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CONDUCTOMETRIC STUDY OF LIGAND STRUCTURE INFLUENCE ON THE Pb(II) COMPLEXATION WITH CROWN ETHERS

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ABSTRACT

- In this paper, the complexation reaction of macrocyclic ligand, 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and Pb(II) cation was studied in different solvents: dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCE). The effects of surfactant structure (Triton X-100 and Triton X-45) on the conductivity of the Pb(II) complex with 18-crown-6 and dibenzo-18-crown-6 ether have been investigated.
- The conductance data showed that the stoichiometry of the complexes in most cases is 1:1(ML). It is also demonstrated that the influence of crown ethers is deeply affected by the organic solvent used. Macrocyclic ligand 18-crown-6 showed more suitable for complexation of Pb(II) ions compared to dibenzo-18-crown-6.
- Adding a surfactant affected the higher absolute values of the conductivity of systems, but not the change in the stoichiometric ratio between a metal ion and macrocyclic ligand.

INTRODUCTION

Conductometric titrations with crown ethers have proved to be very useful in determining the stability constants, selectivity, and also the thermodynamic parameters of the crown ether complexes with various cations in nonaqueous and aqueous/nonaqueous media.

The conductometric study of ligand structure influence on the Pb(II) complexation with crown ethers in different solvents has been investigated.

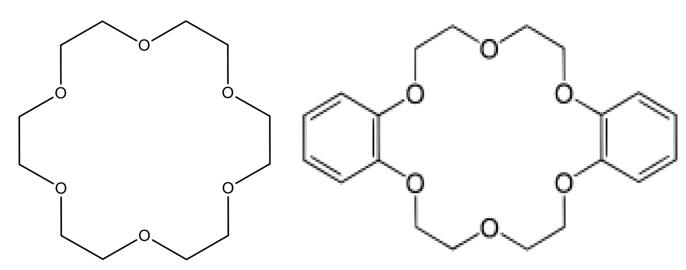

Figure 1. Structures of polyether ligands: macrocyclic "crown ether"

- The cations fitting the cavity best are located in its center and optimize the interactions with the oxygen heteroatoms.
- Table 1. gives the ionic radius of the metal cations as well as the radius of the cavities of the crown ethers determined by CPK (Corey-Pauling-Koltun) molecular models. Specifically, the highest selectivities of cation radius and cavity radius of the ligand are closest to 1.

Table 1. Overview of ion radius of alkali, alkaline earth, and heavy metals cations as well as some crown ethers

Cations	Ionic radius /pm
Ag^+	115
Tl^+	150
Pb^{2+}	120
Cd^{2+}	109
Ligand cavity radius/pm	
Crown ether	Ionic radius /pm
12C4	60-75
15C5	85-110
18C6	134-143
B18C6	134-155
DB18C6	260-320

MATERIALS AND METHODS

Conductometry is an electroanalytical method that measures the electrical conductivity, as a consequence of the existence of free mobile charge carriers (ions) in solution. Ions move freely in solutions under the influence of an electric field and contribute to the overall conductivity of the solution, depending on their concentration and mobility.

Reagents:

The macrocyclic ligand: 18-crown-6, dibenzo-18-crown-6

The nonionic surfactants: Triton X-100; Triton X-45 (p.a. Sigma-Aldrich)

Solvent: dichloromethane, 1,2-dichloroethane

Procedure:

The GLP31 Crison Instruments digital conductometer, presented in Figure 2. was used for the measurements.

Figure 2. GLP31 Crison Instruments digital conductometer

RESULTS AND DISCUSION

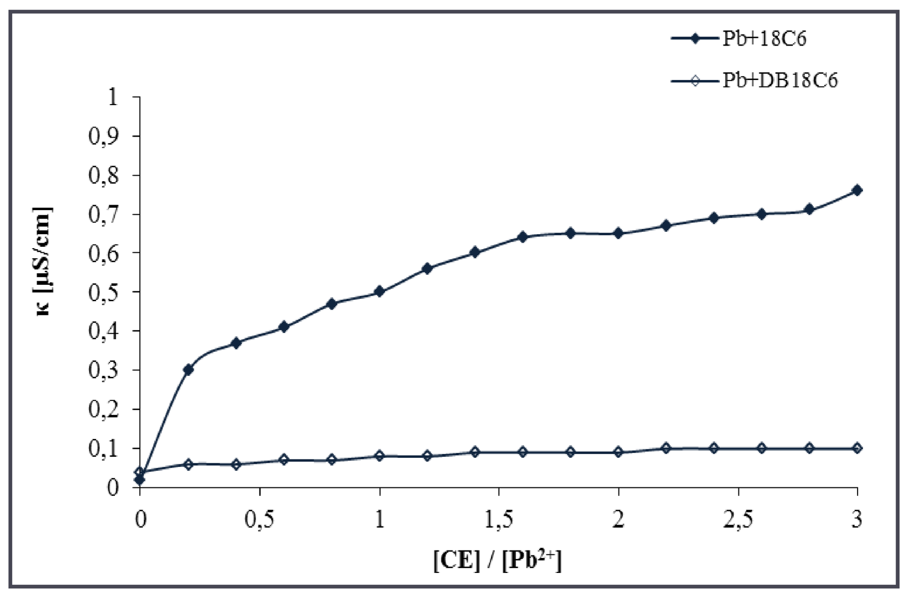

Figure 2. Influence of crown ether structure on the conductivity of 2-component systems:
Pb^{2+} - CE (DCM)

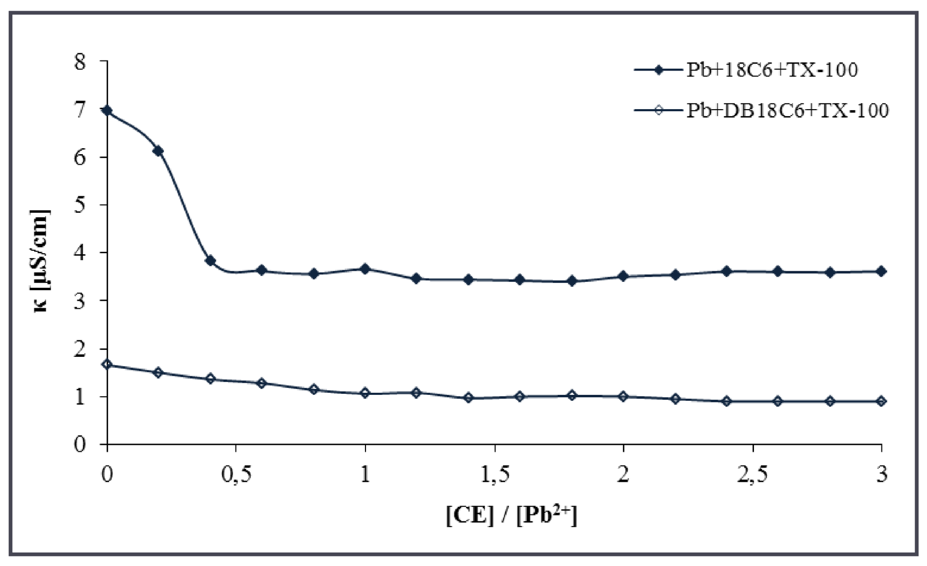

Figure 4. Influence of crown ether structure on the conductivity of 3-component systems:
Pb^{2+} - TX-100- CE (DCM)

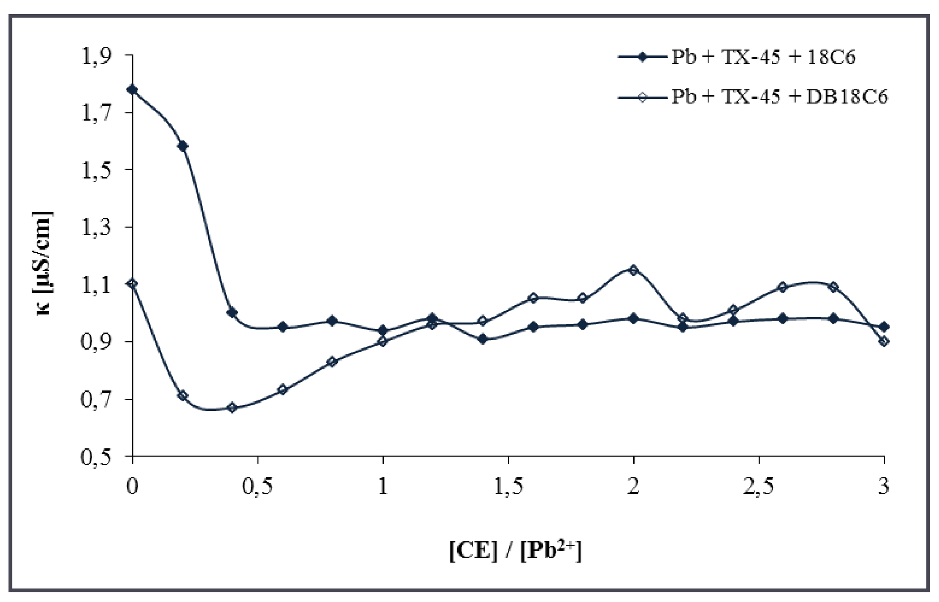

Figure 6. Influence of crown ether structure on the conductivity of 3-component systems:
Pb^{2+} - TX-45- CE (DCM)

18-crown-6 is more suitable for complexation of Cd (II) and Pb(II) ions compared to dibenzo-18-crown-6 ether.

DB18C6 as a ligand gives more less pronounced fractures, which indicates the possibility of forming more complexes with a different stoichiometric composition, as well as with less stability compared to 18C6 as a ligand.

The reason for this behavior of DB18C6 can be attributed to the existence of two substituents on the ring of this ether crown that make the ligand structure less flexible, so the binding of the metal ion is difficult.

Figure 6. and Figure 7. represents the influence of the crown ether structure on tthe conductivity of 2-component system Pb^{2+} -18C6 where a nonionic surfactant Triton X-45 was introduced as the 3rd component. Adding the surfactant did not significantly affect the results in terms of complex stoichiometry, i.e. the same stoichiometry remains 1: 1.

Results also showed sharper curve fracture (better-defined stoichiometry) for 2-component systems Differences can be observed only in the absolute values of conductivity. It is observed that the values of conductivity decrease with an increase in [L]t/[M]t ratio.

The curve shows a breakpoint at [L]t/[M]t ≈ 1 which indicates the formation of 1:1 complexes between the crown ethers and the Pb(II) ions.

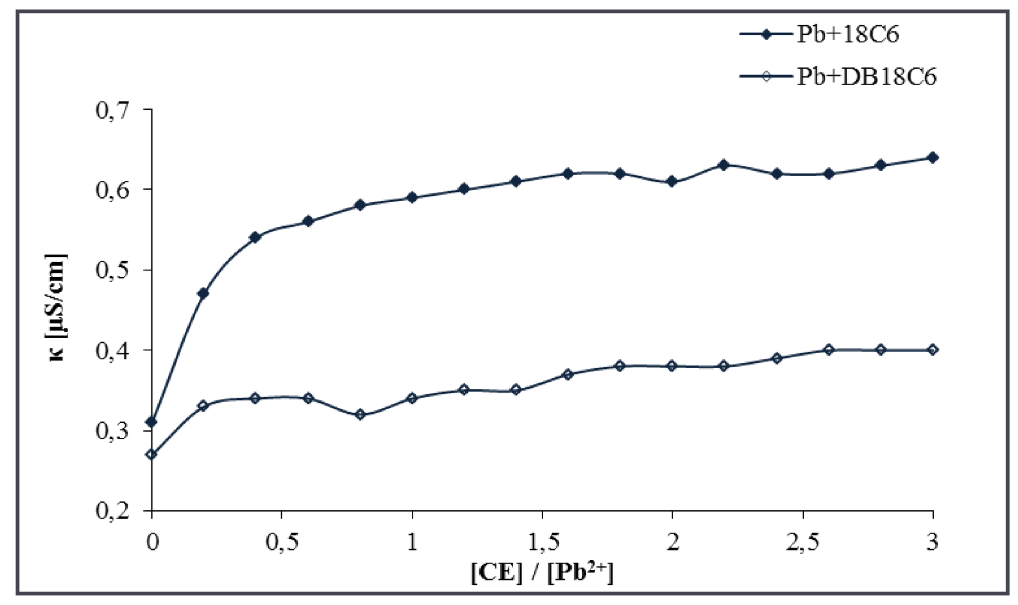

Figure 3. Influence of crown ether structure on the conductivity of 2-component systems:
Pb^{2+} - CE (1,2-DCE)

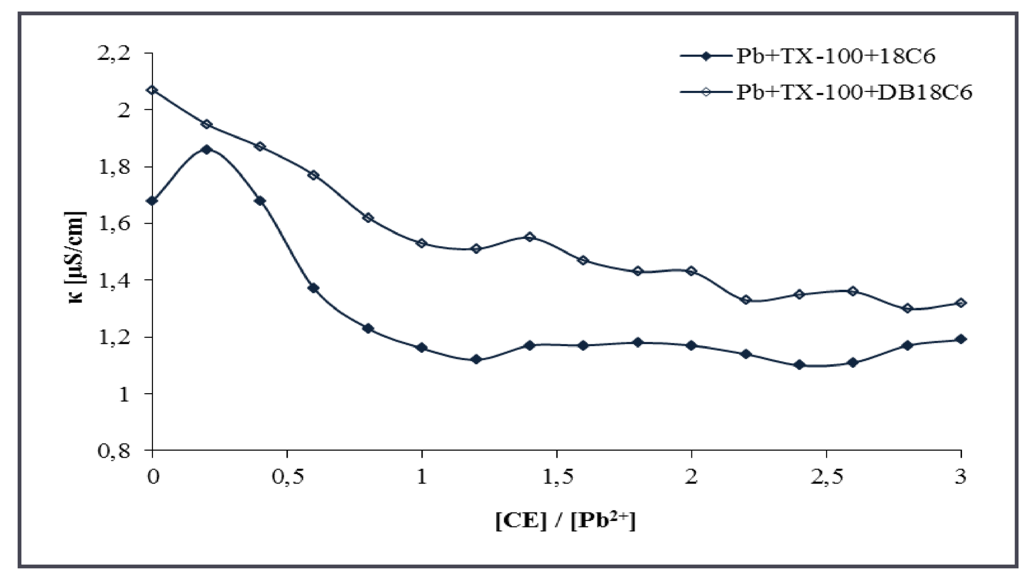

Figure 5. Influence of crown ether structure on the conductivity of 3-component systems:
Pb^{2+} - TX-100- CE (1,2-DCE)

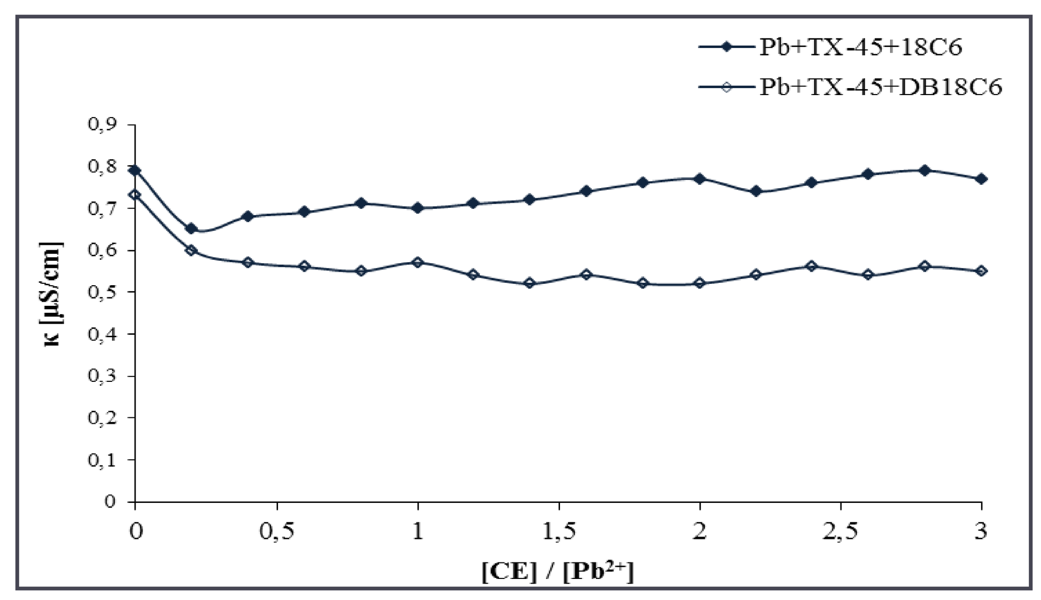

Figure 7. Influence of crown ether structure on the conductivity of 3-component systems:
Pb^{2+} - TX-45- CE (1,2-DCE)

CONCLUSIONS

- 18-crown-6 is more suitable for complexation of Pb(II) ions compared to dibenzo-18-crown-6 due to its greater flexibility; two benzo substituents in DB18C6 molecule make the structure more rigid and reduces the possibility of access for metal ions
- 2-component systems: Pb^{2+} - CE (DCM) showed a nicely expressed curve break which defines the stoichiometry of the formed Pb-DB18C6 complex (1: 1) in the absence of TX-100.
- The same system in 1,2-DCE as a solvent did not lead to similar results, which means that in DCM the interactions are still stronger and lead to greater stability of the complex.
- The influence of the surfactant structure confirms, that the length of the polyether chain affects the metal-surfactant interactions.
- The presence of reverse micellar structures in dichloromethane increases absolute conductivity values and contributes to better definition of stoichiometry and stability of the formed complex.
- Different intensities of conductivity contribute to the earlier assumption of different possibilities of interactions between TX-100 and Pb(II) compared to TX-45, in both solvents.

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