×10^{-4} mol/L Cu^{2+}, 0.75 mol/L SCN^-, and 0.01 mol/L K^+; membrane phase, 30 mL of 5×10^{-3} mol/L DC18C6 in $CHCl_3$; receiving pH = 7.4; time of transport, 2 hours.

stability of a potassium complex with DC18C6 which originates from the convenient fit of the cation inside the crown cavity (21, 23), as well as the suitable lipophilic character of DC18C6. It is interesting to note that in the case of cryptand C222, despite the very high stability of the resulting potassium cryptate, its efficiency for the membrane transport of copper is somewhat less than that of DC18C6. As the data given in Table 5 indicate, after 2 hours the extraction into the organic membrane is complete, emphasizing the good tendency of the resulting potassium inclusion complex (24) to form an ion pair with $Cu(SCN)_4^{2-}$. However, the slow rate of release of copper into the receiving phase seems to be responsible for the lower transport efficiency observed.

The influence of the concentration of DC18C6 in the organic phase on the transport efficiency of copper was also studied (Table 6). As seen, the percentage transport of copper increases with an increase in DC18C6 concentration in chloroform. Maximum transport occurs at a concentration of about 5.0×10^{-3} mol/L. A further excess of ligand has no considerable effect on the transport efficiency.

Figure 1 shows the time dependence of copper transport through the liquid membrane under the optimal experimental conditions. It is seen

TABLE 5
Effect of the Carrier Structure on Copper Transport[a]

Carrier ligand	Log K_f of K^+ complex in methanol[b]	Percentage transported into receiving phase	Percentage remaining in source phase
DC18C6	5.63	92	7
18C6	6.07	65	32
DB18C6	5.00	3	97
DB24C8	3.45	20	80
B15C5	2.90 (1) 2.75 (2)	25	76
15C5	3.86 (1) 2.21 (2)	21	78
22	1.80	0	42
222	10.49	80	0

[a] Conditions: Source phase, 5 mL of 1.26×10^{-4} mol/L Cu^{2+}, 0.01 mol/L K^+, and 0.75 mol/L SCN^-; membrane phase, 30 mL of 5×10^{-3} mol/L of various ligands in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L histidine at pH 7.4; time of transport, 2 hours.

[b] Data taken from Ref. 25.

TABLE 6
Effect of DC18C6 Concentration in the Membrane Phase on Copper Transport[a]

Concentration of DC18C6 × 10^3 (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0	0	95
1	80	17
2.5	85	10
5	92	8
7.5	93	9
10	93	5

[a] Conditions: Source phase, 5 mL of 1.2×10^{-4} mol/L Cu^{2+}, 0.01 mol/L K^+, and 0.75 mol/L SCN^-; membrane phase, 30 mL of varying concentrations of DC18C6 in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L histidine at pH 7.4; time of transport, 2 hours.

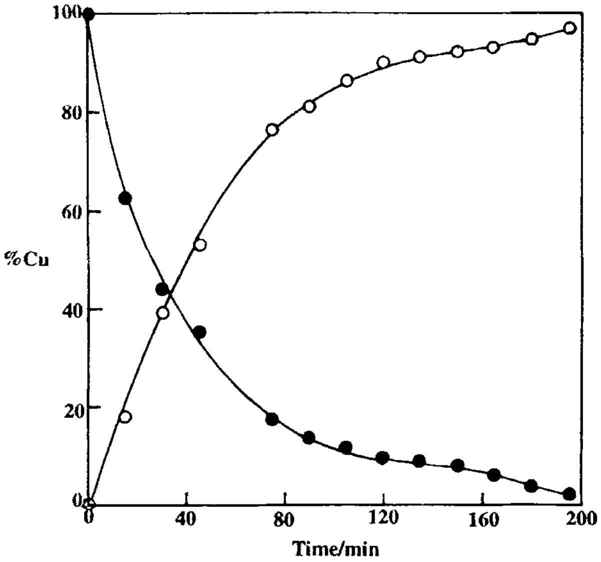


FIG. 1 Time dependence of copper transport: (○) transported; (●) remaining. The conditions are similar to those mentioned in Table 7.

that both the extraction of Cu(SCN)$_4^{2-}$ from the source phase into the membrane and the release of copper from the membrane into the receiving phase are fast (and follow the same trend), so that some 90% copper transport occurs after 2 hours. The reproducibility of copper transport was investigated, and the percent of metal ion transported after 2 hours from 12 replicate measurements was found to be 90.2 ± 1.0.

The selectivity of the membrane system for the transport of copper ion over other cations, in equimolar mixtures, is illustrated in Table 7. As seen, among the different cations tried, cobalt, zinc, lead, and cadmium interfere seriously in the transport of copper ion. However, the interfering effect of these cations was successfully eliminated using $P_2O_7^{4-}$ as a masking agent in the receiving phase. The influence of the concentration of pyrophosphate ion on the masking of the interfering cations, together with the stability constants of the corresponding complexes with SCN^- and $P_2O_7^{4-}$ ions in aqueous solution, are given in Table 8. It is obvious that in the presence of a 8.0×10^{-3} mol/L concentration of pyrophosphate the interfering effect of Co^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions on the transport of copper has been eliminated completely, although the efficiency of Cu^{2+} transport has also decreased some 12%.

TABLE 7
Amount of Cation Transported from Various Cation Mixtures through Membrane[a]

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1:		
Cu^{2+}	90	8
Cd^{2+}	39	32
Zn^{2+}	70	14
Mixture 2:		
Cu^{2+}	90	9
Ni^{2+}	0	100
Fe^{2+}	0	40
Mixture 3:		
Cu^{2+}	91	9
Ag^{+}	0	100
Co^{2+}	75	24
Mixture 4:		
Cu^{2+}	92	5
Bi^{3+}	0	100
Fe^{3+}	0	37
Mixture 5:		
Cu^{2+}	92	6
Pb^{2+}	50	30
Mn^{2+}	0	100
Mixture 6:		
Cu^{2+}	90	9
Cr^{3+}	0	100

[a] Conditions: Source phase, 5 mL of 1.26×10^{-4} mol/L of each cation, 0,01 mol/L K^+, and 0.75 mol/L SCN^-; membrane phase, 30 mL of 5×10^{-5} mol/L of DC18C6 in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L histidine at pH 7.4; time of transport, 2 hours.

In order to further support the fact that the $Cu(SCN)_4^{2-}$ complexed anion should easily accompany the complexed cation K^+-DC18C6 into the membrane phase, the concentration of potassium ion in the receiving phase was determined. It was found that approximately twice as many K^+ as Cu^{2+} ions are transported, indicating that almost all K^+ ions are partitioning as the $(K^+\text{-DC18C6})_2 \cdot Cu(SCN)_4^{2-}$ ion pair. The proposed mechanism of copper transport through the liquid membrane used is sum-

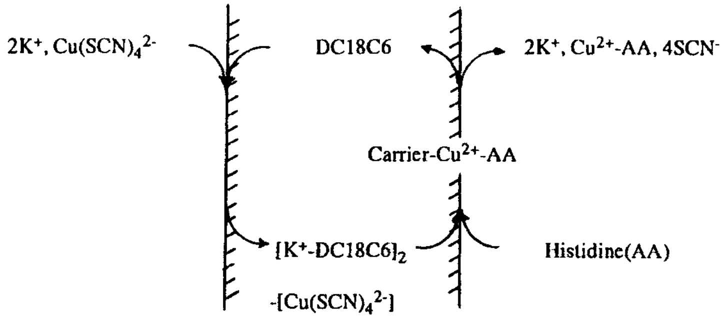
TABLE 8
Amount of Cation Transported from a Cation Mixture through Membrane in the Presence of Varying Concentration of $P_2O_7^{4-}$ as a Masking Agent[a]

Cation	Log β_4 with SCN^- in water[b]	Log K_1 with $P_2O_7^{4-}$ in water[b]	Percentage transported into receiving phase	Percentage remaining in source phase	Concentration of $P_2O_7^{4-}$ in source phase (mol/L)
Cu^{2+}	6.5	5.2	90	8	0.000
Co^{2+}	2.2	4.0	72	24	
Zn^{2+}	3.7	8.7	70	13	
Pb^{2+}	0.8	11.2	50	30	
Cd^{2+}	3.0	5.6	40	30	
Cu^{2+}			84	12	0.005
Co^{2+}			3	95	
Zn^{2+}			2	97	
Pb^{2+}			0	100	
Cd^{2+}			0	100	
Cu^{2+}			78	20	0.008
Co^{2+}			0	99	
Zn^{2+}			0	100	
Pb^{2+}			0	100	
Cd^{2+}			0	100	

[a] Conditions: Source phase, 5 mL of 1.26×10^{-4} mol/L of each cation, 0.01 mol/L of K^+, 0.75 mol/L of SCN^-, and varying concentrations of $P_2O_7^{4-}$; membrane phase, 30 mL of 5×10^{-3} mol/L of DC18C6 in $CHCl_3$; receiving phase, 10 mL of 0.01 mol/L of histidine at pH 7.4; time of transport, 2 hours.

[b] Data taken from Ref. 22.

marized in Scheme 1. The copper ion transport can be explained as follows: 1) At the source phase–membrane interface, the K^+-DC18C6 complex is formed. Since the $Cu(SCN)_4^{2-}$ complex anion is less hydrated than other anions present in the source phase, it would form an ion pair with K^+-DC18C6, and this ion pair distributes preferentially into the organic membrane. 2) The ion pair thus formed diffuses across the membrane. 3) At the membrane–receiving phase interface, histidine with its high affinity for copper ion completes the transport by removing Cu^{2+} from its complex anion. In this case the associated potassium and thiocyanate ions would also release into the receiving phase. 4) The free carrier diffuses back across the membrane to the source phase–membrane interface, where the cycle starts again.



SCHEME 1

CONCLUSION

The excellent efficiency and high degree of selectivity for Cu^{2+} transport demonstrated by the liquid membrane system studied reveals its potential application for the selective removal, concentration, and purification of copper ion from mixtures.

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