

SELECTIVE TRANSPORT OF SILVER IONS THROUGH CROWN ETHER SUPPORTED LIQUID MEMBRANES

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ABSTRACT

The silver content of environmental samples is being increased with the increasing use of silver compounds and silver containing preparations in industry. Silver can enter environment via industrial waters because it is often an impurity in copper, zinc and antimony ores. Recent information about the interaction of silver with essential nutrients, especially Se, Cu, vitamin E and Vitamin B12, have focused attention on potentially toxic nutrients. Thus, separation and recovery of silver ion are of increasing interest. Supported liquid membrane technology has been recently recognized as promising tool for selective separation of metal ions from aqueous solutions. In the present work, a supported liquid membrane (SLM) system for the selective and efficient transport of silver ion is developed. The SLM used is a thin porous polypropylene (PP) membrane impregnated with hexathiacyclooctadecane ($C_{12}H_{24}S_6$) dissolved in alcohol. Crown ether acts as a specific carrier for the uphill transport of Ag^+ ion and its natural complex through SLM. In the presence of thiosulfate ion as a stripping agent in the strip solution, transport of silver occurs almost quantitatively after three hours. The performance of two different membrane materials is compared. The selectivity and efficiency of silver transport from aqueous solutions containing other M^{n+} cations such as Mg^{2+} , Ni^{2+} , Cu^{2+} , K^+ , Cd^{2+} and Cr^{3+} ions were investigated.

Key words: Selective transport, Silver ions, Crown ether and Supported liquid membrane.

INTRODUCTION

Heavy metal contents in environmental media are matter of major concern for metropolitan authorities and environmental protection agencies, worldwide. Recent years have witnessed a growing interest in the recovery of chemical species from wastewaters. There is an increasing need for efficient processes to remove and recover valuable or toxic chemical species from industrial effluents. Membranes and membrane-based processes have attained technical and commercial importance with respect to their industrial and environmental applications. Waste effluents from different industries contain toxic and/or useful organic species that pollute large water bodies meant for irrigation and public utility purposes. Liquid-liquid extraction is certainly a well recognized method for the selective separation of metal ions from complex aqueous solutions because a great number of selective ligands are available which can be used as metal extractants. However, in most instances these ligands are often

quite expensive and their application on a large scale remains limited. Metal transport through supported liquid membranes is another potential possibility for the same purpose, but requiring rather small quantities of ligand (carrier) immobilized in the microporous polymeric film. The possibility of utilizing thin layers of organic solutions, immobilized on microporous inert supports interposed between two aqueous solutions, for removing selectively metal ions from a mixture was first proposed more than two decades ago¹⁻⁴. Such immobilized liquid layers, representing supported liquid membranes (SLM), have since then attracted the interest of a number of researchers⁵⁻⁸. The socio-economic benefits of using SLM technology, in place of conventional separation methods are manifold:

1. Since very small volume of the extractant is required, so highly selective expensive separations can be achieved with much reduced cost.
2. The separation sequence does not involve multi-state separations, hence it is not time

3. consuming.
3. Since, relatively higher feed/strip volume ratios can be achieved with a possibility of back flush more than 90% economy on chemicals is possible.
4. The membrane permeation reactor can easily be scaled-up with low capital and operating costs.
5. The process is gentle, non-destructive, environmental friendly and does not involve handling of large amounts of hazardous chemicals.

Modern electronic industry is responsible for disposing solid waste containing substantial amounts of metals, particularly silver in them. Moreover, pesticide industry is also adding Ag to the natural environment because many pesticidal preparations contain Ag and Hg in them (9). So, developing methodology of selectively removing/recovering silver from aqueous media is of importance.

Present work focuses on developing separation parameters and choosing membrane material for upgrading existing lab-scale model up to many gallons per day by using hollow fibre modules.

METHODOLOGY

Apparatus- The permeation cell used in this study is shown in Figure 1. It is made of Plexiglass and was fabricated in the KFUPM workshop. It has two compartments of equal volumes to house the solutions. The membranes of effective surface area 12.5 cm² were fixed amid the two compartments. No leakage was assured by fixing an O ring between the two compartments. Each chamber was mechanically stirred at variable speeds to eliminate the boundary layer resistance. For this purpose a multivariable power supply was used. All measurements were taken at 25°C.

Membranes

1,4,7,10,13,16 - Hexathiacyclooctadecane (Fluka) was used as membrane carrier. The organic solution was used as liquid membrane was prepared by mixing in an appropriate ratio, the carrier with 1-octanol, which was used as diluent. The hydrophobic organic phase forming liquid membrane was immobilized within the pores of Accural PP micro porous polypropylene film. The characteristics of the films are given below-

Table-1: Properties of support used

Membrane	Pore size (μm)	Thickness (μm)	Porosity (%)	Material
Accural PP2E	0.20	90	69	Polypropylene
Accural PP1E	0.10	75	57	Polypropylene

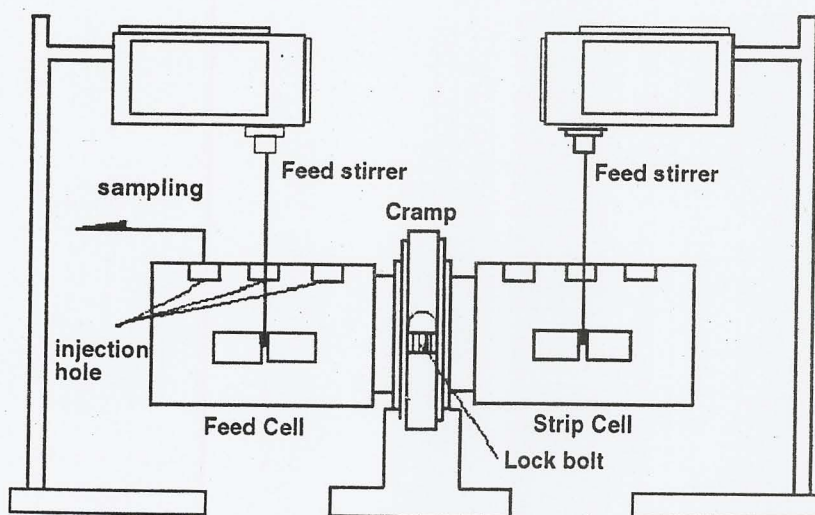
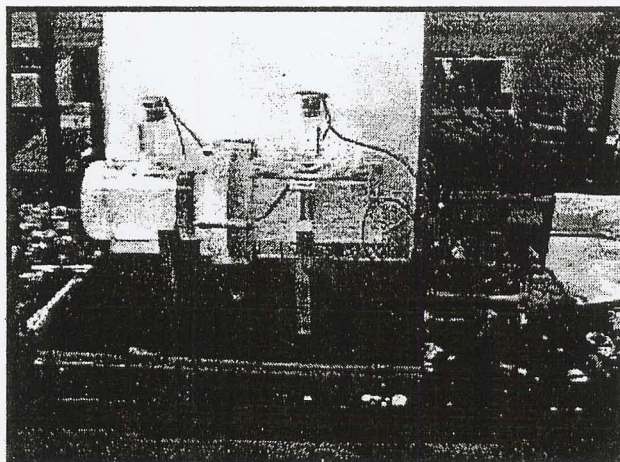


Figure 1. Schematic diagram of permeation cell



Picture of experimental set up used in current study

The polymer sheet was kept soaked in carrier solution for about 24 hours before use. All chemicals used were of AR grade. The Ag ion concentrations were determined by argentometric titrations. Flux (J) of metal ions was measured by using the following relationship;

$$J = \frac{V}{A} \frac{dC}{dt}$$

where V is the volume of feed solution, A the membrane area in contact with the aqueous solution and C is the concentration at any time t^{2-3} .

RESULTS AND DISCUSSION

Selectively in complexation by the macrocycles is primarily based on the hole-size cation diameter relationship, which means that the relative sizes of cation and molecular cavity of the ligand are matched. The process of ion-macrocycle association depends on several factors related to characteristic properties of the ligand, reacting ion and the solvent. Substitution of oxygen atoms by hetero atoms like sulphur gives host molecules different complexation properties. It is well known that Au^+ and Ag^+ ions have great affinity for thiols and thiones¹¹. Based upon this idea a thiocrown ether, hexathiacyclooctadecane ($C_{12}H_{24}S_6$) was selected to be impregnated in porous hydrophobic polypropylene sheets.

Based upon the nature of the carrier, a counter ion transport mechanism was expected. Silver nitrate was used in the feed solution with the

expectation that nitrate ion will act as counter ion. But a rapid decline in flux was observed and transport of silver ions was found to be almost stopped. Blower *et al*¹⁰ have reported complexes of Ag(I) with trithia-9-crown-3 and trithia-12-crown-3. They have shown that presence of aromatic nitrates increase complexation of Ag(I) with thia crowns. Based upon their work, dinitrophenol was added to the system to be used as counter ion. This resulted in significant increase in transportation of Ag ions across the membrane. Thus, it can be concluded that Ag ions make a sort of hydrophobic neutral complex with nitrophenol, which subsequently diffuses into the membrane phase. On the strip side thiosulphate ions was used as receptor for silver. The suitability and efficiency of thiosulphate ion on the strip side is well established and was not further explored¹². Natural pH was maintained on both sides of the membrane throughout the course of work.

Figure 2 shows the dependence of flux upon concentration of crown ether in the membrane for both types of PP films. It is clear that flux is high for PP2E version of PP film. This could be attributed to more thickness and higher porosity of Accural PP2E film. It is possible for more carrier molecules to occupy positions inside the membrane and thus, increase the throughput.

Figure 3 shows the dependence of counter ion concentration upon flux of silver ions through SLM. It seems that there is little change in flux with increasing concentration of DNP. Thus, an optimum concentration of 0.005 M was used throughout the experiments. Once again, PP2E film seems to show better flux throughput for silver ions.

Figure 4 depicts transportation of Ag ions through SLM with respect to time under standard

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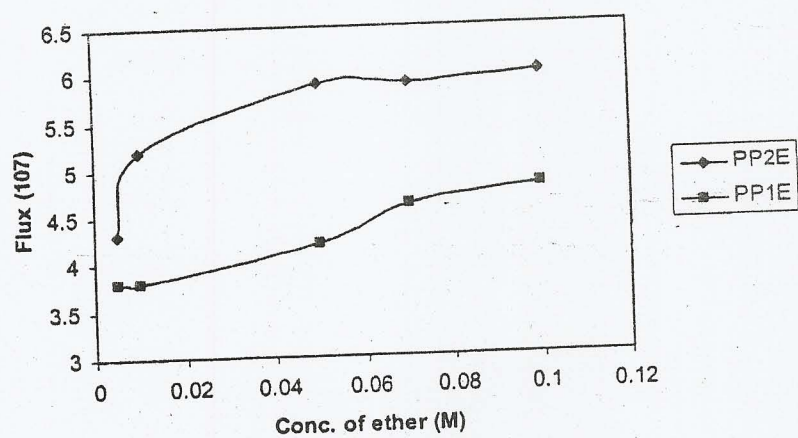


Figure 2

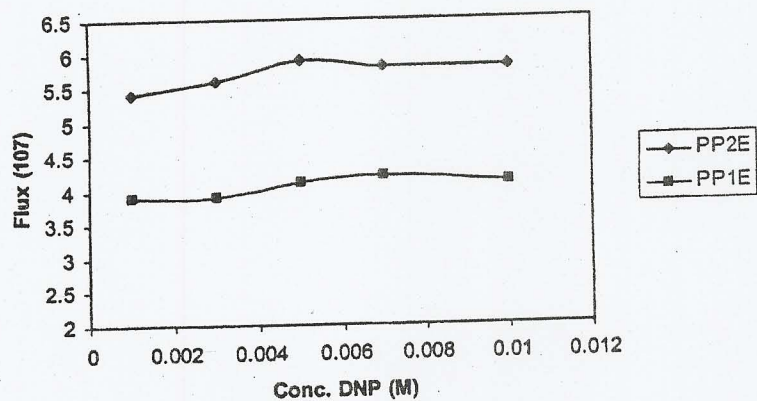


Figure 3

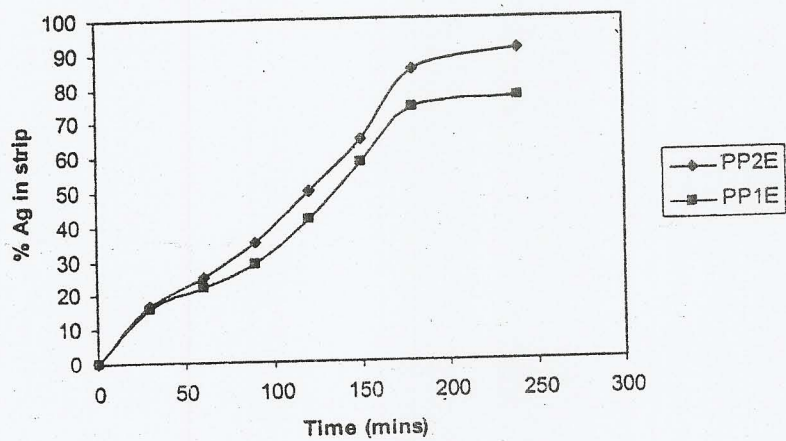


Figure 4

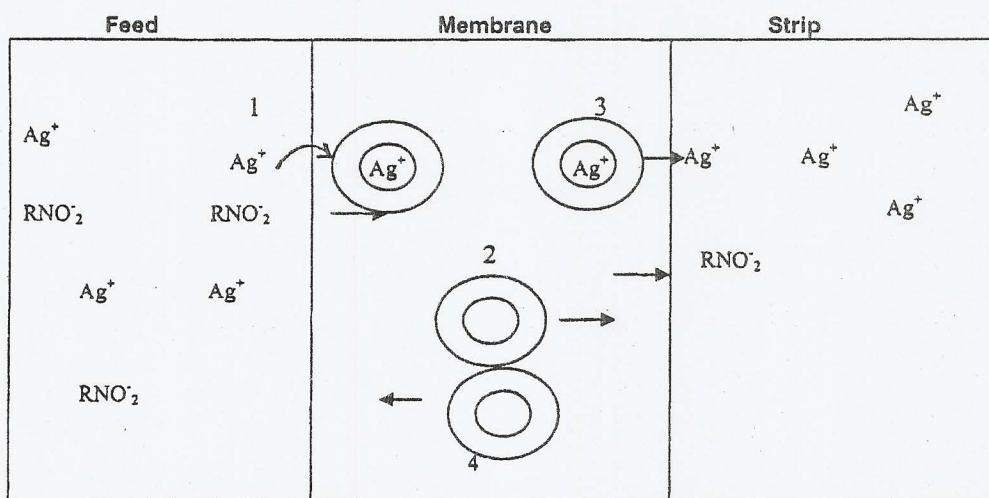


Figure 5. Liquid membrane illustrating the mechanism of carrier facilitated membrane transport of Ag(I) ions with accompanying nitrophenolate ions by macrocyclic carrier (large circle)

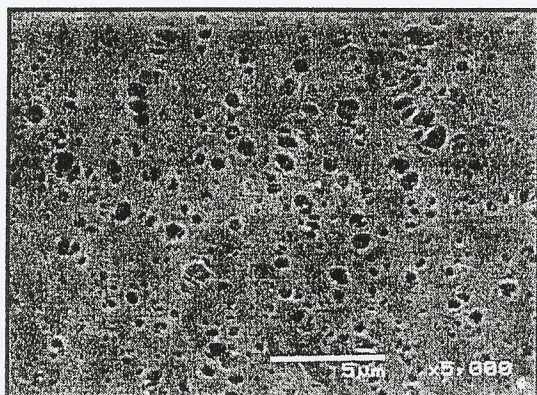


Figure 6. Scanning Electron Micrograph of Accural PP2E membrane

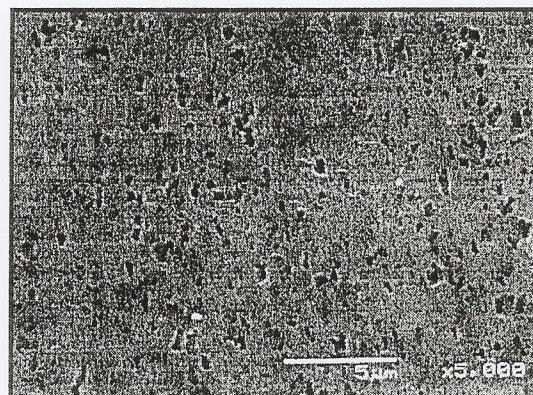


Figure 7. Scanning Electron Micrograph of Accural PP1E membrane

conditions. In about 4 hours time, more than 90% of total Ag in feed is transported to the strip side. For PP1E, it may take a little longer, but a steady rate is expected. It may be due to small pore size and possible clogging during hours of operation.

Normally, waste oozing out of industries contain large quantities of salts and suspended particulate matter. As a part of experimental design and limitation, only filtered wastes can be subjected to recovery with SLM technique. Above stated parameters were examined with different concentrations of various salts in the feed solution.

A closer look at Table 2 reveals that membrane is pretty selective. Little transport of Cr

ions may be due to closeness of ionic radii of both competing ions. Potassium ions may be an impurity in the sodium salt of thiosulphate being used as strip solution.

Table-2: Percentage of Ag ions transported in the presence of selected cations

Metal ion	% Transported	Material
Ag ⁺	90	PP2E
Cd ⁺⁺	BDL	PP2E
Pb ⁺⁺	BDL	PP2E
Cr ⁺⁺⁺	1.2	PP2E
K ⁺	2.8	PP2E

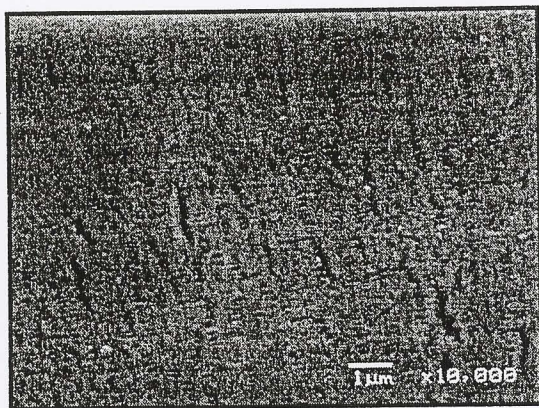


Figure 8. Scanning Electron Micrograph of PP1E membrane after being used for 24 hours

Mechanism of transportation

Figure 5 shows the mechanism of carrier facilitated membrane transport of silver ions with accompanying anions by macrocyclic crown carrier. The mobile carrier mechanism involves four steps; (1) the mobile carrier reacts rapidly with a silver ion at or near the membrane interface, and almost simultaneously an ion pair is formed

between the silver complex and the anion, (2) the carrier-ion pair diffuses through the membrane, (3) at the other interface (strip side) the cation and the anion both leave the carrier, and (4) the uncomplexed carrier diffuses back through the membrane and starts the cycle again.

Morphology of used membranes was studied by using scanning electron microscopy (Figure 6, 7 and 8). The microscopes consisted of elongated slits, arranged in rows. Both sides of each specimen were examined and their appearances were similar. The size and distribution of pores changes considerably over the surface of the membrane. Surface texture of PP2E membrane showed more consistency and stability in structure as compared to PP1E. This can be attributed to higher thickness and porosity of the former. Decline in flux, in case of PP1E can be attributed to pore clogging, a physical evidence of which is shown in the SEM. Some cracks can also be seen after prolonged use of the membrane.

It is, hence, concluded that in order to upgrade the lab-scale model to hollow fibre modules, PP2E should be the preferred material. In addition to that, models made for Ag(I) will be applied to Au(I) as well by using different derivatives of crown ethers. Work in these directions is underway.

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