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## The selective transport of mercury ion through a bulk liquid membrane by 18C 6 and 2-(4-choloro phenyl)-2,3-dihydroquinazoline(1H)-4-one (CPHQO) as counter ion

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### ABSTRACT

*In this work carrier-facilitated transport of mercury(II) against its concentration gradient from aqueous 0.04 M hydrochloric acid solution across a liquid membrane containing 2-(4-Choloro Phenyl) – 2,3 Di Hydro Qinzoline (1- H) – 4 one (CPHQO) as the mobile carrier in chloroform has been investigated. Sodium thiocyanate solution (1.6 M) was the most efficient receiving phase agent among several aqueous reagents tested. Various parameters such as investigated. Under optimum conditions the transport of Hg(II) across the liquid membrane is more than 97% after 2.5 h. The carrier, BHIS, selectively and efficiently could able to transport Hg (II) ions in the presence of other associated metal ions in binary system.*

**Keywords:** bulk liquid membrane; mercury (II) ion; 2-(4-Choloro Phenyl) – 2,3 Di Hydro Qinzoline (1- H) – 4 one (CPHQO).

### INTRODUCTION

Mercury is one of the most abundant heavy metals in the environment, and its toxic effects have been recognized for a long time. The mercury content of air, soil and water has been increasing in the past decades, because of the greater utilization of fossil fuels and for the expanded use in industry and agriculture. Due to its dangerous and harmful properties for the health of human being, the determination of mercury is very important for environmental protection [1]. A wide range of analytical methods have been used for the determination of mercury in real samples. These includes spectrophotometry [2], graphite – furnace atomic absorption spectrometry (GFAAS) [3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4], high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [5], Cloud point extraction [6], anodic stripping voltammetry [7], X-ray fluorescence spectrometry [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], electro thermal atomic absorption spectrometry [10], atomic flurescence spectrometry [11] and cold vaper atomic absorption spectrometry [12]. Numerous extraction and separation methods for mercury determination have been developed [13,14]. Liquid membrane transport mediated with a mobile carrier has been proposed as a promising technology for separation and purification of various metal ions. Liquid membranes (liquid phases), existing in either supported or unsupported

form, serve as selective barriers between liquid or gas phases and have shown great potential and application in separations.

Selective transport of cationic substrates by membrane carriers is of great importance in chemistry, biology, and separation sciences. Compared with conventional separation processes such as liquid–liquid extraction, membrane techniques are characterized by the technical simplicity and high efficiency in separating or enriching material from gaseous or liquid mixtures. Also, these methods reduce the solvent inventory requirements and also allows the use of expensive and highly selective extractant which otherwise would be uneconomic in solvent extractions.

Bulk liquid membrane (BLM) is one of the simple, lowest and efficient types of liquid membranes [15,16]. In this technique similar to liquid membrane configurations, (viz ion transport across membranes) combine the extraction, diffusion, and back extraction of analytes are particularly drawing maximum attention [17]. BLM constitute the cheapest separation techniques because of their relatively small inventory and low capital cost.

In a BLM, a relatively thick layer of immiscible fluid is used to separate the source and receiving phase. There is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility. A recent development in liquid membranes is the incorporation of selective carriers within the liquid membrane phase which selectivity and efficiency via chemical reaction facilitate the transport of a specific compound across the membrane.

Carrier mediated transport through liquid membrane is well known as one of the most powerful tools for such concentration, separation and recovery of target compound. The selective transport of metal ions across a membrane is known to play an essential role in many biological processes [18]. There has been a growing interest in the transport of metal ions mediated by receptor molecules where the carrier operates selective across artificial or biological membranes.

In this regard, there has been considerable interest in the use of proton ionizable carriers for the transport of metal cations between two aqueous solutions through an organic membrane [19]. These pH-regulated ligands described until now present the fact that transfer of the counter-anion from the aqueous phase into the organic medium is avoided. Such chelating agents do not involve concomitant transfer of one or more aqueous phase anions into the organic medium. This factor was of immense importance to potential applications in which hard aqueous phase anions such as chloride, nitrate and sulfate would be involved.

Transport of mercury through liquid membranes using various carriers such as polybutadiene [20]. triisobutylphosphate (TBP) [21]. 18-crown-6 and 21-crown-7 [22]. bis (di (2-ethylhexyloxy)) thiophosphoryl disulfide. have been carried out. The present paper describes the use of 2-(4-Choloro Phenyl) – 2,3 Di Hydro Qinazoline (1- H) – 4 one (CPHQO) [22]. as a selective neutral carrier for  $Hg^{2+}$  ion transport through a bulk liquid membrane. For this purpose the influence of effective parameters such as stirring rate, concentration of HCl in the source phase, concentration of NaSCN in the receiving phase, concentration of CPHQO in the membrane and contact time was optimized.

## MATERIALS AND METHODS

### Reagents

A stock solution of Hg (II) was prepared by dissolving an appropriate and accurately amount of mercuric chloride of analytical reagent grade in 1% (v/v) HCl solution. The working standard solution was prepared by further diluting the stock solution with doubly distilled deionized water.  $SnCl_2$  and Nitrate salts of all other cations used were of the analytical grade and used without further purification. Doubly distilled deionized water was used throughout. Extra pure chloroform purchased from Merck was used as organic phase. (Merck E. Dermstant Germany).

### Synthesis of 2-(4-choloro Phenyl) -2,3 Di Hydro Qinazoline (1 H)- 4 one (CDHQO)

A mixture of isatoic anhydride (1 mmol), 4- choloro benzaldehyde (1 mmol), and ammonium acetate or primary amine (1.1 mmol) in ethanol (5mL) was added silica-bonded N-propylsulfamic acid (0.1 g) and heated at  $80^{\circ}C$  in an oil bath. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and remaining washed with warm ethanol (2-5 mL). After cooling, the corresponding 2,3-dihydroquinazolinone products were obtained which purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for

subsequent runs. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (1:3)] to give pure 2-(4-chloro Phenyl) -2,3 Di Hydro Qinazoline (1 H)- 4 one (CPHQO) in 90% yield, fig. 1, was synthesized according to literature[23].

Mp: 206-208 °C (Lit. 198-200 °C)

$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  : 5.77 (s, 1H), 6.68 (dt, 1H,  $J_1=7.4$  Hz,  $J_2=0.5$  Hz), 6.75 (d, 1H,  $J=8.1$  Hz), 7.15 (s, 1H), 7.25 (dt, 1H,  $J_1=7.8$  Hz,  $J_2=1.5$  Hz), 7.46 (d, 2H,  $J_1=8.6$  Hz), 7.51 (d, 2H,  $J=8.8$  Hz), 7.61 (dd, 1H,  $J_1=7.8$  Hz,  $J_2=1.7$  Hz), 8.34 (s, 1H).

$^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz): 65.7, 114.4, 114.9, 117.3, 127.3, 128.3, 128.7, 132.9, 133.9, 140.6, 147.6, 163.5.  
IR (KBr) ( $\text{cm}^{-1}$ ): 3270, 3125, 1650, 1600, 1505, 1485, 1427, 1378, 1485, 1147, 1094, 1008, 827, 796, 750, 662, 500.

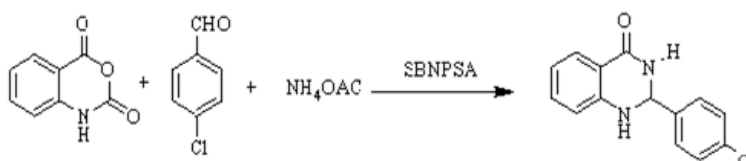


Fig.1: ligand 2-(4-Choloro Phenyl) – 2,3 Di Hydro Qinazoline (1- H) – 4 one (CPHQO)

### Apparatus

The determination of mercury content was carried out with a Shimadzu AA-680 atomic absorption spectrometer equipped with an Hg-hollow cathode lamp (HCL) and an on-line cold vapor generation system using  $\text{SnCl}_2$ . A long path quartz cell (2 cm i.d., 10 cm long) connected to the spectrometer was used as a detection system. A digital pH meter, Metrohm model 632 equipped with a combined glass calomel electrode was used for the pH adjustments. A bulk type liquid membrane cell [24]. (Figure 1) was used in this study. All conductance measurements were carried out with a Metrohm 712 conductivity meter with a dip-type conductivity cell made of platinum black.

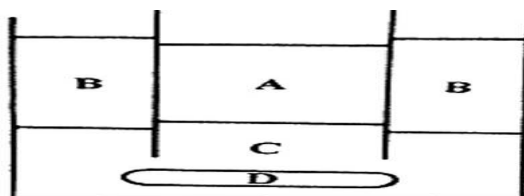


Figure 1. Representation of the bulk type liquid membrane cell used, (A) source phase; (B) receiving phase; (C) membrane phase; (D) magnetic stirrer

### Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (Figure 1) (inside diameter, 4.0 cm) holding a glass tube (inside diameter, 2.0 cm) which separates the two aqueous phases, was used. The inner aqueous phase (source phase, SP) contained mercuric chloride (5 mL,  $2.0 \times 10^{-5}$  M) and 0.04 M hydrochloric acid, while the outer aqueous phase (receiving phase, RP) contained sodium thiocyanate (10 mL, 1.6 M). The membranes phase (MP) is comprised of 20 mL of  $6.0 \times 10^{-3}$  M CPHQO in chloroform below these aqueous phases and bridged the two aqueous phases. The organic layer was magnetically stirred by a Teflon-coated magnetic bar ( $2.0 \times 5$  cm, diameter). Under these conditions, while is the mixing process perfect, the interfaces between the organic membrane and the two aqueous phases remained flat and well defined. Determination of the mercury ion concentration in both aqueous phases was carried out by CV-AAS. A similar transport experiment was carried out in the absence of the carrier for reference.

### Pretreatment and Analysis of Real Samples

The amalgam and omega3 tablet samples were treated according to a reported procedure [25]. blood Radiology wastewater and Natural water samples were prepared as we previously reported [26, 27]. The procedure applied to each sample.

## RESULTS AND DISCUSSION

CPHQO as a sulfur containing ligand is insoluble in water. Due to the existence of four donating sulfur atoms in the flexible structure of CPHQO based on the well known hard-soft acid–base theory [28-30], it was expected that the stability of its complex with  $\text{Hg}^{2+}$  ion be higher than the other ions including alkali, alkaline earth and many transition and heavy metal ions.

### Conductometric investigation of complexation of $\text{Hg}^{2+}$ ion with CPHQO.

In preliminary experiments in order to obtain useful information about the stoichiometry and stability of the complexation of CPHQO with  $\text{Hg}^{2+}$  ion, the system was investigated conductometrically in acetonitrile solution. It is obvious from Figure 2 that a distinct inflection point at L/ $\text{Hg}^{2+}$  molar ratio of 1:1 were occurred. The obtained stability constant for Hg-CPHQO complex using KINFIT program is  $7.94 \times 10^{-5}$ .

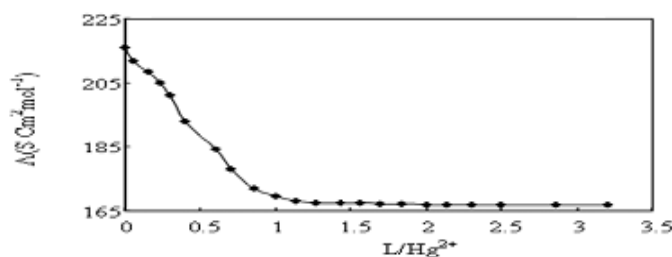


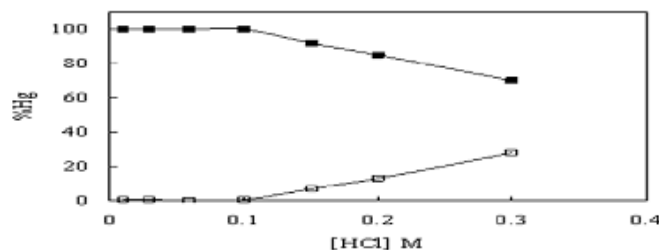
Figure 2. Mole ratio plot of conductometric titration of  $\text{Hg}^{2+}$  (0.002 mM) with CPHQO in acetonitrile solution at  $T=25 \pm 0.1$

### Influence of condition of source phase on $\text{Hg}^{2+}$ ion transport

Most chelating ligands are conjugate bases of weak acid groups and accordingly, have a very strong affinity for hydrogen ions. Therefore the pH, play an important role in the complexation of metal ions by chelation. The pH will determine the values of the conditional stability constants of the complexes of metal ions with a desired ligand. Due to the presence of a sulfur atom in the structure of CPHQO it is expected that the of its complexation ability is sensitive to pH.

It was expected that the efficiency of transport at higher pH values (>2.0) due to the formation of  $\text{Hg}(\text{OH})_2(\text{s})$  precipitate (white precipitate) at top of the chloroform between the source and membrane phases has been reduced. Therefore the source phase must be acidic.

The effect of the presence of 0.1 M of different acids including picric acid, HCl,  $\text{HClO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  in the source phase on the transport of  $\text{Hg}^{2+}$  ion was studied and it was observed that the maximum transport occurs in the presence of 0.1 M HCl. It was found that nitrate ion is not a suitable counter anion to accompany the  $\text{Hg}^{2+}$ -CPHQO complex into the organic phase and only 30% of  $\text{Hg}^{2+}$  ions was transported into the receiving phase in a long time. The transport efficiency was increased to 45% in the presence of perchlorate ion (4 h) in source phase, while addition of picric acid to the source phase increase the transport efficiency of  $\text{Hg}^{2+}$  but not quantitatively. In the presence of hydrochloric acid in the source the percentage of  $\text{Hg}^{2+}$  ion transported to receiving phase quantitatively was increased. The transport efficiency of  $\text{Hg}^{2+}$  ion was also found to be dependent on the concentration of HCl in the SP (Figure 3). Maximum transport occurs at HCl concentration range of 0.01-0.1 M, while further transport studies of  $\text{Hg}^{2+}$  ion was carried out at 0.04 M HCl. At higher HCl concentrations there was a decrease in the percentage of transport of  $\text{Hg}^{2+}$  ion, probably due to the competition of  $\text{H}^+$  with  $\text{Hg}^{2+}$  ion for binding to CPHQO and competition of chloride ion with CPHQO for complexation with  $\text{Hg}^{2+}$  ion. The efficiency of transport decreases at lower HCl concentrations, probably due to hydrolysis of  $\text{Hg}^{2+}$  ion.



**Figure 3.** Effect of HCl concentration in the source solution on the mercury transport: (■)transported in to receiving phase, (□) remaining in source phase. Conditions:  $\text{Hg}^{2+}$ ,  $2.0 \times 10^{-5}$  M; different concentration of HCl in source phase; CPHQO;  $6.0 \times 10^{-3}$  M in membrane phase and 1.6 M of  $\text{SCN}^-$  in receiving phase after 2.5 h

The preferential binding of sulfur containing ligands towards  $\text{Hg}^{2+}$  ion has been reported in the literature [31,32]. The influence of the concentration of CPHQO in the organic phase on the transport efficiency of  $\text{Hg}^{2+}$  ion was studied. It was seen that the percentage of transport of  $\text{Hg}^{2+}$  ion increases with an increase in CPHQO concentration in the organic phase. Maximum transport occurs at concentration range of 0.5 mM-0.04 M CPHQO. A further excess of the carrier had no considerable effect on the transport efficiency. Thus, a concentration of 6.0 mM of CPHQO was adopted for further studies. This is most probably due to the fixed stoichiometry of the resultant 1:1 carrier-  $\text{Hg}^{2+}$  ion complex.

#### Effect of receiving phase agent

The nature and composition of the receiving phase was found to have a dramatic influence on the  $\text{Hg}^{2+}$  ion transport. Preliminary experiments revealed that the nature and composition of the receiving phase could have a significant effect on the efficiency and selectivity of transport. Among different receiving agents used such as hydrochloric acid, hydrobromic acid, bromide, thiosulfate, sulfuric acid, nitric acid, EDTA and thiocyanate,  $\text{SCN}^-$  ion with increased complexing ability towards  $\text{Hg}^{2+}$  ion acts as the most suitable receiver for the release of cation from the membrane phase into the receiving phase.

#### Effect of receiving phase agent

The influence of the concentration of KSCN in the receiving phase on the transport efficiency of  $\text{Hg}^{2+}$  ion was also investigated and the results are shown in Figure 4. As is obvious, while only 20%  $\text{Hg}^{2+}$  ion transport occurs in the absence of the receiving agent, the transport of  $\text{Hg}^{2+}$  ion increases sharply with increasing the concentration of KSCN. Quantitative transport of  $\text{Hg}^{2+}$  ion occurs at a 1.6 M of the receiving agent.

The  $\text{Hg}^{2+}$  ions form a complex with a deprotonated ionophore to be extracted from the source phase into the membrane phase. The thiocyanate plays an essential role in the metal ion releasing process in the receiving phase via the formation of a ternary ligand-metal-thiocyanate complex which has been reported by other researchers. [33-35]. This co-operation probably assists the selective releasing of  $\text{Hg}^{2+}$  ion to the receiving phase, which lead to increase in the percentage of transported  $\text{Hg}^{2+}$  ion. Such a ternary complex has already been recognized as being an important transient species in biological transports [36].

The mechanism of transport in the presence of this carrier could be related to the rapid complex formation and exchange of ions at the membrane interface. In the membrane and receiving phase interface exchange of ligand with thiocyanate for formation of  $\text{Hg}(\text{SCN})_4^{2-}$  take place. Based on the overall stability constant ( $\text{Log } \beta_4$ ) of  $\text{Hg}^{2+}$  ion complexes with respect to  $\text{SCN}^-$ , and  $\text{Cl}^-$  as  $(\text{Hg}(\text{SCN})_4)^{2-}$ ,  $\text{HgCl}_4^{2-}$  : 20.9 and 15.1, [37,38]. one may notice that this is consistent with the selectivity order of described procedure. As is known use of thiocyanate ion as a receiving agent effectively avoids the formation of  $\text{Hg}(\text{OH})_2(\text{s})$  precipitate. Consequently, this compound was used as a receiving phase agent in our later transport experiments.

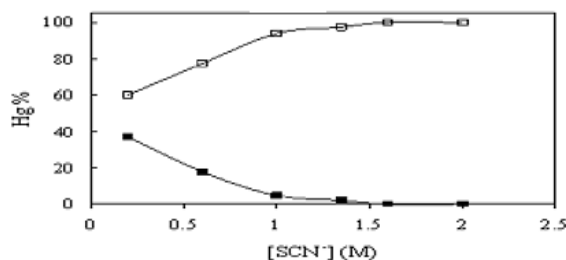


Figure 4. Effect of sodium thiocyanate concentration in the receiving phase solution on the mercury transport: (□) transported into receiving phase, (■) remaining in source. Conditions:  $\text{Hg}^{2+}$ ,  $2.0 \times 10^{-5}$  M; HCl 0.04 M in source phase; CPHQO  $6.0 \times 10^{-3}$  M in membrane phase and various concentration of  $\text{SCN}^-$  in receiving phase, after 2.5 h

### Influence of stirring rate

The effect of stirring speed on  $\text{Hg}^{2+}$  ion transport through bulk liquid membrane was investigated. The effect of stirring rate of organic phase in the range of 50–500 rpm on the  $\text{Hg}^{2+}$  ion transport efficiency was also studied. The results revealed that replicate transport occur in the stirring rate about 300 rpm. The experimental data indicate that beyond 300 rpm the flux of  $\text{Hg}^{2+}$  ions through the bulk liquid membrane becomes independent of the stirring rate. In receiving phase rate of 300 rpm the thickness of the aqueous diffusion films reaches a constant limiting value. Consequently, all subsequent experiments were carried out at a stirring rate of 300 rpm in the source and receiving phase solutions.

### Selectivity

The selectivity of the membrane system in tertiary mixture was studied at optimum conditions for the transport of  $\text{Hg}^{2+}$  ion with respect to other cations which were initially present with in equimolar concentrations. Table 1 shows the percentage of cations transported into receiving phase and remained in source phase. High stability constant of  $\text{Hg}^{2+}$  ion with CPHQO and thiocyanate ion in membrane and receiving phase largely improved the method selectivity. The observed selectivity pattern toward  $\text{Hg}^{2+}$  ion is due to the high tendency of the cation, as a soft acid, towards donating sulfur atoms of the carrier as soft bases.

Table 1. Amount of cation transported from different cation mixtures through the BLM

Percentage transported	Mixture	Percentage transported	Mixture
98/0	$\text{Hg}^{2+}$	98/0	$\text{Hg}^{2+}$
0/0	$\text{Co}^{2+}$	0/0	$\text{Pb}^{2+}$
0/0	$\text{Ni}^{2+}$	0/0	$\text{Cd}^{2+}$
97/0	$\text{Hg}^{2+}$	98/0	$\text{Hg}^{2+}$
1/0	$\text{Cu}^{2+}$	0/0	$\text{Cr}^{3+}$
0/0	$\text{Zn}^{2+}$	0/0	$\text{Tl}^+$
12/0	$\text{Ag}^+$	4/0	$\text{Fe}^{3+}$

<sup>a</sup>Conditions: source solution, 5 mL of  $2.0 \times 10^{-5}$  M  $\text{Hg}^{2+}$ ,  $2.0 \times 10^{-5}$  M of other cations and 0.04 M HCl in source phase 0.006 M CPHQO in Membrane and 1.6 M  $\text{SCN}^-$  in receiving phase.

### Accuracy and Analytical applications

The proposed optical sensor was found to work well under laboratory conditions. To test the practical application of the present sensor, the amalgam and omega3 tablet samples spiked with different amounts of mercury ions were measured by the proposed transport (Table 2). The mercury content of blood Radiology wastewater and Natural water samples were analyzed by standard addition method and then determined by the proposed transport (table 3).

Table 2. Results of mercury (II) ion determination in amalgam and omega3 tablet samples (N=3)

Ion	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	RSD %	Recovery %
Radiology wastewater				
Hg	0	0.17	1.6	---
	0.5	0.66	1.2	98.4
Amalgam				
Hg	0	0.4	1.2	---
	0.5	0.9	0.9	102.1

Table3. Results of mercury (II) ion determination in blood Radiology wastewater and Natural water samples (N=3)

Ion	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	RSD %	Recovery %
Blood				
Hg	0	0.02	1.2	---
	10	0.13	0.9	100.6
Radiology wastewater				
Hg	0	0.04	1.5	---
	10	0.07	1.2	99.0
Natural water				
Hg	0	0.5	1.2	---
	10	1.4	1.1	101.2

### CONCLUSION

The recommended mechanism for the transport of  $\text{Hg}^{2+}$  ion through bulk liquid membrane, which operated in this study, is shown schematically in Figure 6. Movement of the charged species through the hydrophobic organic membrane is accomplished by the presence of host carrier CPHQO ion paired with chloride as a suitable counter anion. The chloride ion not only neutralizes the charged  $\text{Hg}^{2+}$ -CPHQO complex but also induces a more lipophilic character to the mercury complex so that it can be readily extracted into the membrane phase. After complexation of  $\text{Hg}^{2+}$  ion with carrier on the source side of the membrane, the complex diffuses down its concentration gradient [39-41]. On the receiving side of the membrane, the metal ion is released into the receiving phase via formation of a ternary complex (carrier- $\text{Hg}^{2+}$ -SCN). Then the free carrier diffuses back across the membrane and cycle starts again. The net result is the transport of  $\text{Hg}^{2+}$  ion from the aqueous source phase to the aqueous receiving phase across the BLM.

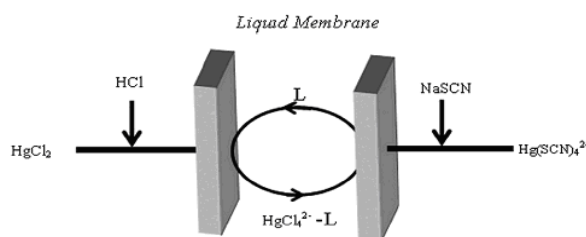


Figure 6. Transport mechanism of Mercury through BLM process

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