Inorganica Chimica Acta, *183* (1991) 65–69

Complex formation of silver, thallium and alkali cations with dibenzo-30-crown-10 in some non-aqueous solutions

Mohammad Kazem Amini and **Mojtaba Shamsipur***

Department of Chemistry, Shiraz University, Shiraz (Iran)

(Received June 25, 1990; revised November 16, 1990)

Abstract

The complexation reactions between dibenzo-30-crown-10 and Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+ and Tl^+ ions have been studied conductometrically in 1,2-dichloroethane, nitromethane, acetonitrile, acetone and dimethylformamide solutions at 25 °C. The stability constants of the resulting 1:1 complexes were determined, and found to decrease in the order $Tl^+ > Rb^+ \approx K^+ > Ag^+ > Cs^+ > Na^+ > Li^+$. In 1,2-dichloroethane solution, the complexation process results in dissociation of ion pairs. There is an inverse relationship between the stabilities of the complexes and the Gutmann donicity of the solvents. The data obtained in this study support the existence of a 'wrap around' structure for the above complexes in solution.

Introduction

Since the first synthesis of macrocyclic polyethers (crowns) by Pedersen [1], the ability of these ligands to selectively complex a wide variety of metal ions has become the subject of extensive research work during the past two decades [2–4]. Among crown ethers, the larger molecules such as dibenzo-30-crown-10 possess some interesting properties. These molecules, because of their high degree of flexibility and increased number of donating oxygen atoms in the macrocyclic ring, show two types of behavior. First, the ligand can wrap itself around the metal ion of proper size to from a three-dimensional 'wrap around' complex in which all oxygen atoms of the ring are coordinated to the central cation. Evidence for the existence of such structures both in solution [5–12] and in the solid state [13, 14] has been reported. Second, the macrocyclic ring can accommodate two cations, if the repulsion forces are not so large, as in the case of Na^+ and K^+ complexes with dibenzo-24-crown-8 [15, 16] and dibenzo-30-crown-10 [6, 9, 17].

It was of interest to us to study the influence of the cation size and solvent properties on the interactions of metal ions with large crown ethers, capable of forming three-dimensional complexes with cations. In this paper we report a conductance study of alkali and of Ag^+ and Tl^+ ions with dibenzo-30-crown-10 in 1,2-dichlorethane, nitromethane, acetonitrile, acetone and dimethylformamide solutions at 25 °C.

Experimental

Dibenzo-30-crown-10 (DB30C10) was synthesized by a slight modification of Pedersen's method [1]. The product was recrystallized from reagent grade n-hexane and vacuum dried. Nitromethane (NM, Merck), acetonitrile (AN, Riedel), acetone (AC, Merck) and dimethylformamide (DMF, Merck) were purified and dried by the previously described methods [18]. 1,2-Dichloroethane (DCE, Reidel) was vaccum distilled and the center fraction was used. Lithium chloride, rubidium chloride, cesium chloride, potassium perchlorate (all from Merck), sodium perchlorate (Fluka), silver perchlorate (Aldrich) and thallium perchlorate (K and K) were all of highest commercial purity available and were used without further purification except for vacuum drying over P_2O_5.

Conductivity measurements were carried out with a model EIL-5003 kent bridge balance and a Consort digital conductimeter. A dip-type cell with cell constant of 0.723 cm^{-1} was used. In all measurements, the cell was thermostatted at 25.00 ± 0.02 °C.

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

In order to determine the formation constants of 1:1 metal ion–DB30C10 complexes, a 50.0 ml portion of the metal ion solution (10^{-4}–10^{-5} M) was placed in the cell and the conductance was measured. Then, a known amount of the ligand was added in a stepwise manner by a micropipet and the conductance was measured after each addition. The complex formation constant can be expressed as [19]

$$K_f = \frac{(\Lambda_m - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_c)[L]} \tag{1}$$

where

$$[L] = [L]_t - \frac{[M]_t(\Lambda_m - \Lambda_{obs})}{(\Lambda_m - \Lambda_c)} \tag{2}$$

and Λ_m = molar conductance of metal ion before addition of the ligand, Λ_{obs} = observed molar conductance of the solution during the titration, Λ_c = molar conductance of the complexed metal ion, $[M]_t$ = total metal salt concentration, $[L]_t$ = total ligand concentration added to the solution, $[L]$ = free ligand concentration.

A computer program based on Powell's algorithm [20] was written to evaluate the best values of K_f and Λ_c from eqns. (1) and (2) by an iterative non-linear least-squares analysis.

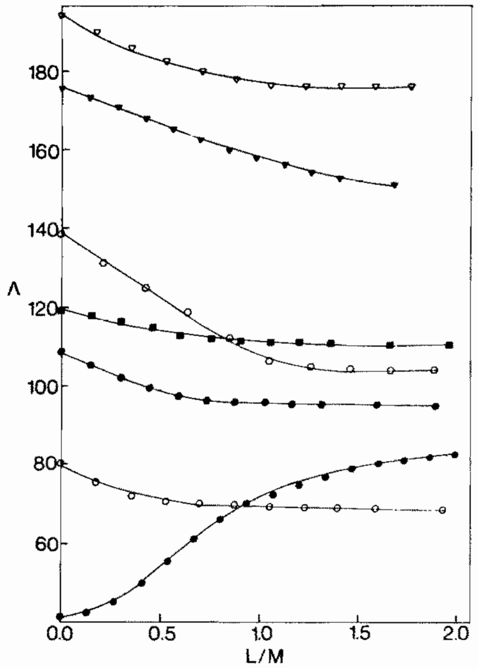

Fig. 1. Λ (ohm^{-1} cm^2 mol^{-1}) vs. [DB30C10]/[M^+] curves in nitromethane. ●: LiCl, 1.8×10^{-4} M; ▼: $NaClO_4$, 1.64×10^{-4} M; O: $KClO_4$, 1.08×10^{-4} M; ⬣: RbCl, 1.55×10^{-4} M; ○: $AgClO_4$, 1.39×10^{-4} M; ▽: $TlClO_4$, 1.4×10^{-4} M.

Results and discussion

The molar conductance of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+ and Tl^+ solutions was monitored as a function of the DB30C10/metal ion mole ratio at 25.0 °C. The resulting plots in various solvents are shown in Figs. 1–4. As can be seen, with the exception of the Li^+–DB30C10 complex in NM, in all other cases studied in NM, AN, AC and DMF solutions, the addition of the ligand to metal salt solution causes a gradual decrease in the molar conductance which tends to level off at high ligand to metal ion mole ratios. The results clearly indicate that the complexed cation is less mobile than the solvated one.

However, an opposite conductance behavior is observed in DCE solutions (Fig. 4). The initial conductance is very low, probably due to a high degree of ion pairing which is common in solvents of low dielectric constant. Addition of the ligand to the metal salt solution then causes a sharp increase in the molar conductance which tends to level off at molar ratios greater than one. It is known that when crown ethers encapsulate metal ions, they impart a lipophilic character to the complexed metal ions [2], so that in the presence of these ligands the ion pairs are expected to dissociate into ions [21]. This process can be

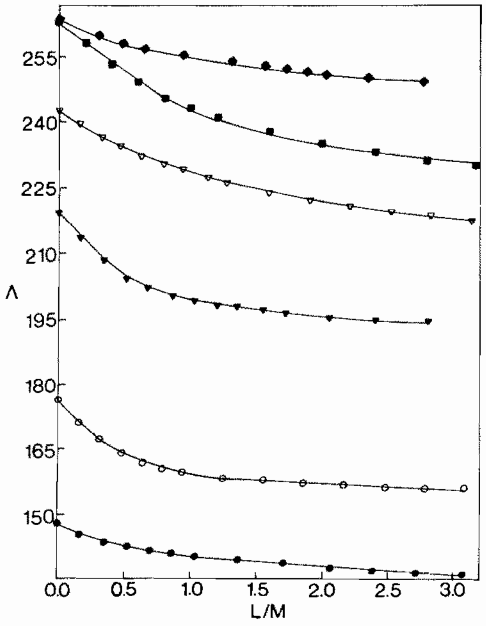

Fig. 2. Λ (ohm^{-1} cm^2 mol^{-1}) vs. [DB30C10]/[M^+] curves in acetonitrile. ◆: $NaClO_4$, 7.93×10^{-5} M; ■ $KClO_4$, 1.08×10^{-4} M; ○: RbCl, 7.96×10^{-5} M; ▽: CsCl, 7.84×10^{-5} M; ●: $AgClO_4$, 6.71×10^{-5} M; ▼: $TlClO_4$, 6.70×10^{-5} M.

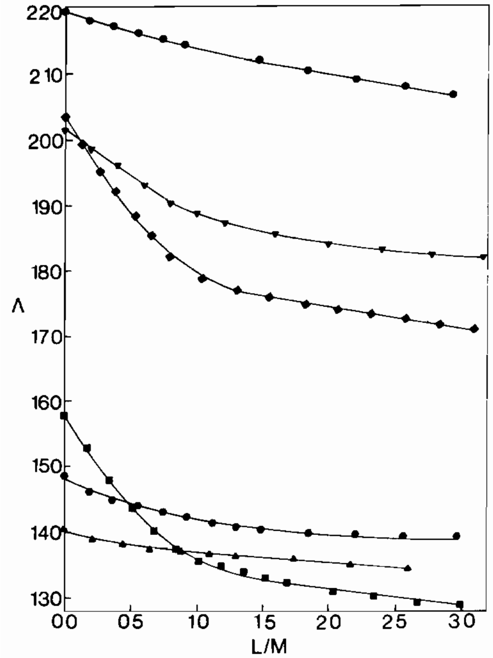

Fig 3 Λ (ohm^{-1} cm^2 mol^{-1}) vs [DB30C10]/[M$^+$] curves in acetone ● NaClO$_4$, 7 93 × 10^{-5} M, ▼ KClO$_4$, 5 20 × 10^{-5} M, ■ RbCl, 7 96 × 10^{-5} M, ⬣ CsCl, 7 84 × 10^{-5} M, ▲ AgClO$_4$, 6 70 × 10^{-5} M, ◆ TlClO$_4$, 1 10 × 10^{-4} M

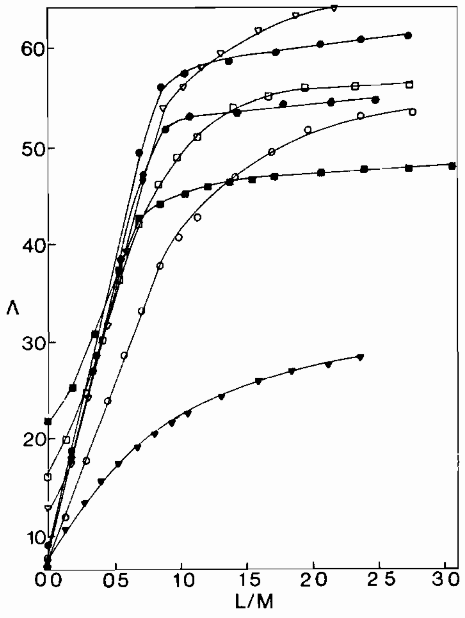

Fig 4 Λ (ohm^{-1} cm^2 mol^{-1}) vs [DB30C10]/[M$^+$] curves in 1,2-dichloroethane ▼ LiCl, 8 67 × 10^{-5} M, ▽ NaClO$_4$, 7 93 × 10^{-5}, ⬣ KClO$_4$, 6 45 × 10^{-5}, □ RbCl, 7 96 × 10^{-5} M, ○ CsCl, 7 84 × 10^{-5} M, ■ AgClO$_4$, 6 71 × 10^{-5}, ● TlClO$_4$, 6 70 × 10^{-5} M

shown by the following equilibria

$$(M^+\bar{A}) + DB30C10 \rightleftharpoons M^+\ DB30C10\ \bar{A}$$

Ion pair Ligand separated ion pair

$$M^+\ DB30C10\ \bar{A} \rightleftharpoons M^+\ DB30C10 + \bar{A}$$

The same kind of conductance behavior in the study of the complexes of crown ethers with organic acids in DCE solutions has already been reported [22]

From Figs 1–4 it is seen that, for all metal ion–DB30C10–solvent systems studied, the slopes of the corresponding molar conductance–mole ratio plots change sharply at the point where the ligand to cation mole ratio is one, indicating formation of a 1 1 complex between DB30C10 and the cations used Although it is known that the formation of a 1 2 (ligand to metal) complex is favored by small cations such as Li$^+$ and Na$^+$ ions [5, 6, 9], no clear-cut evidence for the existence of such complexes in solution was observed during the conductance measurements However, the molar conductance–mole ratio plot for Li$^+$–DB30C10 in NM shows a distinct inflection point at the ligand to metal ion mole ratio of 0 5 (Fig 1) Because of the unexpected increase in conductance upon addition of the ligand in this system, it is hard to consider the inflection point a sign for the formation of a 1 2 complex or a result of ion pair formation in solution

The complex formation constants were evaluted from the computer fitting of the conductance data to eqns (1) and (2) and all of the resulting values are listed in Table 1 The corresponding reported values are also included for comparison As can be seen, some ion pairing undoubtedly occurs in DCE solution and, therefore, the formation constants reported in this solvent indicate only the relative complexing abilities of the cations towards the ligand However, all other solvents used in this study have relatively high dielectric constants and at the very low concentrations used (10^{-4}–10^{-5} M), the degree of ion pairing with the free cation, and especially with the large complex ion, is expected to be negligible Comparison of our values with those reported in the literature (and obtained by different techniques) in most cases show a satisfactory agreement

From Table 1, it is obvious that the nature of the solvent has a very fundamental effect on the stability of the resulting complexes Since, in the complexation process, the ligand must compete with solvent molecules for the cations, variation of the solvent is expected to change apparent binding abilities of the complexes Actually, there is an inverse relationship between the stability of the complexes and the solvating power of the

TABLE 1 Log K_f of different metal ion complexes with DB30C10 in various solvents at 25 °C

Solvent	DN^a	D^b	Log K_f^c						
			Li$^+$ (0 76)^d	Na$^+$ (1 02)^d	K$^+$ (1 38)^d	Rb$^+$ (1 52)^d	Cs$^+$ (1 67)^d	Ag$^+$ (1 15)^d	Tl$^+$ (1 50)^d
DCE	0	10 1	4 68	5 25	5 96	5 60	4 92	5 27	6 30
NM	2 7	35 9	4 49	4 66	5 37	5 26	4 56 4 30^e	4 79	5 48
AN	14 1	38 0		3 14 3 20^f 3 60^g	4 63 4 82^f 4 70^g	4 76 4 49^f 4 70^g	3 81 3 39^e	4 22	5 15
AC	17 0	20 7		3 04	4 39	4 26	3 70 3 96^e	3 88	5 03
DMF	26 6	36 1			3 13 2 22^f				

^{a}DN = donor number, ref 23 ^{b}D = dielectric constant, ref 23 ^{c}Standard deviations = ±0 05 ^{d}Ionic radius in Å, ref 24 ^{e}Ref 6 ^{f}Ref 25 ^{g}Ref 26

solvents, as expressed by the Gutmann donor number [23] That is, the stability of all 1 1 complexes with DB30C10 decreases in the order DCE > NM > AN > AC > DMF There are several earlier reports which clearly show the same type of solvent effect on the stabilities of various metal ion–ligand complexes [4, 7, 11, 27–31]

The stability of the complexes of different cations with DB30C10 in various solvents varies in the order $Tl^+ > Rb^+ \approx K^+ > Ag^+ > Cs^+ > Na^+ > Li^+$ For large crown ethers such as DB30C10, which are capable of forming three-dimensional 'wrap around' complexes with metal ions, the size of the cation is expected to influence strongly the extent of the complexation reaction According to the above stability order, cations with ionic radii of about 1 4 to 1 5 Å (K^+, Rb^+ and Tl^+ ions) seem to have the proper size to fit conveniently inside the cavity formed by twisting of the large molecule, with all ten oxygens of the ring participating in the bond formation with the central cation [5, 6] In the case of larger cations like Cs^+ ion, the complete three-dimensional structure cannot be formed and only some oxygen atoms have the opportunity of bond formation with the cation, consequently, a weaker complex results On the other hand, if the ligand's cavity size is much larger than the cation, as in the case of Li^+ and Na^+ ions, the ligand can still form the 'wrap around' structure, but in this case the oxygen atoms of the ring will have to be in close proximity and, therefore, the resulting repulsive forces will weaken the complex However, the thermodynamic stability constant is not just a measure of the absolute strength of the complex, but a measure of the relative strength as compared to the ionic solvation as well as ligand–solvent interactions [32, 33] Thus the maximum stability for a given metal ion complex results from a balance between the binding and solvation energies

Although, the thallium(I) ion has an ionic radius very close to that of the rubidium ion, the stability of its DB30C10 complex is exceptionally higher than that of the Rb^+–DB30C10 complex This is probably because the Tl^+ ion is bound in the complexes by an ion–dipole interaction with a covalent contribution [2]

Acknowledgements

The authors gratefully acknowledge the support of this study by the Shiraz University Research Council They also acknowledge use of the research facilities of the Department of Chemistry, Esfahan University, during the course of this study

References

1 C J Pedersen, *J Am Chem Soc*, *89* (1967) 7017

2 J M Lehn, *Struct Bonding (Berlin)*, *16* (1973) 1

3 A I Popov and J M Lehn, in G A Melson (ed), *Coordination Chemistry of Macrocyclic Compounds*, Plenum, New York, 1979, Ch 9

4 R M Izatt, J S Bradshaw, S A Nielsen, J D Lamb, J J Christensen and D Sen, *Chem Rev*, *85* (1985) 271

5 D Live and S I Chan, *J Am Chem Soc*, *98* (1976) 3769

6 M Shamsipur and A I Popov, *J Am Chem Soc*, *101* (1979) 4051

7 M Shamsipur, G Rounaghi and A I Popov, *J Solution Chem*, *7* (1980) 701

8 M Bisnaire, C Detellier and D Nadon, *Can J Chem*, *160* (1982) 307

9 H D H Stover, L J Maurice, A Deville and C Detellier, *Polyhedron*, *4* (1985) 1091

10 M B Gholivand and M Shamsipur, *Inorg Chim Acta*, *121* (1986) 53

11 M B Gholivand, S Kashanian and M Shamsipur, *Polyhedron*, *6* (1987) 535

12 M Shamsipur and A I Popov, *J Phys Chem*, *92* (1988) 147

13 M A Bush and M R Truter, *J Chem Soc*, *Perkin Trans*, *2* (1975) 345

14 J Hasek, K Huml and D Hlavata, *Acta Crystallogr*, *Sect B*, *35* (1975) 330

15 D L Hughes, *J Chem Soc*, *Dalton Trans*, (1975) 2374

16 M Mercer and M R Truter, *J Chem Soc*, *Dalton Trans*, (1973) 2469

17 J Owen and M R Truter, *J Chem Soc*, *Dalton Trans*, (1979) 1831

18 M S Greenberg and A I Popov, *Spectrochim Acta*, *Part A*, *31* (1975) 697

19 Y Takeda, *Bull Chem Soc Jpn*, *56* (1983) 3600

20 M J D Powell, *Comput J*, *7* (1964) 155

21 K H Wong, G Gonizer and J Smid, *J Am Chem Soc*, *92* (1970) 666

22 N Nae and G Grodzinski, *J Am Chem Soc*, *99* (1977) 489

23 V Gutmann and E Wychera, *Inorg Nucl Chem Lett*, *2* (1966) 257

24 R D Shannon, *Acta Crystallogr*, *Sect A*, *32* (1976) 751

25 M K Chantooni, G Roland and I M Kolthoff, *J Solution Chem*, *17* (1988) 175

26 A Hofmanova, J Koryta, M Brezina and M L Mittal, *Inorg Chim Acta*, *28* (1978) 73

27 J D Lin and A I Popov, *J Am Chem Soc*, *103* (1981) 3773

28 M Shamsipur and A I Popov, *Inorg Chim Acta*, *43* (1980) 243

29 S Kashanian and M Shamsipur, *Inorg Chim Acta*, *155* (1989) 203

30 M Shamsipur, S Madaeni and S Kashanian, *Talanta*, *36* (1989) 773

31 S Kashanian, M B Gholivand, S Madaeni, A Nikrahi and M Shamsipur, *Polyhedron*, *7* (1988) 1227

32 J A A deBoer, D N Reinhoudt, S Harkema, G J Van Hummel and J F deJong, *J Am Chem Soc*, *104* (1982) 4073

33 P A Mosier-Boss and A I Popov, *J Am Chem Soc*, *107* (1985) 6168