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

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The complexation reaction between Pb^{2+}, Tl^+ and Cd^{2+} ions and macrocyclic ligands, 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6), was studied in dimethylsulfoxide (DMSO)-nitromethane (NM) and dimethyl-formamide (DMF)-nitromethane binary systems by square wave polarography (SWP) technique. The stoichiometry and stability 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 most cases, the stability constants of complexes increase with increasing amounts of the nitromethane in mixed binary solvents used in this study. The complexes formed between 18C6 and DB18C6 and these metal cations in all cases had a stoichiometry of 1 : 1. The results obtained show that there is an inverse relationship between the formation constant of complexes and the donor number of solvents based on a Gatmann donocity scale and the stability constants show a high sensitivity to the composition of the mixed solvent systems. A linear behavior was observed for variation of log K_f of 18C6 complexes vs the composition of the mixed solvent systems in NM/DMSO and NM/DMF, but a non-linear behavior was observed in the case of DB18C6 complexes in these binary systems. In most of the systems investigated, the Pb^{2+} cation forms a more stable complex with the 18C6 than other two cations and the order of selectivity of this ligand for cations is: $Pb^{2+} > Tl^+, Cd^{2+}$.

Introduction

Several hundred papers have been written on crown ether molecules since Pedersen[1] published his pioneering work, in which he described the preparation and complexing properties of these ligands with metal cations in solutions. The discovery that cations and anions form stable complexes with macrocyclic polyethers[2,3] has opened a new door to several broad and fruitful areas of chemical investigations. The interest in these macrocyclic ligands was stimulated when it was found that certain crown ethers formed stable complexes with alkali and alkaline earth metal cations and that preferential cation complexation resulted when the relative sizes of cations and ligand cavities were matched. In addition, these synthetic ligands are similar in their structures and reactions to many naturally occurring macrocyclic compounds, which are known to exhibit selective cation complexation.[4]

Macrocyclic ligands have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes,[5] liquid-liquid or solid-liquid phase-transfer reactions, dissolution in apolar solvents of metal and organic salts,[6-8] preparation of ion-selective electrodes,[9] isotope separations, in the understanding of some natural processes through mimicry of metalloenzymes, as a stationary phase in chromatography,[10] and in preparation and preconcentration of metal cations and the recovery of rare metalic elements.[11-13]

While the investigations of crown ether complexes have been steadily gaining popularity during the past years, it seems that so far most of the research has been focused on alkali and alkaline earth metal ion complexation and little attention has been paid to heavy metal ion complexes. In addition, the complexation reactions of crown ethers with metal cations in mixed solvent systems have been studied only to a very limited extent and these investigations have been predominantly restricted to water-methanol mixtures.[14] The available information of such complexation reactions in solvent mixtures, which do not contain water, appears to be very sparse.

The stability and selectivity of complexations strongly depend on the solvating ability of the solvent not only with respect to cation, but also with respect to the ligand and the resulting complex. It should be noted that the solvating abilities of solvents in mixtures can be very different from those of neat media.[15]

We have reported previously the results obtained in investigations involving complexation of the alkali and a few heavy metal ions with some of macrocyclic crown ethers in several non-aqueous media.[16] We have now extended these studies to complex formation between 18C6 and DB18C6 (both with the same cavity size) and Pb^{2+}, Tl^+ and Cd^{2+} ions in DMSO/NM and DMF/NM binary mixtures in order to see how the variation in the nature and composition of the solvent, the relative size and type of the cation and the effect of the side rings on the polyether ring affect the stability and selectivity of complexation. Since these metal cations are very toxic,[17] investigation of reaction conditions and the design of a highly selective ligand for removal of these harmful cations is of particular importance.

Among various physicochemical methods, which have been used for studying the stability constants and stoichiom-

etry of cyclic polyether complexes,[16-21] polarographic techniques are very useful means for such investigations. Due to the higher speed, higher resolution and also low consumption of mercury in SWP, we preferred to use this technique for the present investigation.

Experimental Section

Reagents and Solvents. Reagent grade 18-crown-6 (Riedel), DB18C6 (Fluka) and lead nitrate, thallium nitrate, cadmium nitrate and tetraethylammonium perchlorate, TEAP (all from Merck), were used without further purification except for drying over P_2O_5 in vacuum for 48h. The organic solvents, dimethylformamide, nitromethane and dimethylsulfoxide (all from Merck) with the highest purity, were used for the preparation of the desired mixed solvents.

Apparatus. The polarographic measurements: square wave polarography, cyclic voltammetry (CV) and direct current polarography (DCP) were carried out on an EG & G Princton applied research (PAR), 384B polarographic analyzer with a static mercury drop electrode (SMDE) in a three-electrode arrangement (EG & G PAR 303A). An Ag/AgCl electrode with a bridge containing the base electrolyte (a solution of 0.025 M TEAP) of the electrolyzed solution was employed. The counter electrode was a Pt wire. The instrumental parameters were: pulse height, 50 mV; equilibration time, 5s; and scan rate, 200 m V/s. All solutions were deaerated for 8 minutes with pure helium and an inert atmosphere was maintained over the solution during the reaction. In all experiments the concentration of metal cations were 2.5×10^{-2} mM.

Results and Discussion

Addition of crown ethers (18C6 and DB18C6) to a solution containing a desired cation in 0.025 M tetraethylammonium perchlorate in different mixtures of DMSO-NM and DMF-NM binary systems, shifts the SWP half-wave ($E_{1/2}$) or peak potentials (E_p) for the reduction of the complexed ion towards more negative values. The reversibility of the systems was studied by CV or DCP, and the one or two electron reduction of cations was studied by the plots of E_{DME} vs. Log ($i/(i_d-i)$). The reduction waves for the complexes in most cases were reversible and diffusion-controlled. The variation of the half-wave potential as a function of the logarithm of the ligand concentration was linear for all cases, showing that a single complex is formed in solution, the slopes of the straight lines suggest that 1 : 1 complexes were formed between 18C6 and DB18C6 with Pb^{2-}, Tl^- and Cd^{2+} ions. As an example, the variations of $\Delta E_{1/2}$ as a function of log $[L]_t$ for the complex formation between 18C6 and Tl^+ ion in DMF-NM binary systems is shown in Figure 1.

For determination of stoichiometry and the stability constants of complexes formed between Pb^{2-}, Tl^-, and Cd^{2-} cations and ligands in these binary non-aqueous solutions, we used the Lingane equation.[22]
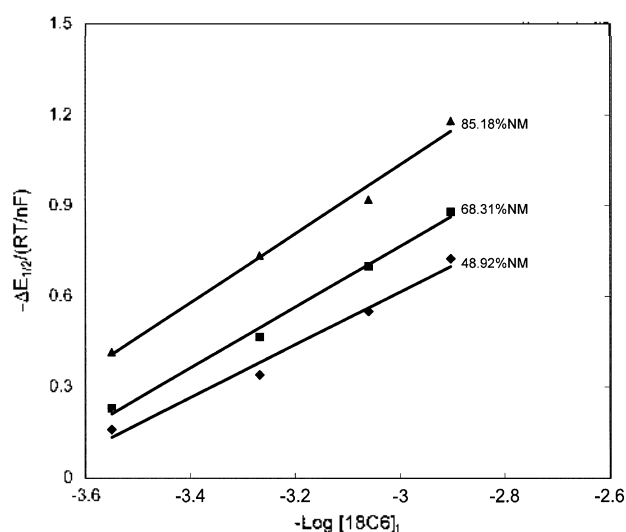

Figure 1. Linear plots of $\Delta E_{1/2}$ (RT/nF) versus log [18C6]$_t$ for the 18C6-Tl$^+$ complex in DMF-NM binary mixtures.

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

where $(E_{1/2})_M$ and $(E_{1/2})_C$ are the half-wave potential of free and complexed metal ion, respectively, n is the number of electrons transferred, $[L]_t$ is the analytical concentration of the ligand, K_f is the complex formation constant and m is the stoichiometry of the complex. The values of log K_f and m can be obtained from the intercept and slope of the linear plots of $\Delta E_{1/2}/(RT/nF)$ vs log $[L]_t$, respectively.

In most of the binary mixed solvent systems used in this investigation, addition of the 18C6 or DB18C6 ligands to the cation solutions in the presence of TEAP, shifts the reduction potential of the metal ions towards a more negative value.
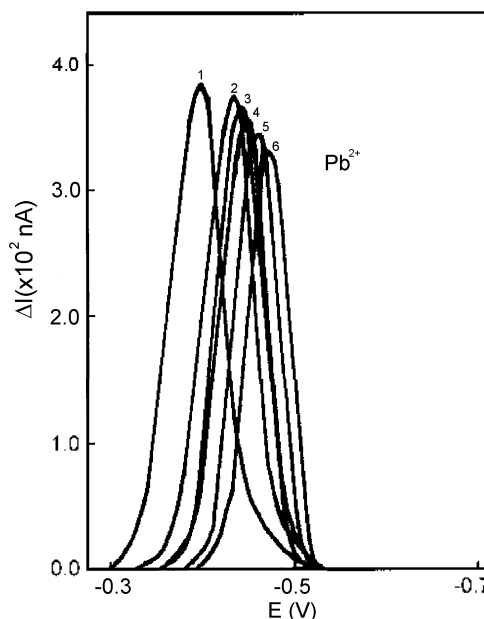

Figure 2. Square wave polarograms of 0.025 mM Pb^{2+} ion in DMSO-NM (84.14% NM – 15.86% DMSO) binary system with different concentration of 18C6 ligand: (1) 0. (2) 0.09. (3) 0.28. (4) 0.54. (5) 0.87 and (6) 1.25 mM.

ence of different concentrations of 18C6 in a DMSO/NM binary system are shown in Figure 2. Similar polarograms were obtained for other systems. In these polarograms the difference between the half-wave potentials of the free and complexed metal ions is a measure of the complex stability.[22]

From Table 1, it is seen that the stability of the complexes of these heavy metal ions with 18C6 decreases in the order $Pb^{2-} > Tl^+$, Cd^{2+} in all of the binary non-aqueous mixtures used in this study. The Pb^{2+} ion, with the least soft character[23] and with a good fit condition for the 18C6 cavity, forms the most stable complex with 18C6 as a hard donating ligand. The greater polarization and the increased nature of the covalent bonding of the Pb^{2-} ion also explain the larger value of the stability constant of the 18C6-Pb^{2+} complex than the other two complexes in these systems. As is evident from Table 1 and Figure 3, the Tl^+ ion forms a more stable complex with 18C6 than Cd^{2+} ion in DMF-NM binary systems. This result seems reasonable, since the Tl^+ ion is bound in the complex by an ion-dipole interaction with a covalent contribution.[21]

The stability of a complex formed in a solution strongly depends on the nature of solvent medium. During the complexation step, the ligand should be able to replace the solvent molecules as completely as possible in the first solvation shell of the cation, or the cation should be able to replace the solvent molecule with the ligand. Therefore, the
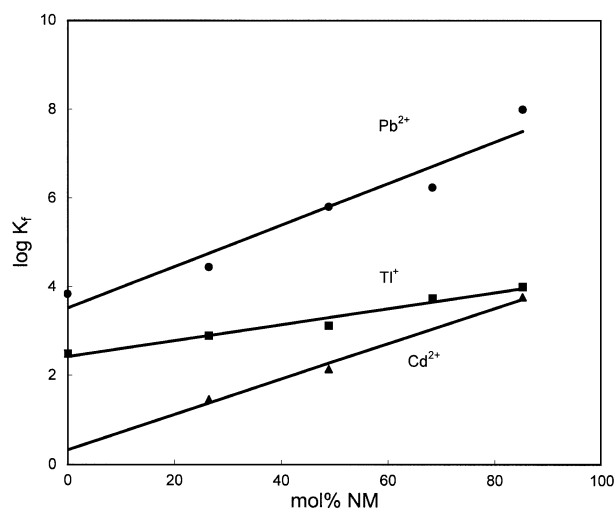

Figure 3. Variation of log K_f for Pb^{2+}-18C6, Cd^{2+}-18C6 and Tl^+-18C6 complexes with solvent compositions in the DMF-NM binary system.

variation of the solvent produces a significant change in the binding properties and selectivity of the ligand for a certain cation over the others. Very few data about the complexation reactions between crown ethers and heavy metal cations in non-aqueous as well as mixed solvents are available in literature. As Izatt *et al.* have suggested,[11] more data valid in a variety of solvent systems are needed in order to understand the effect of solvent parameters on thermodynamic and kinetic values for complexation reactions. As it is evident from Table 1, in general the stability of all complexes increases with an increasing concentration of NM in NM/DMSO and NM/DMF binary systems. In a weakly solvating solvent such as nitromethane, which has a low Gutmann donocity (DN = 2.7), the solvation of the metal cations and possibly of the ligand should be weaker than in solvents with a strong solvating ability such as for dimethylsulfoxide (DN = 29.8) and dimethylformamide (DN = 26.2). Therefore, less energy is necessary for the desolvation step of the Pb^{2+}, Tl^+ and Cd^{2+} cations and probably of the ligand during the complex formation in the case of NM than in DMSO and DMF.

The variation of the stability constants of DB18C6 complexes with Pb^{2+}, Tl^+ and Cd^{2+} ions with solvent compositions in NM/DMSO binary mixtures is illustrated in Figure 4. It is interesting to note that a non-linear behavior is observed for variation of the stability constant (log K_f) of complexes versus the composition of NM/DMSO binary systems. As it is evident from this Figure, when the concentration of NM increases, the stability constants of complexes first increase gradually, and then increase suddenly after about 70 mol% of NM. This behavior may by due to some kind of solvent-solvent interactions between these aprotic solvents when they are mixed with one another or it may be due to preferential solvation of the cations in these binary systems. As it is evident from Figure 4 the order of stability of DB18C6 complexes in all NM/DMSO binary mixtures is: Cd^{2-}-DB18C6 > Pb^{2+}-DB18C6 > Tl^+-DB18C6.

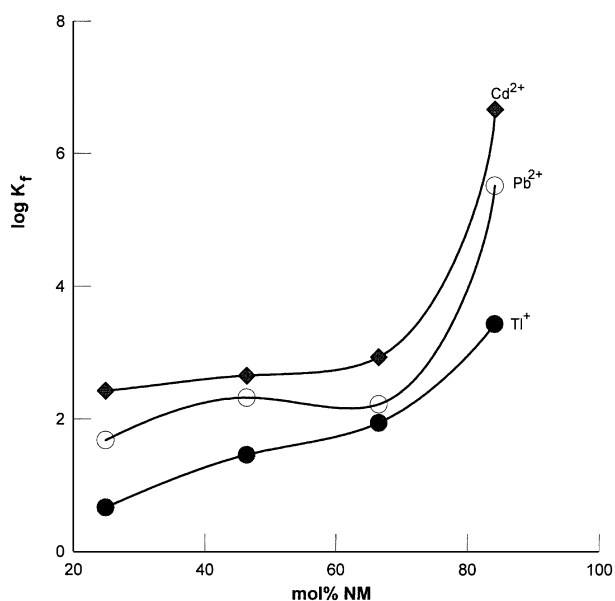Comparison of the results in Table 1 shows that, in most

Table 1. Log K_f values of Pb^{2-}, Tl^+ and Cd^{2+} complexes with 18C6 (T=22 °C) and DB18C6 (T=25 °C) in some binary solvent mixtures

Medium	Solvent Composition	[a]Log K_f		
	Mol%NM	[b]Pb^{2+}	[b]Tl^+	[b]Cd^{2+}
NM-DMSO (18C6)	0	<1	i	i
	24.90	1.46	i	1.02
	46.39	2.64	i	2.93
	66.55	4.48	i	4.94
	84.14	6.66	i	6.52
NM-DMF (18C6)	0	3.83	2.48	−
	26.43	4.44	2.89	1.46
	48.92	5.80	3.12	2.14
	68.31	6.24	3.74	−
	85.18	8.00	4.00	3.77
NM/DMSO (DB18C6)	0	<1	<1	<1
	24.90	1.68	0.66	2.42
	46.39	2.32	1.46	2.65
	66.55	2.22	1.94	2.93
	84.14	5.52	3.43	6.67
NM/DMF (DB18C6)	0	<1	<1	3.17
	26.43	0.89	1.01	3.26
	48.92	2.74	1.86	3.04
	68.31	4.40	1.79	3.33
	85.18	5.15	4.60	4.08

[a]Standard deviation = ±0.08 and ±0.1 for 18C6 and DB18C6, respectively. [b]The concentration of metal ions is 2.5×10^{-5} M. [i]Irreversible

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Figure 4. Variation of log K_f of DB18C6 complexes with Pb^{2+}, Cd^{2+} and Tl^+ ions in NM/DMSO binary systems.
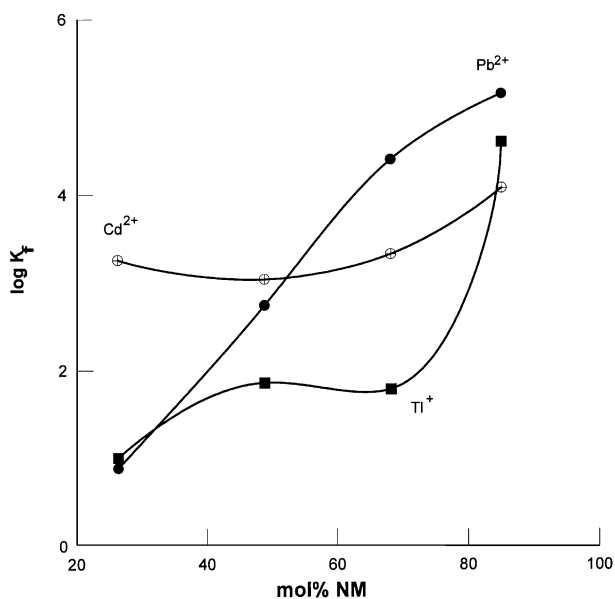

Figure 5. Variation of log K_f of DB18C6 complexes with Pb^{2+}, Cd^{2+} and Tl^+ ions in NM/DMF binary systems.

cases the values of K_f of DB18C6 complexes of Pb^{2+}, Tl^+ and Cd^{2+} ions are smaller than those of 18C6 complexes. Such differences reflect both the electrostatic and the steric effects of the side rings: the strength of the C-O dipoles is affected by the nature of the substituent (*e.g.*, less for aromatic than for acyclic side rings), and the ease of motion and the attainable conformations of the polyether ring depend on the structure near the inter-ring bridges.[25] The aromatic ring lends rigidity to the ligand and withdraws electrons from the basic oxygen donor, thus decreasing the strength of the metal-ligand interaction, or decreasing the stability of the complexes.

As it is evident from Table 1, in some cases the formation

constants of DB18C6 complexes are bigger than those of 18C6 in some binary mixed solvents. In these cases, the DB18C6 ligand may be less stabilized in these solutions than 18C6. Alternatively, the solvation of the DB18C6 cation complexes may make a stabilizing contribution to complex formation relative to 18C6 under the same condition.[26] It may also be explained in terms of ligand bulkiness leading to the isolation of the cation from the solvent. Similar effects have been observed in comparing the selectivity of 18C6 to DB18C6 and also for [2.2.2] cryptand as well as for its benzo derivative, with some alkali and alkaline earth metal cations in methanol and its 95% mixture with water.[27] Somewhat similar behavior was observed in the case of DB18C6 complexes in NM/DMF binary systems (Figure 5). As it is evident from Figure 5, several reversals of stability constants can be observed in some compositions of NM/DMF binary mixed solvents. These reversals of stabilities indicate the possibility of changes in stabilities and, therefore, reversals of cation selectivities, which may be obtained in certain selected mixed solvent systems.

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