



Study of Competitive Behavior of Cd(II) and Pb(II) Ions Through a Bulk Liquid Membrane

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors designed this study. Author MS carried out the experiment and wrote the first draft of the manuscript. Author JS managed the literature searches. Both authors discussed the results and contributed to the final manuscript.

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ABSTRACT

Aims: To investigate the competitive behavior of Cd(II) and Pb(II) ions within their equimolar mixtures, during transportation through a bulk liquid membrane, using macrocyclic carriers.

Study Design: Study was based on transport experiments, using homemade transport cell.

Place and Duration of Study: Department of Analytical Chemistry, Faculty of Technology, between September 2017 and February 2018.

Methodology: The bulk liquid membrane systems consisted of homemade transport cell constructed for transport of cations. Cell contained three separated phases: two aqueous and non-aqueous membrane phase between them. 1,2-dichloroethane (1,2-DCE) and dichloromethane (DCM) were used as liquid membranes. Macrocyclic ligands: benzo-18-crown-6 (DB18C6) and 18-crown-6 (18C6) were used as ligands for cations within the membranes. Both aqueous phases were buffered at pH = 5. Source phase contained an equimolar mixture of investigated metal ions and picrates as counter ions. Receiving phase contained thiosulphate as stripping agent. Duration of transport experiments were 3 hours and concentration of transported cations was measured using flame atomic absorption spectrometry.

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Results: Higher ligand selectivity for Pb(II) ions resulted with higher transport rates compared to Cd(II) ions: 63.25% of Pb(II) > 51.80% of Cd(II) using 18C6 in 1,2-DCE; 38.90% of Pb(II) > 30.50% of Cd(II) using DB18C6 in 1,2-DCE; 43.15 % of Pb(II) > 35.40 % of Cd(II) using 18C6 in DCM and 26.75% of Pb(II) > 8.90% of Cd(II) using DB18C6 in DCM. Higher selectivity of 18C6 as ionophore is also evident here. 1,2-DCE showed higher efficiency compared to DCM in competitive experiments (unlike individual experiments). Overall transport of Pb(II) in competitive experiments is lower compared to individual ones in DCM membrane: 40.30% < 70.40% (with 18C6) and 26.75% < 36.05% (with DB18C6). Overall transport of Cd(II) in competitive experiments is lower compared to individual ones in DCM membrane: 35.40% < 48.10% (with 18C6) and 8.90% < 38.25% (with DB18C6).

Conclusion: The results showed that higher ligand selectivity for Pb(II) ions lead to higher transport rates compared to Cd(II) ions from their equimolar mixtures. 18C6 was more selective for both cations as ionophore compared to DB18C6. 1,2-DCE showed higher efficiency as membrane solvent in competitive experiments compared to DCM, unlike the individual experiments. Competition between cations decreased their overall transport in DCM, but increased in 1,2-DCE membrane.

Keywords: Bulk liquid membrane transport; dibenzo-18-crown-6; 18-crown-6; Cd(II); Pb(II).

1. INTRODUCTION

Attempts to remove toxic heavy metal ions from the environment and biological systems have utilized a variety of analytical separation methods. Among numerous methods (adsorption, precipitation, solvent extraction, liquid membrane transport), transport of cations through the liquid membranes attracts attention of numerous researchers, as new separation process based on solvent extraction [1-5]. Driving force of transport process is diffusion of analytes from higher concentration solution to lower concentration solution, through the liquid membrane, with a suitable carrier [5,6]. Extraction, complexation and stripping operation conducted simultaneously, enabled successful removal of heavy metal ions which make the transport process very attractive [4,5]. Among numerous ligands for metal ions, macrocyclic crown ethers and their derivatives have been used most successfully as suitable neutral carriers through the liquid membranes. Interactions between metal ions and macrocyclic ligands are generally ruled by the level of their compatibility [7]. Numerous researchers concluded that the nature of cation and the nature of ligand (the cavity size, number and orientation of the donor atoms) determine the interactions between them [1,4,5,8]. Recently, there have been some studies of selective membrane transport for different cations using neutral ionophores [1-5]. The bulk liquid membrane systems contain three physically separated phases: two aqueous and one non-aqueous. Non-aqueous phase functions as the organic liquid membrane

(bulk liquid membrane) which separates two aqueous phases (source and receiving phase). The membrane phase provides transportation of cations from the source to the receiving phase, based on their complexation with ligands within the membrane. However, the uptake of cations on the source phase/membrane interface is probably higher than the release of cations on the membrane/receiving phase interface. In previous investigations of cation transport, during 4 hours of experiment, researchers measured decreasing concentration of cations within the source phase of BLM system. They assumed that the limiting step for overall transportation of cations is actually release of cations from formed complexes within the membrane into the receiving phase [5,9]. Based on proposed mechanism of transport [5], it was concluded that established equilibria within the membrane determine the amount of cations incorporated in the macrocyclic cavities of ligands as well as the amount of cations released from formed coordination compounds. For successful formation of complexes, it is required that their stability constants (K_{st}) have higher values (higher possibility of quantitative complexation and higher stability of formed complexes). However, very high values of K_{st} are not desirable for transportation process because the decomposition of complexes and release of cations into the receiving phase is difficult (although the uptake of cations from source phase is high). Based on these facts, researchers assume that certain compromise between complexation/decomplexation rates is required in transport experiments [9].

In this study, transport experiments for Cd(II) and Pb(II) metal cations using 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) as carriers were performed. 1,2-dichloroethane (1,2-DCE) and dichloromethane (DCM) were used as liquid membranes. The possibility of Cd(II) and Pb(II) ions separation from their mixtures is very challenging, due to their similar affinity toward certain ligands during complexation. In previous investigations, optimal experimental conditions for individual transport of Pb(II) and Cd(II) ions through the bulk liquid membranes were established [10]. In this paper, competitive behavior of these two cations which resulted with different transport rates compared to individual experiments, were investigated.

2. MATERIALS AND METHODS

2.1 Materials

Preparation of aqueous and non-aqueous solutions for the bulk liquid membrane system, were performed using following materials.

Source Phase preparation (aqueous solution):

- Standard Cd(II) solution (1000 mg/L), ($\text{Cd}(\text{NO}_3)_2$ in 0,5 mol/L HNO_3), Merck.
- Standard Pb(II) solution (1000 mg/L), ($\text{Pb}(\text{NO}_3)_2$ in 0,5mol/L HNO_3), Merck.
- $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ (picric acid); 99%, Kemika.
- Acetate buffer solution (pH = 5), prepared from CH_3COOH (purris. p.a., Fluka) and NaOH (g.r., Merck).

Membrane Phase preparation (non-aqueous solution):

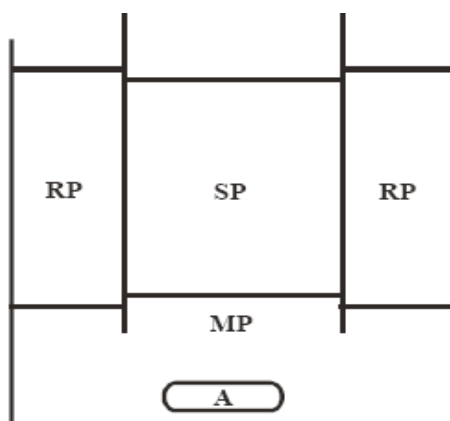
- Organic solvents: dichloromethane (CH_2Cl_2) and 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) (all from Kemika) were used with the highest purity.
- Macrocyclic ligands: 18-crown-6 ($\text{C}_{12}\text{H}_{24}\text{O}_6$) and dibenzo-18-crown-6 ($\text{C}_{20}\text{H}_{24}\text{O}_6$), were all from ACROS ORGANICS and used with the purity >99%

Receiving Phase preparation (aqueous solution):

- Acetate buffer solution (pH = 5), prepared from CH_3COOH (purris. p.a., Fluka) and NaOH (g.r., Merck).
- Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), purrum.p.a. Sigma-Aldrich.

2.2 Transport Procedure and Spectrometric Measurements

Cylindrical glass container, i.e. "transport cell", with inner diameter of 5 cm and central glass tube (2 cm in diameter), have been used for this study (Fig. 1). Implementation of this type of transport cell was reported earlier [11]. Central tube provides physical separation of two aqueous phases: source phase, SP and receiving phase, RP. Membrane phase, MP lies under the aqueous phases and connects them. Constant stirring with a magnetic stirrer is essential to provide that contact surfaces: RP/MP/SP remain flat and well defined.



(a)



(b)

Fig. 1. (a) Scheme of transport cell: SP-source phase; RP-receiving phase; MP-membrane phase; A-magnetic stirrer (b) Homemade cell used in transport experiments

For this study, BLM systems have been prepared as follows. The source aqueous phase (10 mL volume solution, buffered to pH=5) contained the equal amount of Pb(II) and Cd(II) ions (10^{-3} mol/L) and counter ions (picrate, Pic⁻) at the beginning of the experiment. The membrane phase (50 mL of organic solvent) contained macrocyclic ligand (10^{-3} mol/L) were placed on the bottom of transport cell (Fig. 1) and mixed with magnetic stirrer continuously. The receiving aqueous phase (30 mL volume solution, buffered to pH=5) contained the stripping agent (thiosulphate, 10^{-3} mol/L) at the beginning of the experiment. Both aqueous phases were buffered with acetate buffer solution and pH value controlled with pH meter using a combined glass electrode (Crison Instruments). All aqueous solutions were prepared using deionized double distilled water. Membrane phase, MP contained macrocyclic ligand (10^{-3} mol/L), dissolved in 50 mL of organic solvent. During the experiment, the amount of cations in source phase is decreasing due to their uptake on the interface between this aqueous phase and the membrane. Within the membrane, complexation of cations with suitable ligands occurs, and based on resulting interactions, formed complex compounds tends to decompose, enabling the release of cations into the receiving phase (where the amount of cations is increasing during the experiment). 3 hours of transport duration were chosen based on the individual transport results, so that comparison can be made.

AAS technique with flame atomization (apparatus: Atomic Absorption Spectrometer Perkin Elmer AAnalyst 200), was implemented for measurements of metal ion concentration at wavelengths for Pb(II) and Cd(II): 261,40 nm and 326,10 nm, respectively. Measurements were performed in receiving aqueous phases of transport system, after 3 hours of transport through the liquid membrane. Measurements were also made for the series of standard cation solutions (prepared similarly), in order to convert the atomic absorption signals to concentration units.

3. RESULTS AND DISCUSSION

3.1 Study of Cation Selectivity

Competitive transport study was made considering previously published results for individual transport of Cd(II) and Pb(II) ions, which showed that, under certain experimental conditions, it is possible to effectively transport

approximately 70% of Pb(II) and 50% of Cd(II) to the receiving phase [10]. Different transport efficiencies obtained for both cations were based primarily on different macrocyclic ligands used as carriers within the liquid membranes. Also the application of different organic solvents as membranes contributed to it. For instance, the best results for Pb(II) removal were obtained using 18C6 as ligand in DCM membrane phase (70,40%). Identical experimental conditions using DCM membrane and 18C6 as ligand obtained the best results for Cd(II) removal as well (48,10%). In the previous individual transport experiments, higher efficiency of transport and hence the overall removal of Pb(II) compared to Cd(II) was explained based on the size compatibility between the radius of the cation and the ring size, e.g. the radius of the macrocyclic cavity of ligand [10]. Compatibility between 18C6 (and analogs DB18C6, B18C6) with the cavity size in range of 2.6 to 3.2 Å is very high for Pb(II) ions with ionic radius of 2.4 Å. However, ionic radius of 0.97 Å for Cd(II) is less compatible. Actually, the incorporation of Cd(II) ion within the macrocycle occurs, but the level of interactions for smaller cation is probably lower, resulting with lower transport efficiency. The aim of this study was to investigate the possibility of transport for these cations from their equimolar mixtures, compared to individual transport. Same model systems of bulk liquid membrane were created and similar behavior was expected for cations in their mixtures compared to their individual transport. Behavior of both cations were observed through the efficiency of their transport and explained based on different extraction selectivity. In the experiments of transport from the source phase containing equimolar mixture of cations, different amount of transported cations in the receiving phase is probably related to different values of extraction constants (K_{ex}) [11]. Authors in similar investigations suggested that in competitive experiments, the mechanism of cation-ligand interactions within the membrane and cation release at membrane surface are different compared to individual experiments [11]. At the interface between the source phase and membrane, competitive behavior of two cations probably occurs and when their concentrations are equal, different stability constants (K_{st}) of formed complexes results with different transport rates for each cation. The size of Pb(II) ionic radius is probably the main reason for the higher transport efficiency compared to Cd(II), similar to individual experiments. Higher selectivity for Pb(II) ions lead to formation of stronger complex

compound within the membrane which caused higher extraction efficiency, and overall higher transport rates for Pb compared to Cd in these experiments.

Table 1 shows the results of measured concentration of cations (%) in the receiving aqueous phase, after 3 hours of competitive transport experiment, for both used membranes and both ligands.

3.2 Study of Membrane Type Influence

The ability of the solvent molecules to compete with the donor atoms of the ligand towards the coordination sites of cation is one of the factors that can thermodynamically influence the complexation process. Previous experiments of individual cation transport [10] resulted with higher efficiency of DCM membrane compared to 1,2-DCE, which was explained based on some physicochemical properties of solvents: the lower viscosity of DCM (0.41) compared to 1,2-DCE (0.84) and also the lower dielectric constant of

DCM (8.93) than those of 1,2-DCE (10.66). However, in all competitive experiments (for both cations and both ligands), lower transport efficiency is detected using DCM membrane compared to 1,2-DCE (Fig. 2). Obviously the competition between cations during transport can affect the mechanism of complexation in terms of solvent interaction within the membrane. The higher value of the dipole moment for 1,2-DCE (1.88) compared to DCM (1.55) and lower density of 1,2-DCE (1.25) than DCM (1.33) could be also related to higher transport rate for 1,2-DCE in competitive experiments.

3.3 Study of Competitive Behavior of Cations

Comparison between individual [10] and competitive experiments for different membranes showed different effect of cation competition during transport. It is obvious that in competitive experiments 1,2-DCE provided better conditions for cation transport compared to DCM and enabled higher transport rates for both cations

Table 1. Results of measured concentration of cations in RP (%) after 3 hours of competitive transport from their equimolar mixtures in SP ($1 \cdot 10^{-3}$ mol/L), using macrocyclic ligands ($1 \cdot 10^{-3}$ mol/L) within the membrane

Membrane solvent	Pb (%)		Cd (%)	
	18C6	DB18C6	18C6	DB18C6
1,2-Dichloroethane	63.25	38.90	51.80	30.50
Dichloromethane	43.15	26.75	35.40	8.90

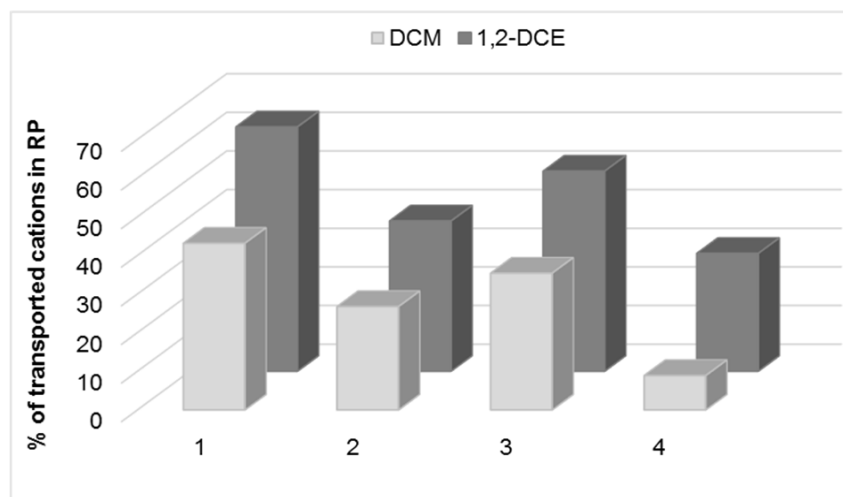


Fig. 2. Comparison of competitive transport results using different membrane solvents and different ligands

1,2 for Pb; 3,4 for Cd; 1, 3 for 18C6 and 2,4 for DB18C6
 SP: $1 \cdot 10^{-3}$ mol/L of cations + $1 \cdot 10^{-3}$ mol/L Pic;
 RP: 0,10 mol/L $S_2O_3^{2-}$

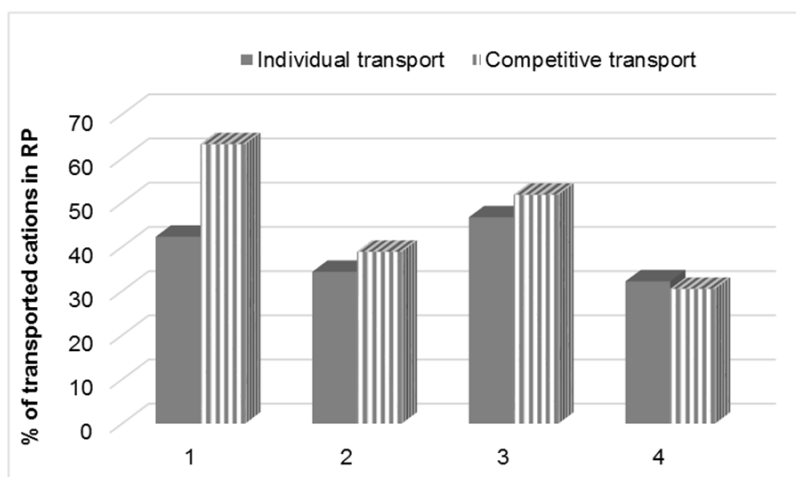


Fig. 3. Comparison of competitive and individual transport results through 1,2-DCE membrane
 1,2 for Pb; 3,4 for Cd; 1,3 for 18C6 and 2,4 for DB18C6
 SP: $1 \cdot 10^{-3}$ mol/L of cations + $1 \cdot 10^{-3}$ mol/L Pic⁻;
 RP: 0,10 mol/L S₂O₃²⁻

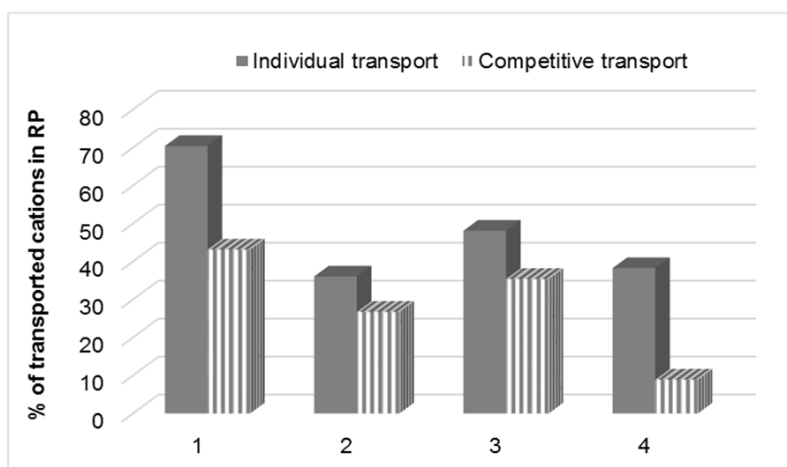


Fig. 4. Comparison of competitive and individual transport results through DCM membrane
 1,2 for Pb; 3,4 for Cd; 1,3 for 18C6 and 2,4 for DB18C6
 SP: $1 \cdot 10^{-3}$ mol/L of cations + $1 \cdot 10^{-3}$ mol/L Pic⁻;
 RP: 0,10 mol/L S₂O₃²⁻

(Fig. 3). Lower transport efficiency for both cations using DCM membrane is also evident (Fig. 4) for competitive transport experiments.

3.4 Study of Ligand Structure Effect

Previously published results for individual transport [10] showed that the selectivity of ligands for investigated metal cations remains the same regardless the identity of organic solvents used as membrane phase during experiments. Obtained results in competitive experiments showed accordance with individual

experiments: higher transport efficiencies for both cations using 18C6 compared to DB18C6 (Table 1). Probably the rigidity of DB18C6 due to presence of two substituents limited the access for cations, hence the higher flexibility of 18C6 enabled better conditions for interactions with cations and resulted with higher transport rates.

4. CONCLUSION

Competitive behavior of metal ions Pb(II) and Cd(II) during their transport through a bulk liquid

membrane reflected in different transport mechanism compared to individual transport. Higher selectivity of ligands for Pb(II) ions caused higher transport rates compared to Cd(II) ions from their equimolar mixtures. 18-crown-6 showed better selectivity for both cations as ionophore compared to dibenzo-18-crown-6 due to its flexibility. 1,2-dichloroethane showed higher efficiency as membrane solvent in competitive experiments compared to dichloromethane, unlike the individual experiments. Competition between cations decreased their overall transport in dichloromethane, but increased in 1,2-dichloroethane membrane.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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