ORIGINAL ARTICLE

Conductometric studies of the thermodynamics complexation of Li$^+$, Na$^+$, K$^+$, Mg^{2+}, and Ba^{2+} ions with 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6 ligand in acetonitrile, ethanol and methanol solutions

Mahmood Payehghadr · Rahman Heidari

Abstract The complexation reaction between 4′,4″(5″)-di-tert-butyldibenzo-18-crown-6, ligand and Li$^+$, Na$^+$, K$^+$, Mg^{2+}, and Ba^{2+} ions were studied conductometrically in acetonitrile, ethanol, and methanol solutions. The formation constants of the 1:1 and 2:1 complexes (metal to ligand) were calculated from the computer fitting of the molar conductance in various mole ratios at 10, 20, 30, and 40 °C. The enthalpy and entropy changes of the complexation reactions in acetonitrile, ethanol, and methanol were estimated at four different temperatures.

Introduction

After the introduction of crown ethers by Pedersen [1] in 1967 and his fundamental studies of their characteristics, many papers have reported some of their chemical properties including their complexes with cations. Frensdorff [2] reported some more properties of crown ethers, together with Pedersen [3], and reviewed the chemistry and applications of crown ethers known in the early 1970.

The synthesis of macrocyclic crown ethers [4] and the discovery of their ability to form stable inclusion complexes with a variety of metal ions have led to an extensive study of these ligands and their complexes. It is well known that several factors influence the formation of crown ether complexes of metal ions in solution. The most emphasized factor is the crown's cavity size-cation diameter ratio despite the fact that its importance has been questioned in the case of large crown ethers [1, 5, 6]. Actually, large crown ethers (i.e., larger than 18-crown-6) possess highly flexible geometries in liquid solution and adapt their conformations for optimum complexation of guest cations. Thus, there is evidence reported in the literature for the formation of tridimensional "wrap-around" complexes between large crown ethers and some alkali metal ions both in the solid state [7, 8] and in solution [9–11]. Other important factors include the number and the nature of heteroatom's participating in cation binding, the nature of the substituent groups on the macrocyclic ring and especially the solvent properties [1]. The nature of the solvent has been found to strongly influence the stoichiometry, selectivity, thermodynamic stability, and exchange kinetics of metal ion-crown ether complexes [1, 5, 6, 11].

The thermodynamics of complexation of crown ethers has been mainly studied with alkali and alkaline earth cations in water and in various non-aqueous solvents [1, 5]. Crown ethers and related compounds are capable of forming complexes with many metal salts, with organic salts (such as organic ammonium, arenediazonium, and guanidinium salts) and with many neutral organic molecules. For determination of the thermodynamic stability of these complexes, a large variety of methods and procedures have been reported [12].

In this work, we report a study of the influence of cation size, cation nature, and solvent properties on the interactions of some alkali and alkaline earth metal ions with 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6 (Fig. 1).

M. Payehghadr (✉) · R. Heidari
Department of Chemistry, Payame Noor University, PO Box 19395-3697, Tehran, Iran
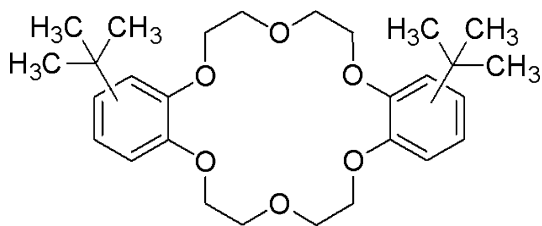e-mail: mahmood_payehghadr@yahoo.com

Fig. 1 The 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6, ligand (DTB 18C6)

Experimental

Reagents

Reagent grade 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6 (DTB18C6), and perchlorate salts of lithium, sodium, potassium, magnesium and barium and solvents acetonitrile (AN), ethanol (EtOH) and methanol (MeOH) (all from Merck) were of the highest purity available and were used without any further purification. The conductivity of the solvents was $<1 \times 10^{-7}$ S cm^{-1}.

Conductometric titrations

Conductometric measurements were carried out using a Metrohm 712 conductometer equipped with a Grant PE26 1LF circulator. In a typical experiment, 10.0 mL of metal ion solution (5.0×10^{-5} mol L^{-1}) in AN, EtOH, or MeOH was placed in the two wall conductometer glass cell and the conductance of solution was measured at a fixed temperature. Then a known amount of the concentrated solution of DTB18C6 in AN (5.0×10^{-3} mol L^{-1}) was added in a stepwise manner using a Hamilton syringe. The conductance of the solution was measured after each addition. The DTB18C6 ligand solution was continually added until the desired ligand-to-metal ion mole ratio was achieved.

In all measurements, cell was thermostated at desired temperature ±0.1 °C; the cell constant at the different temperature used was determined by measuring the conductivity of 1×10^{-2} mol L^{-1} solution of analytical grade KCl in triply distilled de-ionized water. The specific conductances of this solution at various temperatures have been reported in the literature [13]. The corresponding cell constant at 10, 20, 30, and 40 °C were 0.833, 0.830, 0.827, and 0.822 cm^{-1}, respectively. A dip-type conductivity cell made of platinum black was used.

Estimation of the stability constants of metal ions-ligand complexes

The metal ion-ligand (ML) complex formation constant (K_f) was estimated from molar conductance versus C_L/C_M

molar concentration ratio data using the KINFIT program. Adjustable parameters were the K_f, the molar conductance of free metal ion, and the molar conductance of complex.

The free metal ion concentration [M] was calculated by a Newton–Raphson procedure. Once the values of [M] were estimated, the corresponding concentrations of all other species involved were calculated from the mass balance equations by using the estimated value of the formation constant at the current interaction step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed molar conductance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum of squares and the standard deviation of the data [14].

Thermodynamic parameters of metal ions–ligand complexes

In order to have a better understanding of the thermodynamics of complexation between DTB18C6 and metal ions in AN, EtOH, and MeOH, it is useful to consider the enthalpic and entropic contributions to those reactions. The enthalpy and entropy changes of the complexation reactions were determined by measuring the complex formation constants of the resulting complexes as a function of temperature Van't Hoff equation (Eq. 1).

$$2.303 \log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (1)$$

Results and discussion

The molar conductance of the perchlorate salts of Li$^+$, Na$^+$, K$^+$, Mg^{2+}, and Ba^{2+} in AN, EtOH, and MeOH solvents was monitored as a function of the DTB18C6-to-metal ion mole ratio, and the stoichiometry of the complexes in AN, EtOH, and MeOH was examined by the mole ratio method at variable temperatures. A sample of the resulting plots for all metal ions in AN at 20 °C is shown in Fig. 2 and for K$^+$ ion complex in AN at different temperatures is shown in Fig. 3. A consistent decrease in the molar conductance of the metal ion with an increase in the ligand-to-metal ion molar ratio indicates that ML complexes are formed in solution. This is clearly seen in AN solvent, where addition of the ligand to the metal ions solutions causes a continuous decrease in molar conductance of the metal ion in solutions due to a lower mobility of the complexed than the solvated metal ion. As is seen in Fig. 2, in the complexation of K$^+$ ion with DTB18C6, addition of the ligand to the metal ion solution causes a continuous decrease in the molar conductance, which begins to level off at a mole ratio greater than one, thus
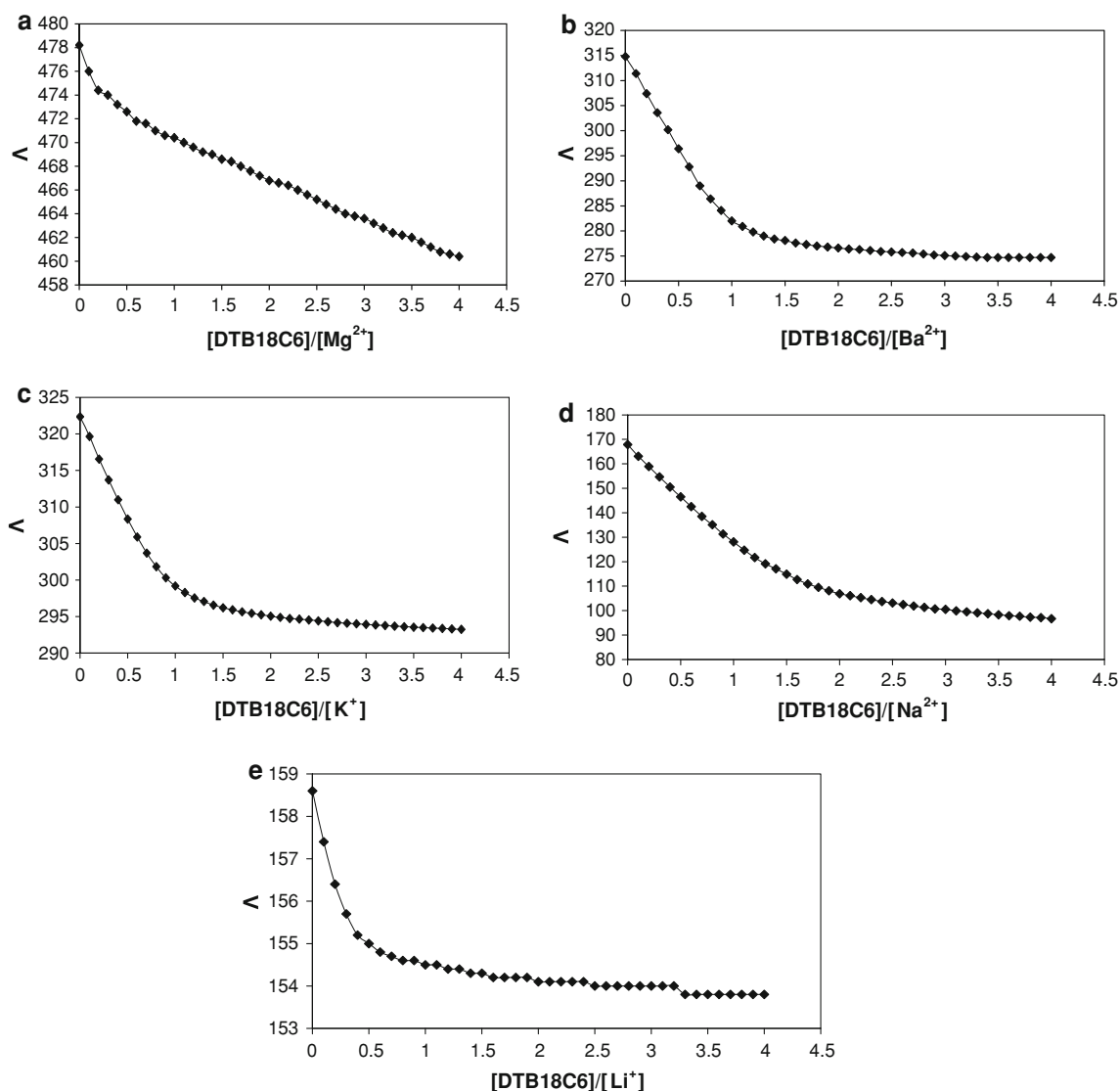
Fig. 2 Molar conductance–mole ratio plots of the metal ions (5.0×10^{-5} mol L^{-1}) with DTB18C6 ligand (5.0×10^{-3} mol L^{-1}) in AN at 20 °C. **a** Mg^{2+}, **b** Ba^{2+}, **c** K^+, **d** Na^+, **e** Li^+

indicating the formation of a stable 1:1 complex. The molar conductance-mole ratio plots of DTB18C6 and its complex with K^+ at 20 °C in EtOH and MeOH solvents are shown in Fig. 4.

The enthalpy (ΔH) and entropy (ΔS) of the complexes in different solvents were evaluated from the temperature dependence of the complex formation constants by applying a linear least-squares analysis according to Eq. 1.

The formation constants of the resulting Li_2L and ML (M: Na^+, K^+, Mg^{2+}, and Ba^{2+}) complexes were obtained by molar conductance measurements of solutions in which varying concentrations of ligand (5.0×10^{-3} mol L^{-1}) were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of metal ions in solution. The entire resulting molar

conductance-mole ratio data were best fitted to Eq. 2 for ML complexes and Eq. 3 for M_2L complex, which further supports the formation of mixed complex for lithium ion and ML for other ions in solution.

$$K_f[L]^2+(1 + K_fC_M - K_fC_L)[L] - C_L = 0 \qquad (2)$$

$$K_{f1}K_{f2}[L]^3 + K_{f1}(1 + K_{f2}(2C_M - C_L))[L]^2$$
$$+ (1 + K_{f1}(C_M - C_L))[L] - C_L = 0 \qquad (3)$$

For evaluation of the formation constants from molar conductance versus C_L/C_M mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the molar conductance–mole ratio data is shown in Fig. 5. The resulting K_f of the DTB18C6 complexes at 20 °C are listed in Table 1.
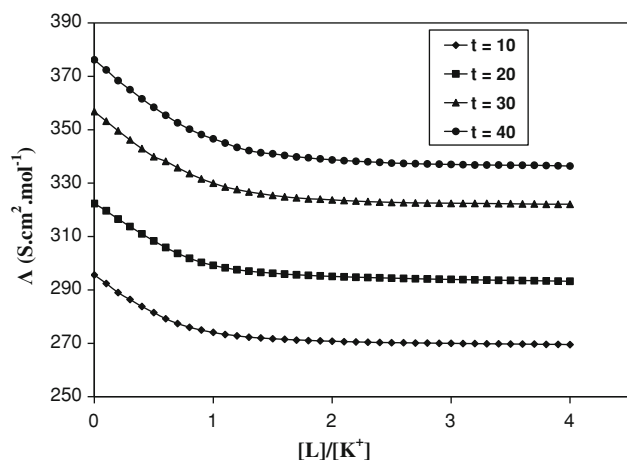
Fig. 3 Molar conductance–mole ratio plots of K^+ ion complexing with DTB18C6 in AN at temperatures 10, 20, 30, and 40 °C

Fig. 5 Computer fit of molar conductance versus (DTB18C6)/(K^+) mole ratio plot in AN at 20 °C, ($\times$) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot Λ

All of the $\log K_f$ values evaluated from the computer fitting of the corresponding molar conductance–mole ratio data are listed in Table 1.

Van't Hoff plots of $\log K_f$ versus $1/T$, for metal complexes in AN were linear and are shown in Fig. 6.

ΔH^0 and ΔS^0 values were determined from Van't Hoff equation (Eq. 1). Comparison of the data given in Table 1 indicate that the stability of the complexes to vary in AN solvent was in the order of $Li^+ > Ba^{2+} > K^+ > Na^+ > Mg^{2+}$. In MeOH and EtOH solvents, complexation stability process of cations with DTB18C6 ligand was in the order of $Li^+ > K^+ > Ba^{2+} > Na^+ > Mg^{2+}$ and $Li^+ > K^+ > Na^+ > Ba^{2+} > Mg^{2+}$ at 20 °C, respectively.

In the case of complexation of macrocyclic ligands, there are at least three factors which can make significant contributions to the stability of their metal ion complexes: (i) the cation size, (ii) the ionic solvation of the charged species involved, and (iii) conformations of the free and complexed crown ethers. The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the M^{n+}-DTB18C6 complexation reactions studied. In the case of all cations, the stability of the resulting complexes with DTB18C6 varied in the order AN > MeOH > EtOH.
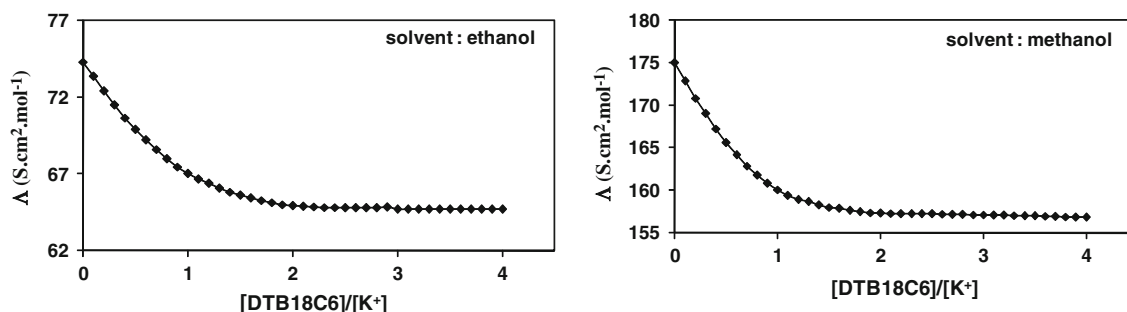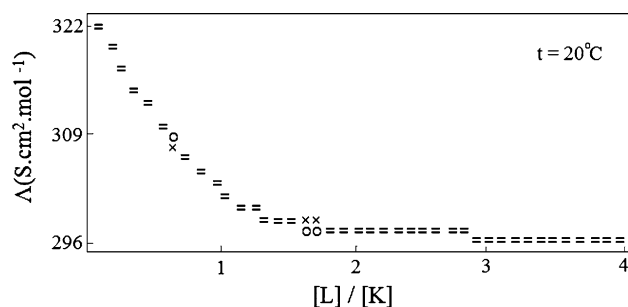
It is well known that the salvation ability of the solvent, as expressed by the Gutmann donor number [15], plays an important role in complexation reactions [16–21]. There is actually an inverse relationship between the stabilities of the complexes and the solvation abilities of the solvents. AN has a lower donicity (DN = 14.1) than MeOH (DN = 19.0), and EtOH (DN = 31.5) and it shows less competition with the crown ether for mentioned ions; thus, it is not unexpected to observe the highest stability of the complexes in AN and the lowest in EtOH.

Table 1 shows that, as expected, for M^{n+}-DTB18C6 complexes, the thermodynamic data vary significantly with the solvent properties. However, the observed increase or decrease depends on the nature of the metal ion.

The structure of Li^+-DTB18C6 is M_2L, but for other M^{n+}-DTB18C6 complexes is ML, because lithium ion diameter is small and two of it can be placed inside of the ligand cavity. Theoretical study on lithium ion interaction with crown ethers [22] shows that for Li^+-crown complex, the cavity is twisted, and the ions are placed inside the cavity.

Ionic diameters of Li^+, Na^+, and K^+ are 180, 132, and 304 pm, respectively. The narrow section of the cavity in DTB18C6 has about 253 pm diameter. So, it is clear that the potassium ion is placed out of the cavity plane. In comparison with the above alkaline ions, Mg^{2+} and Ba^{2+}

Fig. 4 Molar conductance–mole ratio plots of K^+ complexing with DTB18C6 at 20 °C in MeOH, AN, and EtOH solvents

Table 1 Formation constant values and thermodynamic parameters for metal crown ether complexes at different temperatures

| Solvent	Metal ion	Log K_f ± SD at various temperature				Thermodynamic parameters	
		10 °C	20 °C	30 °C	40 °C	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Acetonitrile	Li$^+$ (0.74°A)	9.83 ± 0.01	9.55 ± 0.01	9.52 ± 0.01	9.42 ± 0.01	−21.2 ± 0.3	111.8 ± 1.0
	Na$^+$ (1.02°A)	4.76 ± 0.01	4.62 ± 0.01	4.60 ± 0.01	4.53 ± 0.01	−11.9 ± 0.1	48.4 ± 0.5
	K$^+$ (1.38°A)	5.66 ± 0.01	5.50 ± 0.01	5.36 ± 0.01	5.28 ± 0.01	−21.4 ± 0.1	31.8 ± 0.3
	Mg^{2++} (0.72°A)	4.07 ± 0.02	3.60 ± 0.02	3.36 ± 0.02	2.53 ± 0.02	−80.6 ± 0.8	−205.8 ± 2.8
	Ba^{2+} (1.35°A)	5.60 ± 0.02	5.57 ± 0.02	5.45 ± 0.02	5.36 ± 0.02	−14.0 ± 0.1	58.0 ± 0.4
Ethanol	Li$^+$	9.13 ± 0.01	9.10 ± 0.01	9.01 ± 0.01	8.98 ± 0.01	−8.4 ± 0.1	144.5 ± 0.3
	Na$^+$	4.48 ± 0.01	4.42 ± 0.01	4.22 ± 0.01	4.11 ± 0.01	−21.8 ± 0.2	8.8 ± 0.5
	K$^+$	5.46 ± 0.01	5.30 ± 0.01	5.23 ± 0.01	5.18 ± 0.01	−15.3 ± 0.1	49.6 ± 0.5
	Mg^{2+}	3.52 ± 0.02	3.44 ± 0.02	3.04 ± 0.02	2.80 ± 0.02	−42.3 ± 0.4	−81.0 ± 1.3
	Ba^{2+}	4.36 ± 0.01	4.28 ± 0.01	4.20 ± 0.01	4.18 ± 0.01	−10.3 ± 0.1	46.1 ± 0.3
Methanol	Li$^+$	9.20 ± 0.01	9.01 ± 0.01	8.98 ± 0.01	8.96 ± 0.01	−12.6 ± 0.2	130.0 ± 0.8
	Na$^+$	4.50 ± 0.01	4.44 ± 0.01	4.24 ± 0.01	4.12 ± 0.01	−22.4 ± 0.2	7.5 ± 0.6
	K$^+$	5.90 ± 0.01	5.65 ± 0.01	5.35 ± 0.01	4.94 ± 0.01	−53.0 ± 0.3	−77.3 ± 1.0
	Mg^{2+}	3.86 ± 0.02	3.32 ± 0.02	3.06 ± 0.02	2.95 ± 0.02	−50.5 ± 0.5	−106.8 ± 1.8
	Ba^{2+}	5.33 ± 0.02	5.04 ± 0.02	4.93 ± 0.02	4.83 ± 0.02	−27.2 ± 0.3	5.0 ± 0.9

SD standard deviation
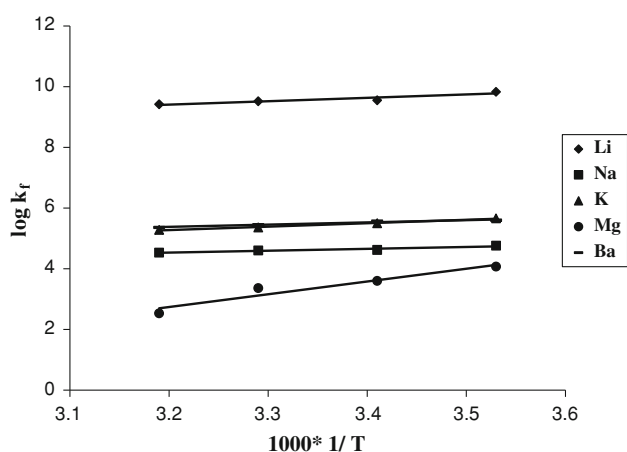
Fig. 6 Log K_f versus 1,000/T for the ML metal ions complexes with DTB18C6 in AN solvent

ions have higher charge density; therefore, it can be concluded that their binding energy should be larger. With enlarging the ionic radius from Mg^{2+} to Ba^{2+}, the crown cavity in the complex form tends to be planer.

References

1. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. J. Am. Chem. Soc. **89**, 7017–7036 (1967)
2. Frensdorff, H.K.: Stability constants of cyclic polyether complexes with univalent cations. J. Am. Chem. Soc. **93**, 600–606 (1971)
3. Pedersen, C.J., Frensdorff, H.K.: Macrocyclic polyethers and their complexes. Angew. Chem. Int. Ed. Engl. **11**, 16–25 (1972)
4. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J., Sen, D.: Thermodynamic and kinetic data for cation-macrocycle interaction. Chem. Rev. **85**, 271–339 (1985)
5. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interactions with cations and anions. Chem. Rev. **91**, 1721–2085 (1991)
6. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interaction with cations, anions, and neutral molecules. Chem. Rev. **95**, 2529–2586 (1995)
7. Hasek, J., Huml, K., Hlavat, D.: The structure of a complex between rubidium thiocyanate, water and dibenzo[b,q][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontane (dibenzo-30-crown-10). Acta Crystallagr. **35B**, 330–334 (1975)
8. Buchanan, G.W., Lear, Y., Bensimon, C.: The sodium perchlorate complex of cis-syn-cis dicyclohexano-24-crown-8 ether. X-ray crystal structure and solution conformations as studied by variable temperature 13C NMR spectroscopy at 125 MHz. An example of eight-coordinate sodium. Can. J. Chem. **70**, 1688–1695 (1992)
9. Live, D., Chan, S.I.: Nuclear magnetic resonance study of the solution structures of some crown ethers and their cation complexes. J. Am. Chem. Soc. **98**, 3769–3778 (1976)
10. Shamsipur, M., Popov, A.I.: Multinuclear NMR study of dibenzo-30-crown-10 complexes with sodium, potassium, and cesium ions in nonaqueous solvents. J. Am. Chem. Soc. **101**, 4051–4055 (1979)
11. Shamsipur, M., Rounaghi, G., Popov, A.I.: Sodium-23, cesium-133 and thallium-205 NMR study of sodium, cesium and thallium complexes with large crown ethers in nonaqueous solutions. J. Solution Chem. **9**, 701–714 (1980)
12. Zollinger, D.P., Bulten, E., Christenhusz, A., Bos, M., Van Der Linden, W.: Computerized conductometric determination of stability constants of complexes of crown ethers with alkali metal salts and with neutral molecules in polar solvents. Anal. Chim. Acta **198**, 207–222 (1987)
13. Wu, Y., Koch, W.: Absolute determination of electrolytic conductivity for primary standard KCl solutions from 0 to 50 °C. J. Solution Chem. **20**, 391–401 (1991)

14. Shamsipur, M., Avanes, A., Aghapour, G., Sharghi, H.: Spectrophotometric studies of acidity constant and Cu^{2+} ion complexation of 1-hydroxy-2-(prop-2'-enyl)-4-(prop-2'-enyloxy)9-, 10-anthraquinone in methanol: water mixtures. Pol. J. Chem. **75**, 1533–1541 (2001)

15. Gutmann, V.: The Donor-Acceptor Approach to Molecular Interactions. Plenum Press, New York (1978)

16. Katsuta, S., Ito, Y., Takeda, Y.: Stabilities in nitromethane of alkali metal ion complexes with dibenzo-18-crown-6 and dibenzo-24-crown-8 and their transfer from nitromethane to other polar solvents. Inorg. Chim. Acta **357**, 541–547 (2004)

17. Christy, F.A., Shrivastav, P.S.: Conductometric studies on cation-crown ether complexes: a review. Crit. Rev. Anal. Chem. **41**, 236–269 (2011)

18. Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., Montgomery Jr, J., Vreven, T., Kudin, K., Burant, J.: Revision, b 3 (2003)

19. Glendening, E.D., Feller, D.: An ab initio investigation of the structure and alkaline earth divalent cation selectivity of 18-crown-6. J. Am. Chem. Soc. **118**, 6052–6059 (1996)

20. Ray, D., Feller, D., Michelle, B., Glendening, E.D., Armentrout, P.: Cation-ether complexes in the gas phase: bond dissociation energies and equilibrium structures of Li + (1, 2-dimethoxyethane) x, x = 1 and 2, and Li + (12-crown-4). J. Phys. Chem. **100**, 16116–16125 (1996)

21. Sargent, A.L., Mosley, B.J., Sibert, J.W.: A theoretical investigation on the Wurster's crown analogue of 18-crown-6. J. Phys. Chem. A **110**, 3826–3837 (2006)

22. Masiker, M.C., Mayne, C.L., Boone, B.J., Orendt, A.M., Edward, M., Eyring, E.M.: 7Li NMR chemical shift titration and theoretical DFT calculation studies: solvent and anion effects on second-order complexation of 12-crown-4 and 1-aza-12-crown-4 with Lithium cation in several aprotic solvents. Magn. Reson. Chem. **48**, 94–100 (2010)