

# Influence of Solvent Properties on Their Efficiency As Liquid Membranes For Metal Ion Removal

Edita Bjelić<sup>1</sup>, Mersiha Suljkanović<sup>2\*</sup>, Jasmin Suljagić<sup>1</sup>, Azra Kovačević<sup>1</sup>

<sup>1</sup>Faculty of Technology, University of Tuzla

<sup>2</sup>Faculty of Natural Sciences and Mathematics, University of Tuzla

Univerzitetska 4, 75000 Tuzla

Bosnia and Herzegovina

## Abstract

Among numerous experimental conditions for metal ion removal by the technique of bulk liquid membrane transport, effects of different membrane solvents were investigated. Polyether ligands dissolved within liquid membranes were used as electron donors for metal ions. The overall transport process (extraction, diffusion and re-extraction of analytes) depends on the numerous interactions within the membranes and on their surface.

In this paper, research was performed on "model transport systems", composed of: divalent metal ions (Cd, Pb) and counter ions (picrate) in "source" phase, polyethers (18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, Triton X-100) in different solvents (dichloromethane, 1,2-dichloroethane, chloroform and nitrobenzene) as "membrane phase" and stripping agents (thiosulfate) in "receiving phase". Spectrometric (UV/VIS and AAS) techniques were used for quantification of removed metal ions. Among the solvents used as liquid membranes, dichloromethane resulted with the highest efficiency for removal of metal ions with 18-crown-6 (61.26% for Cd and 70.40% for Pb), but also for other ligands. Higher dielectric constant ( $\epsilon = 8.93$ ) and lower viscosity (0,41) for dichloromethane contributed to higher removal rate, thus giving the advantage to this solvent for preparing the liquid membrane for transport of metal ions.

**Keywords:** solvent parameters, liquid membrane transport

## I. INTRODUCTION

Among numerous techniques for the effective removal of metal ions from natural sources based on complexing reactions between cations and suitable ligands, transport through the liquid membranes (BLM "Bulk Liquid Membranes") is increasingly attracting the attention of researchers. [1, 2]

This relatively simple technique includes three steps: extraction, diffusion and re-extraction of analytes. [2] Since the ligand-cation ("host-guest") interactions and the stability of the formed complexes depend on a number of experimental conditions, by varying

them we can actually increase the transport efficiency. The most important of all parameters, however, is the compatibility of the metal cation and the ligand. However, also important parameters are: the type of membrane solvent, the type of counter-ion, the presence of coexisting species, stripping agents, etc. The theoretical model of this type of transport was set by Reusch and Cussler [3]. Since the ligands are the "carriers" of metal ions through the membrane, appropriate values of the stability constants of their complexes, adequate solubility within the membrane, as well as lipophilicity are required to prevent the ligand from leaking out of the membrane into the solution of the analyte itself. This actually highlights the importance of ligands and their interactions with the membrane solvent.

Since the transport of ions occurs between two aqueous phases through the organic phase-membrane, the driving force is the cation concentration gradient. [4] However, the importance of the medium itself, in which the metal-ligand interactions take place, should be emphasized.

The nature of the membrane solvent is one of the main factors in establishing transport efficiency. Several parameters of the membrane solvent can affect the transport of metal ions through bulk liquid membranes. The physical and chemical properties of solvents are closely related to their structures and play important roles in solute-solvent and solute-solute interactions in solutions. The basis for understanding the influence of solvents is the principle of dividing solvents into polar and nonpolar ones, but other solvent characteristics (viscosity and dielectric constant) can enhance or limit their application.

When it comes to the interactions of metal ions and ligands, a very significant factor is the solvation of the species involved in complexation: the ligand, the metal ion, and the complex itself.

The effects of the solvent can be explained by Cram's reorganization principle [5], which states that both the host and the guest participate in interactions with the solvent. Essentially, cation-ligand interactions compete with cation solvation, so the balance between these two effects determines both stability and selectivity.

The solvation of a metal ion strongly depends on its size, but also on the nature of the solvent. During complexation, the ligand should have the ability to replace the solvent molecules in the first cation solvation shell or that the cation has the ability to replace the solvent molecules with the ligand molecules.

[6] Therefore, it can be concluded that by changing the type of solvent, we significantly alter the binding properties and selectivity of a particular ligand for a given metal cation. Researchers [7] highlight the necessity of having valid information for different solvent systems to understand their influence on thermodynamics and complexation kinetics. Some significant solvent parameters are given for dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), nitrobenzene (NB) and chloroform (CH) in Table 1.

TABLE 1. Solvent parameters [8]

| Solvent  | Dielectric constant, $\epsilon_r$ | Dipole moment, $\mu$ (D) | Viscosity $\eta$ (mPa.s) | Density, $\rho$ (g/cm <sup>3</sup> ) |
|----------|-----------------------------------|--------------------------|--------------------------|--------------------------------------|
| DCM      | 8.93                              | 1.6                      | 0.41                     | 1.33                                 |
| 1,2- DCE | 10.66                             | 1.8                      | 0.84                     | 1.25                                 |
| NB       | 34.82                             | 4.02                     | 2.03                     | 1.19                                 |
| CH       | 4.81                              | 1.15                     | 0.56                     | 1.49                                 |

The choice of a suitable organic solvent depends on the role expected of it, for example in the process of transport through liquid membranes, it is one of the most critical factors for the functioning of the membrane. The solvent having the role of a liquid membrane should be selected so that it is not miscible with the aqueous phase and has a low viscosity and volatility while allowing a large distribution coefficient. The dielectric constant is also an important parameter. Thus, for example, researchers [9] found that a higher rate of transport of Pb (II) ions was established in chloroform (due to a lower dielectric constant) than in nitrobenzene (with a higher dielectric constant). The high viscosity of nitrobenzene reduces the rate of transport compared to other solvents. [9].

Transport will take place due to diffusion (the difference in ion concentrations between the two aqueous phases is the driving force of the transport) and the difference in solubility between the aqueous phases and the membrane phase. Ligands that interact with metal ions in the membrane phase must hold the ions in the complex as tight as possible in order for the extraction in the organic phase to be complete and the complexes should have the highest stability constant. On the other hand, it is also necessary to release ions from the membrane to the final aqueous phase, so a compromise is required between the ligand-metal binding strength and the ligand dynamics itself. In transport systems, when complex formation between the transported ion and the carrier (ligand) and dissociation of the complex is very fast and the stability constant of the complex at the source

phase / membrane interface and within the membrane is large, the mass transport of the complex in the membrane is the step that determines the reaction rate. Ligand plays the role of an extracting agent that favors the transport of analytes from the original solution to the final stage, due to its ability to build complex with the analyte. The higher the solubility of the ligand in the liquid membrane, the higher the analyte mass flow rates and the better selectivity achieved.

In this paper, "model systems" with known concentrations of metal cations: Cd (II) and Pb (II), and polyether ligands (18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6 and Triton X-100) are examined with counter ions (picrate) present, and in various organic solvents. The aim was to highlight individual solvents as more suitable media for the metal-ligand interactions within transport systems. The desirable physicochemical parameters of the solvent impose its application as liquid membranes, achieving efficient transport of metal ions.

## II. MATERIAL AND METHODS

### Material

For every transport experiment, two aqueous solutions and one non-aqueous organic solution (membrane), were prepared, as follows.

Source Phase solutions were prepared using the AAS standard metal ion solutions (Cd and Pb) from Merck, and picric acid (99%, Kemika) and adjusted to pH = 5, using the acetic buffer solution. Membrane Phase solutions were prepared by dissolving different macrocyclic ligands: 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6 (99%, ACROS ORGANICS) and/or non-ionic surfactant (Triton X-100, p.a. Sigma-Aldrich) in different organic solvents (p.a. Kemika): dichloromethane, chloroform, 1,2-dichloroethane, nitrobenzene. Receiving Phase solutions were prepared also in acetic buffer medium (pH = 5), by dissolving sodium thiosulphate (p.a. Sigma-Aldrich) in it.

### Instruments

pH measurements of aqueous solutions were performed using the pH meter (GLP31 Crison Instruments).

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.

### Procedure

Transport experiments involved the application of a cylindrical glass vessel, "transport cell" (Fig.1), with an inner diameter of 5 cm, containing a glass tube (2cm in diameter) in central position. The central tube represents a physical barrier between the

two aqueous phases. The source phase (SP) contained 10 mL of a mixture of tested metal ion ( $1 \cdot 10^{-3} \text{ mol/L}$ ) and the counter ion, picrate ( $1 \cdot 10^{-3} \text{ mol/L}$ ). The receiving phase (RP), which is outside the central tube, contained stripping agent (thiosulphate). The membrane phase (MP) contained 50 mL of a suitable ligand ( $1 \cdot 10^{-3} \text{ mol/L}$ ) 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. [10] Both aqueous phases were analysed by atomic absorption spectrometry after 3 hours, and the concentration of metal ions transported through the membrane was measured.

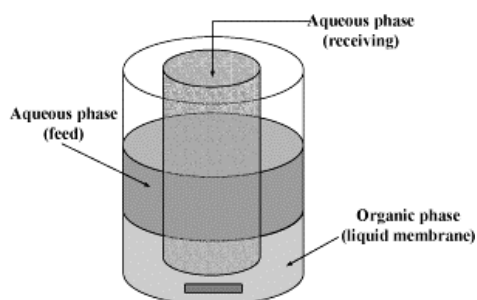


Fig 1: Scheme of a cylindrical glass vessel, "transport cells"



Fig 2: Cylindrical glass vessel before and after transport of metal ions

### III. RESULTS AND DISCUSSION

In previous studies [10, 11], the authors proposed a transport mechanism (Fig. 2), based on the interactions that take place in these systems during the experiment. A key step in transport is the release of metal ions to the receiving phase. By varying the composition of the membrane, the effectiveness of each individual solvent can be examined.

The transport efficiency of Cd (II) ions through four different liquid membranes: dichloromethane, 1,2-dichloroethane, chloroform and nitrobenzene was examined. After 3 h of transport, the highest percentage of Cd (II) ions in the receiving phase was measured for the DCM membrane system (Fig 4.).

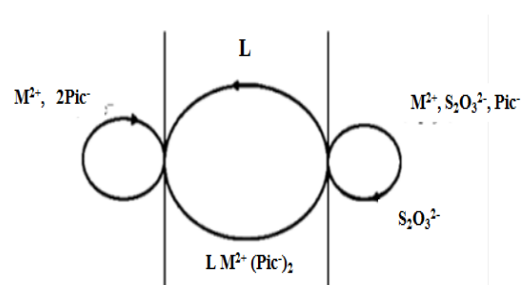


Fig 3: Proposed mechanism of metal ion transport [10] through organic liquid membrane containing dissolved ligand (L), from SP (contains:  $M^{2+}$  cations and counterions picrate  $Pic^-$ ) to RP (contains thiosulphate ions)

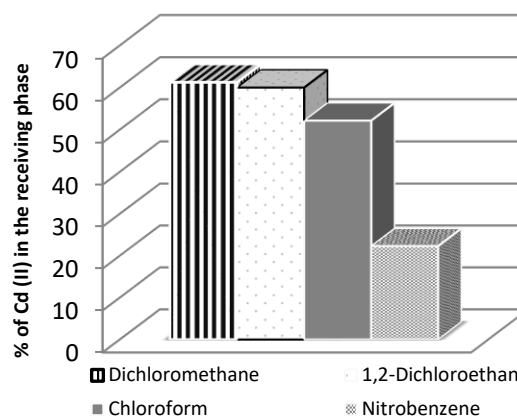


Fig 4: Comparison of Cd(II) transport efficiency through DCM, 1,2-DCE, NB and CH membranes, with 18C6 as membrane ligand

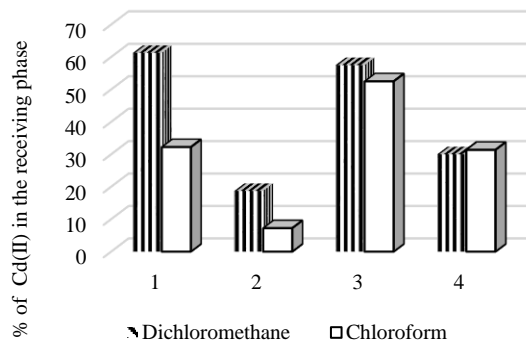
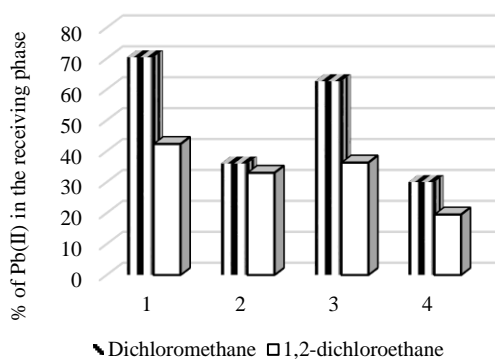


Fig 5: Comparison of Cd(II) transport efficiency through DCM and CH membranes for different ligands: 1 – 18C6; 2 – B18C6; 3 – 18C6+TX-100; 4 – B18C6+TX-100

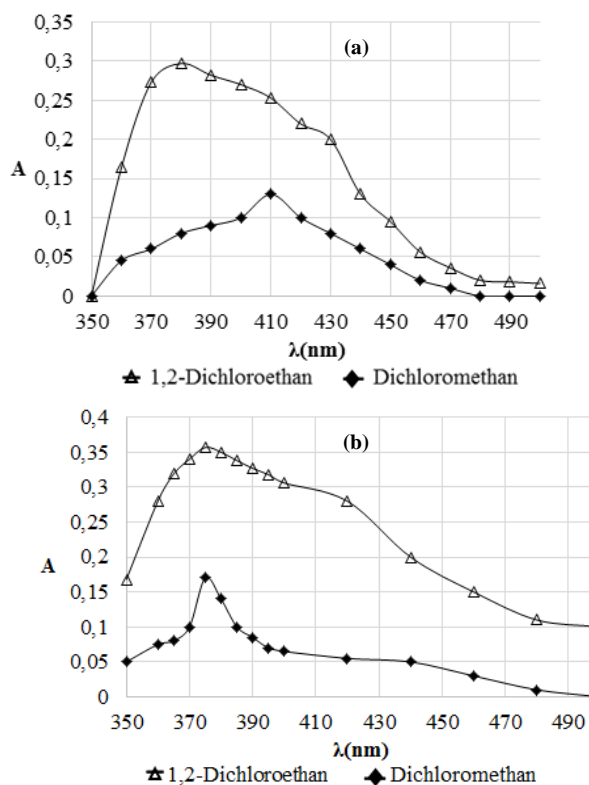
The transport efficiency for Cd (II) ions using different ligands (18-crown-6, 18C6; benzo-18-crown-6, B18C6; combinations of: 18C6 + TX-100 and B18C6 + TX-100) was examined through two different liquid membranes: dichloromethane (DCM) and chloroform (CH). For all investigated ligand systems, better efficiency was obtained using the dichloromethane membrane (Fig. 5).

The transport efficiency for Pb (II) ions using different ligands (18C6; DB18C6; 18C6 + TX-100 and DB18C6 + TX-100) was examined using two different liquid membranes: DCM and 1,2-DCE. DCM membrane showed better transport efficiency, for all ligand systems investigated (Fig. 6).

Double value for viscosity for 1,2-DCE compared to DCM (Table 1) can be possible explanation. The lower viscosity represents the less resistance to movement within the liquid, thus favors the transport of metal ions. Also, the lower dielectric constant for DCM (8.93) compared to 1,2-DCE (10.66) contributed to more efficient transport, since the lower dielectric constant stabilizes ion pairs (between cations and counter ions), and enhance the transport through the membrane.



**Fig 6:** Comparison of Pb(II) transport efficiency through DCM and 1,2-DCE membranes for different ligands: 1 – 18C6; 2 – DB18C6; 3 – 18C6+TX-100; 4 – DB18C6+TX-100



**Fig 7.** Absorption spectra of 3-component systems in different membrane phases: (a) Pb(II)+PA+18C6; (b) Pb(II)+PA+DB18C6

The UV/VIS absorption spectra of 3-component membrane systems (picrate + Pb (II) + ligand) showed a higher intensity of absorption band for 1,2-

DCE as a membrane solvent (Fig.7). 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.

## CONCLUSIONS

The physicochemical properties of solvents are closely related to their effectiveness as liquid membranes in metal ion transport experiments. The solvent viscosity should be as low as possible to minimize the cation diffusion resistance through the membrane. The solvent dielectric constant decreases the electrostatic interactions, so a lower value of this parameter is necessary to stabilize the cation-counter ion pairs in the membrane. The low dielectric constant, as well as the low viscosity of dichloromethane, make this solvent most suitable for the preparation of a liquid membrane for the transport of Cd (II) and Pb (II) ions in investigated systems.

## REFERENCES

- [1] Rosalind Allen, Sanjoy Bandyopadhyay, Michael L. Klein: C12E2 reverse micelle: A molecular dynamics study *Langmuir* 16 (26) (2000) 10547-10552
- [2] M. F. Hsu, E. R. Dufresne, D. A. Weitz: Charge stabilization in nonpolar solvents. *Langmuir* 21 (11) (2005) 4881-4887
- [3] Salman, Salman R., Salem, Mohamed A., Al-Saadi, Hamood M.: Molecular complexes of crown ethers: Part 7. Effect of surfactant on the charge transfer complex between dibenzo-18-crown-6 and tetracyanoethylene. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 42: 3/4 (2002) 289-293
- [4] Semnani A., Shamsipur M.: Spectroscopic study of charge transfer complexes of some benzo crown ethers with  $\pi$ -acceptors DDQ and TCNE in dichloromethane solution. *Spectrochimica Acta Part A: Molecular Spectroscopy*, 49 (3) (1993) 411-415
- [5] D. J. Cram. *From Design to Discovery*, American Chemistry Society, Washington, DC (1991) p. 91.
- [6] A. Nezhadali, Gh. Rounaghi, M. Chamsaz: Stoichiometry and stability of complexes formed between 18-crown-6 as well as dibenzo-18-crown-6 ligands and a few metal ions in some non-aqueous binary systems using square wave polarography. *Bull.Korean Chem.Soc.* 21 (7) (2000) 685-689
- [7] Izatt R.M., Pawlak K., Bradshaw: Thermodynamic and kinetic data for macrocyclic interactions with cations and anions. *J.S. Chem. Rev.* 91 (8) (1991) 1721
- [8] Roya Mohammad Zadeh Kakhki, Gholamhossein Rounaghi: Competitive bulk liquid membrane transport of heavy metal ions. *J. Chem. Eng. Data* 56 (2011) 3169-3174
- [9] Roya Mohammad Zadeh Kakhki, Gholamhossein Rounaghi: Competitive bulk liquid membrane transport of heavy metal ions. *J. Chem. Eng. Data* 56 (2011) 3169-3174
- [10] Nipamanjari Deb, Sanjib Bagchi, Asok K. Mukherjee: Charge transfer complex formation between TX-100/CCl4. *Molecular Physics* 108 (11) (2010) 1505-1511
- [11] Francis A. Christy & Pranav S. Shrivastav: Conductometric studies on cation-crown ether complexes: A review. *Critical Reviews in Analytical Chemistry*, 41 (3) (2011) 236-269