IAU-ARAK

J. Iran. Chem. Res. 3 (2010) 167-177

Journal of the
Iranian
Chemical
Research

www.iau-jicr.com

Conductometric study of the complex formation of Rb^+, Cs^+, NH_4^+, K^+, Tl^+ and Ag^+ ions with several crown ethers in acetonitrile-dimethylsulfoxide and acetonitrile-dimethylformamide binary mixtures

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Received 28 July 2010; received in revised form 26 August 2010; accepted 28 August 2010

Abstract

A conductance study of the interaction between Cs^+, Rb^+, NH_4^+, K^+, $T1^+$ and Ag^+ ions and 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dicyclohexyl-18-crown-6 (DC18C6), dicyclohexyl-24-crown-8 (DC24C8), dibenzo-24-crown-8 (DB24C8) in different binary mixtures of acetonitrile (AN) with dimethylsulfoxide (DMSO) and dimethylformamide (DMF) at 25 °C has been carried out. Formation constants of the resulting 1:1 complexes were determined from the conductance-mole ratio data and found frequently vary in the order DC18C6 > 18C6 > B18C6 > DC24C8 > DB24C8 for Rb^+ ion and DC18C6 > DC24C8 > 18C6 > B18C6 > DB24C8 for NH_4^+ ion, DC24C8 > DC18C6 > 18C6 > B18C6 ≈ DB24C8 for Cs^+ ion, DC18C6
> DC24C8 > 18C6 > B18C6 > DB24C8 for K^+ ion, DC24C8 > DC18C6 > 18C6 > B18C6 > DB24C8 for Tl^+ ion and DC24C8 > DC18C6 > 18C6 > DB24C8 > B18C6 for Ag^+ ion. It was found that the stability of the resulting complexes increased by increasing acetonitrile mole fraction in the solvent mixtures. The interactions of the solvent molecules with metal ions and ligands show an important role for the complex formation process. Therefore, in addition to influences of the solvent, the effects of the number of members in the macrocycle, nature of the substituents in the polyether ring and cavity size are discussed.

Keywords: Cs^+, Rb^+, NH_4^+, $T1^+$, K^+ and Ag^+ complexes; 18- and 24-Crown ethers; Conductance; Mixed solvents.

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1. Introduction

After syntheses of crown ethers by Pedersen in 1967 [1, 2], cryptands by Lehn in 1973 [3, 4] and spherands by Cram in 1974 [5-7] they have found wide spread applications in all sub-branch of analytical chemistry. Their unique property is capability of forming complexes with hard metal cations such as alkali, alkaline earth, lanthanide and organic ammonium ions. They have been extensively utilized as phase-transfer catalysts in organic synthesis [8, 9], as neutral carriers in ion sensors [10], and for enhancing the separation selectivity in chromatography, electrophoresis, membrane transfer and solvent extraction of cations [11–15]. Crown ethers have

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also received special interest from physical chemists, who seek to understand the origins of their complexation selectivity [16].

The crown-ethers are analogous to some bio-ligands, able to selectively interact with metal-ions by including them in a cavity of the molecule [17]. This interaction is similar to the solvation process: the crown-ether molecule behaves like the first solvation shell of the cation [18]. The results of numerous investigations allow to conclude that the complexing properties of crown-ligands could be more effective in mixed and non-aqueous solvents rather than in water [19]. The effect of mixed solvent properties on the formation of crown ether-metal cation complexes is of interest due to, among other things, the fact that the solvation capacities of crown ether molecules and cations change with changing the mixed solvent composition. Some papers on this problem are available in the literature [20-25].

The nature of solvent has found to strongly influence the stoichiometry, selectivity, thermodynamic stability, and exchange kinetics of metal ion-crown ether complexes. While crown ether complexes of alkali and alkaline earth cations in aqueous and neat non-aqueous solvents have been extensively reported in literature, the complexation reaction of these complexes in mixed solvent systems have been investigated only to a very limited extent [26-29]. So it is crucial demand to carry out the determination of those missing data of the comlexation data.

Stability constants of crown compound complexes are determined by various methods, such as potentiometry (with ion selective electrodes), polarography, voltammetry, spectrophotometry, nuclear magnetic resonance, calorimetry, conductometry and solubility. Conductance measurements of an electrolyte solution in the presence of a convenient ligand provide two valuable pieces of information. The first is detection of complexation between the ligands and the cations constituting the electrolyte. Furthermore, the stability constant of the ligand– cation complex can be determined from the conductance data. The second useful piece of information relates to the transport phenomena of the ligand–electrolyte complex in the solution. In this paper, we report the results, which are obtained from conductometric study of the complexation reactions of Rb^+, Cs^+, and NH_4^+ cations with the macrocyclic ligands, 18C6, B18C6, DC18C6, DC24C8 and DB24C8, in different AN-DMSO and AN-DMF binary mixtures at 25°C. The advantage of conductometry is that the measurements can be carried out at low solution concentrations, where the interactions between the cations and anions are known to be small. In addition, conductometry is a highly sensitive and inexpensive technique with a simple experimental arrangement [30].

2. Experimental

2.1. Material

Reagent-grade rubidium nitrate from Aldrich and ammonium nitrate, potassium nitrate, silver nitrate, dried acetonitrile ($H_2O < 0.005$ %), dimethylformamide, from Merck and thallium nitrate, dimethylsulfoxide, 18C6, B18C6, DC18C6, DC24C8 and DB24C8 all from Fluka were of the highest purity available and used as received. $CsClO_4$ were prepared by treating $CsNO_3$, with small excess of 3 mol L^{-1} perchloric acid, evaporation to dryness, recrystallization three times from deionized water and drying at 120 °C [31]. The conductivities of the solvents for AN, DMSO and DMF are 7.5×10^{-7}, 2.23×10^{-6} and 1.53×10^{-6} S cm^{-1} respectively.

2.2. Apparatus

Conductance measurements were carried out with a JENWAY 4320 conductivity meter. A dip-type conductivity cell made of platinum black was used. The cell constant was determined by conductivity measurements of a 0.1000 M solution of analytical-grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures has been reported in the literature [32]. The cell constant was 0.98 cm^{-1}. In all measurements, the cell was thermostated at the desired temperature ±0.03 °C using an HUBER POLYSTAT model K6-3 thermostat-circulator water bath.

2.3. Procedure for conductometry

In a typical experiment, 10 mL of the desired metal ion ($\sim 1.0 \times 10^{-4}$ mol L^{-1}) was placed in the titration cell, thermostated to the desired temperature (25 °C) and the conductance of solution was measured. Then, a known amount of a concentrated crown ether solution (1.0×10^{-2} mol L^{-1}) was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. The ligand solution was continually added until the desired ligand to cation mole ratio was achieved.

2.4. Stability constants calculations

The formation constants, K_f, and the limiting molar conductances, Λ_o, of the resulting 1:1 complexes between 18C6, B18C6, DC18C6, DC24C8, DB24C8 and the mentioned univalent cations, were calculated in different AN–DMSO and AN–DMF mixtures. These calculations were done by fitting the observed molar conductance, Λ_{obs}, at varying $[L]/[M^+]$ mole ratios to the equation which express Λ_{obs} as a function of the free and complexed metal ions [33, 34]. Moreover, the formation constants were evaluated using a non-linear least-squares curve-fitting program that written by the authors using spreadsheet Excel Solver add-in. It is noteworthy that, in the process of calculation of formation constants, the association between M^+ and NO_3^- or ClO_4^- ions was considered negligible, under the highly dilute experimental conditions used (1.0×10^{-4} mol L^{-1}) [35]. Since the concentration of macrocycles was kept below 1.0×10^{-2} mol L^{-1} during the experiments, correction for the viscosity changes was also neglected.

3. Results and discussion

In order to evaluate the influence of adding crown ethers (18C6, B18C6, DC18C6, DC24C8 and DB24C8) on the molar conductance of Cs^+ ,Rb^+ ,NH_4^+ ,$T1^+$,K^+ and Ag^+ ions in different AN–DMSO and AN–DMF mixtures, the molar conductance at a constant salt concentration (1.0×10^{-4} mol L^{-1}) was monitored while increasing the crown ethers concentration at 25 °C. Some of the resulting molar conductance's versus $[L]/[M^+]$ mole ratio plots are shown in Figs. 1.

As shown in Figs. 1, in all cases, except for thallium nitrate in pure acetonitrile, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates the lower mobility of the complexed cations compared to the solvated or free ions. In some conductance profiles, addition of the ligand to a cation solution causes a continuous decrease in the molar conductance, which begins to level off at a mole ratio greater than one, indicating the formation of a stable 1:1 complex. In other cases, although the molar conductance does not show any tendency for leveling off even at a molar ratio of about 4, the corresponding molar ratio data show a considerable change in their slopes at a molar ratio of about one, emphasizing the formation of some weaker 1:1 complex.

As seen from Fig. 2, addition of crowns to thallium nitrate in pure AN solutions at 25 °C results in an increase in molar conductivity which indicates that the crown-$T1^+$ complex in the AN solvent is more mobile than free solvated Tl^+ ion. Since the crown-ion complex is generally heavier than ion alone, why the conductivity increased after addition of the crown to the metal ion solution? Because there is another not surprising chemical phenomena that is not related to the complexation but it reveal the existence of the ion pairing. The slope of the corresponding molar conductivity versus $[L]/[Tl^+]$ plots changes sharply at the point where the ligand to cation mole ratio is 1, which is evidence for formation of a relatively high stable 1:1 complex.

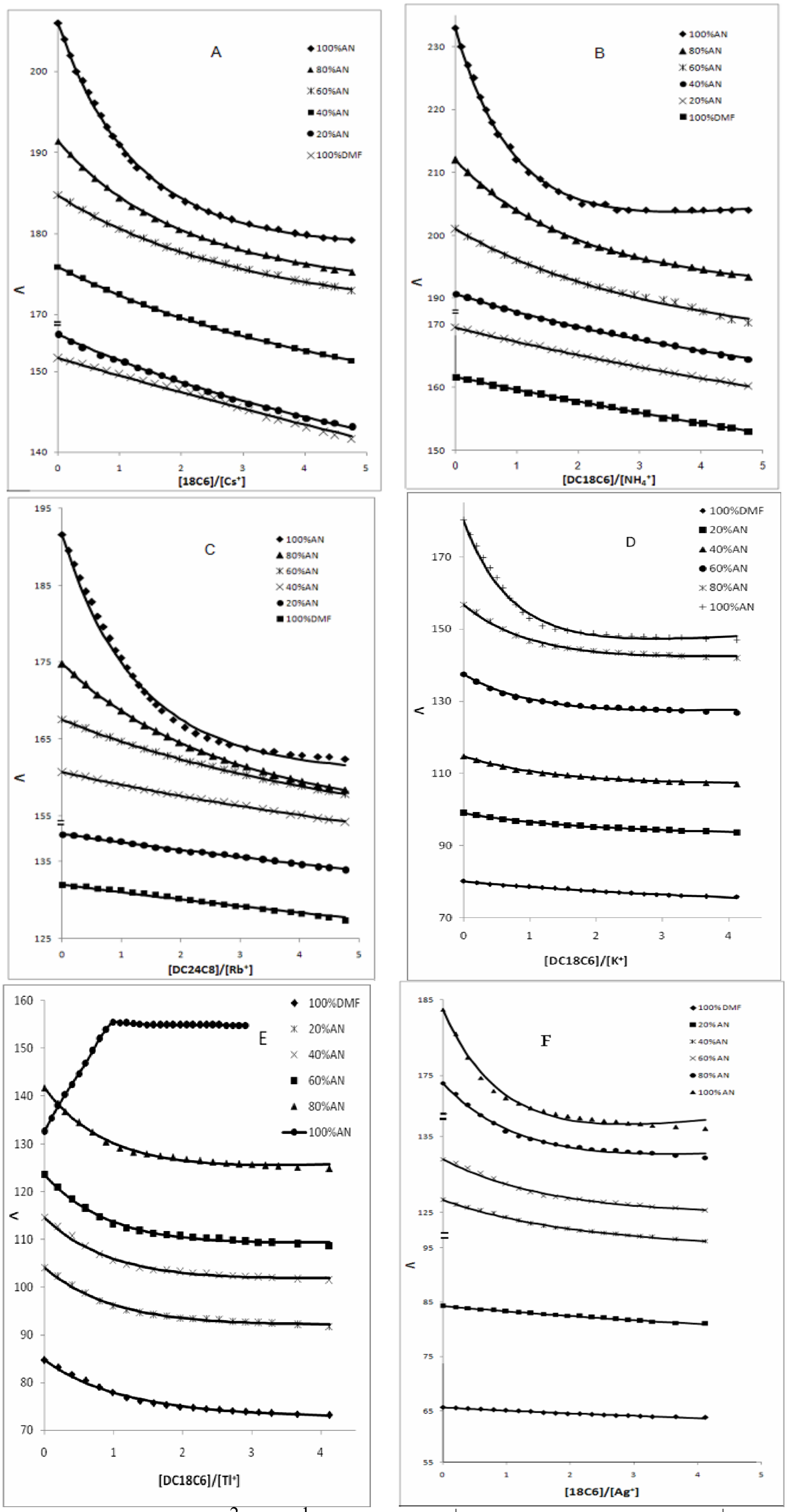

Fig. 1. Molar conductance (S cm^2 mol^{-1}) *vs.* [L]/[M$^+$] plot at 25 °C for Cs$^+$–18C6 (A), NH$_4^+$–DC18C6 (B), Rb$^+$–DC24C8 (C), K$^+$–DC18C6 (D), Tl$^+$–DC18C6 (E) and Ag$^+$–18C6 (F) complexes in different AN–DMF mixtures.

The formation constants of all crowns-cations complexes in different solvent mixtures at 25 °C, obtained by computer fitting of the molar conductance-mole ratio data, are summarized in

Table 1 and 2. A sample computer fit of the molar ratio data is shown in Fig. 3. Our assumption of 1:1 stoichiometry for the resulting complexes of these cations were further supported by excellent agreement between the observed and calculated molar conductance in the process of computer fitting of the mole ratio data. The data given in Table 1 and 2 clearly illustrate the fundamental role of the solvent properties in the complexation reactions of crowns-cations studied. In all cases, the stability of the resulting complexes decreases rapidly with decreasing volume percent of AN in the solvent mixture. It is known that the solvating ability of the solvent, as expressed by the Gutmann donor number [36], plays an important role in different complexation reactions [31, 37-41]. There is actually an inverse relationship between the stability of the complexes and the solvating ability of the solvents. DMSO and DMF are solvents of high solvating ability (DN =29.8 and 26.6 respectively) which can strongly compete with macrocycles for the cation. Thus, it is not unexpected to observe that addition of AN as a relatively low donicity solvent (DN = 14.1) to DMSO and DMF will increase the stability of the complexes.

Table 1

log K_f for different M^+–L complexes in various AN–DMSO mixtures.

cation	**vol% AN**	**Crown ether**				
		18C6	**B18C6**	**DC18C6**	**DC24C8**	**DB24C8**
Rb^+	**100**	3.58 ± 0.005	3.50 ± 0.003	3.61 ± 0.01	3.51 ± 0.01	3.34 ± 0.003
	80	3.13 ± 0.02	3.03 ± 0.01	3.33 ± 0.01	3.26 ± 0.01	2.15 ± 0.65
	60	2.06 ± 0.76	2.55 ± 0.15	3.08 ± .003	2.48 ± 0.11	2.01 ± 0.92
	40	2.84 ± 0.03	2.41 ± 0.31	2.96 ± 0.01	2.21 ± 0.19	1.91 ± 0.80
	20	2.68 ± 0.05	2.39 ± 0.11	2.56 ± 0.06	2.64 ± 0.06	1.75 ± 0.67
	0 (Pure DMSO)	2.47 ± 0.02	2.09 ± 0.27	2.53 ± 0.05	1.98 ± 0.44	1.59 ± 1.22
NH_4^+	**100**	3.57 ± 0.01	3.47 ± 0.01	3.66 ± 0.01	3.59 ± 0.01	3.29 ± 0.005
	80	2.54 ± 0.16	2.29 ± 0.49	2.95 ± 0.01	2.56 ± 0.11	2.31 ± 0.20
	60	2.38 ± 0.20	2.21 ± 0.66	2.61 ± 0.07	2.42 ± 0.29	2.26 ± 0.30
	40	2.15 ± 0.59	2.16 ± 0.17	2.47 ± 0.06	2.36 ± 0.16	2.19 ± 0.19
	20	2.06± 0.36	2.01 ± 0.38	2.38 ± 0.08	2.24 ± 0.34	2.13 ± 0.14
	0 (Pure DMSO)	2.00 ± 0.28	1.95 ± 0.45	2.31 ± 0.08	2.17 ± 0.08	1.72 ± 0.45
Cs^+	**100**	3.53 ± 0.003	3.35 ± 0.01	3.57 ± 0.005	3.65 ± 0.01	3.36 ± 0.002
	80	3.10 ± 0.004	2.96 ± 0.01	3.07 ± 0.01	3.29 ± 0.001	2.92 ± 0.01
	60	2.69 ± 0.06	2.53 ± 0.09	2.38 ± 0.08	2.55 ± 0.09	2.13 ± 0.62
	40	2.81 ± 0.03	2.15 ± 0.26	2.01 ± 0.12	2.47 ± 0.08	2.30 ± 0.29
	20	2.55 ± 0.16	1.98 ± 0.68	2.06 ± 0.20	2.38 ± 0.17	2.07 ± 0.75
	0 (Pure DMSO)	1.93 ± 0.33	1.90 ± 0.31	1.96 ± 0.28	2.34 ± 0.23	1.88 ± 0.35
K^+	**100**	3.74 ± 0.01	3.70 ± 0.005	3.80 ± 0.01	3.72 ± 0.01	3.62 ± 0.01
	80	3.39 ± 0.005	3.43± 0.004	3.54± 0.01	3.57± 0.01	3.38± 0.01
	60	3.29 ± 0.01	3.36± 0.01	3.52± 0.004	3.37±0.01	3.34± 0.01
	40	3.15 ± 0.01	3.17± 0.01	3.39± 0.005	3.19± 0.01	3.16± 0.01
	20	2.54 ± 0.07	2.50 ± 0.07	3.19± 0.01	2.33± 0.11	2.47± 0.09
	0 (Pure DMSO)	2.31± 0.03	2.41± 0.02	2.92± 0.01	2.04± 0.02	2.35± 0.02
Ag^+	**100**	3.58 ± 0.005	3.48± 0.004	3.59 ± 0.01	3.66 ± 0.01	3.52 ± 0.01
	80	3.37± 0.01	3.34± 0.01	3.50 ± 0.01	3.39 ± 0.01	3.35 ± 0.01
	60	3.29± 0.01	3.15± 0.01	3.41 ± 0.01	3.27 ± 0.01	3.27 ± 0.01
	40	3.18± 0.01	3.12± 0.01	3.25± 0.005	3.16 ± 0.01	3.14 ± 0.01
	20	2.82± 0.03	2.81± 0.03	2.72 ± 0.03	2.77 ± 0.03	2.79 ± 0.03
	0 (Pure DMSO)	2.59± 0.03	2.56± 0.03	2.65± 0.01	2.40± 0.03	2.65± 0.01
Tl^+	**100**	a	a	a	a	a
	80	3.57 ± 0.01	3.57 ± 0.01	3.62 ± 0.01	3.63 ± 0.01	3.44 ± 0.01
	60	3.55 ± 0.01	3.55 ± 0.01	3.61 ± 0.01	3.6 ± 0.01	3.38 ± 0.01
	40	3.48 ± 0.004	3.48 ± 0.006	3.6 0± 0.01	3.58 ± 0.01	3.32 ± 0.01
	20	3.39 ± 0.004	3.39 ± 0.006	3.58 ± 0.01	3.6 ± 0.01	3.29 ± 0.01
	0 (Pure DMSO)	3.20± 0.01	3.15± 0.03	3.54± 0.02	3.57± 0.01	3.11± 0.03

The data given in Table 1 and 2 revealed that, in pure AN, DMSO and DMF, the selectivity order of 18-crowns (18C6, DC18C6, B18C6) is $K^+ > Tl^+ > Rb^+ > Ag^+ > NH_4^+ > Cs^+$, while that of large crown ethers used (DC24C8 and DB24C8) is $K^+ > Tl^+ > Cs^+ > Ag^+ > NH_4^+ > Rb^+$. Potassium ion has more stable complex rather than other cations used. K^+ ion form steadier and stable complex beacuse: the size of potassium ion (2.76 Å) is rather smaller than other, so large crown ethers are enable to twist around a metal ion of suitable size to envelop it completely and form a "wrap around" complex in which all oxygen atoms of the ring are coordinated to the central cation. The increased stability of 18-crowns with Rb^+ ion and 24-crowns with Cs^+ ion is mainly due to more convenient fitting of rubidium and cesium ions (with cationic size of 3.02 Å and 3.34 Å respectively) inside the macrocyclic cavity (2.8-3.2 Å for 18-crowns and >4 Å for 24-crowns used). In other compositional mixtures this trend cannot be observed completely, probably due to different behavior of the solvent mixture in the salvation processes.

Table 2
log K_f for different M^+–L complexes in various AN–DMF mixtures.

Cation	**vol% AN**	**Crown ether**				
		18C6	**B18C6**	**DC18C6**	**DC24C8**	**DB24C8**
Rb^+	**100**	3.58 ± 0.01	3.50 ± 0.01	3.61 ± 0.01	3.51 ± 0.01	3.34 ± 0.01
	80	3.29 ± 0.01	3.18 ± 0.01	3.41 ± 0.01	3.23 ± 0.01	2.63 ± 0.03
	60	3.19 ± 0.004	2.86 ± 0.02	3.21 ± 0.01	2.95 ± 0.01	2.21 ± 0.12
	40	3.08 ± 0.01	2.65 ± 0.08	3.17 ± 0.01	2.72 ± 0.03	2.10 ± 1.12
	20	3.06 ± 0.01	2.35 ± 0.11	3.05 ± 0.01	2.50 ± 0.09	1.86 ± 0.60
	0 (pure DMF)	2.80 ± 0.04	2.60 ± 0.03	3.01 ± 0.05	2.41 ± 0.19	1.73 ± 0.75
NH_4^+	**100**	3.57 ± 0.01	3.47 ± 0.01	3.66 ± 0.01	3.59 ± 0.01	3.29 ± 0.01
	8	3.16 ± 0.01	2.78 ± 0.07	3.32 ± 0.01	2.86 ± 0.02	2.60 ± 0.11
	60	2.86 ± 0.04	2.56 ± 0.33	3.11 ± 0.01	2.66 ± 0.09	2.32 ± 0.81
	40	2.54 ± 0.09	2.18 ± 0.31	2.88 ± 0.02	2.57 ± 0.05	2.23 ± 0.40
	20	2.49 ± 0.04	2.10 ± 0.14	2.62 ± 0.02	2.51 ± 0.10	2.11 ± 0.26
	0 (pure DMF)	2.39 ± 0.04	2.06 ± 0.14	2.54 ± 0.03	2.47 ± 0.10	2.02 ± 0.71
Cs^+	**100**	3.53 ± 0.01	3.35 ± 0.01	3.57 ± 0.01	3.65 ± 0.01	3.36 ± 0.01
	80	3.30 ± 0.01	3.01 ± 0.01	3.25 ± 0.01	3.24 ± 0.004	2.88 ± 0.02
	60	3.13 ± 0.01	2.53 ± 0.02	3.06 ± 0.01	2.95 ± 0.01	2.48 ± 0.09
	40	3.01 ± 0.01	2.78 ± 0.01	2.87 ± 0.01	2.81 ± 0.01	2.36 ± 0.06
	20	2.89 ± 0.02	2.22 ± 0.14	2.67 ± 0.02	2.29 ± 0.14	2.26 ± 0.18
	0 (pure DMF)	2.25 ± 0.18	2.09 ± 0.08	2.48 ± 0.03	2.55 ± 0.02	2.08 ± 0.13
K^+	**100**	3.76 ± 0.01	3.72 ± 0.01	3.80 ± 0.01	3.76 ±0.01	3.62 ± 0.01
	80	3.40 ± 0.01	3.44 ± 0.01	3.55 ± 0.01	3.55 ± 0.01	3.38 ± 0.01
	6	3.32 ± 0.004	3.37 ± 0.01	3.52 ± 0.01	3.40 ± 0.01	3.35 ± 0.01
	40	3.19 ± 0.01	3.21 ± 0.01	3.40 ± 0.01	3.18 ± 0.01	3.20 ± 0.01
	20	2.64 ± 0.04	2.62 ± 0.05	3.27 ± 0.01	2.65 ± 0.05	2.51 ± 0.07
	0 (pure DMF)	2.54± 0.05	2.57± 0.04	3.02± 0.03	2.50± 0.01	2.42± 0.02
Ag^+	**100**	3.57 ± 0.01	3.49 ± 0.01	3.61 ± 0.01	3.67 ± 0.01	3.53 ± 0.01
	80	3.43 ± 0.01	3.34 ± 0.005	3.5 ± 0.01	3.37 ± 0.01	3.35 ± 0.01
	60	3.28 ± 0.01	3.17 ± 0.01	3.44 ± 0.01	3.30 ± 0.01	3.28 ± 0.01
	40	3.18 ± 0.01	3.11 ± 0.01	3.24 ± 0.01	3.21 ± 0.01	3.12 ± 0.01
	20	2.76 ± 0.03	2.72 ± 0.03	2.87 ± 0.02	2.70 ± 0.04	2.69 ± 0.02
	0 (pure DMF)	2.71± 0.01	2.62± 0.03	2.77± 0.01	2.68± 0.01	2.42± 0.03
Tl^+	**100**	a	a	a	a	a
	80	3.58 ± 0.01	3.56 ± 0.01	3.63 ± 0.005	3.65 ± 0.01	3.44 ± 0.01
	60	3.57 ± 0.01	3.56 ± 0.01	3.62 ± 0.01	3.62 ± 0.01	3.42 ± 0.01
	40	3.53 ± 0.01	3.52 ± 0.01	3.6 ± 0.01	3.6 ± 0.01	3.36 ± 0.01
	20	3.43 ± 0.01	3.39 ± 0.01	3.58 ± 0.01	3.59 ± 0.01	3.30 ± 0.01
	0 (pure DMF)	3.21± 0.02	3.18± 0.03	3.55± 0.02	3.57± 0.01	3.13± 0.03

a=The data cannot be fitted in equations.

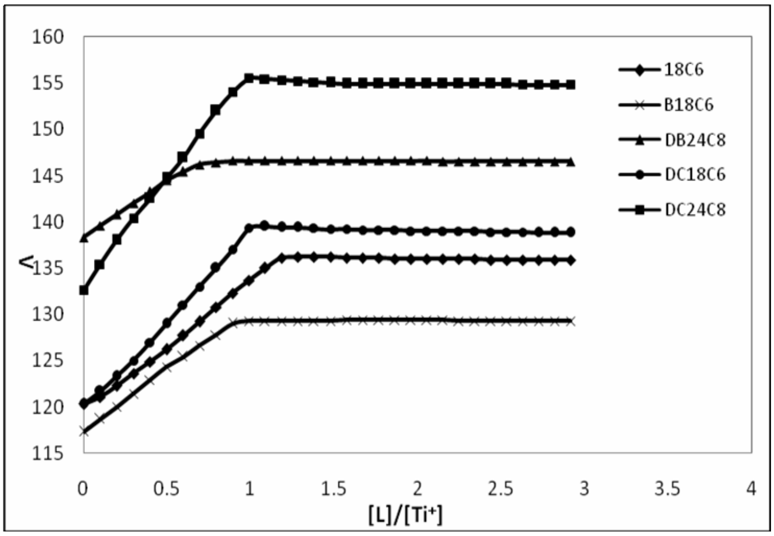

Fig. 2. Molar conductance (S cm^2 mol^{-1}) vs. [L]/[Tl$^+$] for various L–Tl$^+$ systems at 25 °C in 100% AN.

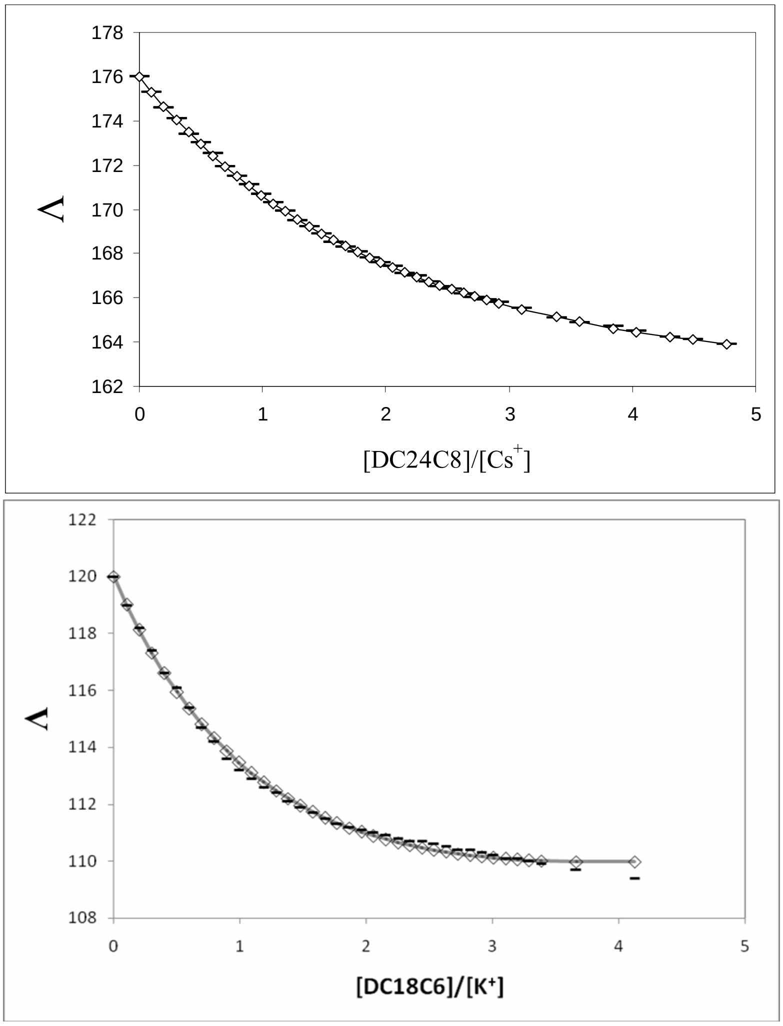

Fig. 3. Computer fit of the molar conductance–mole ratio data for the (A) Cs$^+$–DC24C8 in 80%AN–20%DMSO solution and K$^+$–DC18C6 in 60%AN–40%DMSO solution at 25°C : **(–)** experimental; (◇) calculated.

For small crown ethers such as the 18 crown ether series, rubidium complexes are generally more stable than the corresponding cesium complexes. For smaller ligands the relative size of the cation and the diameter of the crown ether cavity seem to play the most important roles with regard to the stability and the stoichiometry of the complexes. However, for larger crown ethers other factors such as the degree of flexibility of the ligand might become the dominant factor. For DC24C8 and DB24C8 in all solvent mixture used, rubidium complexes are weaker than the corresponding cesium complexes. For DC24C8 and DB24C8, probably more conformational changes of the ligand are needed to accommodate the smaller rubidium cation than are needed for the larger cesium cation. We should mention that the solvent plays an important role in these conformational changes.

Thallium and silver ions have soft natures, so that we expect to form the least stable complex in this series, but we observe that Tl^+ produces the stronger complexes than Rb^+ and Cs^+ ions with hard nature. This observation is due to that, the monovalent thallium ion is a polarizable metal ion that leads to strong interaction (ion-dipole interaction) between ligand (crown) and metal ion.

Comparison of the data given in Table 1 and 2 reveals that the stability of the resulting cation-macrocycle complexes, in most solvent mixture used varies in the order:

Rb^+	DC18C6 > 18C6 > B18C6 > DC24C8 > DB24C8
NH_4^+	DC18C6 > DC24C8 > 18C6 > B18C6 > DB24C8
Cs^+	DC24C8 > DC18C6 > 18C6 > B18C6 ≈ DB24C8
K^+	DC18C6> DC24C8 > 18C6 > B18C6 > DB24C8
Tl^+	DC24C8 > DC18C6 > 18C6 > B18C6 > DB24C8
Ag^+	DC24C8 > DC18C6 > 18C6 > DB24C8 > B18C6

As it is seen, in the case of all cations, among three 18-membered crown ethers used, where the ring frame remains the same, the stabilities of the resulting complexes fall in the order DC18C6 > 18C6 > B18C6. The presence of two cyclohexyl groups in DC18C6 can pump electrons into the ligand ring and thus increase the basicity of the oxygens, while the flexibility of the macrocycle remains more or less the same as 18C6. Thus, it is not unexpected to observe the highest stability for DC18C6 complexes among the 18-crowns used. On the other hand, the addition of benzo group to 18C6 markedly lowers the stability of the cations-complexes. This behavior may be attributed to some combination of the electron-withdrawing property of the benzo groups, which weakens the electron-donor ability of the oxygen atoms of the ring and reduces flexibility of the ligand, which prevents the macrocyclic molecule from wrapping itself around the cation. The net result is a weaker cation–ligand interaction.

In this manner, presence of two cyclohexyl groups substituted on the 24-membered crown ethers instead of two benzo groups, increased stability of the cation-crown ether complexes. The DB24C8 molecule has neither a proper size for the formation of two-dimentional structure nor enough flexibility for a complete wrap-around complex [39] with cations used, so that the resulting complexes are the least stable among the series. In order to show the effect of cavity and substituent group of crown on complex formation and their stability constant the plots of molar conductance, Λ_{obs}, vs. [Crown]/[Ag^+] mole ratios for five crown in five mixtures are shown Fig. 4.

The variation of stability constants of the ligand-cation complexes versus the solvent composition in AN–DMSO and AN–DMF mixtures are not linear. This behavior may be related to changes occurring in the structure of the solvent mixtures and therefore, changing in the solvation properties of the cyclic polyether, cations and even complexes in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes.

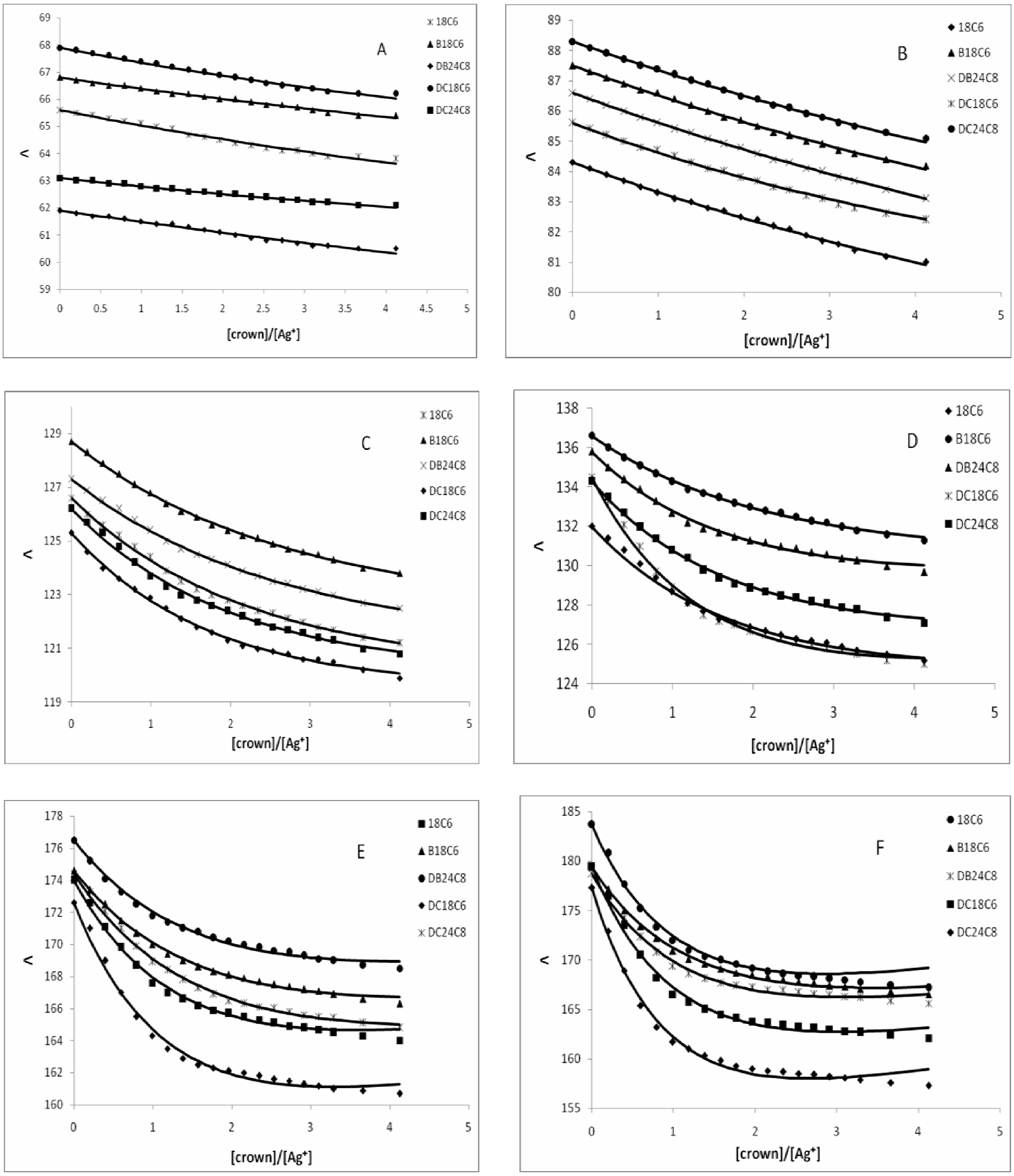

Fig. 4. Molar conductance (S cm^2 mol^{-1}) vs. [L]/[Ag$^+$] for various L–Ag$^+$ systems at 25°C in different AN–DMF mixtures. volume percent of AN in the binary mixtures are: (A)100% DMF, (B) 20% AN, (C) 40% AN, (D) 60% AN, (E) 80% AN and (F) 100% AN.

In addition, the heteroselective solvation of the cation, anion and ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in these complexation processes. In this regard, the interactions between molecules in some mixture solvents have been studied [42].

It is interesting to note that there is a linear relationship between logK_f of DC18C6-M$^+$ complexes and mole fraction of AN (X_{AN}) in their binary mixtures with DMF (Fig. 5). The same trends have already been reported for various complexes in different solvent mixtures [37, 41]. It has reasonably assumed that the preferential solvation of the ligand by DMF is mainly responsible for such a monotonic dependence of the stability constant of the DC18C6 complexes on the solvent compositions.

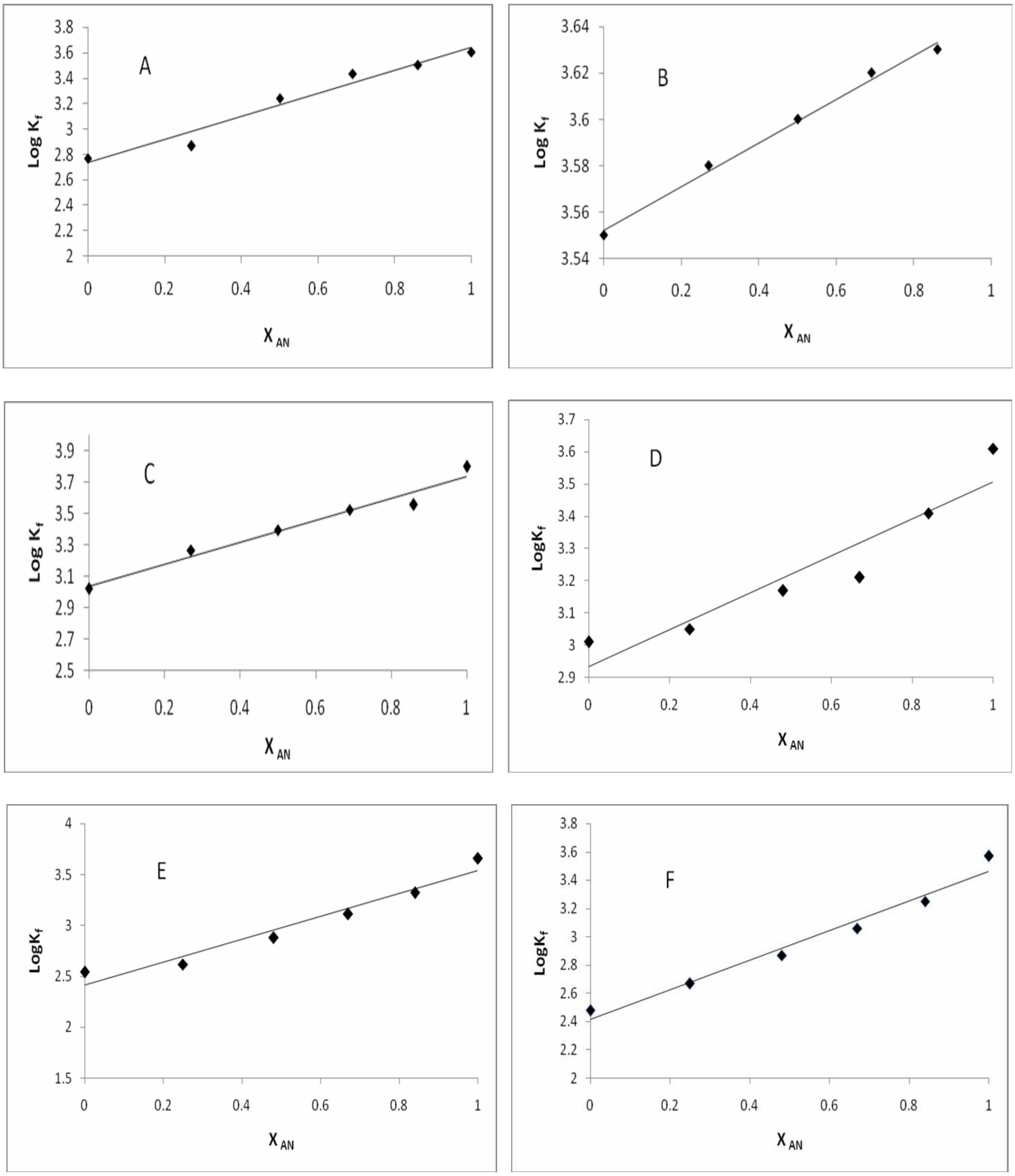

Fig. 5. variation of stability constants of various DC18C6–M$^+$ system with the composition of the AN–DMF for Ag$^+$ (A), Tl$^+$ (B), K$^+$ (C), Rb$^+$ (D), NH$_4$$^+$ (E), and Cs$^+$ (F).

4. Conclusion

Our results demonstrate that the stoichiometry and stability of complexes depends not only on the relative size of the cation and the ligand cavity, but also on the nature of the substituent groups on the crown ether ring as well as the degree of the flexibility of the ligand. In some mixtures used, the ionic salvation of the charged species involved, probably become the dominant factor in the complexation reaction.

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