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# Facilitated Transport of Cadmium Ions from Hydrochloric Acid Solutions through a Liquid Membrane Containing Dicyclohexyl-18-Crown-6 as Extractant-Carrier

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**Abstract:** The transport of cadmium ions from hydrochloric acid solutions across a bulk liquid membrane by using dicyclohexyl-18-crown-6 (DC18C6) dissolved in dichloromethane has been studied at 25°C. The effect of the fundamental parameters influencing the transport, e.g., hydrochloric acid concentration in the feed phase, DC18C6 concentration and the type of diluent used in the membrane and time of transport have been investigated. The transported amount of the cadmium ions (initial concentration 0.001 M) from a 6 M hydrochloric acid solution across a dichloromethane solution of DC18C6 (0.05 M) into distilled water (receiving phase) was found to be 98.3 ($\pm$1.8) percent after 6 h. The selectivity and efficiency of the method toward cadmium ions were tested by performing the competitive transport experiments on the mixtures containing $Cd^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Pb^{2+}$, and $Fe^{2+}$ ions. The best selectivity was found for the recovery of the cadmium ions from its mixture with $Ni^{2+}$, $Mn^{2+}$, $Co^{2+}$, and $Pb^{2+}$ ions. Thus, the method can be proposed for the application in cadmium recovery from the sources containing these ions such as spent rechargeable nickel-cadmium batteries.

**Keywords:** Cadmium, transport, liquid membrane, crown ethers, hydrochloric acid media

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## INTRODUCTION

Separation and recovery of heavy metals from wastes, industrial residuals, and various spent products are important from environmental aspects as well as economical viewpoint. Among the heavy metals, cadmium is known as one of the most toxic elements (1). This metal and its alloys find extensive applications in chemical, electroplating, batteries, and specialized electronic industries (2). Cadmium is mainly obtained as a byproduct in the hydrometallurgical processing of other metals such as zinc, copper, and lead. The residual of these industries contains a considerable amount of cadmium. In addition, the spent rechargeable nickel-cadmium batteries are another important sources for producing of this metal (3).

It has been demonstrated that the transport through liquid membranes act as effective techniques in many applications such as resource recovery and the removal of pollutant from a variety of sources (4). Low capital costs, space requirements, and energy consumptions are certain advantages offering by this class of separation techniques (5).



Liquid membrane acts as a solvent for a transported solute and the transport of that solute is governed by its solubility in the membrane. The most interesting case arises when this solubility can be governed by a chemical reaction between the transported solute and an "extractant-carrier" molecule which forms a solute-carrier complex. This kind of transport is called "facilitated" or "carrier-mediated" transport (6). The selection of a suitable extractant-carrier plays a crucial role in order to selective extraction of the desired substances on one side of the membrane and to release them on the other side.

The transport of cadmium ions from chloride solutions has been subject of some recent studies. He et al. have used tri-*n*-octylamine and tricaprylamine as carrier dissolved in carbon tetrachloride for the transport of cadmium ions as anionic chloride complexes (7). It is demonstrated that the transport of Cd ions is coupled by co-transport flow of protons. The method needs to use ammonium acetate for stripping of the extracted cadmium ions in the receiving phase. A mathematical approach to the transport of cadmium complex anions from hydrochloric acid solutions using (PVC)-based membranes mediated by Aliquat 336 was studied by Wang et al. (8). Alguacil et al. have studied (9, 10) cadmium ion transport from aqueous $HCl/H_3PO_4$ solution through a polymer-immobilized liquid membrane using Cyanex 923 as mobile-carrier. A value of 86% of the initial cadmium concentration ($0.89 \times 10^{-6}$ M) from aqueous phase (100 g/L HCl and 100 g/L $H_3PO_4$) was transported into receiving phase (water) after 3 h through the membrane (30% v/v Cyanex 923 in xylene on a Durapore support).

Crown ethers are known as a class of size selective receptors. These molecules have been largely used as extracting and phase transfer reagents in solvent extraction and liquid membrane process, respectively (11–14). In many applications, they act as neutral solvating agents for extraction and transport of metal cations or metallic salts. However, they are frequently

used in ion pair formation phase transfer experiments in which the crown ether forms a cationic complex for the extraction of metallic species that are included in a complex anion (15–20).

Recently we examined the extraction of cadmium complex anions from hydrochloric acid media using dicyclohexyl-18-crown-6 (DC18C6) as extractant in dichloromethane (21). The results revealed that the cadmium ions are extracted as ion pairs $[HL^+][CdCl_3^-]$ and $[HL^+]_2[CdCl_4^{2-}]$ (L = DC18C6) depending on the acid concentration in the aqueous phase. With the aim of the study of the recovering cadmium from spent rechargeable nickel-cadmium batteries and residual of the zinc hydrometallurgical production plants, in this work we present the transport of the cadmium ions as their chloride complexes from hydrochloride solutions into water, as the stripping phase, through a bulk liquid membrane containing dicyclohexyl-18-crown-6. The parameters influencing the efficiency of the transport are verified. The selectivity of the method is checked by performing the competitive transport experiments of cadmium ions from its mixtures with some interfering ions.



## EXPERIMENTAL

### Materials

Crown ethers 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and dicyclohexyl-18-crown-6 (DC18C6, mixture of isomers), were used as received (Fluka). Diluents (Merck) used were washed three times with distilled water in order to remove the diluent stabilizers and saturated themselves by water. Stock solutions of cadmium, zinc, iron, lead, nickel, cobalt, and manganese were prepared from weighed amount of the corresponding chlorides (Fluka). These solutions were standardized complexometrically. All other reagents were of laboratory reagent grade.

### Analysis and Transport Experiments

The metal concentrations were determined by atomic absorption spectrometry (AAS: Varian 110 AA). The experimental setup used for the transport experiments was a glass apparatus shown in Fig. 1. Temperature of the solutions was kept constant using a thermostated water circulating through the jacket of the transport cell. The source phase contained 10 mL of 0.001 M cadmium in hydrochloride acid solution (6 M). The receiving phase included 10 mL of distilled water. A dichloromethane solution (20 mL) of DC18C6 (0.05 M) placed below these two aqueous phases and bridge them. The organic layer was stirred constantly (100 rpm) by a Teflon-coated magnetic bar. The reproducibility of the transport was investigated and the percent of metal ions transported after 6 h obtained from five replicate measurements was found to be

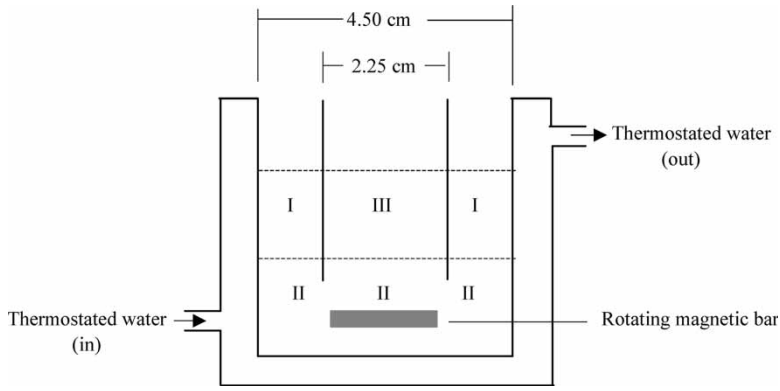


***Figure 1.*** Experimental setup for the transport experiments: (I) feed phase, 10 mL; (II) membrane, 20 mL; (III) receiving phase, 10 mL.



98.3 ± 1.8%. It is confirmed that without DC18C6 in the organic phase, transfer of cadmium ions across the membrane does not take place.

## RESULTS AND DISCUSSION

### Comparison of 18C6, DB18C6 and DC18C6 as the Mobile Carrier Agents

In preliminary experiments, the transport of cadmium ions (0.001 M) from hydrochloric acid solution (4 M) into water across dichloromethane solution of 18C6, DB18C6, and DC18C6 (0.05 M) has been performed. The results are shown in Table 1. The best performance is presented by DC18C6.

***Table 1.*** Comparison of the percent of cadmium ions extracted from feed phase into the membrane containing 18C6, DB18C6, and DC18C6 and the release into receiving phase[a]

| Crown ether | Uptake of $Cd^{2+}$ (%)[b] (feed phase to membrane) | Release of $Cd^{2+}$ (%)[b] (membrane to receiving phase) |
|---|---|---|
| 18C6 | 27.1 | 5.7 |
| DB18C6 | <1 | <1 |
| DC18C6 | 96.5 | 60.6 |

[a]Feed phase: $Cd^{2+}$ (0.001 M), HCl (4 M); membrane: crown ether (0.05 M) in dichloromethane; receiving phase: distilled water; time of transport: 4 h; stirring rate: 100 rpm; temperature: 25°C.
[b]$\sigma_{N-1} < 0.3\%$.

Lower transport efficiency of the transport by 18C6 with respect to DC18C6 can be attributed to the lower lipophilic nature of the former. This characteristic causes the distribution of 18C6 between dichloromethane and water to be reduced. The presence of phenyl groups in DB18C6, as electron withdrawing moieties, diminishes the complexive abilities of this extractant-carrier toward oxonium ions. In addition, the order of the efficiency in the transport presented by these crown ethers, i.e., DC18C6 > 18C6 > DB18C6 is in good agreement with the stability constant reported for the corresponding $H^+$ ion complexes with the studied crown ethers (22).

## Effect of Hydrochloric Acid Concentration in the Feed Phase

In chloride solutions cadmium ions are found as anionic chloride complexes (23, 24). In our recent paper we have found that the composition of the anionic cadmium chloride complexes formed in hydrochloric acid solutions depends on the acid concentration and the corresponding extraction equilibrium for which can be considered as

$$CdCl_{2+n}^{n-} + nH^+ + nL_{org} \rightleftharpoons (HL^+)_n(CdCl_{2+n}^{n-})_{org}$$

Therefore, the chloride concentration can alter the transport efficiency. In order to verify this assumption, the variation of the concentration of cadmium ions in the feed and receiving phases as a function of the hydrochloric acid concentration in the feed phase in the range 2–10 M was studied (Fig. 2). As it is seen, the cadmium concentration in the feed phase decreases with increasing the hydrochloric acid concentration in this phase. However, for the concentration higher than 5 M, the concentration of cadmium in the feed phase is independent to the acid concentration. Variations of the cadmium concentration in the receiving phase by increasing $c_{HCl}$ up to 6 M is agreement with the favorable condition for the formation of the higher chloride containing cadmium complexes. The diminishing of the transport efficiency beyond this concentration of acid can be attributed to the formation of the more stable complexes of $(HL^+)_2$ $(CdCl_4^{2-})$. The possibility of the formation of such complexes is reported previously (21).

## Influence of the Carrier Concentration

The effect of the concentration of DC18C6 in the membrane phase on the transport of cadmium was studied and the results are shown in Fig. 3. It is obvious that a nearly quantitative extraction of the cadmium ions from feed to the membrane is occurred when the concentration of DC18C6 is reached to 0.05 M. A further excess of carrier has no considerable effect on the uptake of the cadmium ions into the membrane. However, in the experimental

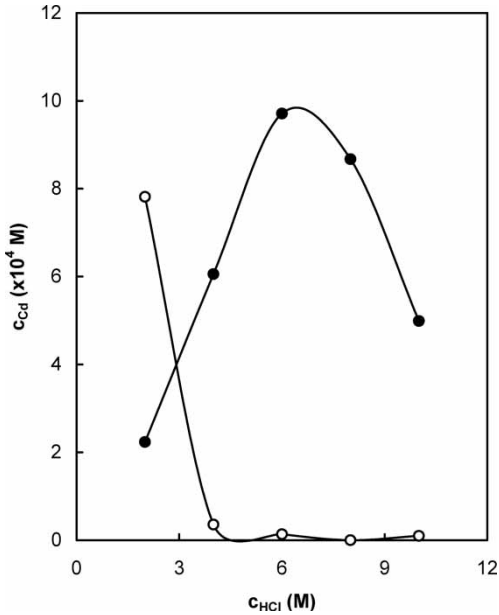


***Figure 2.*** Variation of cadmium concentration in the feed (○) and receiving (●) phases as a function of hydrochloric acid concentration in the feed phase. Other experimental conditions are the same as given in Table 1.



conditions the cadmium concentration in the receiving phase increases with increasing the DC18C6 concentration in the membrane. This can be explained by considering that the rate determining step governed by the stripping step of the transport process.

## Effect of Organic Diluent

The efficiency of the transport process was compared by changing the diluent used in the membrane. The diluents tested were chloroform, dichloromethane (DCM), 1,2-dichloroethane (DCE), and carbon tetrachloride (Fig. 4). The order of both extraction and transport efficiency varies as 1,2-dichloroethane $>$ dichloromethane $\gg$ chloroform $>$ carbon tetrachloride. This order is in good agreement with polarity of the studied diluents (25). However, because of the low cost of dichloromethane, this diluent was selected throughout the study.

## Effect of Time

The time dependency of cadmium transport through the proposed liquid membrane was investigated (Fig. 5). It is clear that the extraction from the

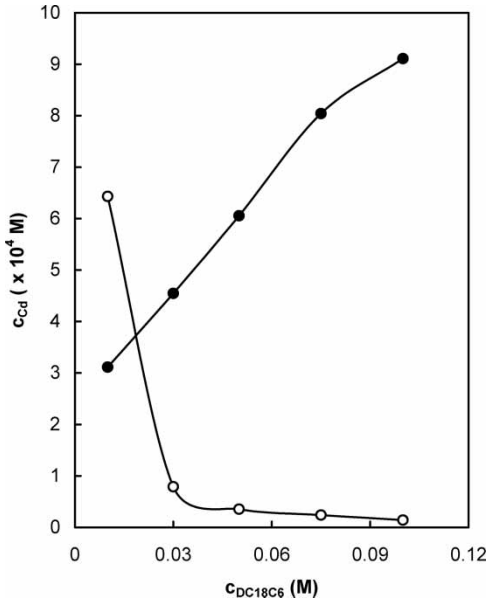


***Figure 3.*** Variation of cadmium concentration in the feed (○) and receiving (●) phases as a function of the DC18C6 concentration in the membrane. Other experimental conditions are the same as given in Table 1.

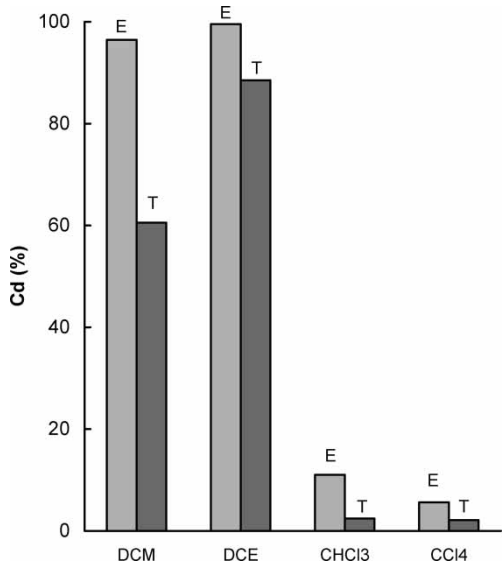


***Figure 4.*** The effect of the diluent used in the membrane on the extracted (E) and transported (T) values of cadmium ions (in percent). Other experimental conditions are the same as given in Table 1.

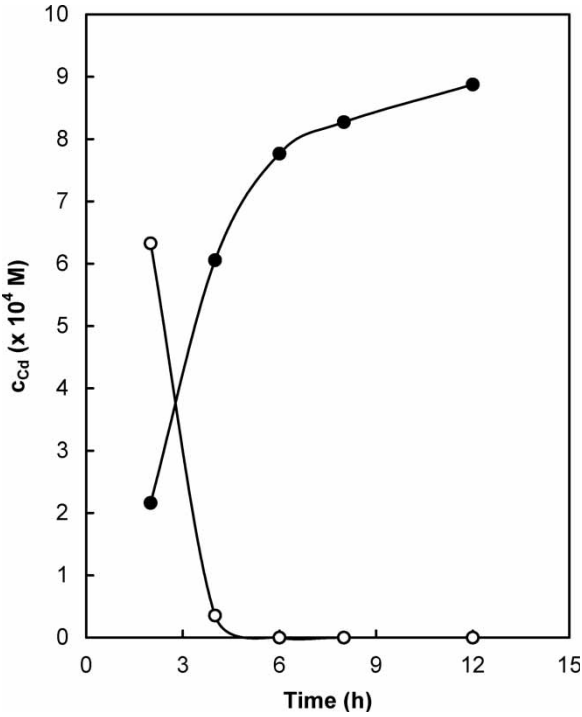


*Figure 5.* Variation of cadmium concentration in the feed (○) and receiving (●) phases as a function of the time of transport. Other experimental conditions are the same as given in Table 1.



feed phase into the membrane occurs at a faster rate than the release to the receiving phase. Therefore, it seems reasonable to assume that the release of cadmium from its ion-paired complex is the rate determining step of the transport process, as it is concluded based on the results found in the study of the effect of the carrier concentration in the membrane.

## Selected Conditions of the Transport Process

Based on the results obtained in the experiments verifying the influence of the parameters affecting the transport efficiency, the following conditions were selected for the transport of cadmium ions: feed phase, 10 mL, $Cd^{2+}$ (0.001 M), HCl (6 M); membrane, 20 mL, DC18C6 (0.05 M) in dichloromethane; receiving phase, 10 mL, distilled water; time of transport, 6 h; stirring, 100 rpm. Under these conditions, the results of five replicates experiments show a value of 98.3 ($\pm$1.8) percent of the initial amount of cadmium ions (0.001 M) is transported.

## Stability of the Membrane

The stability of the membrane was tested by measuring the transported amount of cadmium in repeated transport experiments which were carried out by renewal the source and receiving phases. An average value of 98.6 ($\pm$0.9) percent of the transported cadmium, for five replicate experiments, reveals a good stability of the membrane.

## Selectivity and Application of the Method

The selectivity of the transport toward cadmium ions was tested by performing the transport of these ions in binary mixtures with $Ni^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Pb^{2+}$, and $Fe^{2+}$ ions (Table 2). In addition, the recovery of cadmium ions



***Table 2.*** Comparison of the amount of transported cadmium ions from its mixtures with $Mn^{2+}$, $Ni^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Fe^{2+}$, and $Zn^{2+}$ ions[a]

| Mixture | Cation | Transported (%) |
|---|---|---|
| Mix 1 | $Cd^{2+}$ | 100.0 |
| | $Mn^{2+}$ | 0 |
| Mix 2 | $Cd^{2+}$ | 100.0 |
| | $Ni^{2+}$ | 0 |
| Mix 3 | $Cd^{2+}$ | 96.2 |
| | $Pb^{2+}$ | 0 |
| Mix 4 | $Cd^{2+}$ | 92.0 |
| | $Co^{2+}$ | 6.3 |
| Mix 5 | $Cd^{2+}$ | 100 |
| | $Fe^{2+}$ | 46.7 |
| Mix 6 | $Cd^{2+}$ | 97.2 |
| | $Zn^{2+}$ | 73.8 |
| Mix 7 | $Cd^{2+}$ | 80.2 |
| | $Mn^{2+}$ | 0 |
| | $Ni^{2+}$ | 0 |
| | $Pb^{2+}$ | 0 |
| | $Co^{2+}$ | 0 |
| | $Fe^{2+}$ | 46.2 |
| | $Zn^{2+}$ | 39.0 |

[a]Feed phase (10 mL): metal ions (0.001 M), HCl (6 M); membrane (20 mL): DC18C6 (0.05 M) in dichloromethane; receiving phase (10 mL): distilled water; time of transport: 6 h; stirring: 100 rpm.