

## Potentiometric Study of the Complexation of Silver Ions with Some Crown Ethers in Binary Acetonitrile-Water Solutions

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A potentiometric study concerning the interaction between silver ion and several crown ethers in different acetonitrile-water mixtures has been carried out at 25°C. The formation constants of the resulting 1 : 1 complexes were determined from the potentiometric data and found to vary in the order: C222 > DA18C6 > A18C6 > 18C6 > 15C5 > DB18C6 > DB30C10 > B15C5 > 12C4 > DB24C8. The stability constants of complexes increased with increasing the water content of the solvent mixtures until 20% (w/w). However, in further water percentages, the formation constants will reduce. The possible reasons for such observation has been discussed in terms of the topology of the ligands and the specific interactions of the acetonitrile with the ligands and silver ion.

**Key Words:** Potentiometry, Formation constant, Crown ethers, Silver ion.

### INTRODUCTION

Since Pedersen's first synthesis of crown ethers capable of forming selective and stable complexes with metal ions<sup>1</sup>, studies of these ligands and their interactions with a wide variety of cations have become a popular field of research<sup>2-4</sup>. Because of their selectivity and extraction efficiency, macrocyclic crown ethers have been widely used as suitable neutral carriers for the selective transport through liquid membranes<sup>5-7</sup> and for constructing membrane-selective electrodes for different metal ions<sup>8-10</sup>. Information about the selectivity of Ag<sup>+</sup> ion complexes with macrocyclic ligands is of special interest. This is because of the increased industrial use of silver, on one hand, and its hazardous effect to human health, on the other, which emphasizes the need for the specific ion carriers in the development of new methods for selective removal, concentration and determination of silver from its mixtures.

It is well known that the topological features of the macrocyclic crown ethers involving the cavity size, the nature and number of donor atoms in the ring and

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the type of substituents on the ligand, as well as the nature of solvent, play an important role in both selectivity and stability of the resulting macrocycle-metal ion complexes<sup>2,3</sup>.

We have been currently involved in the study of complexes of crown ethers<sup>11-15</sup>. In this paper we report a potentiometric study of the stability of  $\text{Ag}^+$  ion complexes with macrocyclic crown ethers: 12-crown-4 (12C4), 15-crown-5 (15C5), Benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), aza-18-crown-6 (A18C6), diaza-18-crown-6 (DA18C6), dibenzo-24-crown-8 (DB24C8), dibenzo-30-crown-10 (DB30C10) and cryptand 222 (C222) in acetonitrile-water mixtures. The structure of the ligands is shown in Fig. 1.

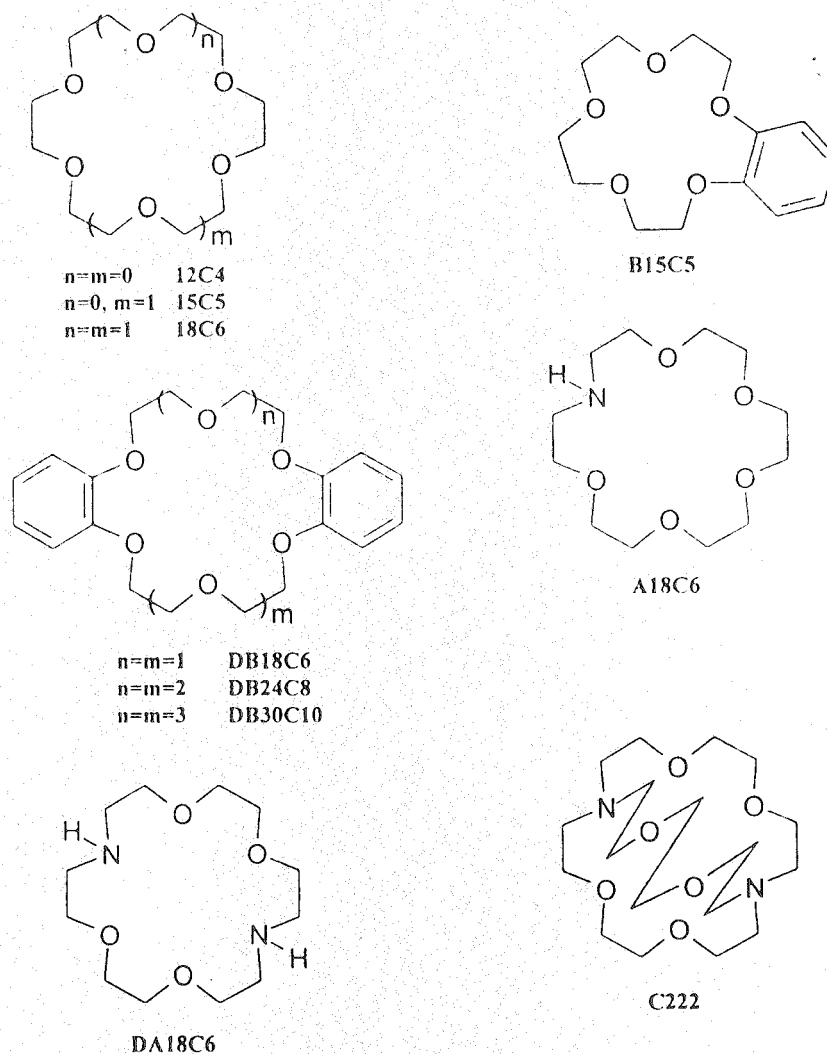


Fig. 1. Structure of the macrocyclic ligands

### EXPERIMENTAL

Reagent grade silver nitrate from Merck Company was used without any further purification except vacuum drying over  $\text{P}_2\text{O}_5$ . Crown ethers B15C5, DB18C6, DB24C8, A18C6, DA18C6 and C222 (all from Merck) were used after

recrystallization in *n*-hexane followed by drying over P<sub>2</sub>O<sub>5</sub>. DB30C10 (Fluka) was recrystallized from acetone and vacuum dried. 12C4 and 15C5 (both from Merck) were used without any further purification. 18C6 (Merck) was precipitated as its acetonitrile complex. The crystals were filtered and the solvent removed by placing the complex under vacuum for at least 24 h<sup>2</sup>.

Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Merck) and perchloric acid<sup>16</sup>. Different acetonitrile-water mixtures were prepared from acetonitrile (Merck) and triply distilled deionized water by weight.

An Ag<sup>+</sup>/Ag concentration cell was used to monitor the concentration of silver ion during the potentiometric titration of Ag<sup>+</sup> ion with a solution of the crown ethers. The concentration of free silver ions was measured with a silver electrode, potentials being measured with a digital voltmeter (Corning 113). The reference electrode was an Ag<sup>+</sup>/Ag electrode, immersed in the desired solvent mixture and separated from the test cell by a salt bridge containing 0.1 M TEAP in the same solvent. In all experiments, the cell was thermostated at 25.0 ± 0.05°C using a Lo-Temprol 154 precision scientific thermostat. All titrations were carried out using a Metier DV10 electronic burette with a precision ± 0.002 mL.

During each titration, the following reaction is assumed to take place between silver ion and macrocyclic ligand used.



The formation constant of the resulting complex is defined as (the charges are ignored for simplicity).

$$K_f = [\text{AgL}]/([\text{Ag}][\text{L}]) \quad (1)$$

On the other hand, from the Nernst equation:

$$E_{\text{cell}} = C + S \log [\text{Ag}] \quad (2)$$

Actually, the values of C and S can be determined, from each titration, from the intercept and slope of the corresponding calibration curve. From eqn. (2) we have

$$[\text{Ag}] = 10^{(E - C)/S} \quad (3)$$

The mass balance equations for various species can be written as:

$$[\text{AgL}] = C_{\text{Ag}} - [\text{Ag}] \quad (4)$$

$$[\text{L}] = C_{\text{L}} - [\text{AgL}] = C_{\text{L}} - C_{\text{Ag}} + [\text{Ag}] \quad (5)$$

where C<sub>L</sub> and C<sub>Ag</sub> are the analytical concentrations of the ligand and silver respectively. Combination of eqn. (1) with the mass balance eqns. (4) and (5) and proper rearrangement results in:

$$K_f[\text{Ag}]^2 - (K_f(C_{\text{L}} - C_{\text{Ag}}) + 1)[\text{Ag}] - C_{\text{Ag}} = 0 \quad (6)$$

from which [Ag] can be obtained:

$$B = (K_f(C_{\text{L}} - C_{\text{Ag}}) + 1)$$

$$[\text{Ag}] = (-B + (B^2 + 4K_f C_{\text{Ag}})^{1/2}) / (2K_f) \quad (7)$$

By using an estimated value of K<sub>f</sub> the positive root of eqn. (7) is obtained and

used to find the calculated potential ( $E_{\text{calc}}$ ) from the corresponding calibration eqn. (2). A BASIC program written based on an iterative method using Newton algorithm was then used to minimize  $\Sigma(E_{\text{calc}} - E_{\text{exp}})^2$ . The refined complex stability constant was then evaluated by this procedure.

The procedure for the titration of  $\text{Ag}^+$  ion with the crown ethers was conducted as follows: The silver electrode was placed in 50.0 mL of a constant ionic strength in the desired solvent mixture (0.05 M in TEAP). The reference cell contained 0.05 M TEAP and  $1.0 \times 10^{-4}$  M silver nitrate in the same solvent. A concentrated silver nitrate solution was added gradually and the cell potential was measured. A plot of the emf vs.  $\text{Ag}^+$  ion concentration gave the calibration curve. The same solution then back titrated with a ligand solution in the same solvent.

## RESULTS AND DISCUSSION

The calibration and titration curves of DB18C6- $\text{Ag}^+$  system are shown in Figs. 2 and 3 respectively. Because of similarity the curves due to other systems are not shown. In all case the slopes of calibration curves were  $59 \pm 3$  mV indicating reversibility in various solvent mixtures and with different ligands. Formation constants of the silver ion complexes with different crown ethers were evaluated from the potentiometric data and all the resulting values are summarized in Table-1.

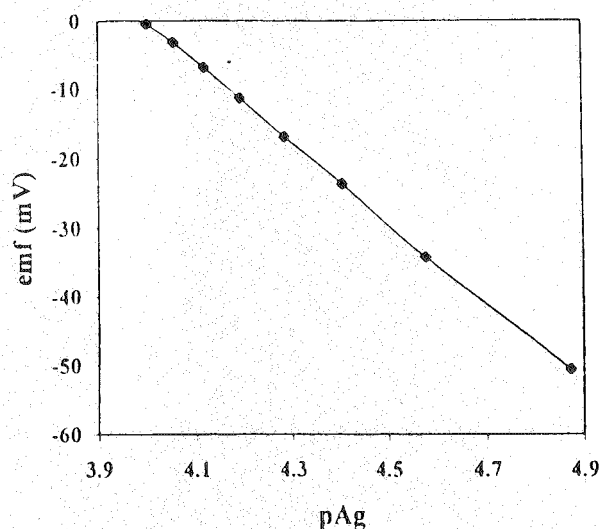


Fig. 2. Calibration plot of emf vs. pAg in acetonitrile solution

Comparison of the data given in Table-1 indicates that among 18-crowns used, where the ring frame remains the same, the stability of the resulting complexes falls in the order DA18C6 > A18C6 > 18C6. This means that substitution of oxygen atoms increases the stability. These results are not surprising since heavy metal ions as soft acids would interact more strongly with the nitrogen atom of the ring as soft base<sup>17-19</sup>. This effect is pronounced in the case of DA18C6- $\text{Ag}^+$  complex.

It is interesting to note that in all solvent mixtures the stability of 18C6 complexes is more than 12C4, 15C5, B15C5 (with lower cavity sizes) or

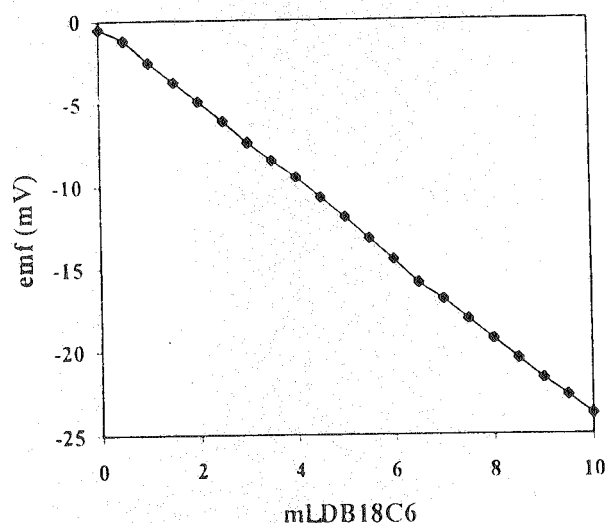


Fig. 3. Titration plot of emf vs. mL DB18C6 ( $2.2 \times 10^{-3}$  M) in acetonitrile solution

DB30C10, DB24C8 (with larger cavity sizes). It seems that  $\text{Ag}^+$  ion with an ionic size of  $2.3 \text{ \AA}^{20}$  to have the most convenient filling condition for the cavity of 18C6.

TABLE-I  
log  $K_f$  OF SILVER ION COMPLEXES WITH SOME MACROCYCLIC LIGANDS IN VARIOUS ACETONITRILE-WATER MIXTURES AT 25°C

Ligand	% H <sub>2</sub> O				
	—	10	20	30	40
DB24C8	1.93 ± 0.01	2.11 ± 0.03	2.27 ± 0.05	1.84 ± 0.07	1.32 ± 0.01
12C4	2.11 ± 0.04	3.32 ± 0.05	2.55 ± 0.07	2.05 ± 0.02	1.56 ± 0.01
B15C5	2.53 ± 0.01	2.71 ± 0.07	2.81 ± 0.07	2.22 ± 0.01	1.78 ± 0.01
DB30C10	2.98 ± 0.05	3.11 ± 0.02	3.29 ± 0.01	3.07 ± 0.02	2.91 ± 0.01
DB18C6	3.36 ± 0.02	3.65 ± 0.04	3.96 ± 0.02	3.26 ± 0.04	3.01 ± 0.09
15C5	4.10 ± 0.01	4.29 ± 0.07	4.68 ± 0.04	4.40 ± 0.09	3.99 ± 0.01
18C6	5.07 ± 0.06	5.83 ± 0.01	5.92 ± 0.01	5.72 ± 0.03	5.18 ± 0.01
A18C6	6.81 ± 0.06	6.27 ± 0.09	6.46 ± 0.06	6.25 ± 0.02	6.01 ± 0.01
DA18C6	6.75 ± 0.03	6.93 ± 0.06	7.11 ± 0.04	6.96 ± 0.04	6.62 ± 0.08
C222	7.63 ± 0.05	7.85 ± 0.01	7.96 ± 0.02	7.81 ± 0.03	7.70 ± 0.07

The cavity size of DB18C6<sup>21</sup> is the same as 18C6. However, this ligand forms weaker complexes. The stability of DB18C6 is also less than 15C5 with no convenient fitting size. Such observation originates from the substitution of two benzo groups on 18C6. This behaviour may be attributed to some combinations of the electron withdrawing property of the benzo groups which weaken the electron-donor ability of the oxygen atoms of the ring and the reduced flexibility of the ligand which prevents the macrocyclic molecule wrapping itself around the cation. The net result is a weaker cation-ligand interaction<sup>22</sup>.

On the other hand, larger crown ethers DB24C8 and DB30C10, despite the increased number of donating atoms in their structures, fail to form stable complexes with silver ion. However, the ion-in-the-hole model<sup>20</sup> is of little use in predicting the stability of metal ion complexes of large crown ethers. In these cases, the increased flexibility of the macrocyclic molecule in solution makes it difficult to define a fixed cavity diameter for the ligand. Actually, the high degree of flexibility in large crown ethers facilitates the twisting of these molecules around the cations of proper size to form a stable three-dimensional wrap around complex. Evidences for the formation of such a three-dimensional structure for K<sup>+</sup>-DB30C10 complex, both in crystalline state<sup>23</sup> and in solution<sup>24</sup>, have been previously reported. In the case of Ag<sup>+</sup>-DB30C10 complex, despite the smaller size of Ag<sup>+</sup> than K<sup>+</sup> ion<sup>20</sup>, the macrocycle can still form a three-dimensional structure, but in this case the oxygen atoms of the ligand will have to be in close proximity so that the resulting repulsive forces will weaken the complex. On the other hand, DB24C8 with lower flexibility and less donating oxygen atoms than DB30C10 form a less stable complex. This means that the solution structure of this complex should be considerably different from that of Ag<sup>+</sup>-DB30C10<sup>22</sup>.

The Gutmann donor numbers for water and acetonitrile are 33 and 14.1 respectively<sup>25, 26</sup>, indicating the higher solvating ability of the former. On the other hand, the dielectric constant of water is more than acetonitrile, which causes the weaker electrostatic attraction between silver ion and the ligands in this solvent. Consequently, it is predicting that the presence of water will diminish the stability of the complexes. However, at water percentages less than 20% (w/w), the reverse is observed (Table-1). Such an unusual solvent effect could be most specific interactions between acetonitrile and the initial reactants. Acetonitrile as a nitrogen donating solvent may have stronger interactions than that predicted by Gutmann donor number<sup>25, 26</sup> with soft metal ion such as Ag<sup>+</sup> ions<sup>27-29</sup>. Moreover, the equally important, but often less appreciated, is the interaction of solvent molecules with macrocyclic ligands<sup>30</sup>. It is well known that acetonitrile would have a rather appreciable interaction with crown ethers in solution<sup>31-33</sup>. 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.

Apparently, at water percentages more than 20% (w/w), the donicity and dielectric constant properties of water<sup>25, 26</sup> overcome the specific interactions of acetonitrile and a usual trend is observed.

Finally, as a result of the formation of the cryptate type inclusion complex between Ag<sup>+</sup> ion and three-dimensional ligand C222<sup>28, 29</sup>, the C222-Ag<sup>+</sup> show a sharp cryptate effect over the other two-dimensional ligands, which evolves a large enhancement in complex stability<sup>28</sup>. The formation of inclusion complex also protects the cation from the solvent. This causes that the solvent dependency of Ag<sup>+</sup>-C222 stabilities to be less than the others (Table-1).

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