

# The Liquid Membrane Process Optimization for Separation of Cadmium Cations Using D2EHPA as Carrier

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*The cadmium cation separation through bulk liquid membranes containing D2EHPA (di-2-ethylhexylphosphoric acid) as carrier has been investigated. In order to optimize the process for the separation of cadmium, the efficiency of the type of solvent (kerosene and toluene) in the organic phase and the influence of the receiving phase acidity on the transport were studied. The best separation for cadmium was observed when kerosene was used as solvent in the organic membrane phase. Under optimal conditions, the maximum transport of cadmium cations through the liquid membrane was 96%.*

*Keywords: D2EHPA carrier, bulk liquid membrane process, cadmium separation*

The liquid membrane process has been used for many years in the chemical industry due to its advantages as simultaneous removal and recovery of solutes in a single unit, more effective separation of elements with similar properties, and small amounts of extractants needed [1]. Also, its utilization in the treatment of liquid waste that contain solute in low concentration was proposed [2].

Liquid membranes are classified into three types: bulk, emulsion and supported liquid membranes (SLM). Compared with other liquid membrane systems, bulk liquid membrane (BLM) is the simplest type for the selective separation, is easy to manipulate, while offering good membrane stability [3]. It has been used in various applications such as precious metal recovery [4], toxic metal [5], non-metal [6], and organic pollutant [7] removal from wastewater.

The BLM usually consists of an aqueous feed and a stripping phase that are separated by a water-immiscible liquid membrane phase [8, 9]. The efficiency and selectivity of the ion transport in the liquid membranes process are influenced by many factors as: the type of the carrier or solvent used in the organic phase, the carrier concentration in membrane, and the nature and acidity of the receiving phase [10-13]. Due to the high toxicity of cadmium to the environment and human health, several studies have been performed for cadmium transport through different liquid membrane configurations using various carriers such as Alamine 304, Alamine 336 [14], D2EHPA, PC-88A, Cyanex 272 [15,16], TOA [17], Tri-iso-octyl amine (TIOA) [18], Cyanex 302 [19].

Kamal Kumar Bhatluri and collaborators investigated simultaneous extraction and recovery of heavy metals (cadmium and lead) from aqueous solutions through a coconut oil-based Flat Sheet Supported Liquid Membrane (FS-SLM). *N*-Methyl-*N,N*-dioctyloctan-1-ammonium chloride (Aliquat 336) was used as carrier for the transportation and Ethylenediaminetetraacetic acid (EDTA) was selected as stripping agent in the liquid membrane. The optimum extraction and recovery of cadmium were 79% and 67%, respectively [20]. The extraction and transport of cadmium (II) and lead (II) in supported liquid membrane (SLM) using tributylphosphate (TBP), tri-ethylhexyl phosphate (TEHP), trioctylphosphine oxide (TOPO), and di-2-ethylhexyl phosphoric acid (D2EHPA)

as mobile carriers were studied by S. Azzoug and others [21].

N. Dalali and others studied selective transport of Cd(II) and Zn(II) ions from sodium chloride medium through a bulk liquid membrane by using trioctyl methyl ammonium chloride (Aliquat 336) dissolved in benzene. In their study was investigated the influence of experimental parameters on the transport efficiency, including the chloride concentration in the sample solution, the reagent concentration and the type of organic solvent in the membrane phase, and the type and concentration of the stripping solution in the receiving phase [22]. Cd(II) transport from an aqueous feed chloride solution to an ammonium acetate strip solution through a bulk liquid membrane (BLM) consisting of tri-*n*-octylamine (TNOA) or tricapryl amine (N235) as carriers in carbon tetrachloride solution was made by He et al [23]. A bulk liquid membrane system contained Aliquat 336, Heavy Polyamine X, and di-(2-ethylhexyl)-phosphoric acid (DEHPA) as mobile carrier dissolved in kerosene was studied [24 - 26].

In the present paper, the transport of cadmium cations through a bulk liquid membrane with D2EHPA as carrier in the organic phase was studied. To optimize the separation process, the influence of the type of solvent used in the organic phase and the effect of receiving phase acidity on the process of transport through liquid membranes were investigated.

## Experimental part

### Materials and method

The chemicals used in this study were analytical grade and were used without further purification. The salt of cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\geq 99.2\%$ , Scharlau firm) was used for preparation of the feed phase. A solution of 1 M sulfuric acid ( $\text{H}_2\text{SO}_4$ , purchased from Scharlau) was used as stripping phase. Kerosene (b.p. = 175-325 °C, the vapor pressure 0.23 mmHg (20 °C)) and toluene (99.5%, the vapor pressure 22 mm Hg (20 °C)), products from Sigma Aldrich, were used as organic solvents in the membrane. Di-(2-ethylhexyl) phosphoric acid (D2EHPA), from Alfa Aesar, having 95% purity and density  $d = 0.965 \text{ g cm}^{-3}$  was used as carrier in the membrane.

The experimental studies were carried out in a bulk liquid membrane using a cylindrical glass cell. The cell design

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and the transport process were previously described [24]. The membrane phase was made of 0.1 M D2EHPA in 25 mL kerosene or toluene. The feed phase contained 105 mL solution of 0.0005 M Cd (II) and the stripping phase was 27.5 mL H<sub>2</sub>SO<sub>4</sub> of various concentrations (1 M, 0.1 M, 0.01 M, 0.001 M, and 0.0001 M). The stirring speed was 250 rpm and all experiments were carried out at room temperature for 20 h. The contact area between the feed phase and liquid membrane (AF/M) was 16.5 cm<sup>2</sup> whereas the contact area between the liquid membrane and the stripping solution (A<sub>M/S</sub>) was 5.5 cm<sup>2</sup>. Cadmium (II) ion concentrations in both the feed and product phases were analyzed with a Varian Liberty ICP emission spectrometer 110.

The transport Q<sub>s</sub> (mol/cm<sup>2</sup>) was calculated with the equation (1):

$$Q_s = \frac{C_{s,t} \times V_{s,t}}{1000 \times A_{s/M}} \text{ mol / cm}^2 \quad (1)$$

where:

Q<sub>s</sub> is the amount (in moles) of metal species transported into the stripping solution (s) after the time t through 1 cm<sup>2</sup> of the working membrane area;

C<sub>s,t</sub> is the concentration of metal species in the stripping phase after the transport time t (mol/dm<sup>3</sup>);

V<sub>s,t</sub> is the volume of the stripping (s) solution (cm<sup>3</sup>) after the time t and A<sub>s/M</sub> (cm<sup>2</sup>) is the area of the stripping solution/membrane interface [27].

The concentration factors (CF), defined as the ratio of metal concentration in the stripping solution after the time t to the initial feed concentration [28], were calculated from eq. (2):

$$CF = \frac{C_{s,t}}{C_{f,t=0}} \quad (2)$$

## Results and discussions

### Effect of organic solvent in the membrane phase on the cadmium transport

The influence of two types of solvent, kerosene and toluene, as organic phase on the cadmium separation through the liquid membrane was examined. In all experiments, the feed phase contained 0.0005 M Cd (II) and the stripping phase 1 M H<sub>2</sub>SO<sub>4</sub>. The organic phase was 0.1 M D2EHPA in kerosene and toluene, respectively.

The experimental data (figs. 1- 3) indicate that the nature of solvent in the organic phase affects the efficiency and selectivity of cadmium transport through the liquid membrane. The highest transport efficiency was obtained when kerosene was used as solvent in the organic phase.

As seen in figure 1, when the organic phase contains kerosene, the concentration of transferred cadmium cations achieves 93% after 20 h. In the experiment of cadmium separation with toluene in the organic phase, the amount of cadmium transferred to the receiving phase is lower, only a maximum of 47% is attained after 20 hours (fig. 2). It is known that kerosene has a lower dielectric constant (ε= 1.8) [27] compared to toluene (ε = 2 to 2.4) [28], but close enough values, so a further explanation for this behaviour can be found in the solubility of D2EHPA that is better in kerosene than in toluene, resulting in a higher transfer of cadmium through the liquid membrane that contains kerosene. The significant difference between the two systems can be observed in figure 3 that shows the

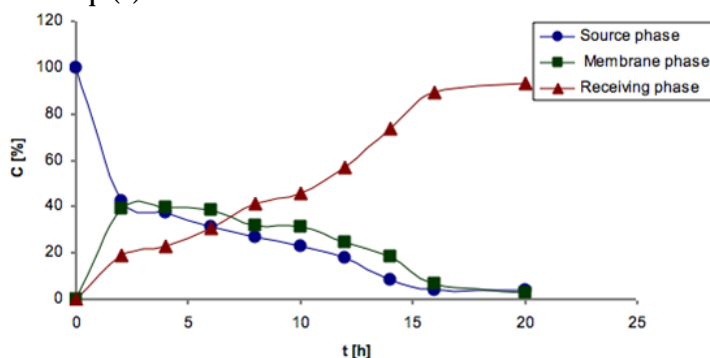


Fig. 1. Cadmium concentration in the liquid membrane with 0.1 M D2EHPA in kerosene vs. time

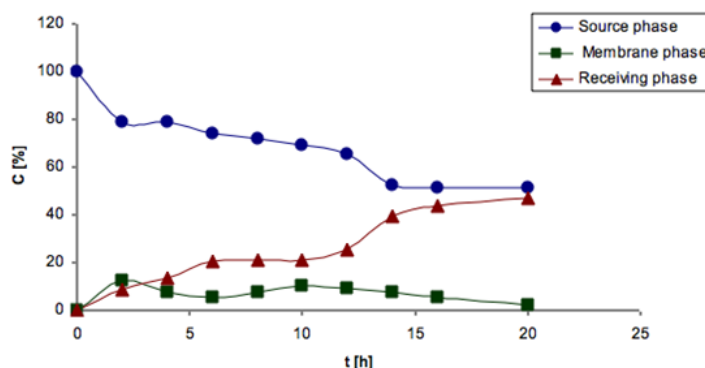


Fig. 2. Cadmium concentration in the liquid membrane with 0.1 M D2EHPA in toluene vs. time

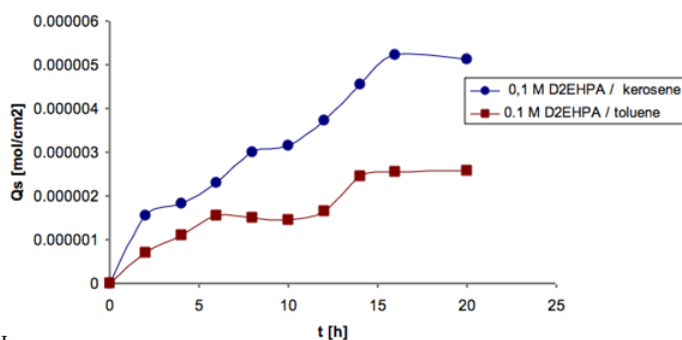


Fig. 3. Effect of organic solvents (kerosene and toluene) on the transport Q<sub>s</sub> of cadmium cations in the stripping solution

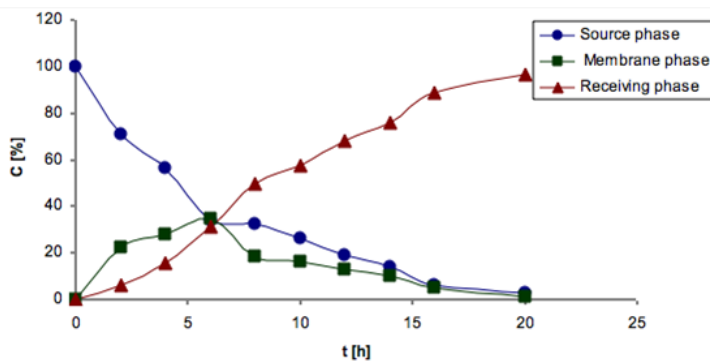


Fig. 4. Percentage concentration of cadmium in liquid membrane with 1 M  $H_2SO_4$  in the receiving phase vs. time

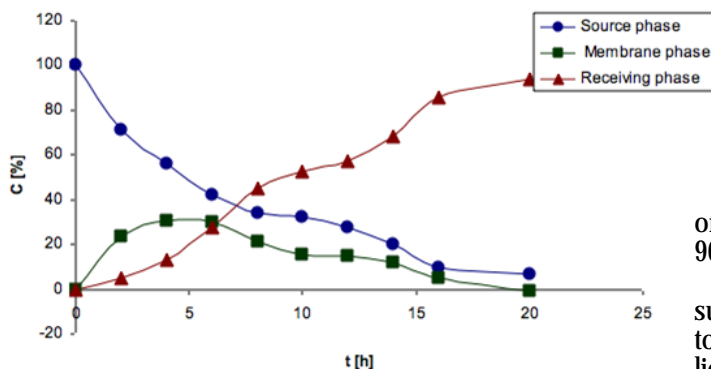


Fig. 5. Percentage concentration of cadmium in liquid membrane vs. time with 0.1 M  $H_2SO_4$  in the receiving phase.

data for the transport  $Q_s$  of cadmium cations in the stripping solution.

#### Effect of receiving phase acidity on the cadmium transport

In order to determine the effect of the receiving phase acidity on the cadmium separation across liquid membrane, the experiments were performed at five different  $H_2SO_4$  concentrations in the receiving phase: 1 M, 0.1 M, 0.01 M, 0.001 M, and 0.0001 M, respectively. The source phase contained 0.0005 M  $Cd^{2+}$  and the organic phase was made of 0.1 M D2EHPA dissolved in kerosene. The results for cadmium separation concentrations are presented in figures 4-8. It can be seen that reducing the ionic strength of  $H_2SO_4$  in the receiving phase decreases the transport of cadmium. When the sulfuric acid concentration in the receiving phase was 1 M, 0.1 M, 0.01 M, 0.001 M, and 0.0001 M, respectively, the maximum value

of cadmium separation through liquid membranes was 96, 94, 92, 27 and 14 %, respectively.

Figures 4, 5 and 6 indicates that by decreasing the sulfuric acid concentration in the receiving phase from 1 M to 0.01 M, the process of cadmium cations transfer through liquid membranes is not significantly affected. As can be seen, the separation efficiency of cadmium was diminished only by four percent (from 96 to 92) and the separation of the cadmium was maintained at a high transfer through the membrane. In the experiments where the receiving phase concentration was under 0.01 M  $H_2SO_4$ , the cadmium transfer through liquid membrane was substantially reduced to values of 27 and 14 % (figs. 7 and 8). This phenomenon can be explained by the fact that decreasing the acidity of the receiving phase, the availability of protons in the separation solution is reduced, resulting an incomplete protonation and a diminished extracting ability of metallic cations - D2EHPA carrier at the receiving phase/membrane interface.

The results for the transport  $Q_s$  of metal species into the stripping solution are shown in figure 9. As is seen, the highest transport of cadmium moles in the stripping solution was realized when the separation solution concentration

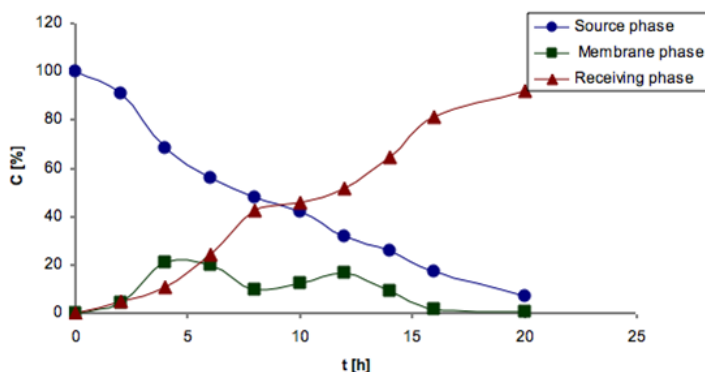
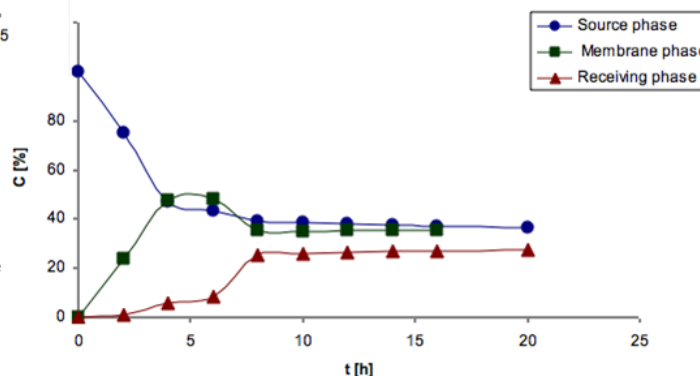


Fig. 6. Percentage concentration of cadmium in liquid membrane vs. time with 0.01 M  $H_2SO_4$  in the receiving phase.

Fig. 7. Percentage concentration of cadmium in liquid membrane vs. time with 0.001 M  $H_2SO_4$  in the receiving phase



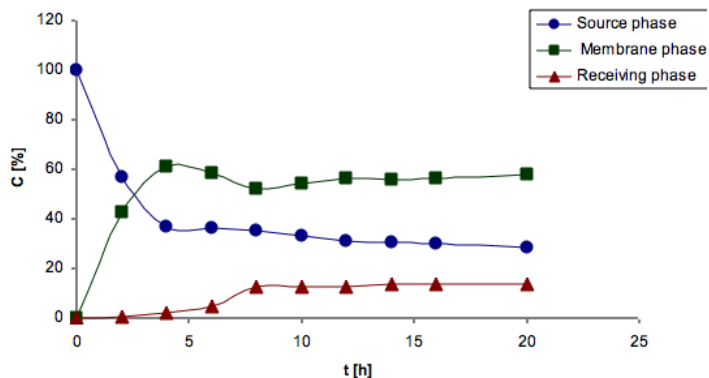


Fig. 8. Percentage concentration of cadmium in liquid membrane vs. time with 0.0001 M  $H_2SO_4$  in the receiving phase.

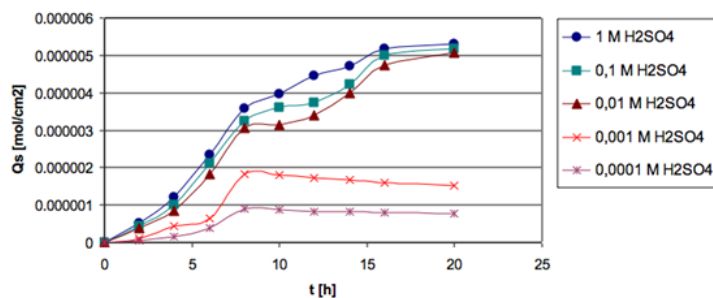


Fig. 9. Effect of the receiving phase acidity on the transport  $Q_s$  of cadmium cations in the stripping solution versus time.

**Table 1**  
THE CONCENTRATION FACTOR (CF) FOR CADMIUM SEPARATION THROUGH LIQUID MEMBRANE WITH VARIOUS  $H_2SO_4$  CONCENTRATIONS IN THE RECEIVING PHASE

Time [h]	CF for the experiment with 1 M $H_2SO_4$	CF for the experiment with 0,1 M $H_2SO_4$	CF for the experiment with 0,01 M $H_2SO_4$	CF for the experiment with 0,001 M $H_2SO_4$	CF for the experiment with 0,0001 M $H_2SO_4$
2	0.243	0.198	0.184	0.042	0.022
4	0.590	0.490	0.410	0.213	0.080
6	1.184	1.060	0.924	0.331	0.191
8	1.893	1.721	1.613	0.969	0.478
10	2.200	1.998	1.738	0.999	0.480
12	2.598	2.181	1.981	1.006	0.486
14	2.900	2.598	2.467	1.032	0.515
16	3.384	3.264	3.096	1.038	0.524
20	3.680	3.590	3.520	1.048	0.532

was in the range 1 - 0.01 M  $H_2SO_4$ . A further diminution in  $H_2SO_4$  concentration under 0.01 had resulted in a pronounced decrease of the efficiency transport  $Q_s$  of cadmium moles through membrane.

The concentration factors CF (table 1) were calculated to demonstrate possible up-hill transfer of cadmium cations from the feed phase to the stripping solution, when  $CF > 1$ . The data in table 1 show that the CF value for cadmium cations after 20 h of transport across the membrane was maintained at a high level (between 3.680 and 3.520) when the acidity of the received solution was in the range 1 M - 0.01 M  $H_2SO_4$ . At a further diminution of the receiving phase acidity to 0.001 M and 0.0001 M  $H_2SO_4$ , an obvious decrease of the CF values to 1.048 and 0.532 can be observed.

## Conclusions

This study demonstrated that the nature of the organic solvent used in membrane phase has a significant influence on the efficiency of cadmium cations transport through liquid membranes. The experimental data show that toluene is a less suitable solvent in the membrane that contains D2EHPA, only 47% of cadmium cations are transported into the receiving phase. A better transfer rate in the membrane system, 93%, is obtained in the presence of kerosene as solvent in the organic phase.

The permeability of the membrane system for  $Cd^{2+}$  cations was found to be largely dependent on the concentration of stripping solution used in the receiving phase. The optimum concentration of sulfuric acid in the receiving phase was found to be from 1 M to 0.01 M, when the separation process of cadmium cations across bulk liquid membrane was maintained at maximum levels



(from 96 to 92 %), but a further decrease in the sulfuric acid concentration had resulted in a pronounced decrease in the transport efficiency of Cd<sup>2+</sup> cation (to 14 % for 0.0001 M H<sub>2</sub>SO<sub>4</sub>).

Therefore, the liquid membrane process from this study could be a potential candidate for practical use in cadmium (II) cation separation, especially as it has the advantages of high precision, efficiency, selectivity and simplicity.

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