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Competitive Potentiometric Study of a Series of 18-Crown-6 with Pb^{2+}, Ag^+, and Tl^+ Ions in Methanol Using Ag^+/Ag Electrode

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The complexation of Ag^+, Tl^+ and Pb^{2+} with 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexyl-18-crown-6 (DCY18C6), and dibenzopyridino-18-crown-6 (DBPY18C6) in methanol solution have been studied by a competitive potentiometry, using Ag^+/Ag electrode as a sensor. The stoichiometry and stability constants of resulting complexes have been evaluated by MINIQUAD program. The stoichiometry for all resulting complexes was 1:1. The order of stability of Ag^+ complexes with used crown ethers varied as DBPY18C6 > DCY18C6 > 18C6 > DB18C6. For Pb^{2+}, and Tl^+, the sequence of stability of complexes with each of these crown ethers (except of DBPY18C6) varied in the order $Pb^{2+} > Ag^+ > Tl^+$. The major trend of stability of resulting complexes of these macrocycle with Pb^{2+} and Tl^+ varied in the order DCY18C6 > 18C6 > DBPY18C6 > DB18C6 with few exceptions.

Key words: competitive potentiometry, Ag^+/Ag electrode, dibenzopyridino-18-crown-6, stability constant

Among the heavy metal ions, Pb^{2+}, Ag^+, and Tl^+ play an important role. This is due to their biological and environmental effects, as well as industrial applications. The synthesis of new crown ethers, which exhibit larger tendencies for binding with transition and heavy metal ions, was the stimulated goal for ligand designing research [1].

The new macrocyclic polyethers, which introduced N, S and the pyridil unit into the macrocycle ring have been synthesized [2]. Among the recently synthesized crown ethers, the dibenzopyrdino-18-crown-6 is a new one, for which the reports about its chemical behaviors are rare [3,4]. Recently, we were interested to study the comparison of complexation reaction of dibenzopyridino-18-crown-6 and other 18-ring member with various groups of metal ions [5–9]. Such comparison of complexation of these ligands with Pb^{2+}, Ag^+ and Tl^+ in methanol solution was the major goal of this work. A simple potentiometric system with Ag^+/Ag electrode as a probe was the measurement technique [6,10,11].

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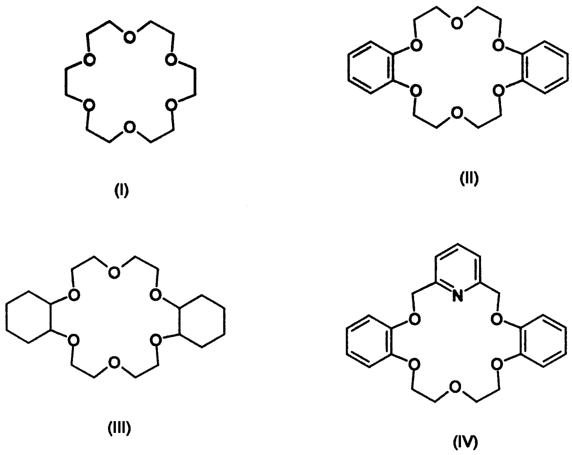
EXPERIMENTAL

Reagent grade 18-crown-6 (18C6, **I**), dibenzo-18-crown-6 (DBl8C6, **II**), dicyclo-18-crown-6 (DCYlB6, **III**), dibenzopyridino-18-crown-6 (DBPY18, **IV**, Figure 1), and the nitrate salts of silver, thallium, and lead (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Absolute methanol (Merck) was used as solvent. Tetrabutylammonium perchlorate (TBAP) was prepared from the 1:l interaction of reagent grade perchloric acid and tetrabutylammonium bromide (both from Merck). The resulting TBAP salt was recrystallized three times from triply distilled deionized water and dried at 110°C for 72 h. The stock solution of crown ethers (0.02 M) and metal ion (0.01 M) were prepared in methanol and kept in darkness.



(I)

(II)

(III)

(IV)

Figure 1. Structures of ligands.

An Ag^+/Ag concentration cell was used to monitor the concentration of silver ion during the potentiometric titration of Ag^+ ion with a solution of the crown in the presence and absence of other metal ions used [11–13]. The concentration of free silver ion was measured by a silver electrode, potentials being measured with a digital voltmeter (model 624 Metrohm). The reference electrode was an Ag^+/Ag electrode, immersed in a known solution of $AgNO_3$ (2.50×10^{-4} M) in methanol and separated from the test solution by a salt bridge containing 0.1 M TBAP in the same solvent. In all experiments, the cell was thermostated at the desired temperature ±0.05°C. All titrations were carried out using a Metrohm electronic burette with a precision of ± 0.001 ml. In all experiments, the ionic strength was kept constant at $I = 0.05$ M using TBAP as supporting electrolyte. The schematic diagram of the used cell is:

Ag $|Ag^+(2.50\times10^{-4}$ M), $M^{n+}(2.50\times10^{-4}$ M), TBAP (5×10^{-2} M) || TBAP (5×10^{-2} M),

(2.50×10^{-4} M) $Ag^+|Ag$

To evaluate the stability constants, the following procedure was conducted. The silver electrode was placed in the reaction vessel containing 20 ml of 0.05 M TBAP in methanol. The reference compartment contained 0.05 M TBAP and 2.50×10^{-4} M silver nitrate in the same solvent. First, a concentrated silver nitrate (0.01 M) was added gradually until Ag^+ ion concentration of 2.50×10^{-4} M was achieved, and the cell potential was measured. Plot of emf *versus* log $[Ag^+]$ was strictly linear (slope: 58.9, intercept: 215, r: 0.9980) at 25°C. The same solution was then back titrated with a concentrated crown solutions (0.02 M), in the presence and absence of other metal ions M^{n+}, in the same solvent.

RESULTS AND DISCUSSION

The stability constant of the Ag^+- crown complex (1), K_{Ag}, can be determined by a simple potentiometric titration of a Ag^+ ion solution with a solution of the ligand (crown ether):

$$Ag^+ + \text{crown} \overset{K_{Ag}}{\rightleftarrows} Ag^+\text{-crown} \qquad (1)$$

The stability constants of the M^{n+}(M^{n+}: Pb^{2+}, Tl^+ and Ag^+) ion complexes, K_M, with each crown ether (2) can be determined by the double decomposition reaction of M^{n+} with the corresponding Ag^+ complex (3) by monitoring the equilibrium concentration of silver ion in the presence of M^{n+} ions, using the equilibrium constant $K_E = K_M/K_{Ag}$ for reaction (3) together with the stability constant K_{Ag} obtained from direct titration of Ag^+ ion with the ligand.

$$M^{n+} + \text{crown} \overset{K_M}{\rightleftarrows} M^{n+}\text{-crown} \qquad (2)$$

$$M^{n+} + Ag^+\text{-crown} \overset{K_E}{\rightleftarrows} M^{n+}\text{-crown} + Ag^+ \qquad (3)$$

In this case, the total concentrations of M^{n+} and of each crown is written as

$$[M^{n+}]_{tot} = [M^{n+}] + [M^{n+}\text{-crown}] \qquad (4)$$

$$[\text{crown}]_{tot} = [\text{crown}] + [Ag^+\text{-crown}] + [M^{n+}\text{-crown}] \qquad (5)$$

A MINIQUAD program was used to compute the formation constants K_{Ag} and the resulting K_M from potential-concentration data [14–16]. By using the Gauss-Newton least-squares method, MINIQUAD refines the formation constants of the simultaneous complexation equilibria. Using the initial estimates of the formation constants, the set of simultaneous normal equations is built up and then solved in order to obtain the corrections to be applied to the K values. The new values of the formation constants are a better approximation to the final values and, consequently, are employed in the next refinement cycle. Such an iterative procedure provides K values, that result in the best agreement between calculated and experimental data. The acceptance of the final results at the desired significance levels is based upon such statistical parameters as standard deviation, sum of square of residuals, χ^2 value as a measure of the normality of residuals and R factor.

During running the MINIQUAD program for each experimental point of a titration curve, the mass balance equations (4,5) are valid. In these equations the c_{Ag^+}, $c_{M^{n+}}$, c_{crown} are the total (analytical) concentration of the independent reactants: Ag^+ , M^{n+}, and crown. The program computes the formation constants, which minimize the sum of the squared residuals between observed and calculated analytical concentration

$$U = \Sigma(c_i^{obs} - c_i^{calc})^2 \tag{6}$$

where the sum covers all the mass balance equations for all experimental points. For evaluation of stability constants of each desired 18-crown-6 with Ag^+ ion and M^{n+} ions each (M^{n+}: Pb^{2+}, Tl^+ and Ag^+), potentiometric titration of Ag^+ with a solution of the desired crown in absence and presence of metal ions have been carried out at 25°C as described in the procedure section [11–13,17]. The potentiometric profiles are shown in Figures 2 and 3. These plots are well S-shaped and clearly show the 1:1 stoichiometry. The MINIQUAD program was used to support the stoichiometry and to compute the formation constants K_{Ag} and K_M from the resulting potential-concentration data [14–17]. The resulting data are listed in Table l.

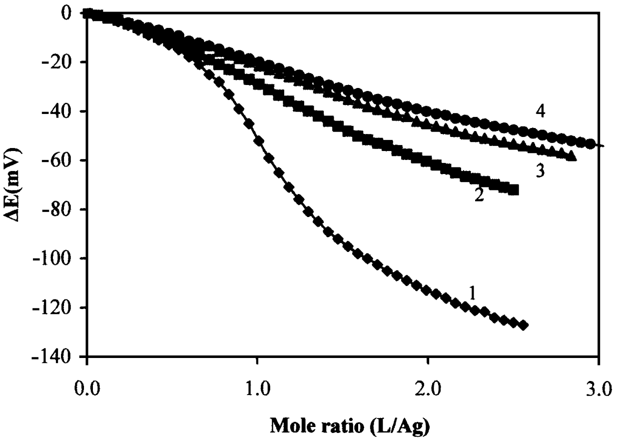


Figure 2. Potential difference *versus* mole ratio (L/Ag^+) plots for complexation of $AgNO_3$ (2.5×10^{-4} M) solutions with 0.02 M: (1) DBPY18C, (2) DCYl8C6, (3) 18C6, (4) DB18C6 in methanol at 25°C and ionic strength 0.05 M TBAP.

For evaluation of stability constants of each used 18-crown-6 with Ag^+ ion and M^{n+} ions (M^{n+}: Tl^+, and Pb^{2+}), potentiometric titration of Ag^+ solution with a solution of the desired crown ether in the absence and presence of metal ions have been done at 25°C as described in the procedure section [6,10,11]. The potentiometric profiles are shown in Figures 2–5. These plots are well S-shaped and clearly show the l:l stoichiometry. The MINIQUAD program was used to support the stoichiometry and compute the formation constants K_{Ag} and K_M from the resulting potential concentration data [14,17]. The resulting data are listed in Table 1.

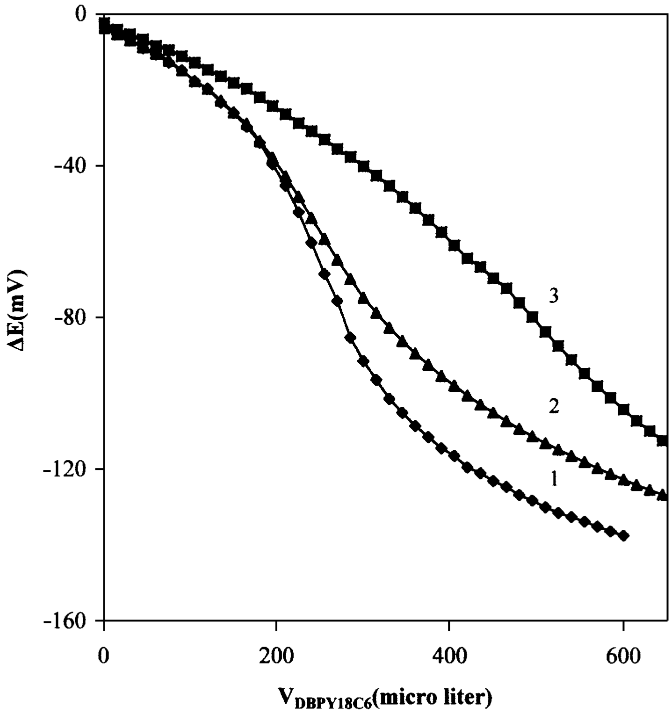


Figure 3. Potentiometric titration plots for $AgNO_3$ (2.5×10^{-4} M) solutions with DBPY18C6 (0.02 M) in the absence (1) and presence of equimolar concentrations of (2) Pb^{2+}, and (3) Tl^+ in methanol at 25°C and ionic strength 0.05 M TBAP.

Table 1. The logarithm of stability constants ($\log K_f \pm \sigma$) for resulting complexes of a series of 18-crown-6 ligands with some heavy metal ions in methanol at 25°C.

Cation	Size (Å)	DBPY18C6	DCY18C6	18C6	DB18C6
Pb^{2+}	2.38	5.16±0.08	5.78±0.06	5.54± 0.07	4.10±0.05
		5.14±0.05^a		6.50^{cd}	4.15^{bd}
Ag^+	2.30	5.64±0.02	4.62±0.01	4.29± 0.01	4.16±0.01
		5.63±0.01^a		4.57^{bc}	4.04^{bd}
Tl^+	3.0	4.19±0.05	4.40±0.05	4.10± 0.06	3.64±0.07
		4.04±0.01^a		5.26^{bc}	3.8^{bc}

a: Ref. [25], 5.63±0.01; b: Ref. [3,4]; c: ISE; d: Cal.

From the consideration of data in Table 1, two trends are obvious among these stability constants. First, from metal ions view (for Ag^+ ion), the sequence of stability of resulting complexes varies in the order DBPY18C6 > DCY18C6 > 18C6 > DB18C6 [8]. The stability of Pb^{2+} and Tl^+ complexes with used 18-crowns-6 varies as follows DCY18C6 > 18C6 > DBPY18C > DB18C6. In this sequence there is an exception for

18C6 complex with Tl^+. This may be due to some softer behavior of Tl^+ relative to Pb^{2+}. Second, for each desired crown, we can also see a general trend as $Pb^{2+} > Ag^+ > Tl^+$. This trend is clearly in accordance with the size effect for ftting into 18-membered rings and HSAB principle (Hard and Soft acid and base) interactions [18,19]. In the sequence of Ag^+-complexes, this cation has a proper size (2.30 Å) for fitting into 18-crown-6 ring (2.68–2.86 Å) [20], but the variation seen among the Ag^+-complexes is mainly due to different substitution groups on 18-crown-6 ring. The effect of introducing such groups as dicyclohexyl-, and dibenzo- into 18-crown-6 has been described before [21–23]. Such unexpected stability of the Ag^+-DBPY18C6 complex could be partly due to the stronger interaction of the pyridino nitrogen of the ligand as a soft base with Ag^+ ion, as a much softer acid than other used cations [6].

Consideration of data given in Table 1 shows the major sequence of stability constants of resulting complexes of Pb^{2+} and Tl^+ ions with 18-crowns-6 varies in the order DCY18C > 18C6 > DBPY18C6 > DB18C6 with some minor exceptions. This general trend is expected, because the presence of cyclohexyl groups allows the pumping of the electrons into the ligand ring and increases the basicity of the oxygen atoms. The flexibility of the ligand remains more or less the same as 18C6. The substitution of two benzo- groups on the 18C6 ring results in a remarked lowering of the stability of the complex. It should be noted that introducing electron withdrawing groups reduces the donicity of the oxygen atoms in the ring and hence the cation-crown interaction [21–24].

Consideration of the sequence of stability constants for each used 18-crown-6 complexes with Pb^{2+}, Tl^+ and Ag^+ shows a general trend as $Pb^{2+} > Ag^+ > Tl^+$ with an exception of DBPY18C6 for which stability varies in another sequence $Ag^+ > Pb^{2+} >$

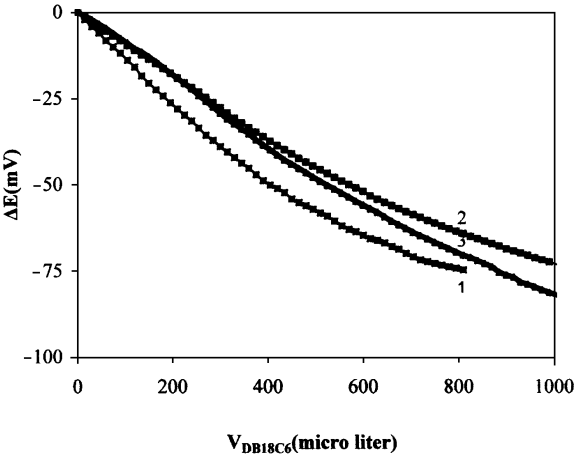


Figure 4. Potentiometric titration plots for $AgNO_3$ (2.5×10^{-4} M) solutions with DB18C6 (0.02 M) in the absence (1) and presence of equimolar concentrations of (2) Tl^+, (3) Pb^{2+} in methanol at 25°C and ionic strength 0.05 M TBAP.

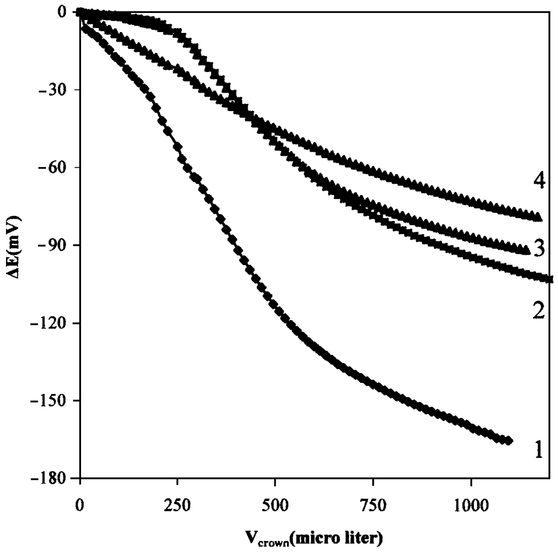


Figure 5. Potentiometric titration plots for complexation of Pb^{2+} (2.5×10^{-4} M) in the presence of equimolar concentration of Ag^{+} solution with 0.02 M: (1) DBPY18C, (2) DCY18C6, (3) 18C6, (4) DB18C6 in methanol at 25°C and ionic strength 0.05 M TBAP.

Tl^{+}. This trend is expected [6]. Moreover, it should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the complexes, an understanding from the "ion-in-the-hole" model [3], but a measure of the relative strength as compared to the ionic solvation. Thus, only for the weakly solvated larger univalent ions, such as Ag^{+}, and Tl^{+}, the cation size can be considered primarily responsible for the complexing characteristics. Bivalent cations (such as Pb^{2+} cation) are so strongly solvated, that considerably more energy must be expended in the desolvation step, than for univalent cations. Contributions of the solvent-complex and even solvent-ligand interactions on the stability of the resulting complexes cannot be ignored [25,26].

To compare the results of this work with the literature stability constants for the complexation of 18C6 and DB18C6 with Pb^{2+}, Tl^{+} and Ag^{+} ions, these data are summarized in Table 1. For DBPY18C6 and DB18C6 the stability constants measured are in agreement with the literature values. Some variations are observed for 18C6, which may be due to various accuracy and reproducibility of different experimental techniques and the conditions used such as: solvent, electrolyte, and ionic strength [27,28].

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