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

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ABSTRACT

The conductometric study of ligand structure influence on the Pb(II) complexation with crown ethers in different solvents has been investigated. 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. In the solvents studied, the stability of the resulting complexes showed higher stability in dichloromethane comparing with 1,2- dichloroethane. 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.

Keywords: crown ethers, Pb(II), conductometry, 18-crown-6.

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 media.

Macrocyclic polyethers (crown ethers), ever since their first discovery by Pedersen first in the 1960s (Pedersen, 1967), constitute an important class of host molecules that have found broad application to studies of molecular recognition (Aragoni, Arca, & Demartin, 2002), and inclusion phenomena (Blasius & Janzen, 1985). Macrocyclic crown compounds have gained a great deal of attention due to their wide applications in chemistry (Christy & Shrivastav, 2011) such as microanalysis, sensing and separation of metal ions, and extraction of biogenic amines (Saaid, Saad, Rahman, Ali, & Saleh, 2010). Crown ethers have a strong affinity for alkali and alkaline earth metal ions. The main factor governing the binding strength and selectivity is the size compatibility between the cation radius and the ligand cavity. The selectivity and stability of crown ethers are also influenced by their structural flexibility, the number and type of donor atoms on the cavity of the crown, and the solvation energy of the metal ion. Crown ethers have the specific macrocyclic structure of their molecules, consists of the polyether chain-forming "the crown" with hydrophilic cavity and hydrophobic surface.

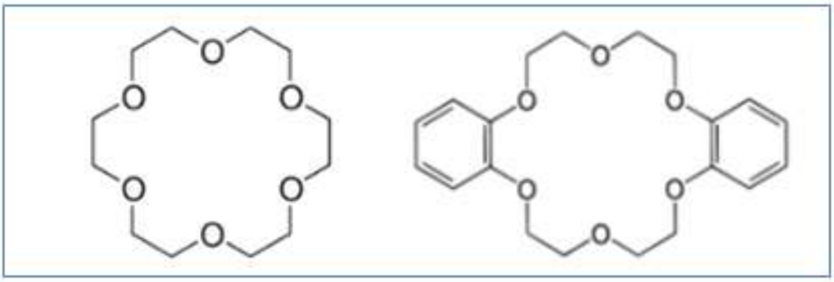

Figure 1. Structures of polyether ligands: macrocyclic "crown ethers" a)18-crown-6; b) dibenzo-18-crown-6;

The metal ion is held in the crown ether cavity by electrostatic attraction between the charged cation and dipoles created by the nonbonding electrons of donor atoms (Atwood & Lehn, 1996). These hosts have three-dimensional structures and therefore, can form a stable complex with various cations. Moreover, due to different hole sizes, they can form various types of complexes with high selectivity. Also, the interaction between crown ether and target ion is non-covalent. The cations that best fit the cavity are located in the center and optimize interactions with heteroatoms (oxygen atoms). Specifically, the highest selectivities are expected in cases where the ratios of cation radius and cavity radius of the ligand are closest to 1. Table 1. gives the ionic radius of alkali, alkaline earth, and some of the heavy metal cations, as well as the radius of the cavities of the crown ethers determined by CPK (Corey-Pauling-Koltun) molecular models (Vögtle, 1995).

Table 1. Overview of ion radius of used metal cation Pb(II) as well as some crown ethers (Vögtle, 1995)

Cations	**Ionic radius (A^0)**
Pb^{2+}	1.19
Crown ether	**Ionic radius (A^0)**
12C4	0.60-0.75
15C5	0.85-1.1
18C6	1.34-1.43
B18C6	1.34-1.55
DB18C6	2.6-3.20

Some techniques such as potentiometry (Bradshaw, Maas, Lamb, Izatt, & Christensen, 1980) have been used to study the complex formation between macrocyclic compounds with different metal ions in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations. The study of various macrocyclic compounds in different solvents may indicate new approaches for developing pharmaceutical systems. 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 also been investigated.

MATERIALS AND METHODS OF WORK

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. The electrical conductivity (κ) is directly related to the concentration (C), through the value of molar conductivity (Λ).

Reagents:

The macrocyclic ligand: 18-crown-6, 18C6, dibenzo-18-crown-6, DB18C6 (99%, ACROS ORGANICS).
The nonionic surfactants: Triton X-100; Triton X-45 (p.a. Sigma-Aldrich).
Solvents: dichloromethane,
1,2-dichloroethan.

All measurements were carried out at 25º C with a GLP31 Crison Instruments digital conductometer, which was calibrated regularly with the Mettler Toledo standard solutions. All molar conductivities were calculated after correcting for the solvent conductivity. The uncertainty in the measurement of conductivities was ±0.1 µS.

Procedure:

The GLP31 Crison Instruments digital conductometer, presented in Figure 2. was used for the measurements. Measurements were performed at room temperature. The change in the electrical conductivity of the solution depending on the change in the ligand concentration was monitored. Namely, the titration of the metal ion solution ($1\cdot10^{-3}$ mol/L) with a ligand solution was performed until the molar ratio of ligand: metal = 3: 1 was reached. The results presented by the diagram of the dependence of electrical conductivity on the molar ratio of ligand / metal made it possible to define the complex stoichiometry. The Pb(II) nitrate ($1\cdot10^{-3}$ mol/L) dissolved in surfactant TX-100 ($4\cdot10^{-3}$ mol/L) was placed in the cell and the conductivity was measured. The crown ether solution (~0.02 mol/L) was added to the cell in small increments until the total concentration of the crown ether was approximately 2 to 3 times as large as that of the metal nitrate. The conductivity was measured after each addition as above.

Figure 2. GLP31 Crison Instruments digital conductometer

RESULTS AND DISCUSSION

In order to evaluate ligand structure influence on the Pb(II) complexation with crown ethers in different solvents, the molar conductance was monitored while increasing the crown ether concentration. The measured values of electrical conductivity in different organic solvents (DCM and 1,2-DCE) are represented by the curves, in Figures 3 and 4. Namely, in both organic solvents, the conductivity increases with the increase of the ligand/metal molar ratio. The increase in conductivity by the addition of ligands in organic solvents indicates the fact that the mobility of the formed complex is higher than the metal ions themselves, as indicated by the researchers (Rounaghi & Razavipanah, 2008) examining the complexation of alkaline earth metals with 15C5 in methanol and acetonitrile. The increase in conductivity by the addition of ligands in organic solvents indicates the fact that the mobility of the formed complex is higher than the metal ions themselves. Figures 3. and 4. represent the results of conductivity measurements for Pb^{2+}-18C6 and Pb^{2+}-DB18C6 complexes in dichloromethane and 1,2-dichloroethane, respectively. From the forms of the dependence curves, it is seen that the stability of the Pb^{2+}-DB18C6 complex is lower, in both solvents. DB18C6 as a ligand gives less pronounced fractures, which indicates the possibility of forming more complexes with different stoichiometric compositions, as well as less stability compared to 18C6 as a ligand. The reason for this behavior of DB18C6 probably is attributed to the existence of two substituents on the ring of this crown ether that make the ligand structure less flexible, so the binding of the metal ion is difficult. The host 18-crown-6 forms complexes for which the reaction enthalpy and entropy are quite high. Host molecules with benzene side groups form complexes of lower reaction enthalpy and entropy and therefore the complexes formed are less stable than that of the analogous crown ethers without aromatic groups.

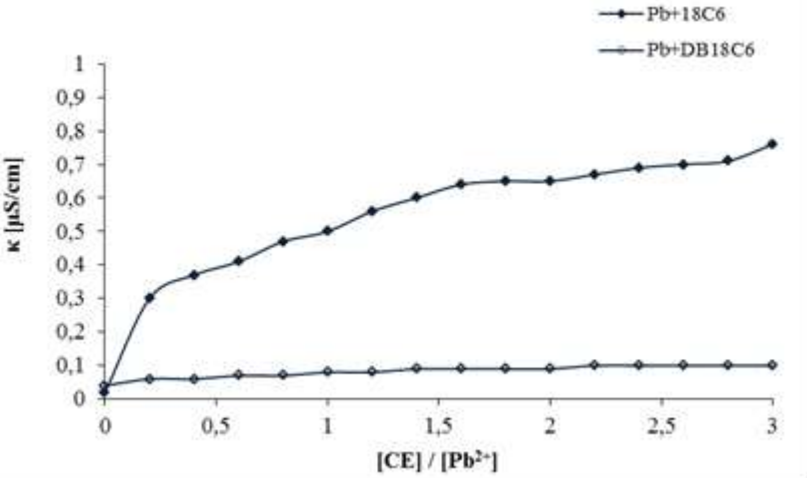

Figure 3. Influence of crown ether structure on the conductivity of 2-component systems: Pb^{2+} - CE (DCM)

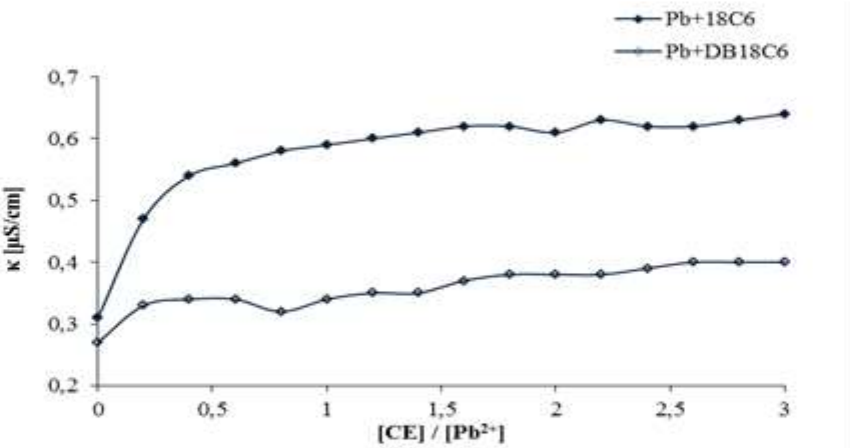

Figure 4. Influence of crown ether structure on the conductivity of 2-component systems: Pb^{2+} - CE (1,2-DCE)

The same study of the influence of the crown ether structure on the conductivity of 2-component systems Pb^{2+} -18C6 and Pb^{2+}-DB18C6 where a nonionic surfactant Triton X-100 was introduced as the 3rd component was investigated. In Figure 5. And Figure 6., the dependence curves of the electrical conductivities were compared for 3-component systems: Pb^{2+}-18C6-TX-100 and Pb^{2+}-DB18C6-TX-100, in DCM and 1,2-DCE, respectively. Results showed that 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. The influence of TX-100 is evident from the shape of the curves: better-defined stoichiometry of Pb(II) complex in the presence of TX-100 (sharper curve fracture at the same position). A possible explanation could be an aggregation of nonionic surfactant TX-100 in organic solvents and the formation of "reverse" micellar structures, which allow the dissolution of polar compounds in a non-polar medium. The addition of the surfactant did not affect the stoichiometry. In the case of a 3-component system involving the DB18C6 ligand, it can be observed that the introduction of the surfactant component significantly contributes to the stability of the complex and a better definition of its stoichiometry. In Figure 5. and Figure 6. where the conduction dependence curves of the ligand / metal molar ratio in organic solvents are presented (conductivity decreases with increasing molar content), we observe a different shape of the curve in relation to the same systems without surfactant component Figure 3. and Figure 4. and especially in DCM as a solvent. The same system in 1,2-DCE as a solvent did not lead to similar results, which means that in DCM the interactions are stronger and lead to greater stability of the complex.

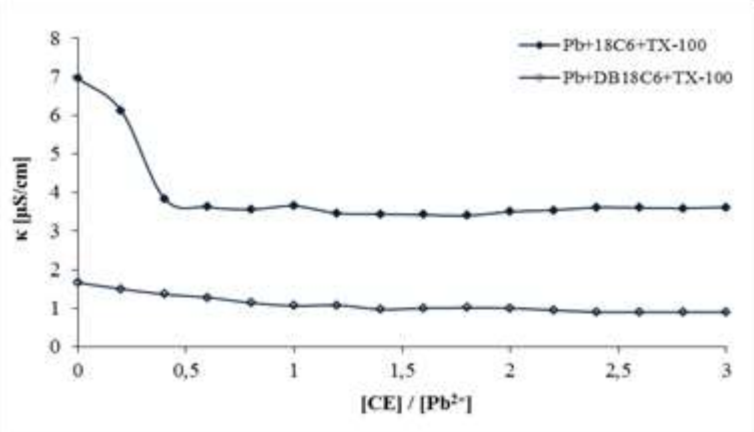

Figure 5. Influence of crown ether structure on the conductivity of 3-component systems: Pb^{2+} - TX-100- CE (DCM)

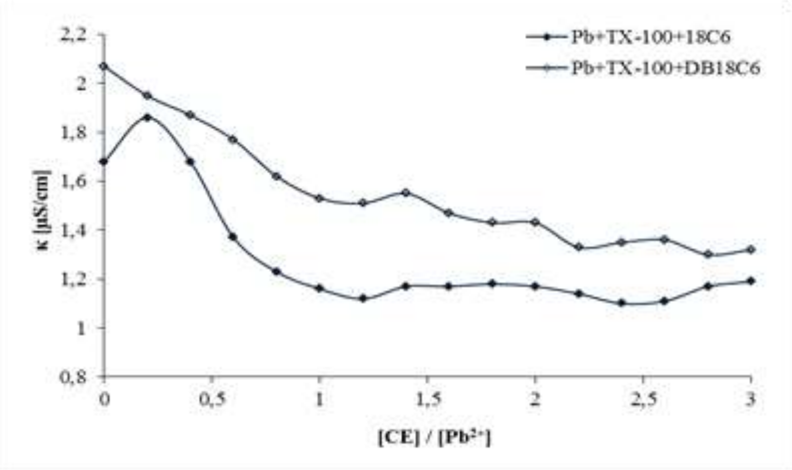

Figure 6. Influence of crown ether structure on the conductivity of 3-component systems: Pb^{2+}- TX-100- CE (1,2-DCE)

The dependence curves of the electrical conductivities were presented for 3-component systems Pb^{2+}-18C6+TX-45 and compared with the Pb^{2+}-DB18C6-TX-45 system in Figure 7. and Figure 8. The strength of cation surfactant interactions can be observed by comparing the results gained for different surfactants. From the values of conductivity, it can be seen that the stoichiometric composition of the complex (1:1) does not change, but the absolute values of electrical conductivity are lower in the presence of Triton X-45 comparing with the TX-100. A possible explanation is in the structure of used surfactants. The higher number of oxyethylene units in the nonionic surfactant chain TX-100 (9,5) compared to TX-45 (contains 4,5 oxyethylene units) affected the higher absolute values of the conductivity of systems of different complexity and composition but not the change in the stoichiometric ratio between the metal ion and macrocyclic ligand.

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. A larger number of oxyethylene units (the number of oxygen atoms as electron-donors) means the higher absolute values of the conductivity for TX-100 compared to TX-45, and probably stronger interactions between metal and macrocyclic ligand.

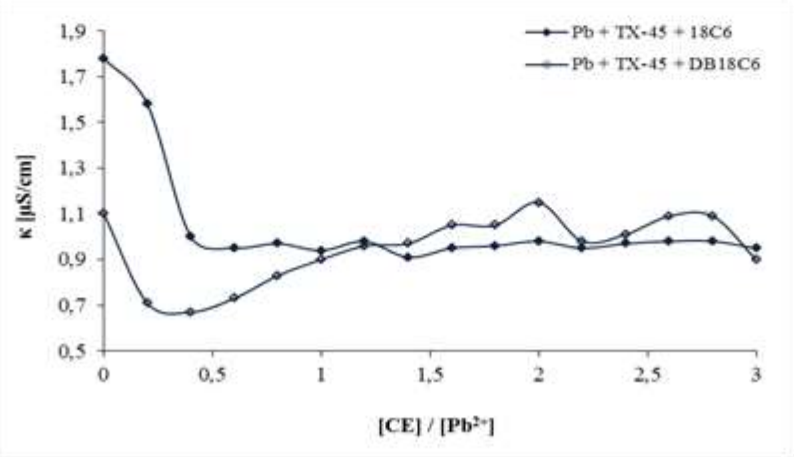

Figure 7. Influence of crown ether structure on the conductivity of 3-component systems: Pb^{2+} - TX-45- CE (DCM)

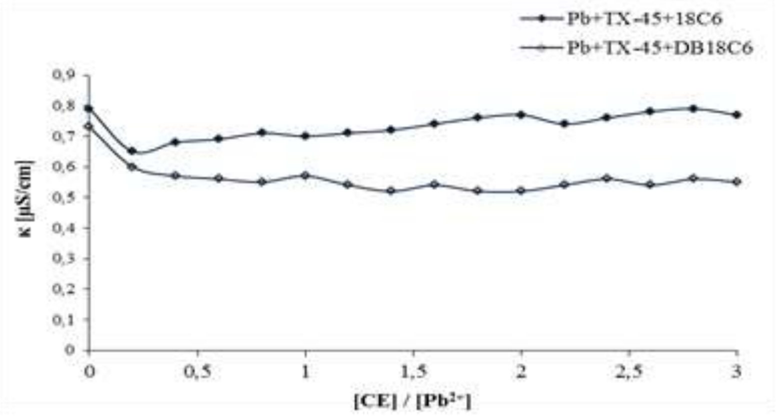

Figure 8. Influence of crown ether structure on the conductivity of 3-component systems: Pb^{2+} - TX-45- CE (1,2-DCE)

CONCLUSIONS

18-crown-6 ether is more suitable for complexation Pb(II) ions compared to dibenzo-18-crown-6 ether 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. Dibenzo-18-crown-6-ether 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. The influence of the surfactant structure confirms, that the length of the polyether chain affects the metal-surfactant interactions. 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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