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Crown Ethers as Carriers for the Transport of Anionic Thiocyanate Complex of Uranyl Ion Across a Bulk Liquid Membrane

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ABSTRACT

Transport of UO_2^{2+} as its anionic thiocyanate complex $[UO_2(SCN)_4]^{2-}$ across a bulk liquid membrane using 18 Crown 6 (18C6) and Dibenzo 18 Crown 6 (DB18C6) as carriers in the membrane phase has been studied. The anionic complex is formed by the addition of KSCN to the feed solution at a pH of 1. A dilute acid (pH = 5) served as the stripping agent in the receiving compartment. The interference from Th(IV) and a few other cations could be eliminated by using EDTA as a masking agent in the feed solution. Various factors influencing the transport process have been studied and an uphill transport (>89%) of UO_2^{2+} from the feed solution could be accomplished under optimum conditions.

Key Words. Crown ethers; Anionic complexes; Uranyl thiocyanate; Bulk liquid membrane; Carriers

INTRODUCTION

Transport of metal ions across a membrane plays an important role in many biological processes (1). The processes are often facilitated by the presence of carrier compounds in the membrane phase (2, 3). The use of carriers to pro-

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mote the transport leads to various possibilities of increasing the selectivity and uphill transport of the ions (4). One interesting possibility for the transport of metal ions of interest involves conversion into an anionic complex in the source phase itself; the anionic complex can then be transported across the membrane. The extraction of the anionic complex due to ion association followed by its transport has been demonstrated in the hydrometallurgical separation of uranium (5) from Mo(VI) and V(V) using tertiary amine as the carrier. The source contains the anionic sulfato complex, which is extracted into the membrane phase due to ion association with the protonated amine carrier, and finally gets transported across the membrane.

Several reports describe the application of cation-selective crown ethers in the transport of anionic metal complexes (6–8). Crown ethers are an important class of synthetic macrocyclic compounds that exhibit unique carrier activity in the selective transport of alkali metal ions (9). The carrier activity of these compounds has been attributed to the accommodation of the cations in the cavity of the macrocyclic compounds forming a stable complex. The cationic carrier complex is transported across the membrane along with the corresponding anions; the net result is the transport of the salt as a whole.

There are several reports in which crown ethers have been used for the transport of metal ions by ion-pair extraction using β-diketones along with crown ethers in the chloroform layer (10–12). In the presence of crown ethers alone in the membrane phase, the transport of the metal ions is negligible, but the presence of β-diketones results in the synergistic extraction of these metal ions into the organic phase.

In the present study, it has been observed that the carrier activity of 18C6 or DB18C6 toward the direct transport of cationic UO_2^{2+} species across a liquid membrane is poor, but the anionic thiocyanato complex of UO_2^{2+} could be transported easily as an accompanying anion during the transport of K^+ using these crown ethers. The choice of thiocyanate was due to its ability to form a stable anionic thiocyanato complex with UO_2^{2+} (13). It was observed that a selective transport of UO_2^{2+} from a mixture of other metal ions could be accomplished by using EDTA as masking agent for interfering ions in the feed solution.

EXPERIMENTAL

Reagents

- Uranyl solution: Standard uranyl solution was prepared by dissolving the appropriate amount of uranium metal (99.999% purity) in dilute nitric acid and made up to the required volume using distilled water.
- Potassium thiocyante (GR): Weighed and dissolved the appropriate amount of the salt using distilled water.

- Crown ethers: The crown ethers 18C6 and DB18C6, obtained from PCR Research Chemicals Inc, USA, were used as such. The solutions of these compounds were prepared using extra-pure AR Grade chloroform. Dilution of the ligand solutions was carried out using chloroform.
- Transition metal-ion solutions were prepared by dissolving their corresponding salts in dilute acid. These solutions were standardized by titrating with EDTA using a suitable metallochromic indicator.

All the other reagents used were of analytical grade.

Procedure

The permeation studies were carried out using a cell as shown in Fig. 1. In a typical experiment, 50 mL of a chloroform solution of crown ether (10^{-4} M) taken in a 250 mL beaker served as the bulk-liquid-membrane phase. A cylindrical tube (i.d. = 24 mM) was used to spatially separate the feed and the receiving solutions. The feed solution contained uranyl ion or a mixture of metal ions including UO_2^{2+} and potassium thiocyanate at a pH of 1; a dilute hydrochloric acid solution (pH = 5) served as the receiving solution. The volumes of the feed and the receiving phases were 10 and 25 mL, respectively. The concentration of UO_2^{2+} in the receiving phase was monitored spectrophotometrically (14) using a mixture of $NaOH–Na_2CO_3–H_2O_2$. Absorbance measurements were carried out at 400 nm using Shimadzu 120 UV-visible double beam spectrophotometer. Vanadium was determined using salicyl hydroxamic acid as the chromogenic reagent, whereas oxine sulfonic acid was used for the determination of molybdneum. The concentration of the other metal ions was estimated by titrating with standard EDTA using suitable metallochromic indicators.

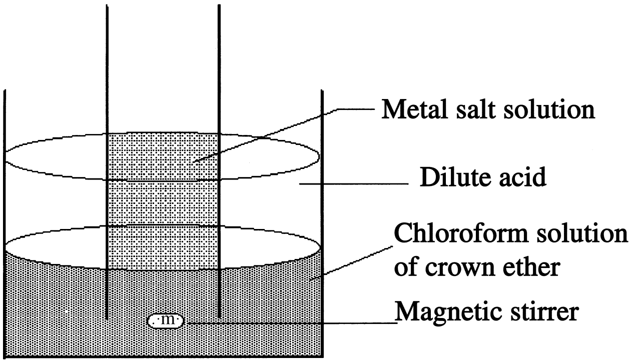

FIG. 1 Permeation cell.

RESULTS AND DISCUSSION

Crown ethers 18C6 and DB18C6 have been successfully used as extracting agents and carriers for the selective transport of potassium salts of different anions across a liquid membrane. Although there are few reports on the transport of uranyl ion across a liquid membrane using crown ethers (15, 16), they generally do not serve as good carriers for direct transport of the cation. Because the crown ethers have been used for the transport of anionic metal complexes, it was felt that they would serve as good carriers for the transport of UO_2^{2+} as its anionic complex.

The experiments with 18C6 and DB18C6 showed that the transport of UO_2^{2+} was greatly enhanced in the presence of thiocyanate in the feed solution (Table 1) because of the formation of a $[UO_2(SCN)_4]^{2-}$ complex. Because the formation of a $[UO_2(SCN)_4]^{2-}$ complex is maximum at $pH = 1$ (17), the feed solution was maintained at that pH in all the experiments. Although the excess of SCN^- is needed for the complete conversion of UO_2^{2+} to $UO_2(SCN)_4^{2-}$ a large excess lowered the permeation, presumably due to the competitive transport between free SCN^- and $[UO_2(SCN)_4]^{2-}$. Variation of SCN^- concentration in the range of 0.004 to 0.6 M showed that the maximum transport of UO_2^{2+} could be accomplished by keeping the SCN^- concentration in the feed solution at 0.1 and 0.04 M when the bulk membrane phase contains DB18C6 and 18C6, respectively.

The crown ethers used have limited solubility in water (18), but they are freely soluble in chloroform. At low concentration levels, variation of the concentration of crown ethers did not show any significant effect on the transport of uranyl ion. Hence, the concentration of the carrier was kept at 10^{-4} M for all the experiments.

TABLE 1
Effect of KSCN Concentration on the Permeation of UO_2^{2+}

	% of Uranyl ion permeated in 5 hours	
Concentration of KSCN (M)	18 C 6	DB 18 C 6
0.000	<0.30	<0.30
0.004	34	22
0.020	35	23
0.040	40.0	26
0.100	25.1	34
0.400	24.0	17
0.600	19.2	13

TABLE 2
Variation of the Amount of UO_2^{2+} Permeated as a Function of the Concentration of UO_2^{2+} in the Feed Solution

Concentration of UO_2^{2+} ($\times 10^3$) M	% of UO_2^{2+} permeated
1.02	40.0
2.31	80.2
5.06	88.9
8.10	89.4

Several water-soluble strong complexing agents like sodium carbonate, Tiron, and dilute acids were tested as stripping agents. More than 89% of uranium could be recovered using dilute hydrochloric acid. The stripping of uranium was always less than 60% with other reagents. The low recovery could be due to the back extraction and transport of the anionic complexes formed with these stripping agents. Therefore, dilute hydrochloric acid at pH of 5 was chosen as the stripping solution.

The percentage of permeated uranium in the receiving solution depends on the initial concentration of UO_2^{2+} in the feed compartment (Table 2). At high concentrations of UO_2^{2+} in the feed solution, the formation of a carrier complex in the membrane phase is high. The anionic complex $UO_2(SCN)_4^{2-}$ strips out of the organic phase in the aqueous receiving phase due to the concentration difference, where the anionic species breaks down into UO_2^{2+} and SCN^- on account of the unfavorable pH condition of the solution. This prevents the transport of uranyl ions back into the feed solution, resulting in the uphill transport of cation. If the concentration of UO_2^{2+} in the feed solution is low, the concentration of the carrier complex in the membrane phase is also low. In the absence of a strong stripping agent, the removal of the anionic complex was partial. This explains the low permeation of uranyl ions at low concentrations of UO_2^{2+} in the feed solution.

In general, metal ions forming anionic complexes are transported from the feed solution along with uranium. The addition of masking agents like EDTA to the feed solution was found to increase selectivity. The selective permeation of UO_2^{2+} from different mixtures is given in Table 3. In the presence of EDTA, UO_2^{2+} could selectively permeate from a feed solution containing a large excess of Th(IV) (10^{-2} M) and Mo(VI). At low pH, the EDTA complexes of interfering transition metal ions were not stable enough to suppress their transport effectively. The interference from V(V) was negligible, whereas Fe^{3+} caused serious interference. Furthermore, the permeation of UO_2^{2+} from a binary or ternary mixture was generally low as compared to that from a pure solution. This is probably due to competition of all the anionic species with $UO_2(SCN)_4^{2-}$ for the crown ethers. Though EDTA does not form a very strong

TABLE 3
Selective Transport of UO_2^{2+} from a Multicomponent Mixture in the Presence of EDTA

Mixture	Feed solution composition	Receiving solution	
		% of UO_2^{2+}	% of Other ions
I	UO_2^{2+}–10^{-3} M Th(IV)–10^{-2} M	43.1	Th(IV): 35%
II	UO_2^{2+}–5×10^{-3} M Fe^{3+}–3×10^{-2} M	40.5	Fe(III): 35.2%
III	UO_2^{2+}–10^{-3}M Th(IV)–10^{-2} M EDTA–3×10^{-2} M	82.6	Th(IV): Negligible
IV	UO_2^{2+}–5×10^{-3} M Fe^{3+}–3×10^{-2} M EDTA–5×10^{-2} M	69.6	Fe(III): <20%
V	UO_2^{2+}–5×10^{-3} M Mo(VI)–3×10^{-2} M V(V)–3×10^{-2} M EDTA–5×10^{-2} M	79.8	Mo(VI): <1% V(V): <2%

complex with UO_2^{2+} (19), lowering of effective concentration of the cation due to the partial complexation contributes to the lowering of UO_2^{2+} transport in the presence of the reagent.

CONCLUSION

Crown ethers like 18 Crown 6 or DB 18 Crown 6 could be successfully used as carriers for the uphill transport of anionic thiocyanate complex of UO_2^{2+} across a bulk liquid membrane (BLM). A selective transport of the uranyl ion from a mixture of Th(IV) and Mo(VI) could be accomplished using EDTA as the masking agent in the feed solution. The interference from Fe^{3+} was very high. Enhanced and selective transport of metal ions across a liquid membrane has great potential in industrial applications because of low cost and energy savings. The present study maybe useful for the separation of uranyl ion from other cations and the recovery of uranium from the leach solution obtained from hydrometallurgical operations and treatment of nuclear materials.

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