

Study of complexation of phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5, and benzo-15-crown-5 with Ag^+ , Tl^+ and Pb^{2+} ions in methanol by competitive potentiometry

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Abstract The complexation reaction of phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5, and benzo-15-crown-5 with Ag^+ , Tl^+ and Pb^{2+} ions in methanol solution have been studied by a competitive potentiometric method. The Ag^+/Ag electrode used both as an indicator and reference electrode in a concentration cell. The emf of cell monitored as the crown ethers concentration varies through the titration. The stoichiometry and stability constants of resulting complexes have been evaluated by MINQUAD. The stoichiometry for all resulting complexes was 1:1. The stability of these metal ions with derivatives of 15-crown-5 are in order phenylaza-15-crown-5 > Benzo-15-crown-5 > 4-nitrobenzo-15-crown-5, and for the each used crown ethers are as $\text{Pb}^{2+} > \text{Ag}^+ > \text{Tl}^+$. The effect of the substituted group on the stability of resulting complexes was considered. The obtained results are novel and interesting.

Keywords Competitive potentiometry · Ag^+/Ag electrode · Phenylaza-15-crown-5 · 4-Nitrobenzo-15-crown-5 · Stability constant · methanol

Introduction

The post transition metal ions such as Pb^{2+} , Ag^+ , and Tl^+ play important role in biological, environmental and industrial process [1, 2]. Since these metal ions are among the hazardous substance, the research for monitoring and control of them are very interested for environmental

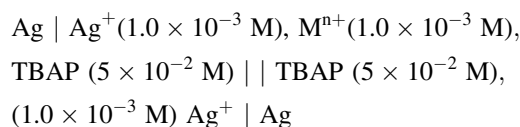
analysis and environmental engineering. Through the synthesis of crown ethers by Pedersen's pioneering work, followed by that Lehn and Cram, opened up the field of supramolecular chemistry [3, 4]. In this field the recognitions of selectivity behavior of macrocyclic polyethers and ligand designing which were using it in various analytical applications [5, 6], stimulating many researchers to synthesize of the new derivatives of macrocyclic polyethers compounds [7, 8]. Thus great number of crown ether derivatives were synthesized [7, 8]. Introducing other heteroatom into macrocycle ring, such as N and S drastically changes the behavior of these compounds [9]. Currently, our research group has been interested to the chemistry of dibenzopyridino-18-crown-6 with several metal ions [10–14], phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5 [15]. We also used dibenzopyridino-18-crown-6, dicyclohexyl-18-crown-6 for ion-transport of the Pb^{2+} , Ag^+ , and Tl^{3+} through bulk liquid membrane [16–18]. Among the recently synthesized crown ethers, phenylaza-15-crown-5 is a new one [19], and also 4-nitrobenzo-15-crown-5, which the reports about their chemical behaviors are rare [7, 8]. Recently, we were stimulated to study the complexation reaction of phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5, benzo-15-crown-5 with various groups of metal ions [15]. So, comparison of chemical behavior of these crown ethers with Ag^+ , Tl^+ and Pb^{2+} in methanol solution was the major goal of this work. Since the potentiometric system is simple, facile and accurate technique for complexation studies, we have interested using Ag^+/Ag electrode as a sensor for monitoring the equilibrium concentration of free metal ions [20, 21]. We also compared the obtained results with literature and our previous work [7, 8, 15]. Throughout the discussion of the results, we have considered the effect of the substituted group on the stability of resulting complexes.

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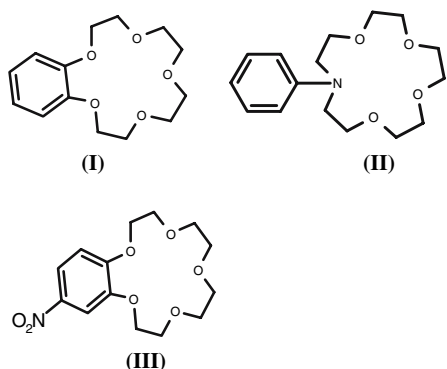
Experimental

Reagent grade benzo-15-crown-5 (B15C5,I), phenylaza-15-crown-5 (PhA15C5,II), and 4-nitrobenzo-15-crown-5 (NB15C5, III) 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 , Scheme 1. Absolute methanol (Merck) was used as solvent. Tetrabutylammonium perchlorate (TBAP) was prepared from the 1:1 mixture 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 and kept under dark condition.

A concentration cell was used for monitoring the concentration of silver ion during the potentiometer titration of Ag^+ ion with a solution of the crown in the presence and absence of other metal ions [20–22]. The concentration of free silver ion was monitored with a silver electrode; potentials being measured with a digital voltmeter (model 624 Metrohm). The reference electrode was also an Ag^+/Ag electrode, immersed in a known solution of $AgNO_3$ (1.0×10^{-3} 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 25 ± 0.1 °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 used cell is:



To evaluate the stability constants, the following procedure was conducted. The silver electrode was



Scheme 1 Structures of crown ethers

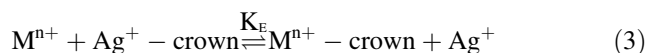
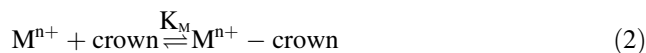
placed in the reaction vessel containing 10 ml of 0.05 M TBAP in methanol. The reference compartment contained 0.05 M TBAP and 1.0×10^{-3} M silver nitrate in the same solvent. First, a concentrated silver nitrate (0.01 M) was added gradually until Ag^+ ion concentration of 1.0×10^{-3} M was achieved, and the cell potential was measured. A Plot of emf versus $\log [Ag^+]$ was strictly linear (slope: 59.3, intercept: 217.2, R^2 : 0.9966) at 25 °C. The same solution was then back titrated 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 (Eq. 1), K_{Ag} , can be 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+} (M^{n+} : Ag^+ , Tl^+ and Pb^{2+}) ion complexes, K_M , with each crown ether (Eq. 2) can be determined by the double decomposition reaction of M^{n+} with the corresponding Ag^+ complex (Eq. 3). 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.



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

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

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

The MINIQUAD program was used to compute the formation constants K_{Ag} and the resulting K_M from potential-concentration data [23–25]. 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 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 the running MINQUAD program for each experimental point of a titration curve the mass balance Eqs. (4, 5) must be 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 values of the formation constants, which minimize the sum of the squared residuals between observed and calculated analytical concentration

$$U = \sum (C_i^{obs} - C_i^{calc})^2 \quad (6)$$

where the sum covers all the mass balance equations for all experimental points.

For evaluation of stability constants of each used 15-crown-5 with Ag^+ , Tl^+ and Pb^{2+} ions, potentiometric titration of Ag^+ with a solution of the desired crown in absence and presence of metal ions have been done at 25 °C as described in the experimental section [20–22, 26]. The potentiometric profiles are shown in Fig. 1, 2, 3. These plots show the variation of difference potential (ΔE) versus addition of crown ethers to solution. It also emphasizes that the complex reaction have been take placed. It is obvious that the extent of variation of ΔE depends on the strength of

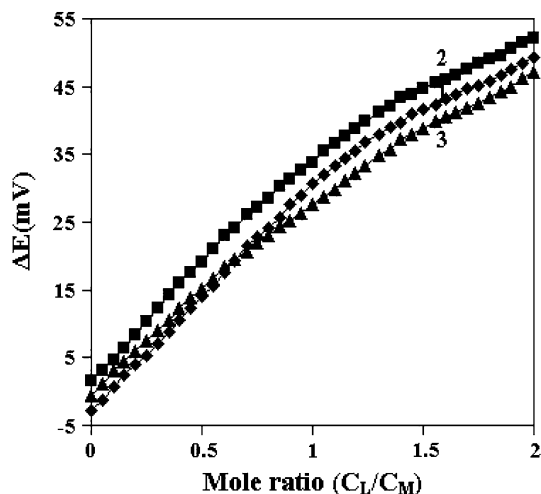


Fig. 1 Potential difference versus mole ratio (L/M) plots for complexation of a $AgNO_3$ (1.0×10^{-3} M) solutions with phenylaza-15C5 (0.02 M) in the presence of equimolar concentrations of (1) Tl^+ , (2) Ag^+ and (3) Pb^{2+} in methanol at 25 °C and ionic strength 0.05 M TBAP

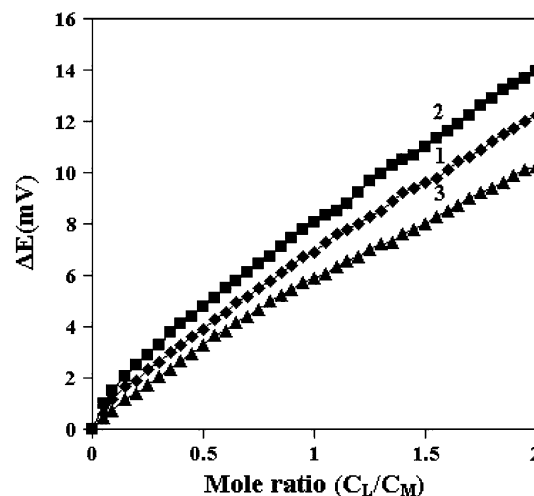


Fig. 2 Potential difference versus mole ratio (L/M) plots for complexation of a $AgNO_3$ (1.0×10^{-3} M) solutions with B15C5 (0.02 M) in the presence of equimolar concentrations of (1) Tl^+ , (2) Ag^+ (3) Pb^{2+} in methanol at 25 °C and ionic strength 0.05 M TBAP

resulting complex, so it is expected that ΔE for phenylaza-15-crown-5 was more than others (Fig 1). Since the MINQUAD program is robust for model selection [27], it was used to support the stoichiometry of resulted complexes and compute the formation constants K_{Ag} and K_M from the resulting potential-concentration data [23–27]. The resulting data are listed in Table 1.

From the consideration of data given in Table 1, two trends are obvious among these stability constants. First, from metal ions view, the sequence of stability of resulting complexes varies in the order as phenylaza-15-crown-5 > Benzo-15-crown-5 > 4-nitrobenzo-15-crown-5. Second for each used crown ethers, it could be seen a general

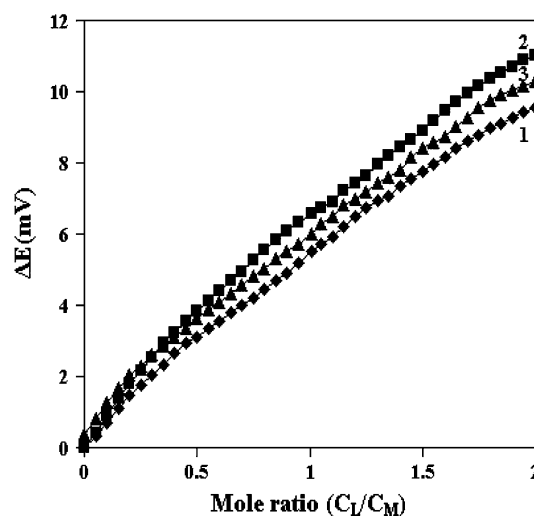


Fig. 3 Potential difference versus mole ratio (L/M) plots for complexation of a $AgNO_3$ (1.0×10^{-3} M) solutions with NB15C5 (0.02 M) in the presence of equimolar concentrations of (1) Tl^+ , (2) Ag^+ (3) Pb^{2+} in methanol at 25 °C and ionic strength 0.05 M TBAP

Table 1 The logarithm of stability constants ($\log K_f \pm \sigma^*$) for resulting complexes of NB15C5, B15C5, phenylaza-15C5 with some post heavy metal ions in methanol at 25 °C, and ionic strength 0.05 M TBAP

Cation	Size (Å)	NB15C5	B15C5	phenylaza-15C5
Pb ²⁺	2.38	3.33 ± 0.02	3.61 ± 0.03 2.36 ^a	3.82 ± 0.02
Ag ⁺	2.30	3.23 ± 0.02	3.51 ± 0.02 3.06 ^a	3.73 ± 0.01
Tl ⁺	3.0	3.13 ± 0.03	3.36 ± 0.02 3.00 ^b	3.45 ± 0.02
Na ⁺	2.04	2.73 ± 0.02 ^c	3.27 ± 0.01 ^c 3.05 ^c 2.87 ^d	3.83 ± 0.02 ^c

*Standard deviation. The sum of squares of residuals ($8.2\text{--}8.8 \times 10^{-8}$), χ^2 and R values associated with formation constants were in the range of $0.4\text{--}2.30 \times 10^{-8}$, 2.2–56.7 and 0.01–0.04, respectively

a, b, c, d : Ref. [7, 8]

e: Ref. [15]

^a Cal, ^b Pol, ^c ISE, ^d Pot, ^e Na⁺-ISE

trend for their complexes in order as $\text{Pb}^{2+} > \text{Ag}^+ > \text{Tl}^+$. This trend is clearly in accordance to both size and charge effects, and is quite expected. All these cations have less proper size for fitting into 15-crown-5 ring (1.72–1.82 Å) and soft behavior [30, 28, 29]. Among these the Pb^{2+} with radius (2.38 Å) has more charge and formed stronger complex. Tl^+ has larger size (3 Å), which has less fitting into 15-crown-5 ring (1.72–1.82 Å) and formed weaker complex [30, 4]. In our experimental set up for all metal ion (especially Tl^+), the molar concentration ratio of crown ethers to the metal ion (C_L/C_M) was varied up to ratio about 2:1. Thus 1:1(M: L) was the major stoichiometry of complexes, but if the excess amount of crown ethers is added, the 1:2 (M: L) stoichiometry is also is realizable [31]. Ag^+ has relatively proper size (2.3 Å) and softer behavior for complex formation with these crown ethers. So the sequence of Ag^+ -complexes varies as phenylaza-15-crown-5 > Benzo-15-crown-5 > 4-nitrobenzo-15-crown-5. The variation, which has seen is mainly due to different substitution groups on 15-crown-5 ring. The effect of introducing such groups as phenylaza-, 4-nitrobenzo, and benzo- into 15-crown-5 ring has been described before [15]. The stability of the Ag^+ -phenylaza-15-crown-5 complex could be partly due to the stronger interaction of the nitrogen of the ligand as a soft base with Ag^+ ion as a much softer acid than other used cations [28, 29]. The induction effect and flexibility of phenyl- group which should increase the electron density around the nitrogen atom in the 15-crown-5 ring may have importance role. In this series, nitrobenzo group because of its electron

withdrawing effect of both nitro and benzo group which lower the electron density on oxygen ring and considerably decreases interaction of this crown ethers with Ag^+ , Tl^+ , Pb^{2+} [15].

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 [7], 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 strongly solvated. So 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 [32, 33].

To compare the results of this work with the literature, stability constants for the complexation of benzo-15-crown-5, 4-nitrobenzo-15-crown-5, and phenylaza-15-crown-5 with Ag^+ , Tl^+ and Pb^{2+} ions, these data are summarized in Table 1. We also compare the recently published results of this used crown ethers with Na^+ ion [15]. The trend of stability of complexes of Na^+ ion is also has the same order as phenylaza-15-crown-5 > Benzo-15-crown-5 > 4-nitrobenzo-15-crown-5. The full agreement has been seen between the trend of these results and our previous study. It should be interested to say that the potentiometric sensor in these two studies is different. The latter was Na^+ -ISE and the former Ag/Ag^+ . Some variations are observed for benzo-15-crown-5, which may be due to various accuracy and reproducibility of different experimental techniques and used conditions such as: solvent, electrolyte, and ionic strength [34, 35]. The behavior of phenylaza-15-crown-5 with Na^+ ion has not seen with Tl^+ ion, because the distance of π system of phenyl ring with p, d and f orbital are so far that interaction between them are negligible [15]. Since the electronic configuration of Ag^+ and Pb^{2+} , are $4d^{10}$ and $5d^{10} 6p^2$ respectively, it is possible that the vacant orbital of the valance shell of Ag^+ and Pb^{2+} interacted with π system of phenyl group in phenylaza-15-crown-5 to stabilize the Pb^{2+} -phenylaza-15-crown-5 and Ag^+ -phenylaza-15-crown-5 complexes. The rigidity of other two used crown ethers, will not give the metal ion thus chance to have this kind of interaction. There are no any report about the chemical behavior of phenylaza-15-crown-5 and 4-nitrobenzo-15-crown-5 in the literature for comparison [7, 8, 15]. So the obtained results in particular stability constants of complexes of phenylaza-15-crown-5 and 4-nitrobenzo-15-crown-5 with Ag^+ , Tl^+ , Pb^{2+} ions are precise, novel and interesting.

References

1. Bremner, I.: Heavy metal toxicities. *Q. Rev. Biophys.* **7**, 75–124 (1974)
2. Catsch, A., Harmuth, A.E.: New developments in metal antidotal properties of chelating agents. *Biochem. Pharmacol.* **24**, 1557–1562 (1975)
3. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **89**, 7017–7036 (1967)
4. Lehn, J.M.: Design of organic complexing agents. Strategies towards properties. *Struct. Bond.* **16**, 1–69 (1973)
5. Hancock, R.D., Martell, A.E.: Ligand design for selective complexation of metal ions in aqueous solutions. *Chem. Rev.* **89**, 1875–1914 (1989)
6. Zoltov, Y.A.: *Macrocyclic Compounds in Analytical Chemistry*. Jon Wiley & Sons Inc, New York (1997)
7. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J., Sen, D.: Thermodynamic and kinetic data for macrocycle interaction with cations. *Chem. Rev.* **85**, 271–339 (1985)
8. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interaction with cations. *Chem. Rev.* **91**, 1721–2085 (1991)
9. Wu, G., Jiang, W., Lamb, J.D., Bradshaw, J.S., Izatt, R.M.: High-specificity thiocrown reagents for silver(I) over bivalent mercury and lead. Thermodynamics and ^{13}C NMR relaxation time studies. *J. Am. Chem. Soc.* **113**, 6538–6541 (1991)
10. Zolgharnein, J., Shamsipur, M.: Spectrophotometric study of the thermodynamics and kinetics of charge-transfer complexation of dibenzopyridino-18-crown-6 with iodine in chloroform solution. *Polish. J. Chem.* **72**, 2486–2492 (1998)
11. Shamsipur, M., Zolgharnein, J.: Competitive potentiometric study of the thermodynamics of complexation of some transition and heavy metal ions with dibenzopyridino-18-crown-6 in methanol using Ag^+ ions as a probe. *J. Incl. Phenom.* **40**, 41–44 (2001)
12. Zolgharnein, J., Riahi, F., Amani, S.: Spectrophotometric study of the complexation of some lanthanide (III) ions with a series of 18-crowns-6 in DMSO solution using murexide as a metallochromic indicator. *J. Incl. Phenom.* **45**, 13–17 (2003)
13. Zolgharnein, J., Zahredini, F., Azimi, G.: Competitive spectrophotometric study of complexation of dibenzopyridino-18-crown-6 with Ca^{2+} , Sr^{2+} , and Ba^{2+} in binary dimethylsulphoxide – acetonitrile solutions. *Polish. J. Chem.* **77**, 813–820 (2003)
14. Zolgharnein, J., Tahmasebi, H., Habibi, M., Amani, S.: Competitive potentiometric study of a series of 18-crown-6 with some alkali and alkaline earth metal ions in methanol using Ag^+ /Ag electrode. *J. Incl. Phenom.* **49**, 231–234 (2004)
15. Zolgharnein, J., Shahmoradi, Gh., Amani, S.: Potentiometric study of complexation of phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5 and dibenzopyridino-18-crown-6 and other derivative of 18-crowns-6 with Na^+ ion in methanol. *J. Incl. Phenom.* doi: 10.1007/s10847-007-9301-8
16. Zolgharnein, J., Hossini, Sh., Sangi, M.R., Dadfarnia, Sh., Shamsipur, M.: Dibenzopyridino-18-crown-6 as highly selective and effective carrier for uphill transport of Pb^{2+} through bulk liquid membrane. *Chem. Anal (Warsaw)*. **48**, 65–76 (2003)
17. Zolgharnein, J., Hosseini, Sh., Azimi, G., Sangi, M.R.: Highly selective and efficient membrane transport of silver as AgBr^{2-} ion using K^+ -decyl-18-crown-6 as carrier. *Anal. Sci.* **19**, 871–875 (2003)
18. Zolgharnein, J., Shams H., Azimi G.: Selective and efficient liquid membrane transport of thallium (III) ion by potassium-dicyclohexyl-18-crown-6 as specific carrier. *Sep. Sci. Technol.* **42**, 2305–2316 (2007)
19. Zhang, X.X., Buchwald, S.L.: Efficient synthesis of *N*-aryl-aza-crown ethers via palladium-catalyzed amination. *J. Org. Chem.* **65**, 8027–8031 (2000)
20. Cox, B.G., Garcia-Rosas, J., Stroka, J.: Kinetics and equilibrium of cryptate in propylene carbonate. *J. Phys. Chem.* **84**, 3178–3183 (1980)
21. Cox, B.G., Schneider, H., Stroka, J.: Kinetics of alkali metal complexes formation with cryptands in methanol. *J. Am. Chem. Soc.* **100**, 4746–4749 (1978)
22. Gutknecht, J., Schneider, H., Stroka, J.: Cryptand formation in nonaqueous solvents: new aspects in single-ion thermodynamics. *Inorg. Chem.* **17**, 3326–3329 (1978)
23. Sabatini, A., Vacca, A., Gans, P.: Miniquad – a general computer program for computation of formation constants from potentiometric data. *Talanta* **21**, 53–77 (1974)
24. Gans, P., Sabatini, A., Vacca, A.: An improved computer program for the computation of formation constants from potentiometric data. *Inorg. Chim. Acta.* **18**, 237–239 (1976)
25. Legget, D.G.: *Computation Methods for the Determination of formation Constants*. Plenum Press, New York (1985)
26. Pettit, L.D., Siddiqui, K.F., Kozlowski, H., Kowalik, T.: Potentiometric and ^1H NMR studies on silver (I) interaction with *S*-methyl-L-cysteine, L-methionine and L-ethionine. *Inorg. Chim. Acta.* **55**, 87–91 (1981)
27. Gans, P., Vaca, A., Sabatini, A.: Investigation of equilibria in solution. Determination of equilibrium constants with HYPERQUAD suite of programs. *Talanta* **43**, 1739–1753 (1996)
28. Pearson, R.G.: Hard and soft acid and bases. *J. Am. Chem. Soc.* **85**, 3533 (1963)
29. Par, R.G., Pearson, R.G.: Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* **105**, 7512–7516 (1983)
30. Shannon, R.D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **32A**, 751–767 (1976)
31. Hofmanová, A., Koryta, J., Březina, M., Mittal, M.L.: Electrochemical reduction of monovalent cation complexes of macrocyclic ionospheres. *Inorg. Chim. Acta.* **28**, 73–76 (1978)
32. Gutmann, V.: *Coordination chemistry in nonaqueous solvents*. Springer-Verlag (1968)
33. Mosier-Boss, P.A., Popov, A.I.: NMR and infrared studies of complexation reaction of 18-crown-6 with some organic solvents. *J. Am. Chem. Soc.* **107**, 6168–6174 (1985)
34. Buschman, H.: A comparison of different experimental techniques for the determination of the stabilities of polyether crown ether and cryptand complexes in solution. *Inorg. Chim. Acta.* **195**, 51–60 (1992)
35. Arnaud -Neu, F., Delgado, R., Chaves, S.: Critical evaluation of stability constants and thermodynamic functions of metal complexes of crown ethers (IUPAC technical report). *Pure. Appl. Chem.* **75**, 71–102 (2003)