

## Performance of hollow fiber supported liquid membrane on the extraction of mercury(II) ions

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**Abstract**—The extraction and recovery or stripping of mercury ions from chloride media using microporous hydrophobic hollow fiber supported liquid membranes (HFSLM) has been studied. Tri-n-octylamine (TOA) dissolved in kerosene was used as an extractant. Sodium hydroxide was used as a stripping solution. The transport system was studied as a function of several variables: the concentration of hydrochloric acid in the feed solution, the concentration of TOA in the liquid membrane, the concentration of sodium hydroxide in the stripping solution, the concentration of mercury ions in the feed solution and the flow rates of both feed and stripping solutions. The results indicated that the maximum percentages of the extraction and recovery of mercury ions of 100% and 97% were achieved at the concentration of hydrochloric acid in the feed solution of 0.1 mol/l, the concentration of TOA at 3% v/v, the concentration of sodium hydroxide at 0.5 mol/l and the flow rates of the feed and stripping solutions of 100 ml/min. However, the concentration of mercury ions from 1-100 ppm in the feed solution had no effect on the percentages of extraction and recovery of mercury ions. Thus, these results have identified that the hollow fiber supported liquid membrane process has high efficiency on both the extraction and recovery of mercury (II) ions. Moreover, the mass transfer coefficients of the aqueous phase ( $k_a$ ) and membrane or organic phase ( $k_m$ ) were calculated. The mass transfer coefficients of the aqueous phase and organic phase are 0.42 and 1.67 cm/s, respectively. The mass transfer coefficient of the organic phase is higher than that of the aqueous phase. Therefore, the mass transfer controlling step is the diffusion of the mercury ions through the film layer between the feed solution and the liquid membrane.

Key words: Mercury, Extraction, Liquid Membrane, Hollow Fiber, Mass Transfer

### INTRODUCTION

Natural water contamination is of great concern worldwide. As water passes over soil in its natural cycle, it carries sediments and mineral deposits. Soil and rocks erode over time and release more minerals into the water. Sediments of soil erosion include some harmless minerals like calcium, magnesium, and potassium, but the more worrisome soil deposits contain heavy metals. Mercury is unique among metals because of its ability to evaporate in soil or water. The most common source of mercury in surface and underground water is natural erosion of soil and ore deposits, runoff from factories and refineries [1]. Mercury is extremely toxic to the body. Short-term exposure to mercury in water results in kidney damage, while a lifetime of exposure can lead to impairments in neurological functioning, which is especially harmful to children.

In a membrane-separation process, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier or membrane through which one or more species move faster than another or other species, where the feed mixture is separated into a retentate (a part of the feed that does not pass through the membrane) and a permeate (a part of the feed that does pass through the membrane). Although the feed, retentate, and

permeate are usually liquid or gas, they may also be solid. The liquid membrane is a hydrometallurgical process for metal recovery from aqueous solutions and seems to be a promising approach due to the selectivity and the facilitated transportation of the desired metal [2]. The simultaneous extraction and stripping operation of the liquid membrane system is very special. Metal ions can move from low to high concentration solutions by facilitated transport. The liquid membrane, which is supported by hollow fibers (supported liquid membrane), has been applied to the recovery of valuable metals as well as fermentation products [3,4] pollutants [5,6] pharmaceutical products [7,8] due to the advantage of accomplishing the extraction and stripping operation with very high enrichment factors in a single stage.

The presence of metal ions in the environment is a major concern due to their toxicity to many life forms. For this reason, the separation of metal ions from solution is of great interest in hydrometallurgical processes for recovering the metal values, as well as abating the environmental pollution problems. This separation can be achieved by liquid membrane systems that have been widely applied to the extraction and recovery of metal ions from solutions [9,10]. The simultaneous extraction and stripping operation is very efficient because metal ions can move from low to high concentration solutions. The membranes contain an extractant or a carrier which possesses the potential for selective permeation by using the facilitated transport mechanism [11,12]. This technique has been

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widely applied to the extraction and recovery of metal ions. One promising technique for liquid membrane is the use of microporous hollow fiber modules as liquid-liquid phase contactors: a new type of liquid membrane configuration, the membrane contactor [13], with the potential to eliminate the shortcomings of supported liquid membranes whilst retaining its advantages is gaining in importance. It has been applied to a large variety of systems including the extraction of fermentation products [3,4,14], pollutants [5,6] pharmaceutical products [7,8], rare earth metals [15-18], heavy metals [18-20] and radioactive metals [21]. The basic principle of the hollow fiber supported liquid membrane (HFSLM) is the immobilization of organic extractant into the pores of a hydrophobic membrane [22,23].

The potential advantages of HFSLMs over traditional separation techniques are as follows: lower capital and operating costs, low energy and low extractant consumption factors and high fluxes compared to solid membranes [23,24]. Due to these advantages, SLMs may be extremely useful for the recovery of metals from the solutions.

In this paper, an HFSLM using TOA as a mobile carrier was studied for the separation of mercury ions from a dilute feed solution and on the modeling of this process. A model, which describes the transport mechanism, was presented. The effect of TOA concentration on the permeability coefficient ( $P$ ) was studied and the mass transfer coefficients of the aqueous phase ( $k_a$ ) and the organic phase ( $k_m$ ) were calculated by this model. In addition, the rate-controlling step was found.

## THEORY

### 1. Liquid Membrane Mechanism for Separation of Mercury Ions

The liquid membrane consists of an organic solution of an extractant. The mechanism which transports the mercury ions through the liquid membrane is schematically illustrated in Fig. 1. The liquid membrane is between the aqueous solution initially containing mercury ions (feed solution) and the aqueous solution initially containing no mercury ions (stripping solution). Transportation of ions results from the driving force between the opposite sides of the aqueous phase. In this experiment, co-transportation [12,22] occurred.

Because of the  $\text{HgCl}_2$  in the presence of higher hydrochloric

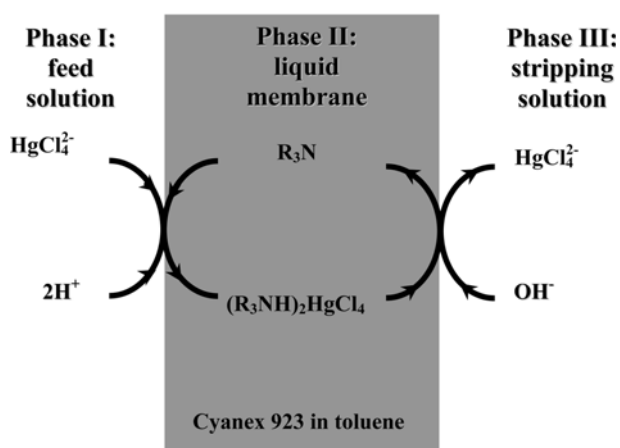


Fig. 1. Co-transport scheme for basic extractant.

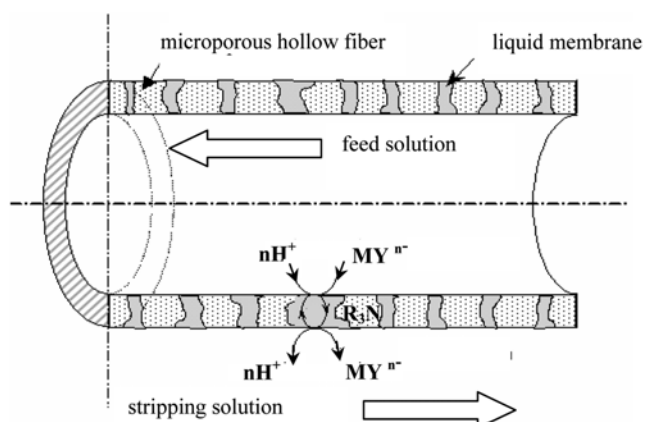
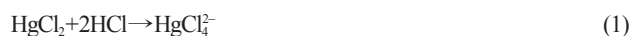


Fig. 2. Flow pattern in a hollow fiber supported liquid membrane.

concentration in  $\text{HgCl}_4^{2-}$  type species will result as shown in Eq. (1):



Mercury ions in an acid solution will form anion species, which is extractable into the organic phase.  $\text{Hg}^{2+}$  ions in hydrochloric acid can be extracted as shown in Eq. (2).



In the presence of sodium hydroxide in the stripping phase, the reaction on the stripping of  $\text{Hg}^{2+}$  side membrane will be as follows in Eq. (3):



An example of the extraction and stripping processes is schematically illustrated in Fig. 1. This occurred in a hollow fiber module as shown in Fig. 2. Inside, the hollow fiber module consists of a liquid membrane and two more sides for aqueous solutions. The liquid membrane is trapped in a hydrophobic micropore and this liquid membrane separates the feed and stripping solutions. The feed solution and the stripping solution flow counter-currently, and the liquid membrane is between them. In this case, the carrier is made up of a basic extractant. The transport mechanism of metal ions that occurs in this case is called co-transport and is depicted in Fig. 1 where the metal ions must be in anion complex form [12].

### 2. The Extraction Equilibrium

When the concentration of TOA is at 3% v/v the bulk of mercury ions can be extracted. From the extract ion reaction described in Eq. (4), the extraction equilibrium constant ( $K_{ex}$ ) of mercury (II) ions can be expressed by the following equation:

$$K = \frac{[(\text{R}_3\text{NH})_2\text{HgCl}_4]}{[\text{HgCl}_4^{2-}][\text{H}^+]^2[\text{R}_3\text{N}]^2} \quad (4)$$

The distribution ratio for mercury,  $D$  is given by:

$$D = \frac{[(\text{R}_3\text{NH})_2\text{HgCl}_4]}{[\text{HgCl}_4^{2-}]} \quad (5)$$

Rearrangement to give the distribution ratio variation as a function of the extraction equilibrium constant ( $K_{ex}$ ) becomes

$$D = K_{ex} [H^+]^2 [R_3 N]^2 \quad (6)$$

The equilibrium constant ( $K_{ex}$ ) of mercury (II) ions extracted with TOA was derived from the experimental data and could be calculated from Eq. (4). Whereas, the value of  $K_{ex}$  was found to be  $1.34 \times 10^5$  (L/mol)<sup>4</sup>.

### 3. Determining the Permeability Coefficients

In considering linear concentration gradients, fast interfacial reactions and the distribution ratio of metal ions between the feed phase and the membrane phase is much higher than that between the membrane phase and the stripping phase. Thus, the final equation obtained for permeability could be expressed as that suggested by Danesi [25]:

$$V_f \ln \left( \frac{C_f}{C_{f,0}} \right) = -AP \frac{\phi}{\phi+1} t \quad (7)$$

$\phi$  is given by a modified form

$$\phi = \frac{Q_f}{PL \varepsilon \pi N r_i} \quad (8)$$

where the unit of the permeability coefficient,  $P$ , is cm/s and that of the mercury ion concentration at time  $t$  and 0,  $C_f$  and  $C_{f,0}$ , are M (mol/l), then the units of the effective areas of the membrane,  $A$  are cm<sup>2</sup>. Normally,  $\pi$  is treated as a constant (3.1416) for which the volume of the feed,  $V_f$ , is cm<sup>3</sup>. This also provides the volumetric flow rate of the feed solution,  $Q_f$ , that flows through the tube side, with a result of cm<sup>3</sup>/s. For the plot  $V_f \ln(C_f/C_{f,0}) = f(t)$ , the following restrictions apply to Eq. (7):  $-AP(\phi/\phi+1)$  is the slope and the value for  $P$  can be obtained by analytical calculation. The length of the fiber ( $L$ ) and the internal radius of hollow fiber ( $r_i$ ) are in cm. The porosity of the hollow fiber,  $\varepsilon$ , is percent. Note that the number of hollow fibers in the module,  $N$ , does not have units.

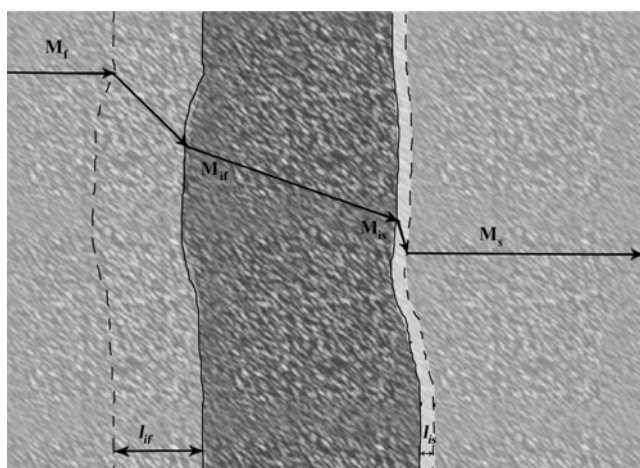


Fig. 3. Schematic representation of mercury transport through a liquid membrane.  $M_f$  is the concentration of mercury ions in the feed solution,  $M_{if}$  is the concentration of mercury ions of the feed solution-liquid membrane interface,  $M_{is}$  is the concentration of mercury ions of the liquid membrane-stripping solution interface and  $M_s$  is the concentration of mercury ions in the stripping solution.  $l_{if}$  is thickness of aqueous film in the feed phase.  $l_{is}$  is thickness of the aqueous film in the stripping phase. The units of  $l_{if}$  and  $l_{is}$ , are cm.  $M_f$ ,  $M_{if}$ ,  $M_{is}$  and  $M_s$  have the same unit in M (mol/l).

### 4. Mass Transfer Modeling and Mass Transfer Coefficient Determination

The mathematical mass transfer model of the hollow fiber supported liquid membrane for the separation of mercury ions uses the mercury permeability coefficient ( $P$ ) to determine other coefficients. The mercury permeability coefficient depends on the three steps of mass transfer resistance [26], as shown in Fig. 3, which are as follows:

(1) Metal ions transfer from the concentration layer of the feed solution to the interface between the feed and the membrane phases.

(2) Metal ions transfer from one side to the other side of the liquid membrane.

(3) Metal ions transfer from the interface between the membrane and the stripping phases to concentration layer in the stripping phase.

Therefore, each steps of mass transfer of metal ions are the mass transfer resistances. The mass transfer resistance is the reciprocal of the mass transfer coefficient and this relation is given as follows [9]:

$$\frac{1}{P} = \frac{1}{k_f} + \frac{r_i}{r_m} \frac{1}{P_m} + \frac{r_i}{r_o} \frac{1}{k_s} \quad (9)$$

In general, the log-mean radius of the hollow fiber is given by

$$r_{lm} = \frac{r_o - r_i}{\ln \left( \frac{r_o}{r_i} \right)} \quad (10)$$

where  $r_o$  is the external radius of the hollow fiber in cm.  $k_f$  and  $k_s$  are the aqueous and the stripping mass transfer coefficients in the tube and shell sides, respectively. The units of  $k_f$  and  $k_s$  are cm/s.  $P_m$  is the membrane permeability coefficient which has the same unit in cm/s, which is related to the distribution ratio ( $D$ ) in Eq. (5). The relation of  $D$  and  $P_m$  is [9] as follows:

$$P_m = D k_m \quad (11)$$

Combining Eqs. (4) and (11), we get:

$$P_m = K_{ex} k_m [R_3 N]^2 [H^+]^2 \quad (12)$$

where  $k_m$  is the membrane mass transfer coefficient.

The mass transfer resistance in the stripping solution can be disregarded since the mass transfer coefficient of the stripping solution ( $k_s$ ) is higher than the mass transfer coefficient of the feed solution or aqueous phase ( $k_f$ ) which is due to:

(1) The film existing between the feed solution and the liquid membrane is much thicker than the film existing between the liquid membrane and the stripping solution, as shown in Fig. 3. This is because at the feed solution interface there was a combination of the mercury ions and the acid ions dissolving in the feed solution; whereas, at the stripping solution, there was only sodium hydroxide stripping solution and no combination of different solvents that would make the film thicker and the sodium hydroxide stripping solution could directly contact to the liquid membrane. From the Eqs. (13) and (14) [27]:

$$k_f = \frac{D}{l_{if}} \quad (13)$$

Similarly, at the other side:

$$k_s = \frac{D}{l_{is}} \quad (14)$$

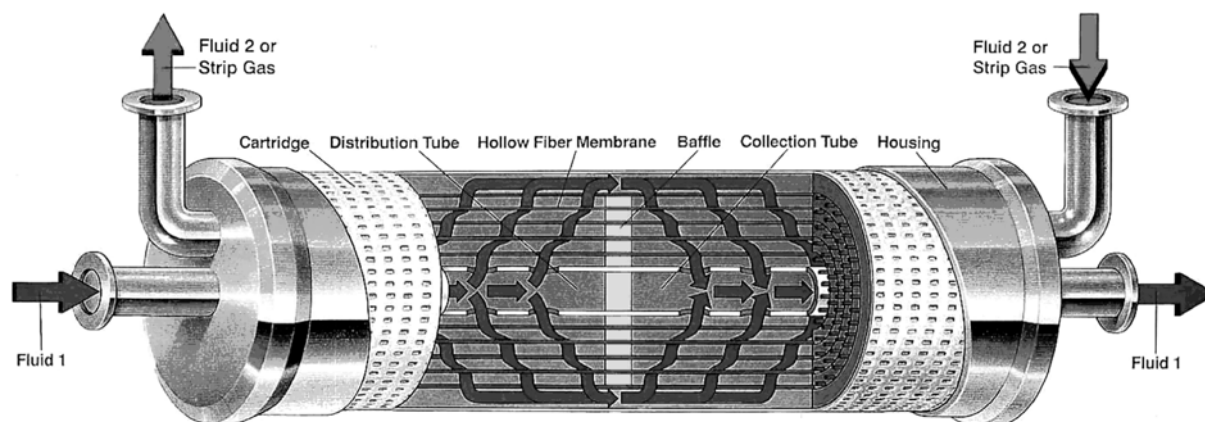


Fig. 4. The Liqui-Cel® Extra-Flow module.

Typically,  $D$  is the diffusion coefficient which makes the mass transfer coefficient of the feed solution ( $k_f$ ) much lower than the mass transfer coefficient of the stripping solution ( $k_s$ ).

(2) From the equation:

$$\text{Flux} = k_f(M_f - M_{fi}) = k_s(M_{si} - M_s) \quad (15)$$

The difference between the mercury ion concentration in the feed solution ( $M_f$ ) and the mercury ion concentration at the interface between the feed solution and the membrane ( $M_{fi}$ ) is higher than that between the mercury ion concentration at the stripping solution - liquid membrane interface ( $M_{si}$ ) and the mercury ion concentration in the stripping solution ( $M_s$ ) [12].

(3) Only sodium hydroxide is used in the stripping side and it directly contacts with the liquid membrane providing rapid dissolution, so, we can discard the last term in Eq. (9).

Hence, when substituting the value of liquid membrane permeability coefficient ( $P_m$ ) from Eq. (12) into the Eq. (9), and assuming the stripping reaction is instantaneous, the contribution of the stripping phase is negligible. Therefore, Eq. (9) is expressed as:

$$\frac{1}{P} = \frac{1}{k_f} + \frac{r_i}{r_{im} K_{ex} k_m [R_3 N]} \quad (16)$$

In this experiment, the percentage of extraction (% E) was determined as follows:

$$\% E = \frac{Hg_{total, extract}}{Hg_{total, feed}} \times 100 \quad (17)$$

Similarly, the percentage of recovery (% R) can be written in terms of

$$\% R = \frac{Hg_{total, recovery}}{Hg_{total, feed}} \times 100 \quad (18)$$

Eqs. (17) and (18) are modified for the flux of extraction ( $J_{extract}$ ):

$$J_{extract} = \frac{Hg_{total, extract}}{A \times t} \times V \quad (19)$$

and the flux of recovery ( $J_{recovery}$ ) is then defined, in general, as

$$J_{recovery} = \frac{Hg_{total, recovery}}{A \times t} \times V \quad (20)$$

## EXPERIMENTAL

### 1. Chemicals

For the liquid membrane, tri-*n*-octylamine (TOA) from Sigma Chemical was used as the extractant and was diluted in kerosene. Mercuric (II) chloride ( $HgCl_2$ ) from Polskie Odczynniki Chemiczne SA was used as the feed solution. Hydrochloric acid (HCl) from Merck was dissolved in the feed solution and sodium hydroxide (NaOH) supplied by Merck was used as the stripping solution (recovery solution). All chemicals were A.R. grade.

### 2. Apparatus

(1) The Liqui-Cel® Laboratory Liquid/Liquid Extraction System, which is composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges was used.

(2) The Liqui-Cel® Extra-Flow module offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), shown in Fig. 4, was used as a support material. This module uses Celgard® microporous polyethylene fibers that are woven into fabric and wrapped around a central tube feeder that supplies the shell-side fluid. The woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The properties of the hollow fiber module are shown in Table 1. The fiber is potted into a solvent-resistant polyethylene tubesheet and the shell casing is polypropylene.

(3) In the separation experiment, the concentrations of mercury

Table 1. Properties of the hollow fiber module [28]

Properties	Description
Material	Polypropylene
Inside diameter of hollow fiber	240 $\mu m$
Outside diameter of hollow fiber	300 $\mu m$
Pore size	0.05 $\mu m$
Porosity	30%
Contact area	1.39 $m^2$
Area per unit volume	29.3 $cm^2/cm^3$
Module diameter	6.3 cm
Module length	20.3 cm
Number of fiber	240

as well as other cations were determined by inductively coupled plasma spectroscopy (ICP).

### 3. Procedures

The feed solution was prepared by dissolution in HCl. The liquid membrane phase was prepared by dissolution of TOA in kerosene. Sodium hydroxide was applied as the stripping solution. The organic solution, which contained TOA, was circulated in tube and shell side for 60 minutes. After that, the experiment was started by flowing the feed solution into the tube side. Simultaneously, the stripping solution was pumped into the shell side of hollow fiber module counter-currently; a one-through-mode operation was used. The

flow diagram is shown in Fig. 5.

## RESULTS AND DISCUSSION

### 1. Effect of HCl Concentration in Feed Solution

In the first five variables, the relationship between the concentration of hydrochloric acid in the feed solution and the percentages of extraction and recovery of mercury ions is shown in Fig. 6. 0.1 M HCl is the best to extract mercury ion. From Eq. (2), we find that mercury (II) ions in hydrochloric solution exist in the anionic complex form  $\text{HgCl}_4^{2-}$  and TOA reacts with the anionic metal complex  $[\text{L}]$ . From Fig. 6, when the HCl concentration increases, the percentages of extraction and recovery increase because the  $\text{H}^+$  is higher to react with TOA. However, TOA is the basic extractant; it can react with metal ions in a basic solution or not high acidity solution [17-19].

Thus, the percentage of extraction decreases when the concentration of HCl is higher than 0.1 M. All of these results also occur in the recovery phase. The extraction and recovery percentages were calculated from Eqs. (17) and (18), respectively.

### 2. Effect of TOA Concentration in the Liquid Membrane

The TOA concentration ranged from 0.1 to 10% v/v. The percentages of extraction and recovery of mercury ions rose gradually when the TOA concentration increased, as shown in Fig. 7. The results showed that at the concentration of TOA of 3% v/v, the percentages of extraction and recovery were maximized and no longer increased. However, when the concentration of TOA exceeded 3% v/v, both the extraction and recovery percentages were constant due to the viscosity of the membrane being increased according to the molecular kinetic interpretation of Stokes and Einstein [2,29,30]. The theoretical equations, based on Boltzmann's kinetic theory, the diffusion coefficient ( $D$ ) can thus be defined as:

$$D = \frac{k_B T}{6 \pi \eta r} \quad (21)$$

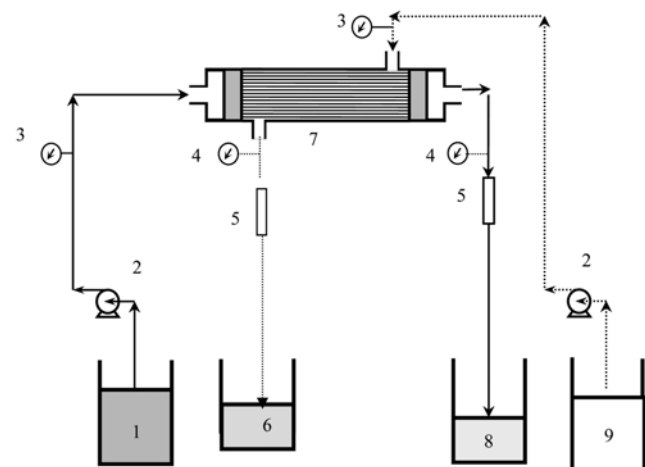


Fig. 5. Schematic counter-current flow diagram for the one-through-mode operation in a hollow fiber supported liquid membrane.

- |                           |                           |
|---------------------------|---------------------------|
| 1. Feed reservoir         | 6. Strip outlet reservoir |
| 2. Gear pumps             | 7. Hollow fiber module    |
| 3. Inlet pressure gauges  | 8. Raffinate reservoir    |
| 4. Outlet pressure gauges | 9. Strip inlet reservoir  |
| 5. Flow meters            |                           |

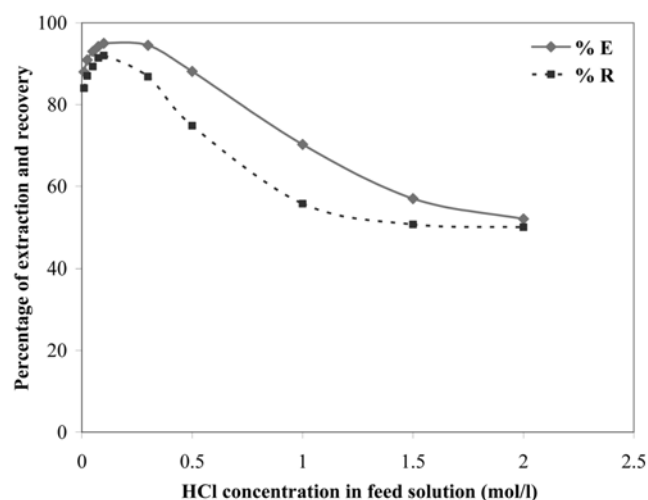


Fig. 6. The percentage of extraction and recovery against HCl concentrations at 1% v/v TOA concentration in the liquid membrane, 100 ppm  $\text{Hg}^{2+}$  in the feed solution and 0.05 M NaOH in the stripping solution. The flow rates of the feed and stripping solutions were both 100 ml/min.

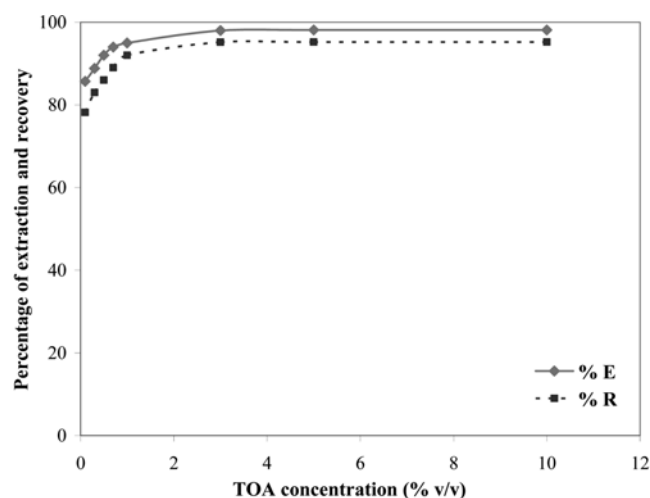


Fig. 7. The percentage of extraction and recovery against the TOA concentration in the liquid membrane at 0.1 M HCl, 100 ppm  $\text{Hg}^{2+}$  in the feed solution and 0.05 M NaOH in the stripping solution. The flow rates of the feed and stripping solutions were both 100 ml/min.

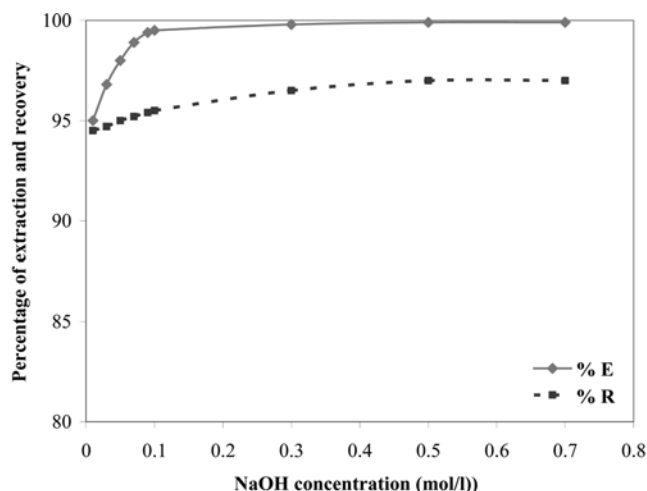


Fig. 8. The percentage of extraction and recovery against NaOH concentration in the stripping solution at 0.1 M HCl, 100 ppm  $\text{Hg}^{2+}$  in the feed solution and 3% v/v TOA concentration in the liquid membrane. The flow rates of the feed and stripping solutions were both 100 ml/min.

in which  $D$  is the diffusion coefficient in  $\text{m}^2/\text{s}$ ,  $k_B$  is Boltzmann's constant, which is  $1.3807 \times 10^{-23} \text{ J/K}$ .  $T$  is the absolute temperature in degrees Kelvin,  $\pi$  is a constant of 3.1416,  $\eta$  is the viscosity of the liquid membrane in  $\text{kg/m-s}$ , and  $r$  is the radius of the diffusion component in  $\text{m}$ .

### 3. Effect of NaOH Concentration in the Stripping Solution

The effect of NaOH concentration is shown in Fig. 8. The recovery of mercury ions by NaOH can be expressed in the reaction of Eq. (3). From Le Chatelier's principle [31]; when the hydroxide ion concentration increased, more mercury ions were extracted and recovered into the stripping solution. However, at NaOH concentration higher than 0.5 M, the percentages of extraction and recovery

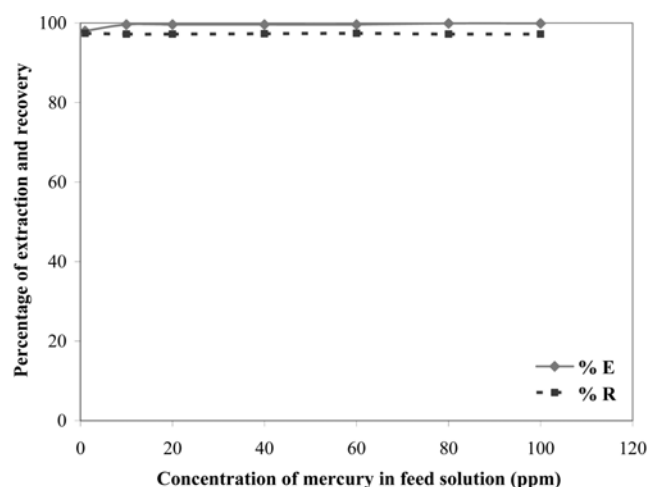


Fig. 9. The percentage of extraction and recovery against the concentration of mercury ions in feed solution at 0.1 M HCl in the feed solution, 0.5 M NaOH in the stripping solution and 3% v/v TOA concentration in the liquid membrane. The flow rates of the feed and stripping solutions were both 100 ml/min.

were constant due to the limitation of the mass transfer area of the hollow fibers [15].

### 4. Effect of Concentration of Mercury Ions in Feed Solution

A mercury concentration in the feed solution range from about 1 to 100 ppm has no effect on the percentages of extraction and recovery, as shown in Fig. 9. These results corresponded to the theoretical model proposed by Rovira and Sastre [32] that the extraction flux of metal ions in the supported liquid membrane is proportional to the concentration of metal ions in the feed solution when the concentration is extremely small.

### 5. Effects of Flow Rates of the Feed and Stripping Solutions

It was also found that when the flow rates of both the feed and stripping solutions ranged from about 20 to 100 ml/min, the percentages of extraction and recovery were constant and then abruptly decreased when the flow rates of both the feed and stripping solutions increased higher than 100 ml/min due to the residence time [22]. The results are shown in Fig. 10. The processes of extraction and recovery should provide high throughput. In other words, the flow rates of both the feed and stripping solutions should be high.

However, from the results in Fig. 10, it was found that the flow rate which gave the highest percentages of the extraction and recovery was less than 100 ml/min. Therefore, the flow rate of 100 ml/min should be the most suitable rate, which is found to be essentially for the separation of mercury (II) ions through a hollow fiber supported liquid membrane.

### 6. Calculation of Equilibrium Constant and Distribution Ratios

The equilibrium constants ( $K_{ex}$ ) and distribution ratio ( $D$ ) can be calculated from Eqs. (4) and (5), respectively, by liquid-liquid extraction process. The equilibrium constant of mercury extraction reaction was calculated by the slope of the graph in Fig. 11 which was found to be  $1.34 \times 10^5 (\text{L/mol})^4$ . The experimental values of the distribution ratios at the TOA concentration from 0.1 to 3% v/v are given in Table 2.

### 7. Calculation of Permeability

Fig. 12 shows the relationship of mercury (II) ion concentration in the feed solution versus time at different concentration of TOA in

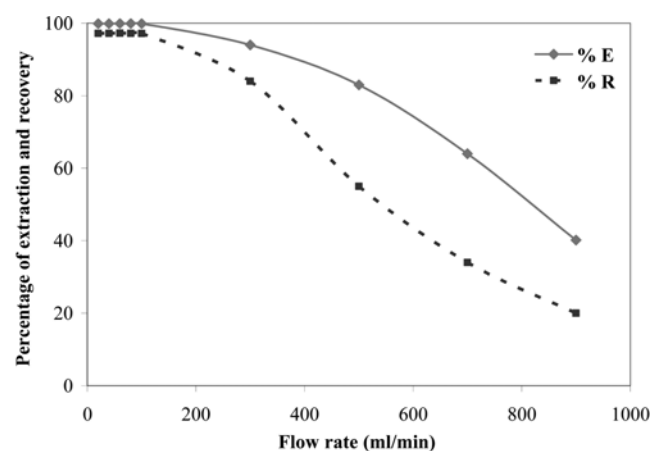


Fig. 10. The percentage of extraction and recovery against flow rates of the feed and stripping solutions at 3% v/v TOA concentration in the liquid membrane, 0.1 M HCl, 100 ppm  $\text{Hg}^{2+}$  in the feed solution and 0.5 M NaOH in the stripping solution.

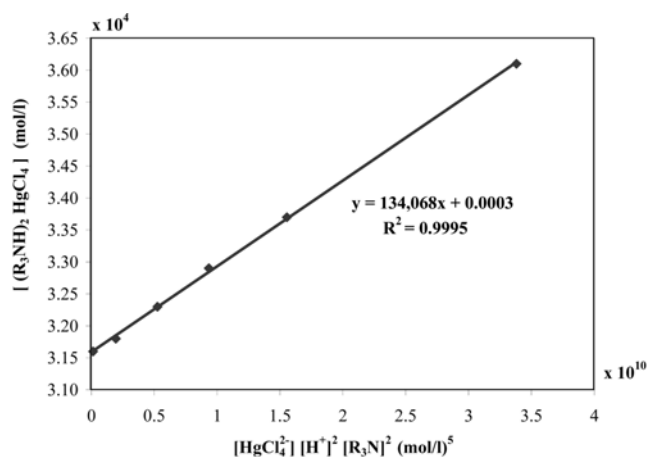


Fig. 11. The relation of TOA concentration between the end of reaction and the initial reaction of  $\text{Hg}^{2+}$  at different TOA concentrations in the liquid membrane and 0.1 M HCl in the feed solution.

Table 2. The distribution ratio (D) at a TOA concentration of 0.1-3.0% v/v

[TOA], % v/v	Distribution ratio, D
0.1	3.0
0.3	9.2
0.5	15.4
0.7	21.5
1.0	30.8
3.0	92.4

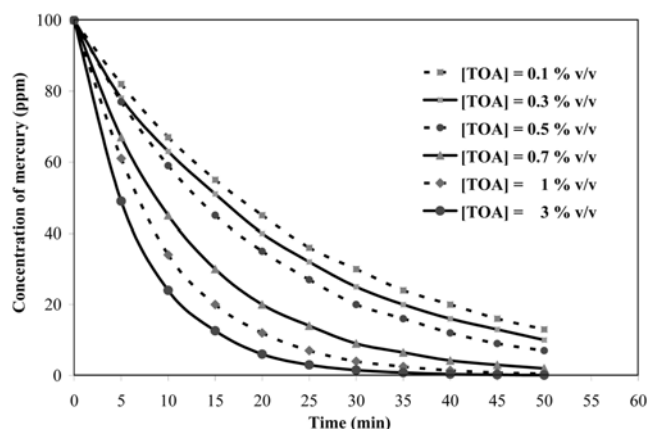


Fig. 12. The relation of mercury (II) ion concentration in the feed solution versus time at different concentrations of TOA in the liquid membrane at 0.1 M HCl and 100 ppm  $\text{Hg}^{2+}$  in the feed solution and 0.5 M NaOH in the stripping solution. The flow rates of the feed and stripping solutions were both 100 ml/min.

the liquid membrane. It was found that the extractability increased when the concentration of TOA increased.

From the above data, the permeability coefficient can be determined. Permeability coefficient can also be calculated from Eqs. (7) and (8) for mercury ions at the TOA concentration of 0.1-3.0%

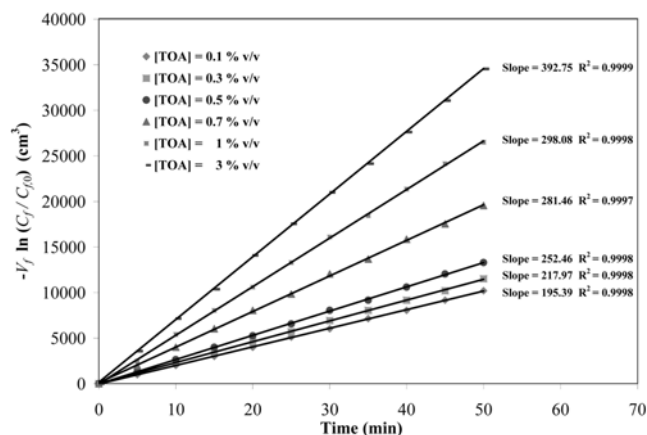


Fig. 13. The relationship of  $-V_f \ln(C_f/C_{f,0})$  of mercury (II) ions in the feed solution versus time at different concentrations of TOA in the liquid membrane when using 0.1 M HCl and 100 ppm  $\text{Hg}^{2+}$  in the feed solution, and 0.5 M NaOH in the stripping solution. The flow rates of the feed and stripping solutions were both 100 ml/min.

Table 3. The permeability (P) at a TOA concentration of 0.1-3.0% v/v

[TOA], % v/v	Permeability, P, $\text{cm/s} \times 10^2$
0.1	2.58
0.3	3.20
0.5	4.45
0.7	5.97
1.0	7.16
3.0	37.80

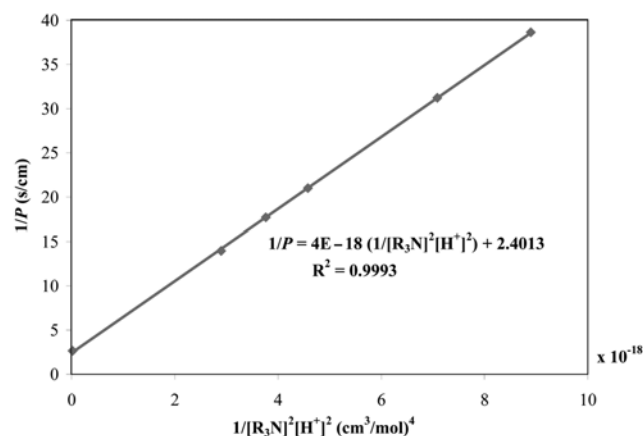


Fig. 14. Plot of  $1/P$  as a function of  $1/([R_3N]^2[H^+]^2)$  of mercury (II) ions.

v/v and are shown in Fig. 13 and Table 3.

## 8. Calculation of the Mass Transfer Coefficient

The aqueous and membrane mass transfer coefficients,  $k_i$  and  $k_m$ , can be evaluated by using Eq. (16). When plotting  $1/P$  as a function of  $1/([R_3N]^2[H^+]^2)$  at different TOA concentrations (shown in Fig. 14), a straight line with the slope  $(\tau_i/\tau_m) (1/(K_{ex}k_m))$  and the ordinate  $1/k_i$  was obtained. Thus, from Fig. 14, the values of  $k_i$  and  $k_m$

calculated from the slope and ordinate were 0.42 and 1.67 cm/s. As a result, the membrane mass transfer coefficient ( $k_m$ ) was higher than the aqueous feed mass transfer coefficient ( $k_i$ ).

## CONCLUSIONS

The mercury (II) ions in the form of  $\text{HgCl}_4^{2-}$  can be extracted and stripped by TOA from a chloride media by microporous hydrophobic hollow fiber supported liquid membrane. The results indicated that the maximum percentages of extraction and recovery of mercury ions of 100% and 97% were achieved at a concentration of hydrochloric acid in the feed solution of 0.1 M, a concentration of TOA at 3.0% v/v, a concentration of sodium hydroxide at 0.5 M, and flow rates of the feed and stripping solutions of 100 ml/min. However, a concentration of mercury ions from 1-100 ppm in the feed solution had no effect on the percentages of extraction and recovery of mercury ions. The mass transfer coefficients of the aqueous phase ( $k_i$ ) and membrane or organic phase ( $k_m$ ) were 0.42 and 1.67 cm/s, respectively. Therefore, the rate-controlling step was the diffusion of the mercuric complex through the film layer between the feed solution and the liquid membrane.

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## NOMENCLATURE

A	: effective area of the membrane [ $\text{cm}^2$ ]
$C_f$	: concentration of feed solution at time t [M]
$C_{f,0}$	: concentration of feed solution at t=0 [M]
D	: distribution ratio [-]
D	: the diffusion coefficient [ $\text{m}^2/\text{s}$ ]
% E	: the percentage of extraction [percent]
$J_{\text{extract}}$	: flux of extraction [ $\text{mol}/\text{m}^2\text{-min}$ ]
$J_{\text{recovery}}$	: flux of recovery [ $\text{mol}/\text{m}^2\text{-min}$ ]
$k_B$	: Boltzmann's constant is $1.3807 \times 10^{-23}$ [J/K]
$k_i$	: aqueous feed mass transfer coefficient [cm/s]
$k_m$	: membrane or organic mass transfer coefficient [cm/s]
$k_s$	: stripping mass transfer coefficient [cm/s]
$K_{\text{ex}}$	: extraction equilibrium constant [ $\text{L}^4/\text{mol}^4$ ]
$l_{\text{if}}$	: thickness of the film existing between the feed solution and the liquid membrane [cm]
$l_{\text{is}}$	: thickness of the film existing between the liquid membrane and the stripping solution [cm]
L	: length of the fiber [cm]
$M_f$	: the concentration of mercury ions in the feed solution [M]
$M_{\text{if}}$	: the concentration of mercury ions of the feed solution-liquid membrane interface [M]
$M_{\text{is}}$	: the concentration of mercury ions of the liquid membrane-stripping solution interface [M]
$M_s$	: the concentration of mercury ions in the stripping solution [M]

N	: number of hollow fibers in the module [-]
$P_m$	: membrane permeability constant [cm/s]
P	: permeability constant [cm/s]
$Q_f$	: volumetric flow rate of feed solution that flows through the tube side [ $\text{cm}^3/\text{s}$ ]
r	: the radius of the diffusion component [m]
$r_{\text{lm}}$	: the log-mean radius of the hollow fiber [cm]
$r_i$	: the internal radius of the hollow fiber [cm]
$r_o$	: the external radius of the hollow fiber [cm]
% R	: the percentage of recovery [percent]
t	: time [min]
T	: the absolute temperature [K]
$V_f$	: volume of the feed [ $\text{cm}^3$ ]

## Greek Letters

$\varepsilon$	: porosity of the hollow fiber [percent]
$\pi$	: constants [3.1416]
$\eta$	: the viscosity of the liquid membrane [kg/m-s]

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