



Competitive Potentiometric Study of a Series of 18-crown-6 with Some Alkali and Alkaline Earth Metal Ions in Methanol Using an Ag^+/Ag Electrode

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Abstract

The complexation of some alkali and alkaline earth cations with 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexyl-18-crown-6 (DCY18C6), and dibenzopyridino-18-crown-6 (DBPY18C6) in a methanol solution has been studied by a competitive potentiometric titration using Ag^+/Ag electrode as a probe. The stoichiometry and stability constants of the resulting complexes have been evaluated by the MINIQUAD program. The stoichiometry for all resulting complexes was 1:1. The order of stability of Ag^+ complexes with desired crown ethers varied as $\text{DBPY18C6} > \text{DCY18C6} > \text{18C6} > \text{DB18C6}$. The stability of the resulting complexes for each of these crown ethers varies in the order of $\text{K}^+ > \text{Na}^+$ and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. For each of the used metal ions the major sequence of the stability constants of the resulting complexes varies as $\text{DCY18C6} > \text{18C6} > \text{DB18C6} > \text{DBPY18C6}$ with minor exceptions.

Introduction

The recognition of the complexing ability of crown ethers with alkali and alkaline earth cations by Pedersen and others [1–3] opened a new area in alkali and alkaline earth metal chemistry [4, 5]. The lack of ability of alkali and alkaline earth metal ions for complexation with N and S donor ligands decreased the attention of researchers for the complexation study of these cations before the 1970s [6, 7]. However, after some reports on the selectivity behavior of macrocyclic polyethers with alkaline cations and similar behavior of these compounds with natural macrocyclic compounds such as valinomycin [8, 9], attempts to use crown ethers for analytical purposes increased [7, 10, 11]. The easy and selective ion transport and also ion selective-electrode designing for alkali cations such as K^+ , and Na^+ with natural macrocyclic compounds such as some antibiotics, stimulated analytical chemists to apply these compounds as carriers and ionophores in analytical techniques [9, 12–14]. Due to the importance of some alkali and alkaline earth metal ions in vital, agricultural, biological and industrial processes, we are interested in a systematic study on the complexation of a series of 18-crown-6 with these cations for further analytical purposes [10, 11, 14]. Among these series dibenzopyridino-18-crown-6 is a new one, and reports about it are quite rare [4, 5, 16–21]. Previous studies show that introducing a pyridyl unit into an 18-membered ring drastically decreases the complexing ability of these compounds toward alkali and alkaline metal ions [22, 23]. Therefore, a comparison of the complexation ability of dibenzopyridino-

18-crown-6 with other 18-crown-6 complexes with K^+ , Na^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} and Mg^{2+} in methanol solution was the major goal of this paper. A simple potentiometric system through using an Ag^+/Ag electrode as a probe was the measurement technique [20, 24].

Experimental

Reagent grade 18-crown-6 (18C6, **I**), dibenzo-18-crown-6 (DB18C6, **II**), dicyclohexyl-18-crown-6 (DCY18C6, **III**), dibenzopyridino-18-crown-6 (DBPY18C6, **IV**, Figure 1), and the nitrate salts of silver, sodium, potassium, magnesium, calcium, strontium and barium (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 the solvent. Tetrabutylammonium perchlorate (TBAP) was prepared from the 1:1 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. Stock solutions of crown ethers (0.02 M) and metal ions (0.01 M) were prepared and kept in the dark.

An Ag^+/Ag concentration cell was used for monitoring the concentration of silver ion during the potentiometric titration of Ag^+ ion with a solution of the crown ether in the presence and absence of other metal ions [24, 25]. The concentration of free silver ions was measured with a metallic silver electrode (Metrohm), potentials being measured with a digital voltmeter (model 624 Metrohm). The reference electrode was an Ag^+/Ag electrode, immersed in a known

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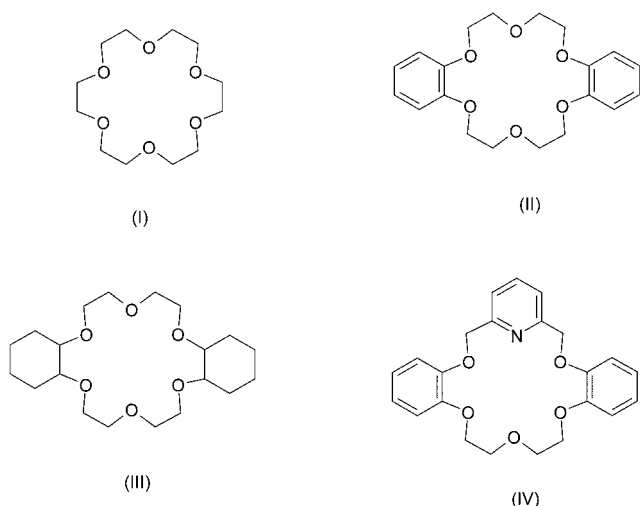
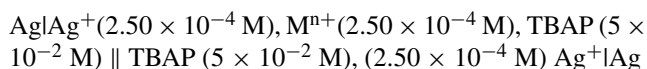


Figure 1. Chemical structures of ligands.

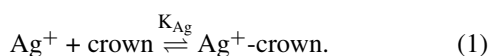
solution of AgNO_3 (2.50×10^{-4} M) in methanol and separated from the test solution by a salt bridge containing 0.1 M TBAP in the same solvent. In all experiments, the cell was thermostated at the desired temperature of ± 0.05 °C, using a Huber thermostat. All titrations were carried out using a Metrohm 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 cell is:



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 an Ag^+ ion concentration of 2.50×10^{-4} M was achieved, and the cell potential was measured. The plot of emf versus $\log [\text{Ag}]$ was strictly linear (slope: 58.9 mV/decade, intercept: 215 mV, $r: 0.9980$) at 25 °C. The same solution was then titrated back with 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 (Equation (1)), K_{Ag} , was determined by simple potentiometric titration of a solution Ag^+ ion with a solution of the ligand (crown ether):



The stability constants of the M^{n+} (K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) ion complexes, K_{M} , with each crown ether (Equation (2)) were determined by the double decomposition reaction of M^{n+} with the corresponding Ag^+

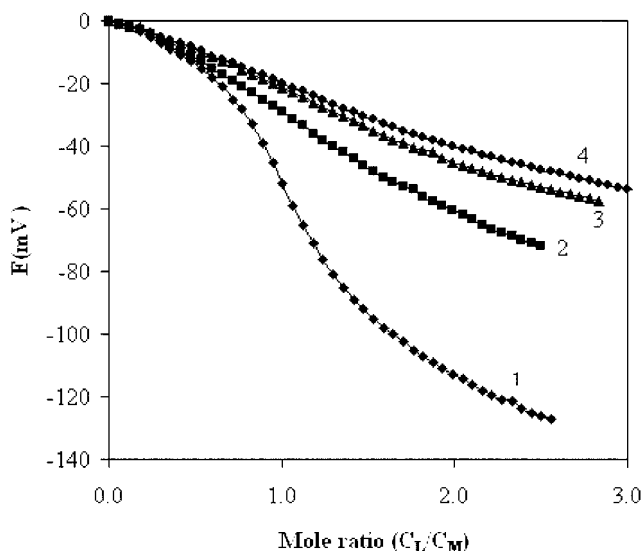
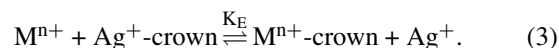
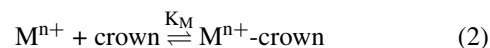


Figure 2. Potential difference versus mole ratio (L/M) plots for complexation of a 2.50×10^{-4} M AgNO_3 solution with 0.02 M: (1) DBPY18C (2) DCY18C6 (3) 18C6 (4) DB18C6 in 0.05 M TBAP methanol at 25 °C.

complex (Equation (3)) by monitoring the equilibrium concentration of silver ion in the presence of M^{n+} ions using the equilibrium constant $K_{\text{E}} = K_{\text{M}}/K_{\text{Ag}}$ for reaction (3) together with the stability constant K_{Ag} obtained from direct titration of Ag^+ ion with the ligand.



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

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

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

The MINIQUAD program was used to compute the formation constants K_{Ag} and the resulting K_{M} from potential-concentration data [26, 27]. 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.

Potentiometric titration of Ag^+ solution with a solution of the desired crown ether in the absence and presence of metal ions was done at 25 °C as described in the procedure section [24, 25, 28]. The potentiometric profiles are shown in Figures 2, 3. These plots are well S-shaped and clearly show the 1:1 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 [26–28]. The resulting data are listed in Table 1.

Table 1. Logarithm of stability constants ($\text{Log } K_f \pm \sigma^*$) for resulting complexes of a series 18-crown-6 with some alkali and alkaline earth cations in methanol at 25 °C, and ionic strength 0.05 M TBAP

| Cation | Size (AA) | DBPY18C6 | DCY18C6 | 18C6 | DB18C6 |
|------------------|-----------|--------------------------|-------------|-------------------------------------------|---------------------------------------------------------|
| Ag ⁺ | 2.30 | 5.64 ± 0.01 ^a | 4.62 ± 0.01 | 4.29 ± 0.01 4.58 ± 0.03 ^{b,c} | 4.16 ± 0.01 4.04 ^{b,c} |
| Na ⁺ | 2.04 | 3.96 ± 0.01 | 4.33 ± 0.03 | 4.25 ± 0.04 4.35 ± 0.02 ^{b,c} | 4.15 ± 0.01 4.36 ^{b,c} |
| K ⁺ | 2.76 | 4.15 ± 0.02 | 4.96 ± 0.03 | 5.06 ± 0.07 5.93 ^{b,c} | 4.86 ± 0.04 4.8 ^{b,c} , 6.06 ^{b,d} |
| Mg ²⁺ | 1.44 | 2.84 ± 0.04 | 3.57 ± 0.01 | 3.36 ± 0.06 | 3.15 ± 0.02 |
| Ca ²⁺ | 2.0 | 3.04 ± 0.03 | 3.94 ± 0.01 | 4.16 ± 0.03 3.90 ^{b,c} | 3.34 ± 0.01 – |
| Sr ²⁺ | 2.36 | 4.03 ± 0.02 | 4.87 ± 0.04 | 4.75 ± 0.09 | 3.96 ± 0.03 3.55 ^{b,c} |
| Ba ²⁺ | 2.70 | 4.64 ± 0.01 | 4.98 ± 0.08 | 4.87 ± 0.09 7.04 ± 0.08 ^{b,d} | 4.43 ± 0.01 4.28 ^{b,d} |

* Standard deviation. The sum of residuals, χ_2 and R values associated with determination of formation constants were in the range of 0.4×10^{-8} – 2.30×10^{-8} , 2.2–56.7 and 0.01–0.04, respectively.

^a Reference [20]: 5.63 ± 0.01 .

^b Reference [4, 5].

^c ISE.

^d Cal.

^e Kin.

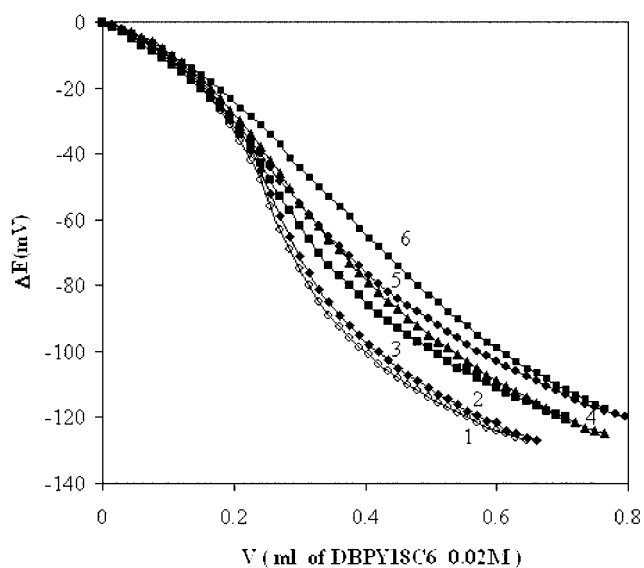


Figure 3. Example of potentiometric titrations plots for a 2.50×10^{-4} M AgNO_3 solution with DBPY18C6 (0.02 M) in the absence (2) and presence of equimolar concentrations of other metal ions in 0.05 M TBAP methanol at 25 °C: (1) Mg^{2+} ; (3) Na^+ ; (4) K^+ ; (5) Sr^{2+} ; (6) Ba^{2+} .

From the consideration of data given in Table 1, two general trends are obvious. First, for Ag^+ ion, the sequence of stability of resulting complexes varies in the order as $\text{DBPY18C6} > \text{DCY18C6} > \text{18C6} > \text{DB18C6}$ and for alkali and alkaline earth metal ions as $\text{DCY18C6} > \text{18C6} > \text{DB18C6} > \text{DBPY18C6}$. Second, for each desired crown, we can also see a general trend as $\text{K}^+ > \text{Na}^+$ for alkaline and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ for alkaline earth metal ions.

This trend is clearly in accordance with the size effect for fitting into 18-membered rings [1–3, 22].

In the sequence of Ag^+ -complexes, this cation has a proper size (2.30 AA) for fitting into an 18-crown-6 ring (2.68–2.86 AA) [2, 3, 29]. 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 [30–31]. The unexpected stability of the Ag^+ -DBPY18C6 complex could be partly caused by the stronger interaction of the pyridino nitrogen of the ligand as a soft base with Ag^+ ion which is a much softer acid than other used cations [20, 32].

Consider now the major sequence of the stability constants for alkali and alkaline earth ions in the order $\text{DCY18C6} > \text{18C6} > \text{DB18C6} > \text{DBPY18C6}$ with some minor exceptions. This general trend is expected, because the presence of cyclohexyl groups allows pumping the electrons into the ligand ring and increasing the basicity of the oxygen atoms, while the flexibility of the ligand remains more or less the same as 18C6. The commercial DCY18C6 is a mixture of two isomers and this may cause the unexpected results. The effect of the substitution of two benzo-groups of the 18C6 macro ring causes a remarkable lowering of the complex stability. It should be noted that introducing two electron withdrawing groups reduces the donicity of the oxygen atoms in the ring and hence the cation–crown interaction [30, 31].

Comparison of the stability of DBPY18C6 with DB18C6 complexes according to the suggested sequence is the interesting result of this work. Introducing a pyridyl group into DB18C6 ring caused a macrocycle with three aromatic moi-

eties, which substantially reduces the affinity of the donor atoms towards hard metal ions such as alkali and alkaline earth cations. In DBPY18C6, the presence of a pyridyl group increases the rigidity of the macrocycle, and on the other hand pyridino nitrogen in the 18-membered ring increased the softness of this ligand remarkably. A few exceptions in 18-crowns-6 trend are (i) 18C6 \approx DCY18C6 for K⁺ and 18C6 > DCY18C6 for Ca²⁺ (ii) DBPY18C6 > DB18C6 for Ba²⁺. These exceptions may be due to conditions such as unpredicted commercial DCY18C6 behavior and more solvated M-18C6 complexes in comparison with DCY18C6.

In the latter trend (for each crown) the Ba²⁺ is an interesting case with ionic radius of 1.35 AA [30] which nicely fits into the cavities of 18-ring crowns. Other cations of the alkaline earth series with smaller ionic sizes are too loose for the size of 18-crowns-6 cavities. On the other hand, among the alkaline earth metal ions, the Ba²⁺ is relatively softer (absolute hardness 12.8 eV) than others such as Mg²⁺ (absolute hardness 32 eV), so due to the HSAB (Hard and Soft Acid and Base) principle the stronger interaction between DBPY18C6 and Ba²⁺ is expected [33]. Therefore, relatively moderate stability constants for complexation of DBPY18C6 with other alkaline ions are observed. The DBPY18C6 has relatively softer behavior than 18C6, so the sequence of DBPY18C6 > DB18C6 for Ba²⁺ – complexes is quite expected. Another important parameter, which can affect the stability constants, is the free energy of the desolvation of cations. So, the Mg²⁺ is more solvated than Ba²⁺, the balance of the strength of the interactions and the free energy of desolvation increases the stability constants of alkaline earth cations as Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺.

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 [4], 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⁺, K⁺, and Na⁺, the cation size can be considered to be primarily responsible for the complexing characteristics. While in the case of bivalent cations such as Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ the cation is 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 [34].

In order to compare the results of this work with data from the literature, the stability constants for the complexation of 18C6 and DCY18C6 with some alkali and alkaline earth metal ions are summarized in Table 1. For 18C6 and DCY18C6 the stability constants measured are in agreement with values from the literature. Some variation are seen which may be due to the accuracy and reproducibility of different experimental techniques [35]. In this work we have done a systematic comparison study of a series of 18-crown-6 with alkali and alkaline earth metal ions with an Ag⁺/Ag electrode about which there is no not any report in the literature [4, 5]. The obtained results, in particular the stability

constants of complexes with DBPY18C6 in comparison with other crowns are novel and interesting.

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References

1. C. J. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).
2. H.K. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).
3. J.M. Lehn: *Structure and Bonding* **16**, 1 (1973).
4. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
5. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
6. W.A. Hart, O.F. Beumel, Jr., and T.P. Whaley: *The Chemistry of Lithium, Sodium, Potassium, Rubidium, Cesium, Francium*, Pergamon Press, New York (1973).
7. R.D. Hancock and A.E. Martell: *Chem. Rev.* **89**, 1875 (1989).
8. P.B. Chock, F. Eggers, M. Eigen, and R. Winkler: *Biophys. Chem.* **6**, 239 (1977).
9. A.Yu. Ovchinnikov, V.T. Ivanov, and A.M. Shkrob: *Membrane-Active Complexones*, American Elsevier, New York (1974).
10. E. Bakker, P. Buhlman, and E. Pretsch: *Chem. Rev.* **97**, 3083 (1997).
11. Y.A. Zoltov: *Macrocyclic Compound in Analytical Chemistry*, Jon Wiley & Sons Inc., New York (1997).
12. E. Grell, T. Funck, and F. Eggers: In G. Eisenman (ed.), *Membranes*, Marcel Dekker, New York, 1975, vol 3, pp. 1–128.
13. R.A. Schwind, T.J. Gilligan, and E.L. Cussler: In R.M. Izatt, and J.J. Christensen (eds.), *Synthetic Multidentate Macrocyclic Compound*, Academic Press, New York, 1978, pp. 289–380.
14. J.D. Lamb, J.J. Christensen, S.R. Izatt, K. Bedke, M.S. Astin, and R.M. Izatt: *J. Am. Chem. Soc.* **102**, 3399 (1980).
15. H.C. Visser, D.N. Reinhoudt, and F.D. Long: *Chem. Soc. Rev.* **75**, (1994).
16. N. Tavakoli and M. Shamsipur: *Talanta* **45**, 1219 (1998).
17. J. Zolgharnein and M. Shamsipur: *Polish J. Chem.* **72**, 248 (1998).
18. K. Tawareh and F. Ababneh: *J. Incl. Phenom.* **29**, 15 (1997).
19. Z. Monsef, G. H. Rounaghi, and A. Sarfaraz: *J. Incl. Phenom.* **39**, 321 (2001).
20. M. Shamsipur and J. Zolgharnein: *J. Incl. Phenom.* **40**, 41 (2001).
21. J. Zolgharnein, F. Riahi, and S. Amani: *J. Incl. Phenom.* **45**, 13 (2003).
22. J.D. Lamb, R.M. Izatt, C.S. Swain, and J.J. Christensen: *J. Am. Chem. Soc.* **102**, 475 (1980).
23. X.X. Zhang, A.V. Bordunov, X. Kou, N.K. Dalley, and R.M. Izatt: *J. Am. Chem. Soc.* **36**, 2586 (1997).
24. B.G. Cox, H. Schneider, and J. Stroka: *J. Am. Chem. Soc.* **100**, 15 (1978).
25. J. Gutknecht, H. Schneider, and J. Stroka: *Inorg. Chem.* **17**, 3326 (1978).
26. A. Sabatini, A. Vaca, and P. Gans: *Talanta* **21**, 53 (1974).
27. D.G. Legget: *Computation Methods for the Determination of Formation Constants*, Plenum Press, New York (1985).
28. L.D. Pettit, K.F. Sodium, H. Kozlowski, and T. Kowalik: *Inorg. Chim. Acta.* **55** 87 (1981).
29. R.D. Shannon: *Acta Crystallogr.* **32A**, 751 (1976).
30. M. Hassani, and M. Shamsipur: *J. Incl. Phenom.* **16**, 123 (1993).
31. H. Parham, and M. Shamsipur: *Talanta* **40**, 1353 (1993).
32. F. Arnaud-Neu, B. Spiess, and M.J. Schwing-Weill: *J. Am. Chem. Soc.* **104**, 5641 (1982).
33. R.G. Parr and R.G. Pearson: *J. Am. Chem. Soc.* **105**(26), 7512 (1983).
34. P.A. Mosier-Boss and A.I. Popov: *J. Am. Chem. Soc.* **107**, 6168 (1985).
35. H-J. Buschmann: *Inorg. Chim. Acta.* **195**, 51 (1992).