A Polarographic Study of Tl^+, Pb^{2+} and Cd^{2+} Complexes with Aza-18-crown-6 and Dibenzopyridino-18-crown-6 in some Binary Mixed Non-aqueous Solvents

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Abstract

The complexation of Tl^+, Pb^{2+} and Cd^{2+} cations by macrocyclic ligands, aza-18-crown-6 (L1) and dibenzopyridino-18-crown-6 (L2) was studied in some binary mixtures of methanol (MeOH), *n*-propanol (*n*-PrOH), nitromethane (NM) and acetonitrile (AN) with dimethylformamide (DMF) at 22 °C using DC (direct current) and differential pulse polarographic techniques (DPP). The stoichiometry and stability constants of the complexes were determined by monitoring the shifts in half-waves or peak potentials of the polarographic waves of metal ions against the ligand concentration. In all of the solvent systems, the stability of the resulting 1:1 complexes was found to be L1 > L2. The selectivity order of the L2 ligand for the cations was found to be Pb^{2+} > Tl^+ > Cd^{2+} and the selectivity of the L1 ligand for Pb^{2+} ion was greater than that of Tl^+ ion. The results show that the stability of the complexes depends on the nature and composition of the mixed solvents. There is an inverse relationship between the stability constants of the complexes and the amount of dimethylformamide in the mixed solvent systems.

Introduction

Macrocylic polyethers have received much attention in the last few years both in biology and in chemistry. These compounds can provide a suitable model for studying the selective transport of ions across cellular membranes by some cyclic antibiotics such as valinomycin and nonactin [1]. Macrocyclic compounds play an important role in chemistry such as their applications in ion-selective electrodes [2–6], membrane separation processes [7], fiber optic chemical sensors [8], chiral separation [9], preconcentration of metal ions [10, 11] and phase transfer catalysts [12].

Macrocyclic polyethers have been found to form very stable complexes with many metal ions [13–17]. Since the complexation reaction is a competition between the ligand and the solvent with respect to the cation, the intrinsic interaction between ligand and the metal cation is affected by the nature and properties of the solvent. Thus the stability and selectivity of the complexes can be altered by changing the solvent properties.

Among the various physicochemical methods which are used for the study of cation-crown ether complexes [18, 19], polarography is a very useful means for studying the electrochemical behavior of macrocyclic compounds. By using this technique, the stoichiometry, stability and selectivity of a number of metal ion complexes in both aqueous and non-aqueous media have been determined [20–27].

Heavy metal ions such as Pb^{2+}, Tl^+ and Cd^{2+} are very toxic [28, 29], therefore, design of a highly selective ligand for removal of these harmful cations with minimum effect on the level of the biologically important ones such as Na^+, K^+, Ca^{2+}, Zn^{2+} and Mg^{2+} is of particular importance [30].

Although the complexation reaction of macrocyclic polyethers with metal cations has been extensively studied during the past two decades, most of these studies have been restricted to neat solvents or partly in mixtures of water with some organic solvents [31–36] and little attention has been paid to the study of such complexations in mixed non-aqueous solvents [37–39].

It is interesting to us, therefore, to study the complexation of some of the macrocyclic ligands with heavy metal ions in mixed non-aqueous solvents in order to see how the nature of the cation and ligand and particularly the solvent properties can affect the selectivity and the stability of macrocyclic complexes.

In this work, we studied the complexation of Tl^+, Pb^{2+} and Cd^{2+} with aza-18-crown-6 and dibenzopyridino-18-crown-6 (Scheme 1) in dimethylformamide/methanol (DMF/MeOH), dimethylformamide/*n*-propanol (DMF/*n*-PrOH), dimethylformamide/acetonitrile (DMF/AN) and dimethylformamide/nitromethane (DMF/NM) binary systems.

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H
N
O O

O O

O

aza-18-crown-6

(L1)

N

O O

O O

O

Dibenzopyridino-18-crown-6

(L2)
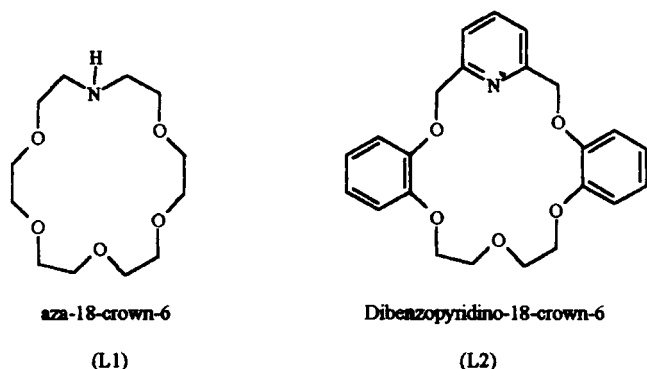
Scheme 1. The structures of the ligands.

Experimental

Reagents

The crown ethers, aza-18-crown-6 (L1) and dibenzo-pyridino-18-crown-6 (L2) (both from Merck) were used without purification except for drying over P_2O_5 in vacuum for 72 h. Reagent-grade thallium(I)nitrate, lead(II)nitrate and cadmium(II)nitrate (all from Merck) and tetraethylammonium perchlorate, TEAP (Merck), were used as received except for drying over P_2O_5 in vacuum for 48 h.

The solvents, dimethylformamide, acetonitrile, methanol and nitromethane (all from Merck) and n-propanol (Riedel) were used as received.

Apparatus

The polarographic measurements were carried out with a dropping mercury electrode (DME) in a three-electrode arrangement. A Pt wire with a considerably larger surface area than that of the DME was used as an auxiliary electrode. A silver-silver chloride reference electrode with a bridge containing the base electrolyte of the electrolysed solution was employed. A solution of 0.025 M tetraethylammonium perchlorate (TEAP) was used as a base electrolyte. All solutions were deaerated for 10 minutes with pure helium and a helium atmosphere was maintained over the solutions during the reduction.

The measurements were carried out on an EG & G Princeton Applied Research (PAR 384B) electrochemical instrument. The usual instrumental parameters were constant drop time, 0.5 s; scan rate, 2 mV s^{-1}; pulse duration, 0.04 s and pulse height, 20 mV. All experiments were carried out at 22 ± 0.5 °C.

Procedure

The stability constants of metal ion-crown ether complexes in different solvent mixtures were determined based on measurement of the shift in Ep (peak potential) caused by addition of an increasing amount of the ligands. The shift in half-wave (or peak) potential toward more negative values upon addition of an excess amount of ligand was found to be in accordance with the Lingane equation [40]:

$$\Delta E_{1/2} = (E_{1/2})_{\text{complex}} - (E_{1/2})_{\text{metal}}$$

$$= \left(-\frac{RT}{nF}\right)(\ln K_f + \rho \ln[L]_t) \qquad (1)$$

where $(E_{1/2})_{\text{complex}}$ and $(E_{1/2})_{\text{metal}}$ are the half-wave potentials of the complexed and free metal ion, n is the number of electrons transferred, K_f is the stability constant of the complex, ρ is the stoichiometry of the complex and $[L]_t$ is the analytical concentration of the ligand. The ρ and log K_f values were obtained from the slope and intercept of the linear plots of $\Delta E_{1/2}/ - 2.303(RT/nF)$ versus $\log[L]_t$, respectively.

Results and discussion

In polarographic investigation of complexation of metal ions by ligands, the difference between the half-wave potentials $(E_{1/2})$ or the differential pulse peak potential (E_p) of the free and complexed metal ion is a measure of the complex stability [40, 41].

The complexation of ligands L1 and L2 with Tl$^+$, Pb^{2+} and Cd^{2+} were studied in DMF/NM, DMF/AN, DMF/n-PrOH and DMF/MeOH binary mixtures. The results show that addition of the ligands to Tl$^+$, Pb^{2+} and Cd^{2+} solutions in 0.025 M tetraethylammonium perchlorate, shifts the differential pulse peak potential (E_p) for the reduction of the complexed ions towards more negative values. As an example, the differential pulse polarograms of the Tl$^+$ ion in different concentrations of L1 in a DMF/n-PrOH (79.54% DMF) binary systems are shown in Figure 1. With the exception of the PbL1 complex in DMF/MeOH mixtures and the CdL1 complex in all solvent systems, the reduction waves for all complexes of L1 with these cations are reversible and diffusion-controlled (Table 1). In addition, as is evident from Table 1, the resulting L2 complexes show an irreversible behavior in DMF/MeOH and some compositions of DMF/AN binary systems.

The plots of EMF$_{\text{(DME)}}$ vs. log $[(i_d - i)/i]$ gave straight lines with Nerstian slopes corresponding to a reversible reduction of one electron (62 ± 3 mV) for Tl$^+$ complexes and a two-electron reversible reduction (30 ± 2 mV) for Pb^{2+} and Cd^{2+} complexes. The variation of $\Delta E_{1/2}/ - 2.303(RT/nF)$ as a function of log $[L]_t$ for PbL1 in DMF/n-PrOH binary mixtures is shown in Figure 2. Similar linear plots were obtained for other systems, indicating the formation of a single complex in solutions. The slopes of these linear plots gave a value of $\rho = 1$, which suggests the formation of a 1:1 complex in solution. The formation constants were obtained by fitting of the polarographic data to equation (1) and the results are listed in Table 1.

It is seen from Table 1 that in all of the solvent mixtures, the stability of PbL1 is much higher than that of TlL1. A similar trend is also observed for PbL2 and TlL2 complexes. This behavior may be due to the relative size of the metal ions and the cavity of the polyether rings. Both macrocyclic ligands L1 and L2 have about the same cavity size of 2.8 Å [42], therefore, the Pb^{2+} ion with ionic size 2.40 Å can attain a more convenient fit condition than the Tl$^+$ (2.90 Å) ion for the ligand's cavity, moreover, the Pb^{2+} ion bears a

Table 1. Log K_f for formation of Tl^+, Pb^{2+} and Cd^{2+} complexes with L1 and L2 in some binary mixed non-aqueous solvents at 22 °C

| Medium | mol% of DMF | Log K_f [a] | | | | |
| | | L1 | | L2 | | |
		Tl^+ [b] $(r = 1.45)$[c]	Pb^{2+} [b] $(r = 1.19)$[c]	Tl^+	Pb^{2+}	Cd^{2+} [b] $(r = 0.95)$[c]
DMF/NM	14.79	5.6 (1.1)[d] [4.00][e]	13.8 (1.1) [8.00]	2.6 (0.9)	4.5 (1.1)	1.7 (0.9)
	31.60	5.0 (1.1) [3.74]	12.3 (1.1) [6.24]	1.9 (0.9)	2.5 (0.9)	1.7 (0.9)
	50.98	4.3 (1.1) [3.12]	11.1 (1.1) [5.80]	1.5 (0.9)	2.0 (0.9)	<1
	73.40	3.7 (1.0) [2.69]	9.8 (1.1) [4.44]	1.2 (0.9)	1.6 (0.9)	<1
	100	3.3 (0.9) [2.48]	7.9 (0.9) [3.38]	<1	1.4 (0.9)	<1
DMF/n-PrOH	19.55	6.2 (1.1)	11.0 (1.0)	3.2 (0..9)	5.2 (1.1)	1.9 (0.9)
	39.31	5.3 (1.1)	10.4 (1.0)	2.6 (0.9)	4.1 (1.0)	1.6 (0.9)
	59.33	4.8 (1.1)	9.7 (0.9)	2.0 (0.9)	3.4 (0.9)	1.2 (0.9)
	79.54	4.2 (1.0)	8.9 (0.9)	1.3 (0.9)	2.3 (1.0)	<1
	100	3.3 (0.9)	7.9 (0.9)	<1	1.4 (0.9)	<1
DMF/MeOH	11.61	5.6 (1.1) [5.11]	I	3.2 (1.0)	I	I
	25.90	5.2 (1.1) [4.40]	I	I	I	I
	44.04	4.7 (1.1) [3.80]	I	I	I	I
	65.49	4.1 (1.0) [3.24]	I	I	I	I
	100	3.3 (0.9) [2.48]	7.9 (0.9)	<1	1.4 (0.9)	<1
DMF/AN	14.46	5.6 (1.1)	9.0 (0.9)	I	4.1 (1.0)	I
	31.09	5.1 (1.1)	8.7 (1.1)	1.7 (1.1)	2.6 (0.9)	I
	50.32	4.6 (1.1)	8.4 (1.1)	1.3 (1.1)	I	<1
	72.30	4.0 (1.0)	8.1 (1.0)	<1	I	<1
	100	3.3 (0.9)	7.9 (0.9)	<1	1.4 (0.9)	<1

[a] Standard deviations = ± 0.1.
[b] Concentration of metal ions 1.0×10^{-5} M.
[c] Ionic radius in Angstroms [50].
[d] The figures in parentheses show the stoichiometric number ρ.
[e] The figures in bracket show the log K_f of 18C6 complexes, from ref 46 and ref 47. I = Irreversible.

high charge density which results in a strong interaction with these ligands. As is evident from Table 1, the Cd^{2+} ion forms the least stable complex with L2 compared with Pb^{2+} and Tl^+ ions (Figure 3). This is because the cation size of Cd^{2+} (1.90 Å) is too small to match the ligand cavity and it also has a higher soft character than the other two cations [43, 44].

The data given in Table 1 show that in all solvent systems, the PbL1 and TlL1 complexes are more stable than the corresponding L2 complexes. As an example, this behavior in n-PrOH/DMF binary systems is shown in Figure 3. This behavior can be attributed to some combination of the electron withdrawing property of benzo groups which reduce the electron donor ability of the oxygen atoms of the macrocyclic ring, and the reduced flexibility of the ligand which prevents a convenient arrangement of the macrocyclic molecule L2 around the cations. On the other hand, although the L1 and L2 ligands have the same kind of donating atoms, in the case of L1, the nitrogen atom has a lone-pair of electrons which conveniently interacts with the metal ion, while in the case of L2, the lone-pair electrons of the nitrogen atom are engaged with the other atoms of the pyridine ring via resonance, therefore, the interaction between L2 with Pb^{2+} and Tl^+ cations decreases compared to L1. The decrease in stability of macrocyclic complexes due to the presence of a benzo group has also been reported in a study of 15C5 and 18C6 and their related benzo substituted analogs upon complexation with some of the metal cations [45].

Comparison of the results obtained in this investigation with those which have been obtained for 18C6 [46, 47] indicates that the substitution of one oxygen donor atom of the 18C6 ring with nitrogen causes a drastic increase in the stability of the resulting complexes with the heavy metal ions (Table 1). These results are not unexpected, because
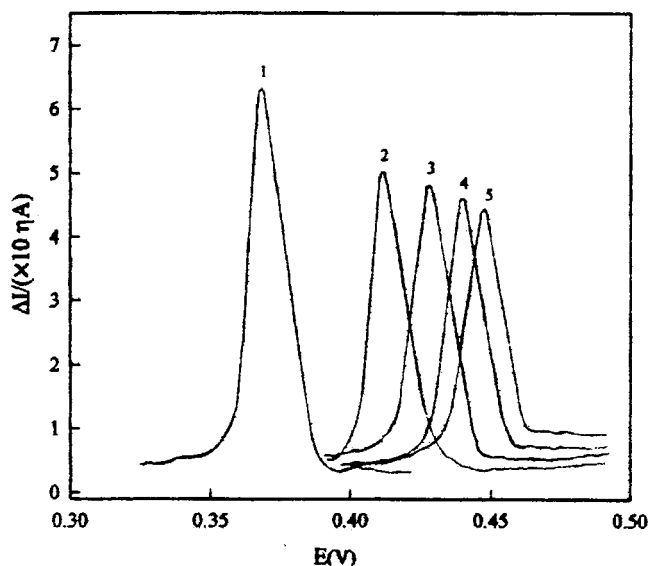
Figure 1. Differential pulse polarograms of 0.01 mM Tl$^+$ ion in *n*-propanol/dimethylformamide (79.54% DMF + 20.46% *n*-PrOH) binary mixture with different concentration of L1 ligand. Concentration of L1/mM: (1) 0; (2) 0.5; (3) 1; (4) 1.4; (5) 1.9.
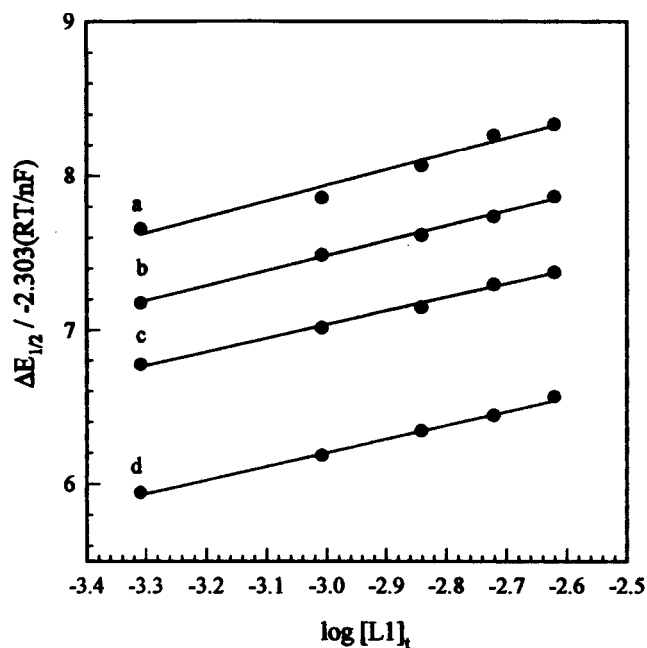

Figure 3. Variation of log K_f of Pb^{2+}, Tl$^+$ and Cd^{2+} complexes with L1 and L2 ligands in different binary *n*-propanol/dimethylformamide mixtures.

Figure 2. Linear plots of $\Delta E_{1/2}/-2.303(RT/nF)$ vs. log [L1]$_t$ for the PbL1 complex in different binary *n*-propanol/dimethylforamide mixtures. Respective mol % of dimethylforamide: *a* (19.55), *b* (39.31), *c* (59.33), *d* (79.54).

Figure 4. Variation of log K_f of PbL1 in different binary systems: (a) AN/DMF, (b) *n*-PrOH/DMF, (c) NM/DMF.

the heavy metal ions as soft acids can interact more strongly with the nitrogen atom of the ring as a soft base compared with the oxygen atom.

The variation of the stability constant of the PbL1 complex as a function of the composition of the mixed solvents is shown in Figure 4. As shown in this Figure, the stability of PbL1 decreases with increasing concentration of dimethylformamide in AN/DMF, *n*-PrOH/DMF and NM/DMF binary systems. In addition, as it is evident from Table 1, in all of the solvent mixtures, the stability of the complexes decreases with increasing concentration of dimethylform-
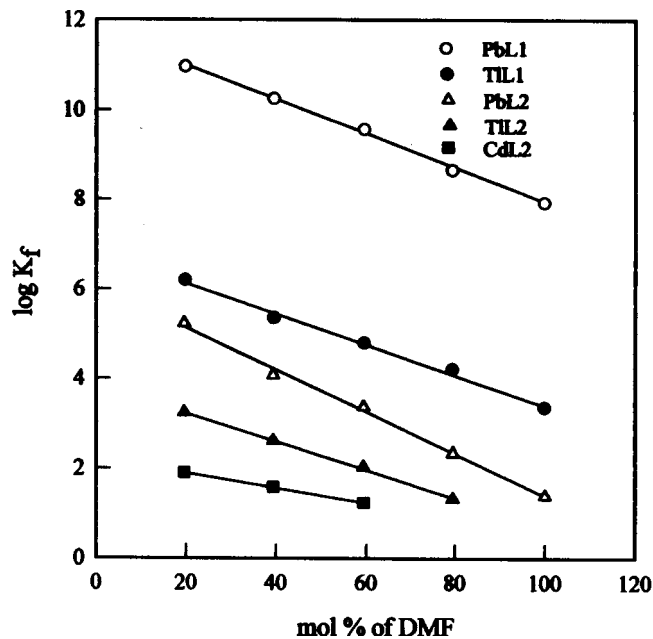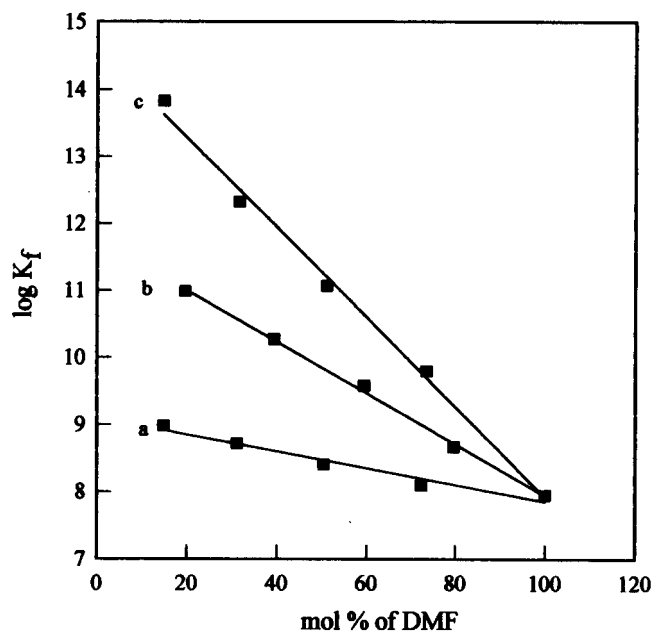
amide. This behavior can be interpreted by considering the relative solvating ability of the neat solvents which form the mixtures. It has been shown that the solvating ability of a solvent, as expressed by the Gutmann donor number [48], plays a fundamental role in complexation reactions. In a solvent with high solvating ability (high donor number), the solvent can compete strongly with the ligand for the cation, therefore, the interaction between the ligand donor atoms and the metal ions will be decreased. Since dimethylformamide is a high donor solvent (DN = 26.6) relative to nitromethane (DN = 2.7), acetonitrile (DN = 14.1), methanol (DN = 20) and *n*-propanol (DN = 18), the stability constant

of the complexes increases as the concentration of DMF is lowered in these binary systems.

As is evident from Table 1, the stability constants of the TlL1 and PbL1 complexes in AN/DMF binary mixtures are lower than those of n-PrOH/DMF and MeOH/DMF binary systems. A similar trend is also observed for the PbL2 and TlL2 complexes. This behavior seems to be unexpected if we only consider the donicity of the solvents. Since the donor number of AN is lower than those of n-PrOH and MeOH, it is expected that the stabilities should be in the order AN/DMF > n-PrOH/DMF > MeOH/DMF. This unexpected behavior may be attributed to the presence of a CN group in AN molecules; because the CN group with a nitrogen atom (as a soft base) can strongly interact with Tl^+ and Pb^{2+} cations and due to this specific interaction between the solvent molecules and these metal ions, the desolvation of cation would be difficult. In addition, the high dielectric constant of acetonitrile (38.0) with respect to n-propanol (20.1) and methanol (32.6) will decrease the electrostatic interaction between the ligand and cation, therefore, the complex formation is weakened in AN/DMF binary mixtures relative to n-PrOH/DMF and MeOH/DMF binary systems. Similar results have been obtained for some of the metal ion complexes of 15-crown-5 and 18-crown-6 macrocyclic ligands in acetonitrile solutions [49].

Acknowledgement

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