

STUDY OF INTERACTIONS BETWEEN METAL IONS AND CROWN ETHERS IN LIQUID ORGANIC MEMBRANE SYSTEMS

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ABSTRACT

Considering the toxic properties of heavy metals and their effects on the environment, there is an increasing interest in studying their interactions with different ligands and searching for possibilities to remove those ions from the environment. Compared to other ligands, crown ethers possess the highest selectivity as ligands for metal cations, due to their “macrocyclic effect”. In this paper, interactions between Pb(II), Cd(II) ions and various crown ethers (18 crown-6, benzo-18-crown-6, dibenzo-18-crown-6, dicyclohexane-18-crown-6 ether), were analyzed. The UV/VIS spectrometric method was used to record absorption diagrams of "model systems" of varying complexity. Cd(II) and Pb(II) ions were monitored using flame atomic absorption spectrometry. In different organic solvents used (chloroform, dichloromethane), UV/VIS and FAAS measurements showed that higher absorption intensity caused more stable complexes in the membrane, complicating the release of ions. With the benzo-18-crown-6 ether as ligand, Pb(II) ions released into the aqueous phase at a rate higher than 60%, compared with Cd(II) ions released at a rate of 49%. In a model system containing a nonionic surfactant (TX-100), metal ions interact more intensely with the membrane, and cation release is reduced in the aqueous phase, indicating that the reverse micellar aggregates incorporate metal ions that result in higher absorption intensities. According to the macrocycle selected, the presence of benzo- and cyclohexyl groups (B18C6, DB18C6, DCH18C6) probably reduces interactions between substituted macrocyclic ligands and metal cations, resulting in lower values of Pb(II) and Cd(II) ions measured in the aqueous phase compared with a model system with 18 crown-6 ether.

1. INTRODUCTION

A major problem in the world is the pollution of water caused by the discharge and accumulation of heavy metals. Natural waters usually contain trace amounts of heavy metals, but many are toxic even at very low concentrations [1]. Controlling Pb(II) and Cd(II) ions in environmental samples is of crucial importance due to their industrial importance and its environmental pollution [2]. In analytical chemistry, and especially in industrial processes, it is critical to separate metal cations from complex matrices. As well as finding the most efficient and reliable methods for determining undesirable components, attention is focused on removing them from the environment. Crown ethers are generally heterocyclic compounds with high binding affinity. The unique structure of crown ethers has made them widely used in drug delivery, solvent extraction, cosmetics manufacturing, material studies, catalysis, separation, and organic synthesis. This class of organic compounds has an interesting structure with a hydrophobic ring surrounding a

hydrophilic cavity [3]. Hydrophobic rings surround hydrophilic cavities in these molecules, enabling them to form stable complexes with metal ions and contribute to host-guest chemistry [4,5]. The interaction between ligands and metal cations is determined by the nature of the metal cation as well as the number, distance, and orientation of the ligand donor atoms structurally accessible to the complex metal cation [6]. Pedersen studied the properties and manufacturing of crown ether for the first time in 1967 [7,8]. According to Pedersen's proposal, metal ions are electrostatically attracted to oxygen atoms in crown ether rings (host-guest complexes), and a ligand that exhibits less affinity for transition metal cations than alkali and alkaline earth metal cations [9].

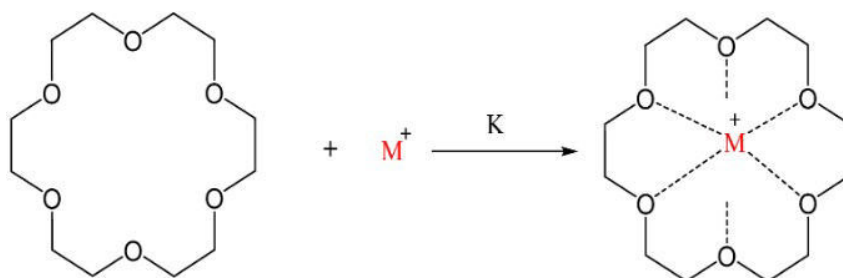


Figure 1. Binding of M^+ by 18-crown-6 ether; K is complex stability constant [10]

In this paper, interactions between Pb(II), Cd(II) ions and various crown ethers (18 crown-6, benzo-18-crown-6, dibenzo-18-crown-6, dicyclohexane-18-crown-6 ether), were analyzed. After complexation of the carrier with Pb(II) and Cd(II) ions on the left side of the membrane ($CE-Pb^{2+}$)($CE-Cd^{2+}$), $(Pic^-)^2$ ion-pair is formed at the SP-MP interface and diffuses down its concentration gradient within the organic phase. Liquid membrane is known as a green technology because of its green characteristics such as being eco-friendly and its low consumption of organic solvent [11]. A liquid membrane system used involves an organic liquid membrane that serves as a semi-permeable barrier between two aqueous phases, the source phase (SP) and receiving phase (RP). On the right side of the membrane, at the MP-RP interface, the metal ion would be released into the receiving phase via the formation of ternary adducts (carrier-metal ion-stripping agents/carrier-metal ion-surfactants).

2. MATERIALS AND METHODS

Materials

Feed solutions were prepared from:

- Standard Pb(II), and Cd(II) solution (1000 mg/L), Merck
- Picric acid ($C_6H_3N_3O_7$), $c = 1 \cdot 10^{-3}$ mol/L, 99%, Kemika
- Formic acid buffer solution (pH=3), prepared from HCOOH and NaOH (g.r., Merck)

Organic solutions were prepared from:

- Organic solvents: chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and 1,2-dichloroethane ($C_2H_4Cl_2$)
- Macrocyclic ligands: 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6)

Stripping solutions were prepared from:

- Triton X-100 surfactant ($1,4 \cdot 10^{-3}$ mol/L)
- Disodium-EDTA ($1 \cdot 10^{-3}$ mol/L)

- Acetic acid buffer solution (pH=5), prepared from CH₃COOH (purris. p.a., Fluka) and NaOH (g.r., Merck).

Extraction procedure

Liquid-liquid extraction – LLE is based on the distribution of the analyzed substance from one liquid phase to another liquid phase. Liquid phases do not mix with each other: e.g. water and hydrophobic organic solvents, then alcohol and ether, etc.

LLE is the most commonly used separation method, where the metal ion from the aqueous phase passes into the organic phase by complexing with some hydrophobic ligand.

In order for the extraction to take place at the molecular level, the metal ion and the ligand must react and diffuse together, which can be shown schematically (Figure 2.).

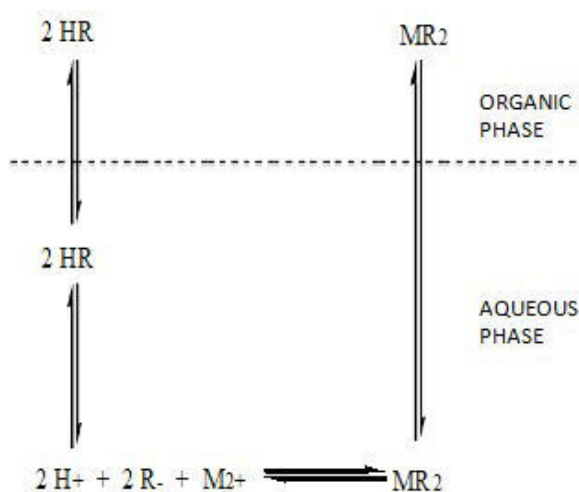


Figure 2. Balances in the system during the extraction of M^{2+} cations by the chelating agent

The source phase (SP) contained 10 mL of a mixture of tested Pb(II) ions ($1 \cdot 10^{-3}$ mol/L) and Cd(II) ($1 \cdot 10^{-3}$ mol/L). The receiving phase (RP), which is outside the central tube, contained a stripping agent. The membrane phase (MP) contained a suitable ligand ($1 \cdot 10^{-3}$ mol/L) dissolved in an organic solvent; the membrane layer lies beneath the aqueous phases and connects them. The membrane phase is mixed with a magnetic stirrer so that under these conditions the contact surfaces between the aqueous phases are straight and precisely defined [12]. Spectrophotometric measurements of the membrane phase were performed with UV/VIS spectrophotometer (CECIL CE 2021).

Quantification of metal ions removed during the transport experiments was obtained by Flame Atomic Absorption Spectrometry technique, using the instrument Perkin Elmer AAnalyst 200.

3. RESULTS AND DISCUSSIONS

The macrocyclic structure of organic ligands ensures high stability of the formed complexes with metal ions due to the "macrocyclic effect" [13]. The affinity of the ligand to the metal ion depends on the structural characteristics of the ligand, primarily on the number and type of donor atoms, polarity, the hydrophilic-lipophilic balance of the ligand, chirality and other stereochemical indicators with heteroatoms (oxygen atoms). In particular, the highest selectivity is expected in cases where the ratios of cation radius and ligand cavity radius are closest to 1. One of the main factors determining transport

efficiency is the nature of the membrane. In complexation, solvation is an important factor in determining the interactions between metal cations and ligands, which includes ligand, metal cation, and complex together. This can be explained by Cram's reorganization principle, which states that both host and guest are involved in solvent interactions [14].

Effective interactions, according to the acid-base concept (classification into so-called hard and soft bases and acids), Pb(II) ions have a less "soft character", so they can form a more stable complex with oxygen atoms that donates B18C6 as a "hard" base.

Experiments involved different ligands dissolved in organic solvents as carriers for Pb(II) and Cd(II) ions. Results showed that benzo-18-crown-6 ether achieved the highest efficiency in removing Pb(II) ions in chloroform (60%) compared with dibenzo-18-crown-6 ether, and dicyclohexano-18-crown-6 ether. In addition, Pb(II) ions carry a high charge density, and consequently in greater transport of Pb(II) ions with B18C6 compared to other ligands. Compared to the system with 18-crown-6 ether, where the ring size and cavity diameter remain the same (1.34 \AA^0), the presence of benzo- and cyclohexyl groups (B18C6, DB18C6, DCH18C6) probably reduces the interactions between substituted macrocyclic ligands and cations, which leads to lower values of measured Pb(II) ions in the final phase compared to the model system with 18C6 (70.4%). Actually, DB18C6 has the most rigid structure among the crown ethers studied [15,16].

The UV/VIS absorption spectra of 3-component systems (picrate + Pb(II) + ligand) showed a higher intensity of absorption band for 1,2-DCE as a membrane solvent (Figure 3). The higher absorption intensity probably refers to stronger interactions for model system PA+Pb+18C6 which result in a more stable complex formed in the membrane compared to model system PA+Pb+DB18C6 for both solvents used.

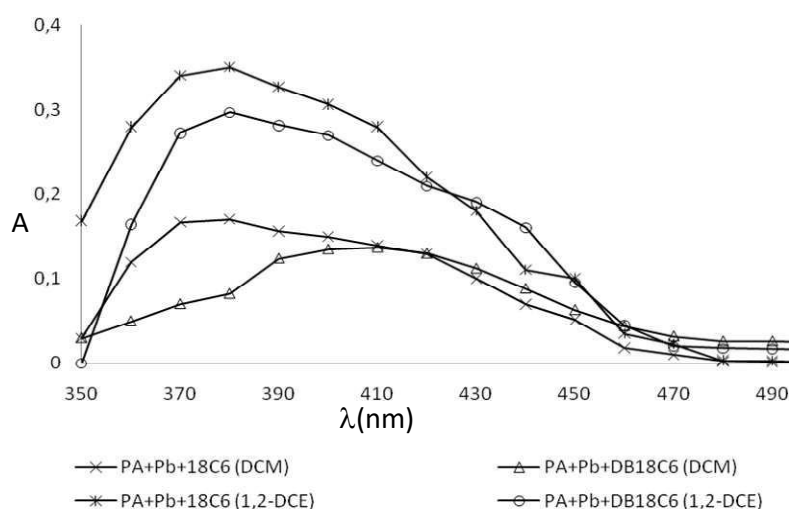


Figure 3. Comparison of absorption diagrams model - system: PA+ Pb(II)+18C6, PA+ Pb(II)+DB18C6 in the presence of different solvents in the liquid membrane

If we observe the absorption diagram of the 3-component system inside the membrane (PA+Cd(II)+ligand), we notice a lower intensity of absorption in chloroform (Figure 4.) compared to dichloromethane (DCM) and 1,2-dichloroethane (DCE) as membranes. Namely, a higher intensity of absorption means stronger interactions within the membrane, the complex formed in the membrane is more stable, and this further complicates the release of cations at the boundary between the membrane and the aqueous phase.

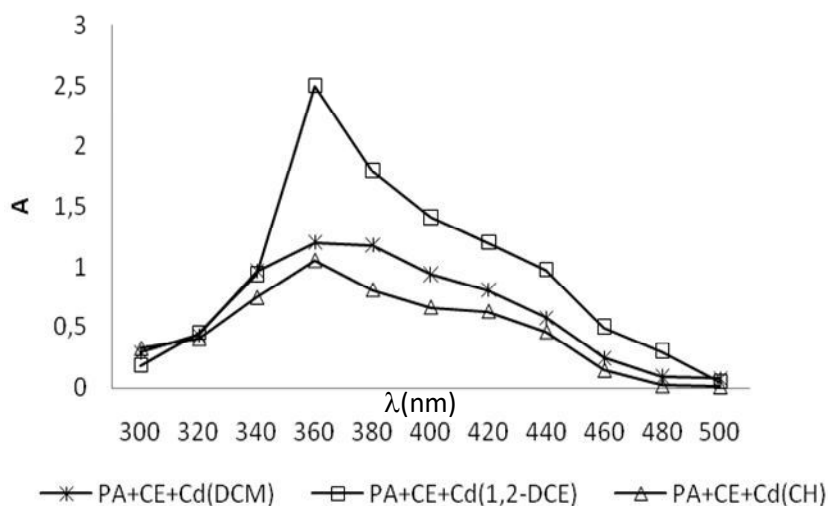


Figure 4. Comparison of absorption diagrams model - system: PA+ Cd(II)+18C6, PA+ Cd(II)+DB18C6 in the presence of different solvents in the liquid membrane

After 3 h of transport, the highest percentage of removed ions in the aqueous phase was measured for the system with a CH membrane, where the efficiency of removed Cd(II) ions was slightly lower (43.2%). For the system with a 1,2-DCE membrane, the efficiency of removed Cd(II) ions was 35.30%.

Interactions between cations and surfactants inside the membrane successfully provide cation removal from the source phase, but not their transfer to the receiving phase. The results show a lower transport efficiency for systems with added surfactants (TX-100 and TX-45), compared to systems containing only macrocyclic ligands. The influence of the surfactant structure is obvious: the comparison of Pb(II) transport results confirms the fact that the length of the polyether chain affects the metal-surfactant interactions. Despite the assumption that the spatial separation of cations from the binding sites of longer-chain surfactants reduces the level of interaction, the greater number of binding sites (oxygen atoms) in the structure of longer-chain surfactants speaks in favor of a greater possibility of interactions. The higher absorption intensity probably refers to stronger interactions within the membrane, the formed complex in the membrane is more stable, and consequently the release of metal ions to the receiving phase is reduced.

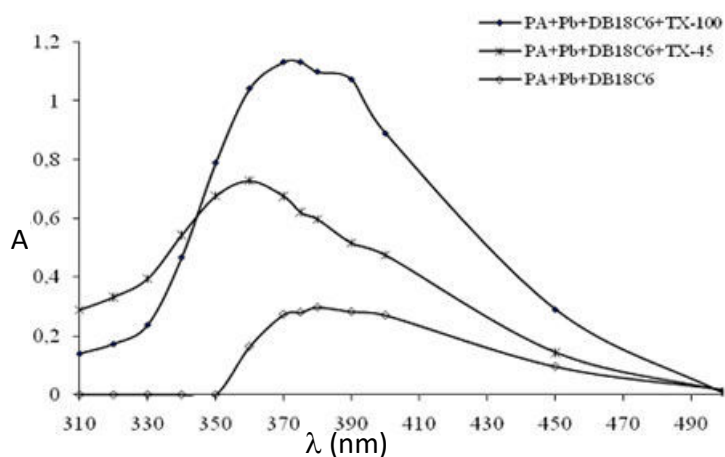


Figure 5. Comparison of absorption diagrams model - system: PA+ Pb(II)+DB18C6, PA+ Pb(II)+DB18C6+TX100, PA+ Pb(II)+DB18C6+TX45, in the presence of 1,2-DCE in liquid membrane

4. CONCLUSIONS

The UV/VIS and FAAS measurements in different organic solvents found that higher absorption intensity caused more stable complexes in the membrane, resulting in a more difficult ion release. In the presence of benzo-18-crown-6 ether, Pb(II) ions release into the aqueous phase at a rate greater than 60%, compared with Cd(II) ions which are released at a rate of 49%. 18-crown-6 ether is the most suitable for the complexation of Cd(II) ions compared to dibenzo-18-crown-6, benzo-18-crown-6, and dicyclohexano-18-crown-6 due to its greater flexibility. The metal ions interact more strongly with the membrane in a model system with a nonionic surfactant (TX-100), reducing cation release in the aqueous phase, indicating that reverse micellar aggregates contain metal ions resulting in higher absorption rates.

5. REFERENCE

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