

# POLAROGRAPHIC STUDY OF THE INTERACTIONS BETWEEN THALLIUM AND LEAD IONS AND SOME CROWN ETHERS IN 90% ACETONITRILE AND 90% ETHANOL SOLUTIONS

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**ABSTRACT:** *The complexation reactions between  $Tl^+$  and  $Pb^{2+}$  ions and crown ethers 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and aza-18-crown-6 (A18C6) were studied in 90% acetonitrile and 90% ethanol solutions at 25°C, using an a.c. polarographic technique. The stoichiometry and stability of the complexes were determined by monitoring the shift in peak potential of the polarographic waves of metal ions against the crown concentration. The stability of the resulting 1:1 complexes of  $Tl^+$  and  $Pb^{2+}$  ions, in both solvent systems used, was found to vary in the order  $A18C6 > DC18C6 > 18C6 > 15C5 > B15C5 > 12C4$ . In 90% ethanol,  $Pb^{2+}$  ion complexes with all crown ethers used were more stable than the corresponding  $Tl^+$  complexes. The influence of substituents in the polyether ring and of the nature of solvent and metal ions on the stability of a number of complexes is discussed.*

**KEY WORDS:** *Crown complexes, Thallium, Lead, Stoichiometry, Stability, Polarography.*

## INTRODUCTION

In 1967 Pedersen reported the first synthesis of the cyclic polyethers (crowns) and detected

their ability to form selective and stable complexes with various cations, particularly with

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alkali ions [1]. Since then, these ligands became the subject of numerous original papers as well as reviews (see, for example, [2-4]). These studies mainly dealt with the stoichiometry and stability of metal complexes with crown ethers [2,4], kinetics of complex formation [2-4], structure of macrocyclic ligands and their complexes [5-8], their role in the ion transport across artificial as well as biological membranes [9-13] and application of their selective complex formation to the design of ion-selective electrodes [14-18]. However, despite the important role of transition and heavy metal ions in matter and life, much less attention has been focused on the study of their crown complexes, as compared to alkali and alkaline earth cations [2,4].

Heavy metal ions such as  $Tl^+$  and  $Pb^{2+}$  cations are found to be very toxic [19,20]. The design of highly selective ligands for the removal of such harmful metal ions, with minimum effect on the level of the biologically important cations such as some alkali and alkaline earth cations, is of fundamental importance [21]. For this purpose, several macropolycyclic ligands, involving appropriate binding sites and suitable cavity sizes have been synthesized [22,23].

We have been recently involved in the study of the effects of variables such as ligand topology, nature and number of binding sites, relative sizes of cation and ligand cavity, nature of the cation and, especially, the solvent properties on the selectivity, stability and kinetics of macrocyclic complexes with heavy metal ions [24-29]. In this paper we report a study of the complexation of  $Tl^+$  and  $Pb^{2+}$  ions with several crown ethers in 90% acetonitrile and 90% ethanol solutions. It should be noted that, 10% (by weight) water was added to pure acetonitrile and ethanol to overcome the solubility problem of the salts used. Moreover, since the polarographic methods have shown their abilities as very powerful means of studying different metal ion-macrocyclic ligand complexes in both aqueous and nonaqueous solvents [25-27, 30-32], we used an a.c. polarographic

method to obtain information about the stoichiometry, stability and selectivity of thallium and lead complexes with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5, (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6), and aza-18-crown-6 (A18C6) in the solvent mixtures used, at 25°C.

## EXPERIMENTAL

Reagent grade nitrate salts of  $Tl^+$  and  $Pb^{2+}$  (both from *Merck*) were used without any further purification except for vacuum drying over  $P_2O_5$ . Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (*Merck*) and perchloric acid (*Fluka*) as described before [33]. The resulting salt was recrystallized several times from triply distilled deionized water and dried in vacuo at 60°C. HPLC grade acetonitrile (*Fluka*) and absolute ethanol (*Merck*) and triply distilled deionized water were used for the preparation of the 90% (w/w) acetonitrile-water and ethanol-water mixtures. Crown ethers B15C5, 18C6 and DC18C6 (all from *Merck*) were purified and dried by the previously described methods [25,34]. A18C6 (*Fluka*) was recrystallized from reagent grade n-hexane and dried under vacuum for 3 days. 12C4 and 15C5 (both from *Merck*) were used as received.

The polarographic measurements were carried out with a dropping mercury electrode (DME) in a three-electrode arrangement. The auxiliary electrode was a Pt-wire with a considerably larger surface area than that of the DME. A silver-silver chloride reference electrode was placed in 0.03 M TEAP and connected to the electrolyzed solution by means of a bridge containing the base electrolyte. All the solutions were deaerated for 10 min with pure nitrogen and an inert atmosphere was maintained over the solutions during the reduction.

All polarographic measurements were made with a polarecord E-506 *Metrohm Herisau* instrument. The usual instrumental parameters were: drop time, 0.4 s; mercury height, 50 cm;

scan rate, 5.0 mVs<sup>-1</sup>; a.c. amplitude, 15 mV. All of the experiments were carried out at 25.0±0.5°C.

## RESULTS AND DISCUSSION

To characterize the complexation equilibria of Tl<sup>+</sup> (in both solvent systems used) and Pb<sup>2+</sup> ions (in 90% ethanol) with crown ethers used, the polarographic measurements were carried out under the same experimental conditions both in d.c. and a.c. modes.

The polarograms obtained by the reduction of Tl<sup>+</sup> and Pb<sup>2+</sup> ions in 0.03 M TEAP were all reversible. The logarithmic analysis of the polarograms in d.c. and a.c. modes showed a linear dependence of  $\log(i_d - i)/i$  vs.  $E_{d.c.}$  and  $\log[(i_p/i)^{1/2} \pm (i_p - i)/i^{1/2}]$  vs.  $E_{a.c.}$ , respectively, with the slopes correspond to a reversible (or quasi reversible in some cases) reduction. All reduction waves were well defined and controlled by diffusion. Plots of  $i_d$  vs.  $h^{2/3}t^{1/6}$  were straight lines with zero intercept ( $h$  is the height of the mercury column after correction for back pressure).

The crown ethers used show no reduction wave within the available potential range. However, addition of the macrocyclic ligands to Tl<sup>+</sup> and Pb<sup>2+</sup> solutions in 0.03 M TEAP resulted in the shifts of  $E_{1/2}$  and  $E_p$  corresponding to the reduction of cations towards more cathodic values. In all metal ion-crown ether systems studied, the reduction waves of the complexed ions were found to be reversible and diffusion controlled. This reversible behavior indicates that the exchange between free cations and corresponding complexes is rapid on the measurement time scale, as expected [35,36]. Sample a.c. polarograms for Tl<sup>+</sup> and Pb<sup>2+</sup> complexes are shown in Figs. 1 and 2, respectively. It should be noted that the considerable decrease in peak current brought about upon addition of the crown ethers to Tl<sup>+</sup> and Pb<sup>2+</sup> solutions is possibly a result of the decreased diffusion of the complexed metal ions compared with that of the free cations in solution [25,26,30-32].

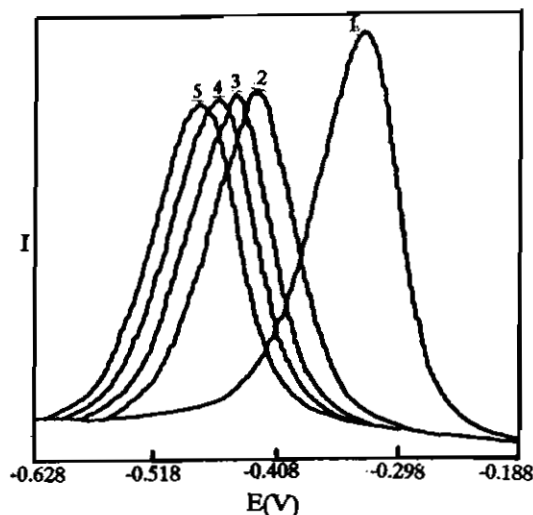


Fig. 1: A.c. Polarograms of 0.2 mM Tl<sup>+</sup> ion in 90% acetonitrile solution in the presence of increasing amounts of 18C6. Ligand concentration/mM: (1) 0.0, (2) 6.0, (3) 13.1, (4) 30.5, (5) 52.8.

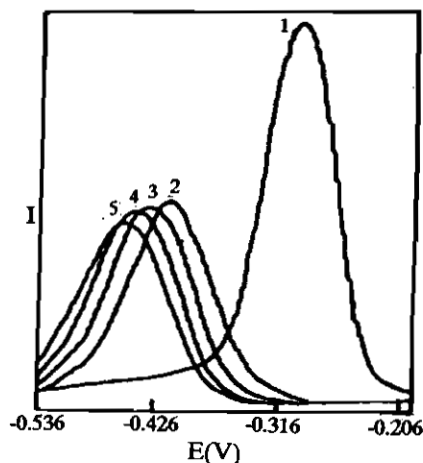


Fig. 2: A.c. Polarograms of 0.2 mM of Pb<sup>2+</sup> ion in 90% ethanol solution in the presence of increasing amounts of DC18C6. Ligand concentration/mM: (1) 0.0, (2) 1.2, (3) 6.0, (4) 14.2, (5) 28.7.

Determination of the stability constants of the Tl<sup>+</sup>-crown and Pb<sup>2+</sup>-crown complexes was based on the measurement of the shifts in  $E_{1/2}$  (or  $E_p$ ) of the cations brought about by the addition of an increasing amount of the crown ether [37]. In the case of the reversible amalgam-forming reduction of labile complexes of relatively high stability, the shift in half-wave (or peak) potentials to more negative values upon addition of an excess amount of ligand was

found to be in accordance with the Lingane equation [38]:

$$\Delta E_{1/2} = (E_{1/2})_M - (E_{1/2})_C = \frac{RT}{nF}(\ln K_f + m \ln [L]_t) \quad (1)$$

where  $(E_{1/2})_M$  and  $(E_{1/2})_C$  are the half-wave (or peak) potentials of the free and complexed metal ions, respectively,  $K_f$  is the complex formation constant,  $[L]_t$  is the analytical concentration of crown ether (where  $[L]_t \gg [M]_t$ ) and  $m$  is the stoichiometry of complex. The value of  $m$  and  $\log K_f$  can be obtained from the slopes and intercepts of the linear plots of  $\Delta E_p / (RT/nF)$  vs.  $\log [L]_t$ , respectively (see, for example, Fig. 3).

As it is seen, in all cases studied, only a 1:1 complex was formed in solution. All the calculated formations constants are listed in Table 1. The available data in pure acetonitrile are also included for comparison [25]. As it is seen, addition of 10% (by weight) water to acetonitrile decrease the stability of the  $Tl^+$  complexes with B15C5, 18C6 and DC18C6 very

drastically (i.e. more than 2-3 orders of magnitude). Water is known as a solvent of high solvating ability, with Gutmann donor number of 33 [39], which can compete strongly with the crown ethers for  $Tl^+$  ion. Thus, it is not surprising to observe such a drastic decrease in the stability of  $Tl^+$ -crown complexes upon addition of even 10% water to pure acetonitrile,

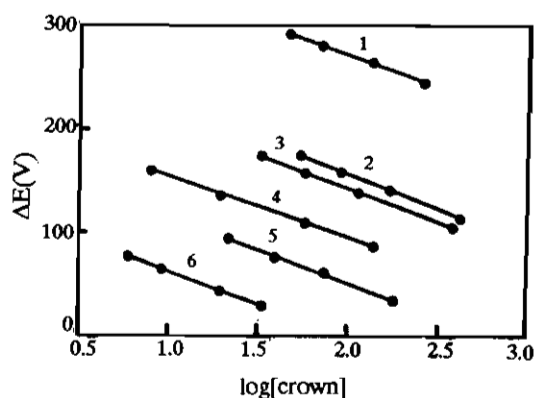


Fig. 3: Linear plots of  $\Delta E$  vs.  $\log [crown]$  for different  $Tl^+$ -crown ether systems in 90% ethanol solution: (1) A18C6, (2) DC18C6, (3) 18C6, (4) 15C5, (5) B15C5, (6) 12C4. The unit of concentration is mM.

Table 1: Formation constants of  $Tl^+$  and  $Pb^{2+}$  complexes with various crown ethers in different solvent mixtures at 25°C.

Crown ether	Cavity size (Å) <sup>a</sup>	$\log K_f^b$		
		90% Acetonitrile $Tl^+$	90% Ethanol $Tl^+$ $Pb^{2+}$	
12C4	1.2-1.5	2.1±0.1	2.18±0.06	3.23±0.04
B15C5	1.7-2.2	3.0±0.1 (5.41) <sup>c</sup>	3.0±0.2	4.3±0.1
15C5	1.7-2.2	3.7±0.1	3.6±0.1	5.1±0.2
18C6	2.6-3.2	4.2±0.2 (7.73) <sup>c</sup>	4.6±0.2	6.4±0.1
DC18C6	2.6-3.2	4.8±0.1 (7.54) <sup>c</sup>	4.9±0.2	8.0±0.2
A18C6	2.6-3.2		6.7±0.2	14.1±0.2

a : Data taken from Ref. 42

b : The errors associated with  $K_f$  values are given as  $\pm SD$  based on four replicate analyses.

c : The  $K_f$  values in pure acetonitrile, taken from Ref. 25.

as a low donicity solvent of  $DN = 14.1$  [40].

The data given in Table 1 indicate that, in 90% ethanol solution, all  $Pb^{2+}$ -crown complexes studied are much more stable than the corresponding  $Tl^+$ -crown complexes (from about 1 to 6 orders of magnitude). The lead ion with an ionic radius of  $1.19 \text{ \AA}$  [41] and two positive charges have a higher charge density than the single charged thallium ion with an ionic radius of  $1.50 \text{ \AA}$  [41]. Thus, observing a higher charge-dipole interaction between the former cation and donating groups of the crown ethers than that of the latter cation is not unexpected. From Table 1, it is also obvious that the stability of the resulting 1:1 complexes of  $Tl^+$  and  $Pb^{2+}$  ions, in both solvent systems used, vary in the order  $A18C6 > DC18C6 > 18C6 > 15C5 > B15C5 > 12C4$ . It is well known that some structural features of the macrocyclic ligands such as the cavity size, the number of donating oxygens participating in metal ion binding and the nature of substituents on the macrocyclic ring may strongly influence the stability and selectivity of the resulting complexes in solution.

Both cations used seem to have the most convenient fitting condition for the cavity of  $18C6$  with the size of  $2.6\text{-}3.2 \text{ \AA}$  [42]. Crown ethers  $15C5$  and, especially,  $12C4$  with too small cavity sizes as well as the decreased number of oxygen atoms in the macrocyclic ring [42] form less stable complexes with both  $Tl^+$  and  $Pb^{2+}$  ions. From the data given in Table 1, it can be seen that the substitution of a benzo group on the ring of  $15C5$  would markedly decrease the stability of its complexes with both  $Tl^+$  and  $Pb^{2+}$  ions. Such a behavior could be related to some combination of the electron withdrawing property of the benzo group which lowers the basicity of the oxygen atoms of the ring, as well as the reduced flexibility of the ligand which prevents the macrocycle wrapping itself around the cation [25]. The net result is a weaker cation-ligand interaction.

Comparison of the data given in Table 1 indicates that among 18-crowns used, where the

ring frame remains the same, the stabilities of the resulting complexes with both cations used fall in the order  $A18C6 > DC18C6 > 18C6$ . The presence of two cyclohexyl groups in  $DC18C6$  molecule can pump electrons into the ligand ring and thus enhance the basicity of the oxygen atoms, while the flexibility of the ligand remains more or less the same as  $18C6$  [25]. Thus it is not unexpected to observe the increased stability of  $Tl^+$ - $DC18C6$  and  $Pb^{2+}$ - $DC18C6$  over the corresponding  $18C6$  complexes.

On the other hand, the substitution of one of the oxygen atoms by a  $-NH-$  group in the  $18C6$  macrocyclic ring increases the stability of  $Tl^+$  and  $Pb^{2+}$  complexes very significantly. These results are not surprising since heavy metal ions as soft acids would interact more strongly with nitrogen atom of the ring as a soft base [43]. It is interesting to note that the effect is surprisingly pronounced in the case of  $Pb^{2+}$ - $A18C6$  complex (about 6 orders of magnitude compared with about 2 orders of magnitude in the case of  $Tl^+$ - $A18C6$  complex). This is probably due to the higher polarizability of  $Pb^{2+}$  ion which cause a higher affinity of this cation for the ligand nitrogen atom, as compared with  $Tl^+$  ion case, resulting in some strong covalent interactions [44].

Finally, comparison of the stability data for the  $Tl^+$ -crown complexes in 90% acetonitrile and 90% ethanol (Table 1) revealed an unexpected solvent effect on the stability of the resulting complexes: Although acetonitrile is a solvent of lower donicity ( $DN = 14.1$ ) [40] than ethanol ( $DN = 20.0$ ) [45], the resulting  $Tl^+$  complexes in 90% ethanol are either more stable (e.g.  $18C6$ ) or of the same stability (within the experimental errors) as those in 90% acetonitrile solution. Such an unusual solvent effect could be most probably related to the existence of some specific interactions between acetonitrile and the initial reactants. Acetonitrile as a nitrogen donating solvent may have stronger interaction than that predicted by the *Gutmann* donor number [40,45] with soft metal ions such as  $Tl^+$  and  $Pb^{2+}$  cations [43]. Moreover, the equally

important, but often less appreciated, is the interaction of solvent molecules with the macrocyclic ligands [46]. It is well known that acetonitrile would have a rather appreciable interaction with crown ethers in solution [47-49]. Since both the cation and the ligand must be at least partially desolvated before the complex can be formed, such specific interactions of acetonitrile with the reactants can weaken the cation-crown interaction, unexpectedly.

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