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Specific Membrane Transport of Mercury as $[Hg(SCN)_4]^{2-}$ Ion Using K^+–Dibenzo-18-crown-6 as Carrier

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ABSTRACT

Potassium-dibenzo-18-crown-6 complex cation was used as carrier for the uphill transport of mercury as $[Hg(SCN)_4]^{2-}$ complex anion through a chloroform membrane system. By using 0.2 mol/L EDTA as a metal ion acceptor in the receiving phase at the optimized pH of 10.0, the amount of mercury transport through the liquid membrane after 120 minutes was 94.2 ± 0.7%. The selectivity and efficiency of mercury transport from aqueous solutions containing equimolar mixtures of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions were investigated. In the presence of 0.05 mol/L EDTA at pH 3.2 as a proper masking agent in the source phase, the interfering effects of Zn^{2+}, Pb^{2+}, and Cu^{2+} ions were eliminated.

Key Words. Liquid membrane; Mercury transport; K^+–Dibenzo-18-crown-6 carrier; $Hg(SCN)_4^{2-}$ anion; EDTA

INTRODUCTION

During the past two decades, the assay of mercury compounds has been of special interest not only because of their widespread agricultural and industrial use in the world, but also because of their hazardous effects on human health (1, 2). Hence, the development of new methods for selective removal of Hg^{2+} ion for environmental remediation and in the treatment of severe and

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chronic mercury poisoning has remained an important objective. A variety of separation methods, such as solvent extraction, adsorption, precipitation, etc., has been utilized to remove toxic heavy metal ions (e.g., Hg^{2+}, Cd^{2+}, and Pb^{2+}) from the environment and from biological systems (3).

Recently liquid membrane systems have been extensively used for selective removal, concentration, and purification of metal ions, particularly alkali and alkaline earth cations (4–8). In recent years, several liquid membrane systems using a variety of cyclic and acyclic ion carriers for the selective transport of heavy metal ions have been reported (9–22). The main advantage of liquid membrane transport of metal ions over their classical solvent extraction is that the amounts of organic solvent and metal ion complexing agent are markedly reduced (8).

In recent years we have been involved in the development of new solvent extraction (23, 24), solid-phase extraction (25), liquid membrane transport (15–17, 20), and PVC membrane selective electrode systems (26, 27) for selective separation and determination of heavy metal ions, mainly based on macrocyclic crown ionophores. In this paper we describe a selective and efficient liquid membrane system containing potassium ion–dibenzo-18-crown-6 for the transport of the mercury ion as $[Hg(SCN)_4]^{2-}$ counterion.

EXPERIMENTAL

Reagents

Dibenzo-18-crown-6 (DB18C6) and other macrocyclic ligands used were purchased from Merck Chemical Co. 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. Triply distilled water was used throughout.

Apparatus

The atomic absorption spectrophotometer used for the measurement of metal ion concentrations was a Shimadzu AA-670 instrument. The determination of mercury in solution was done by cold vapor atomic absorption spectrometry (CVAAS) (25). pH measurements were made with a Metrohm 632 pH-meter using a combined glass electrode. A bulk-type liquid membrane cell (17, 28) was used.

Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used (17, 28). The inner aqueous phase (source phase) contained mercury nitrate (5 mL, 1.0×10^{-3}

mol/L). The outer aqueous phase (receiving phase) contained EDTA at pH 10 (10 mL, 0.2 mol/L). The chloroform solution (30 mL) containing 8.0×10^{-3} mol/L DB18C6 laid below these aqueous phases and bridged the two aqueous phases. The organic layer was slowly stirred by a Teflon-coated magnetic bar (3 cm × 5 mm diameter). Determination of metal concentration was carried out by AAS. Reproducibility was confirmed as ±3% or better. A similar transport experiment was carried out in the absence of the carrier for reference. The detailed conditions are included as footnotes in the tables.

RESULTS AND DISCUSSION

In preliminary experiments it was found that, due to the relatively high hydration energy of Hg^{2+} ion (29) and its weak interaction with DB18C6 (30), DB18C6-mediated mercury transport in a liquid membrane system is very low (i.e., about 5% after 3 hours). However, in the presence of excess potassium thiocyanate, Hg^{2+} exists as a fairly stable anion $[Hg(SCN)_4]^{2-}$ with $\log \beta_4 = 19.77$ (30) and, hence, it can easily accompany the K^+–DB18C6 ion into the liquid membrane (i.e., about 90% transport after 2 hours). In further experiments, such experimental variables as concentration of KSCN in the source phase, nature and concentration of the stripping agent in the receiving phase, pH of the aqueous phases, and nature and concentration of the macrocyclic polyether in the organic membrane phase were optimized in order to achieve the highest efficiency and selectivity of a 1.0×10^{-3} mol/L solution of mercury nitrate across the membrane system used.

The effect of the concentration of DB18C6 in the organic phase on the transport efficiency of mercury was studied, and the results are given in Table 1. The results show that the percentage transport of mercury ion increases with an increase in DB18C6 concentration in chloroform. Maximum transport occurs at a concentration of about 8.0×10^{-3} mol/L. A further excess of carrier has no considerable effect on the transport efficiency.

The influence of the concentration of KSCN in the source phase on mercury ion transport was investigated, and the results are given in Table 2. As seen, the percentage of Hg^{2+} transported into the receiving phase increases with the potassium thiocyanate concentration in the source phase until a reagent concentration of about 0.2 mol/L is reached, beyond which the transport efficiency remains more or less the same.

The nature and composition of the receiving phase was found to have a pronounced influence on the mercury ion transport. Use of EDTA at pH 10 as a stripping ligand in the receiving phase, with $\log K_s = 21.8$ with Hg^{2+} ion (30), caused a rather large enhancement in the efficiency and selectivity of mercury transport, while the presence of other stripping agents, such as thiosulfate, iodide, and chloride, resulted in diminished transport efficiency as well as in-

TABLE 1
Effect of DB18C6 Concentration in the Membrane Phase on Mercury Transport[a]

Concentration of DB18C6 × 10^3 (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
5	57	36
7	64	12
8	74	9
8.5	73	4
9	73	4
10	72	4
12	72	4

[a] Conditions: Source phase, 5 mL of 1.0×10^{-3} mol/L Hg^{2+} and 0.1 mol/L KSCN; membrane phase, 35 mL of varying concentration of DB18C6 in $CHCl_3$; receiving phase, 10 mL of 0.1 mol/L EDTA; time of transport, 3 hours.

creased interfering effects of other cations. The optimum concentration of EDTA in the receiving phase (at pH 8.5) was investigated (Table 3) and found to be 0.2 mol/L. It is interesting to note that the absence of a metal ion acceptor in the receiving phase resulted in no measurable mercury transport even for much longer periods of time.

The influence of the pH of the source and receiving phases on the transport of Hg^{2+} was investigated, and the results are shown in Fig. 1. It is seen that

TABLE 2
Effect of KSCN Concentration in the Source Phase on Mercury Transport[a]

Concentration of KSCN (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.05	53	27
0.10	74	90
0.15	83	3
0.20	90	3
0.25	91	3
0.30	90	3

[a] Conditions: Source phase, 5 mL of 1.0×10^{-3} mol/L Hg^{2+} and varying concentration of KSCN; membrane phase, 35 mL of 8.0×10^{-3} M DB18C6 in chloroform; receiving phase, 10 mL of 0.1 mol/L EDTA at pH 8.5; time of transport, 3 hours.

TABLE 3
Effect of EDTA Concentration in the Receiving Phase on Mercury Transport[a]

Concentration of EDTA (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.05	73	3
0.08	80	3
0.10	90	2
0.15	92	2
0.20	93	2
0.30	93	2

[a] Conditions: Source phase, 5 mL of 1.0×10^{-3} mol/L Hg^{2+} and 0.2 mol/L KSCN; membrane phase, 35 mL of 8.0×10^{-3} mol/L DB18C6; receiving phase, 10 mL of varying concentration of EDTA in water at pH 8.5; time of transport, 3 hours.

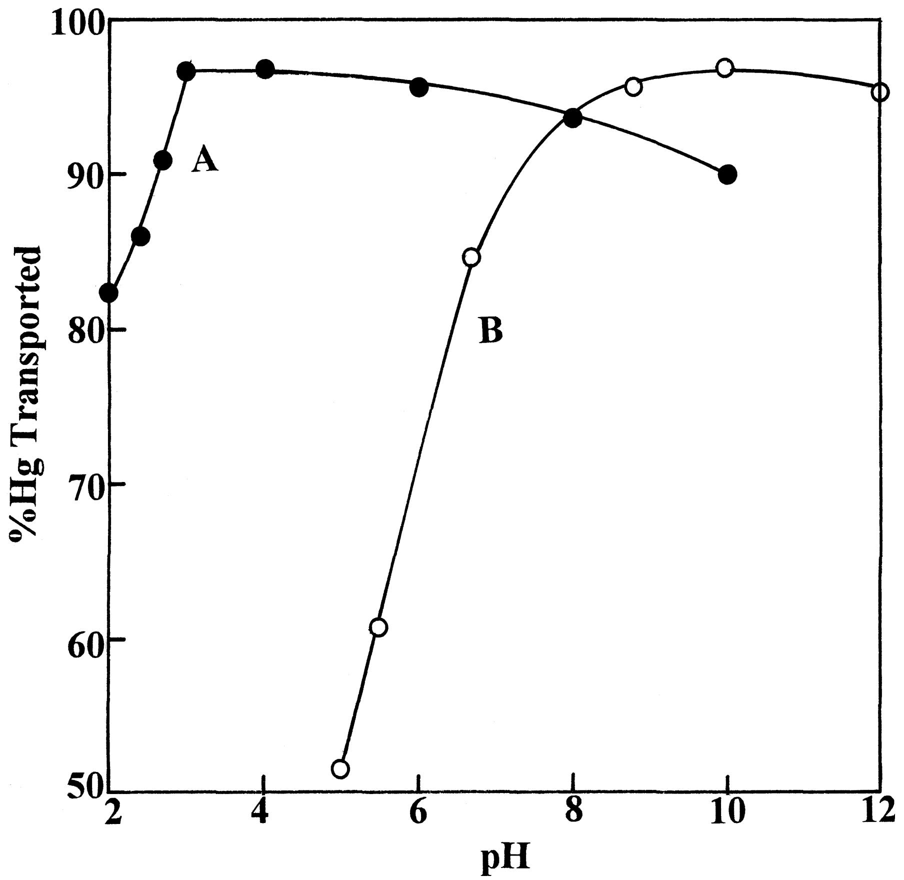


FIG. 1 Effect of pH of the source (A) and receiving (B) phases on mercury transport. Conditions similar to those mentioned in Table 5, except for the varying pH values of the source and receiving phases.

the release of mercury ions into the receiving phase occurs almost completely in the pH range of about 9–12. The decreased release of mercury at lower pH values can be mainly related to the diminished complexing power of EDTA. The best pH region of the source phase for the quantitative transport of Hg^{2+} ion is about 3–6. At pH values smaller than 3 in the source phase, most of the SCN ion exists in the form of HCN, resulting in a diminished amount of $Hg(SCN)_4^{2-}$ ion necessary for the successful extraction of mercury ion into the organic phase. On the other hand, at pH values greater than 6 the formation of some $Hg(OH)_2$ precipitate caused a decreased transport efficiency of mercury ion.

Permeability of the membrane system designed for transport of Hg^{2+} was also found to be critically dependent on the nature of the macrocycle used as carrier in the organic membrane 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 $Hg(SCN)_4^{2-}$ in the presence of K^+ ion, and the results are shown in Table 4. As seen, the three 18-crowns and cryptand C222 are suitable carriers for the transport of mercury, mainly due to their proper cavity sizes for K^+ ions (31) and, consequently, the higher stability of their complexes. However, in the case of macrocycles of smaller (B15C5) and larger (DB24C8) cavity sizes than the 18-crowns used, and diminished stability of their K^+ complexes, the transport of mercury ion through the liquid membrane is very low. It should be noted that, despite some lower efficiency of DB18C6 in comparison with that of 18C6 and DC18C6, this ligand was selected as the ion carrier for the transport system, mainly due to its much lower price.

TABLE 4
Effect of Carrier Structure on Mercury Transport[a]

Carrier ligand	Log K_f of K^+ complex in methanol[b]	Percentage transported into receiving phase	Percentage remaining in source phase
B15C5	3.9 (K_1)	15	58
18C6	6.1	98	0
DB18C6	5.0	96	2
DC18C6	3.4	98	0
DB24C8	3.5	14	79
C222	10.4	96	0

[a] Conditions: Source phase, 5 mL of 1.0×10^{-3} mol/L Hg^{2+} and 0.2 mol/L KSCN; membrane phase, 35 mL of 8.0×10^{-3} mol/L macrocycle; receiving phase, 10 mL of 0.2 mol/L EDTA at pH 10; time of transport, 2.5 hours.

[b] Ref. 31.

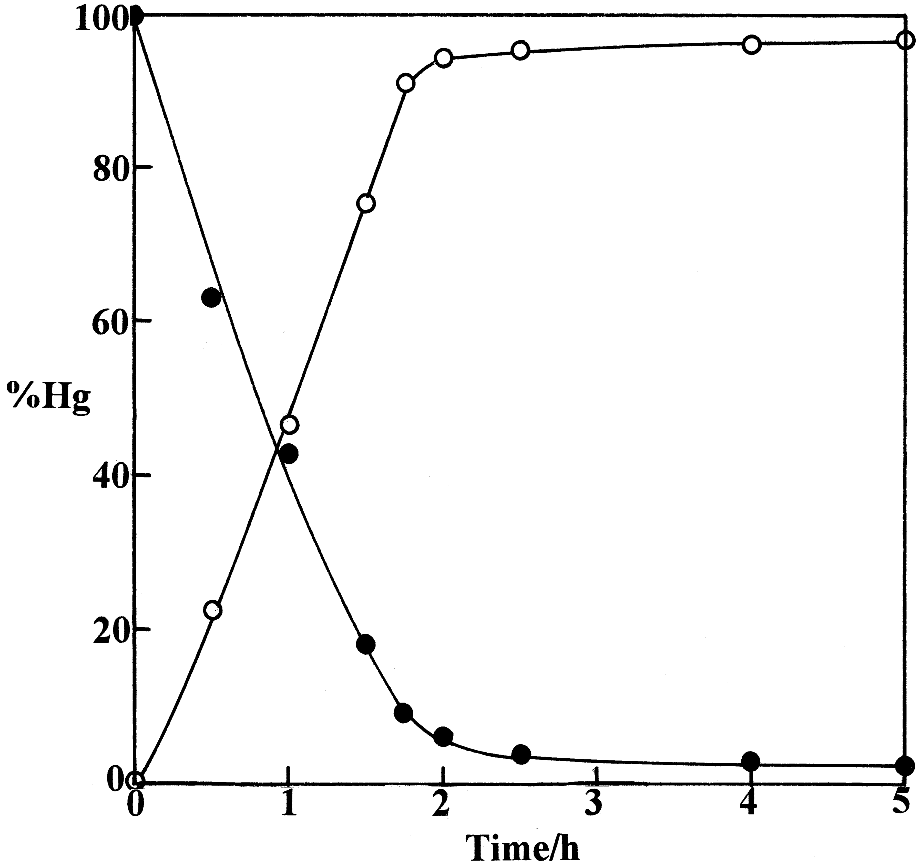


FIG. 2 Time dependence of mercury transport: (○) transported, (●) remaining. Conditions similar to those mentioned in Table 5.

Figure 2 shows the time dependence of mercury transport through the liquid membrane under the optimal experimental conditions. It is seen that both the extraction of $Hg(SCN)_4^{2-}$ from the source phase into the membrane and the release of mercury from the membrane into the receiving phase are fast (and follow the same trend), so that some 95% mercury transport occurs after 2 hours. The reproducibility of mercury transport was investigated, and the percent of metal ion transported after 2 hours from seven replicate measurements was found to be 94.2 ± 0.7.

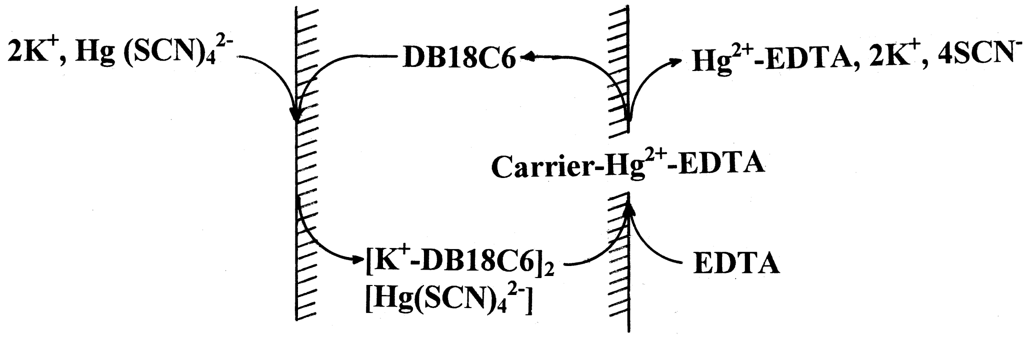
The selectivity of the membrane system for the transport of mercury ion over some other transition and heavy metal ions, in equimolar mixtures was studied and the results are summarized in Table 5. As seen, among the different cations tried, copper, lead, and especially zinc interfere seriously in transport of mercury ion. However, the interfering effect of these cations was eliminated by adding 0.05 mol/L EDTA at pH 3.2 as a suitable masking agent in the source phase (Table 5).

TABLE 5
Amount of Cation Transported from a Cation Mixture in the Absence (A) and Presence (B) of 0.05 mol/L EDTA at pH 3.2 as Masking Agent in the Source Phase[a]

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
	Mixture A	
Hg^{2+}	95	2
Zn^{2+}	90	1
Pb^{2+}	33	65
Cu^{2+}	17	80
Ni^{2+}	0	98
Cd^{2+}	0	98
Co^{2+}	0	99
	Mixture B	
Hg^{2+}	93	5
Zn^{2+}	3	95
Pb^{2+}	0	100
Cu^{2+}	0	100
Ni^{2+}	0	100
Cd^{2+}	0	100
Co^{2+}	0	100

[a] Conditions: Source phase, 5 mL of 1.0×10^{-3} mol/L of each cation and 0.2 mol/L KSCN; membrane phase, 35 mL of 8.0×10^{-3} mol/L DB18C6; receiving phase, 10 mL of 0.2 mol/L EDTA at pH 10; time of transport, 2.5 hours.

In order to further support the concept that tetracyanatomercury(II) complexed anion accompanied the K^+–DB18C6 complexed cation into the membrane phase in this study, the concentration of K^+ after the transport period in the receiving phase was determined. It was found that approximately twice as many K^+ ions as Hg^{2+} ions were transported, emphasizing that almost all potassium ions are participating as the $(K^+\text{-DB18C6})_2 \cdot Hg(SCN)_4^{2-}$ ion pair. A proposed mechanism of mercury transport through the liquid membrane is presented in Scheme 1. At the source phase–membrane interface, the K^+–DB18C6 complex is formed. Since the $Hg(SCN)_4^{2-}$ complex anion is less hydrated than other anions present in the source phase, it will form an ion pair with the potassium–crown complex cation, and this ion pair distributes preferentially into the chloroform phase, then diffuses across the membrane. At the membrane–receiving phase interface, EDTA with high affinity for mercury ion (30) com-



SCHEME 1

pletes the transport process by removing Hg^{2+} ion from its complex anion. Finally, the free carrier (i.e., DB18C6) diffuses back across the membrane to the source phase–membrane interface, where the cycle starts again. Actually, the transport process of mercury through the liquid membrane is illustrated by the following equations:

1. The Hg^{2+} ion in the source phase reacts with SCN^- to form a very stable $Hg(SCN)_4^{2-}$ complex anion:

$$Hg^{2+}_{(SP)} + 4SCN^-_{(SP)} = Hg(SCN)^{2-}_{4(SP)} \tag{1}$$

2. The macrocycle DB18C6 in the membrane phase reacts with K^+ ion to form a $K^+{-}DB18C6$ complex acting as a suitable lipophilic counterion for the formation of a $Hg(SCN)_4^{2-}\cdot(K^+{-}DB18C6)_2$ ion pair which is readily extractable in the membrane phase:

$$Hg(SCN)^{2-}_{4(SP)} + 2K^+_{(SP)} + DB18C6_{(MP)} = Hg(SCN)_4^{2-}\cdot(K^+{-}DB18C6)_{2(MP)} \tag{2}$$

3. EDTA (Na_2Y) in the receiving phase reacts with the ion pair to strip mercury into the receiving phase:

$$Hg(SCN)_4^{2-}\cdot(K^+{-}DB18C6)_{2(MP)} + Na_2Y_{(RP)} = HgY_{(RP)} + 2NaSCN_{(RP)} + 2KSCN_{(RP)} + DB18C6_{(MP)} \tag{3}$$

CONCLUSION

The very high efficiency and excellent degree of selectivity for mercury transport shown by the membrane system introduced demonstrate its potential application to selective removal, concentration, or purification of Hg^{2+} ion from different real samples.

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