329

Conductance Study of Complex Formation of Thallium and Silver Ions with Several Crown Ethers in Acetonitrile, Acetone and Dimethylformamide Solutions

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Abstract. The complexation reactions between Tl^+ and Ag^+ ions and several crown ethers have been studied conductometrically in 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 DA18C6 > DC18C6 > DB30C10 > 18C6 > DB21C7 > DB24C8 > DB18C6 > B15C5 > 12C4, in the case of Tl^+ complexes, and in the order DA18C6 > DC18C6 > 18C6 > DB18C6 > DB24C8 > DB30C10 ≈ B15C5 > DB21C7 for Ag^+ complexes. There is an inverse relationship between the stabilities of the complexes and the Gutmann donicity of the solvents. The influence of a number of atoms in the macrocycle and of substituents in the polyether ring on the stability of the complexes is discussed.

1. Introduction

The first report of the synthesis of macrocyclic polyethers (crowns) and the formation of stable complexes between these ligands and alkali and alkaline earth cations by Pedersen [1] opened the door to several broad and fruitful areas of chemical investigation. During the past two decades several hundreds of macrocyclic ligands have been synthesized and their complexation reactions with a variety of metal ions and with neutral molecules have been studied by a number of different physiochemical techniques [2–4].

Perhaps the most fundamental thermodynamic property of a metal complex is its stability, in a given medium and at a given temperature, as expressed by its formation constant. In order to understand the formation of a macrocyclic complex it is important to elucidate various factors that affect the complexation reaction equilibria. The relative size of the cation and the macrocyclic cavity, the number and the nature of binding sites, the flexibility of the ligand structure, the acid–base character of metal ions and, especially, the nature of the solvent are among the important factors which influence both the stability and selectivity of

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the macrocyclic complexes [2,3].

Because of the importance of both thallium and silver ions in biological and environmental processes [5–7], studies on the selective complexation of these cations with macrocyclic ligands are of particular interest. Both Tl^+ and Ag^+ are polarizable, soft ions [8] with the respective ionic radii of 1.49 Å and 1.15 Å [9]. In this paper we report a conductometric study of the complexation reactions between Tl^+ and Ag^+ ions and the macrocyclic poly-ethers 12-crown-4 (12C4), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), 1,13-diaza-18-crown-6 (DA18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8) and dibenzo-30-crown-10 (DB30C10) in acetonitrile (AN), acetone (AC) and dimethylformamide (DMF) solutions at 25°C.

2. Experimental

Reagent grade thallium perchlorate (K and K) and silver perchlorate (Fluka) were of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Crown ethers DB30C10, DB24C8, DB21C7 (all from Parish), DB18C6, DC18C6, DA18C6, 18C6 and B15C5 (all from Merck) were purified and dried using the previously reported methods [10–13]. 12C4 was used as received .

HPLC grade acetonitrile (Fluka) and acetone (Merck) were used as received. Dimethylformamide (Merck) was purified and dried by the previously described method [14]. The conductivities of the solvents were less than $1 \times 10^{-7} \, \Omega^{-1} \, cm^{-1}$.

The conductance measurements were carried out with a General Radio 1608-A Impedence Bridge. A dip-type conductivity cell, made of platinum black, with a cell constant of $0.4358 \, cm^{-1}$ was used. In all measurements the cell was thermostated at $25.00 \pm 0.03°C$ using a Lo-Temtrol 154 Precision Scientific thermostat.

In a typical experiment, 50 mL of the salt solution in the desired solvent (1.0×10^{-4} M; 1 M = 1 mol dm^{-3}) was placed in the titration cell, thermostated to 25°C, and its conductance was measured. A known amount of the crown ether solution, prepared in the same solvent, was then added in a stepwise manner using a precalibrated micropipette. The conductance of the solution was measured after each addition. Addition of the crown ether solution was continued until the desired crown ether-to-metal ion mole ratio was achieved.

The 1 : 1 binding of Tl^+ and Ag^+ ions with various crown ethers can be expressed by the following equilibrium

$$M^+ + crown \underset{}{\overset{K_f}{\rightleftarrows}} M^+\text{-crown} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[M^+\text{-crown}]}{[M^+] \, [crown]} \cdot \frac{f(M^+\text{-crown})}{f(M^+) \, f(crown)} \tag{2}$$

where [M$^+$-crown], [M$^+$], [crown] and f represent the equilibrium molar concentrations of complex, free metal ion, free ligand and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, the activity coefficient of uncharged crown ether, f(crown), can be reasonably assumed as unity [10, 15–17]. The use of the Debye–Hückel limiting law of 1 : 1 electrolytes [18] leads to the conclusion that f(M$^+$-crown) $\approx f$(M$^+$), so the activity coefficients in Equation (2) cancel.

Thus the complex formation constant in terms of the molar conductance can be expressed as [19,20]

$$K_f = \frac{[\text{M}^+\text{-crown}]}{[\text{M}^+]\,[\text{crown}]} = \frac{(\Lambda_m - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_c)\,[\text{crown}]} \tag{3}$$

where

$$[\text{crown}] = C_{\text{crown}} - \frac{C_{\text{M}^+}(\Lambda_m - \Lambda_{obs})}{(\Lambda_m - \Lambda_c)} . \tag{4}$$

Here, Λ_m is the molar conductance of metal ion before addition of crown ether, Λ_{obs} the molar conductance of solution during titration, Λ_c the molar conductance of the complexed metal ion, C_{crown} the analytical concentration of crown ether added and C_{M^+} the analytical concentration of metal perchlorate. Upon rearrangement of Equation (4)

$$K_f\,[\text{crown}]^2 + (1 + K_f C_\text{M} + -K_f C_{\text{crown}})\,[\text{crown}] - C_{\text{crown}} = 0 \tag{5}$$

For the evaluation of the formation constants from molar conductance vs. mole ratio data, a nonlinear least-squares curve fitting program, KINFIT, was used [21]. The program is based on the iterative adjustment of the calculated values of the molar conductance to the observed values and the adjustable parameters are K_f and Λ_c. The free crown ether concentration was calculated from Equation (5) by means of a Newton–Raphson procedure. Once the value [crown] had been obtained, the molar conductance was calculated by using the estimated values of K_f and Λ_c at the current step of the program. Refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of the molar conductance for all experimental points is minimized. The output of the program comprises refined parameters, the sum-of-squares and the standard deviation of the data.

3. Results and Discussion

In order to evaluate the effect of adding crown ethers on the molar conductance of thallium and silver perchlorates in AN, AC and DMF solutions, the conductivity at a constant salt concentration (1.0×10^{-4} M) was monitored while increasing the crown ether concentration at 25°C. The corresponding molar conductance vs. crown ether/metal ion mole ratio plots are shown in Figures 1–4. In the case of silver
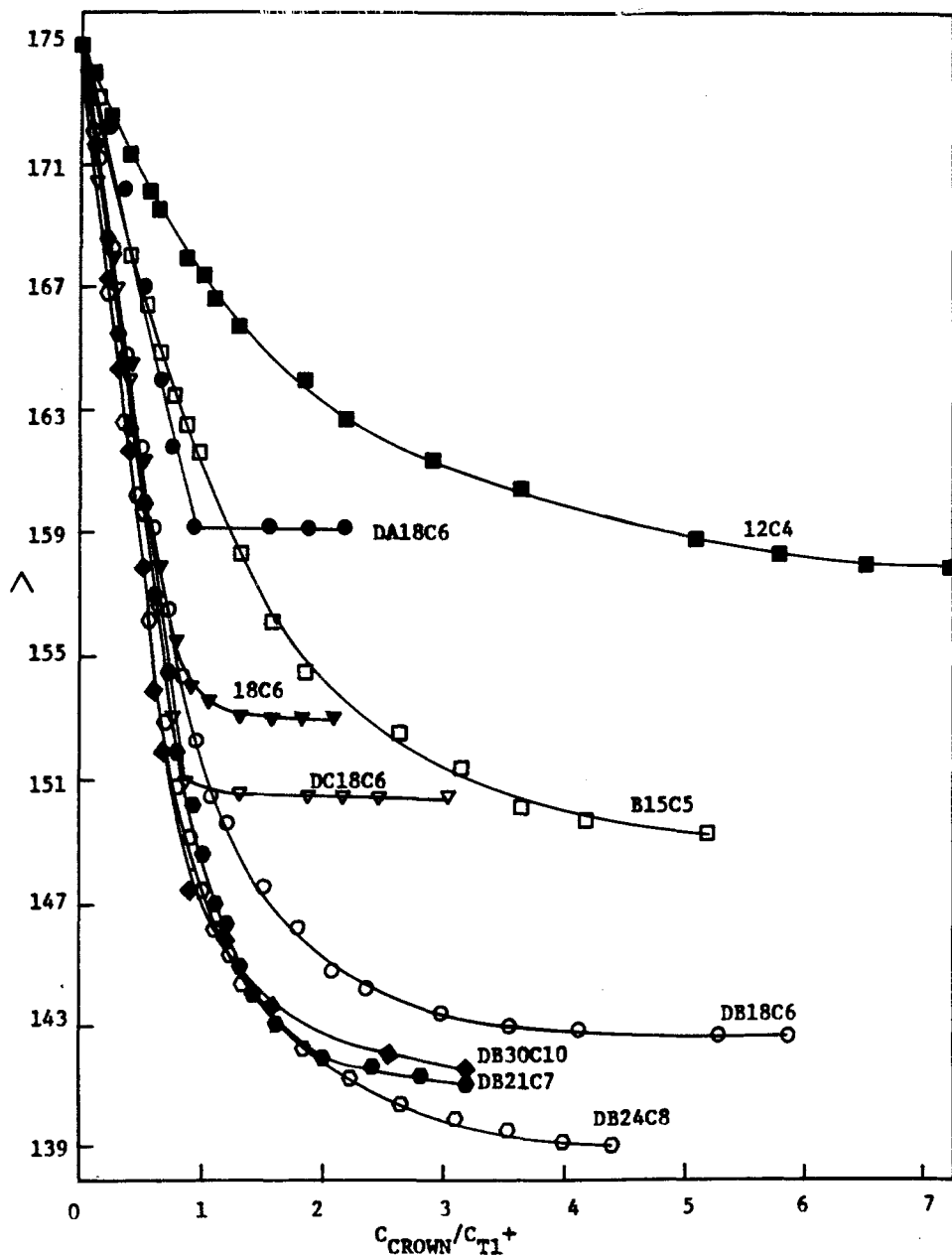
Fig. 1.   Molar conductance vs. C_{crown}/C_{Tl^+} curves in acetonitrile solution.

perchlorate solution in AN, addition of the crown ethers to the solution caused no significant change in the molar conductance of the salt, even at ligand/silver ion mole ratios of 10. This behavior is probably a result of the very strong solvation of Ag^+ ion by acetonitrile molecules [22–24] which strongly compete with the
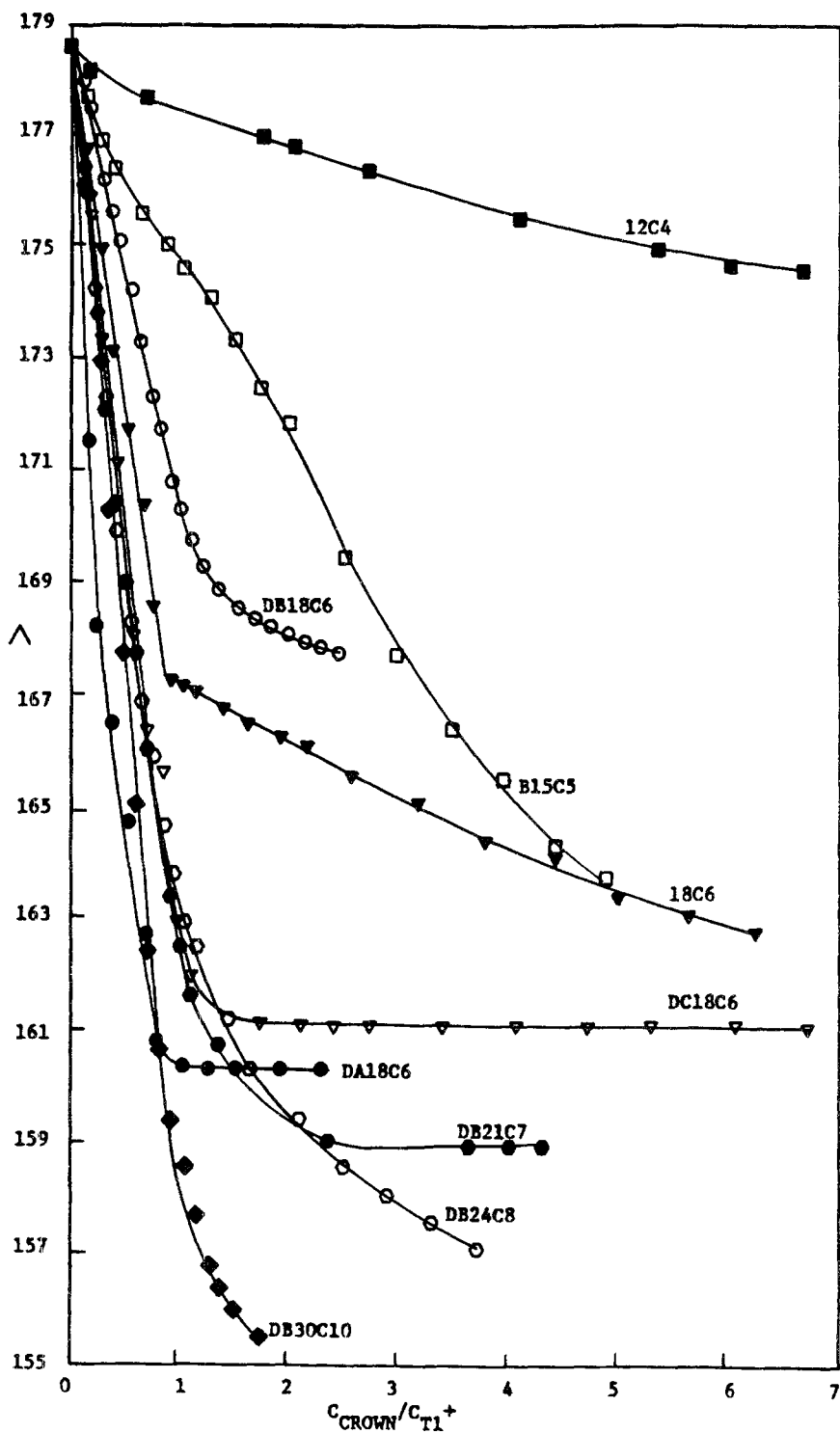
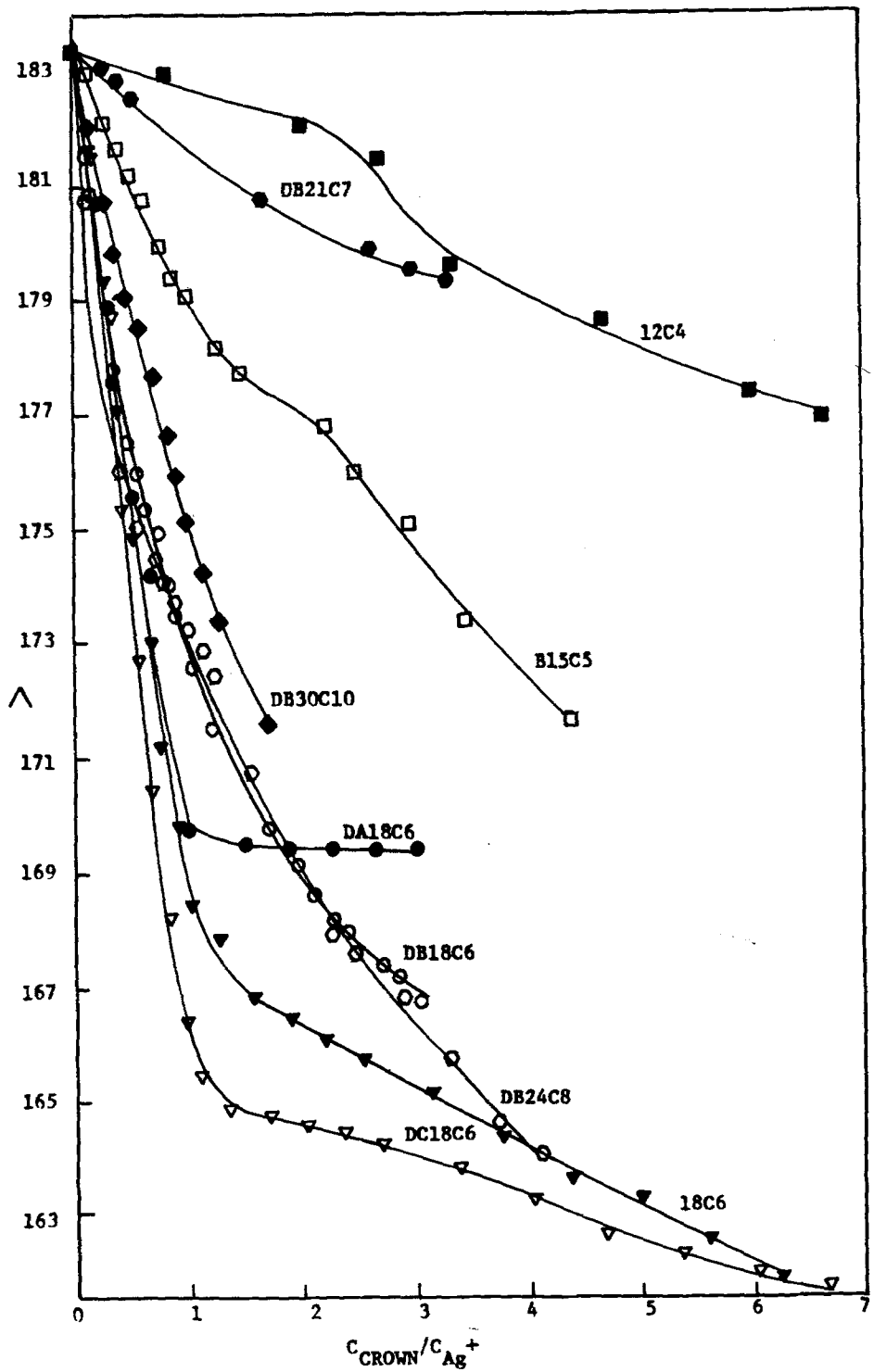Fig. 2.   Molar conductance vs. C_{crown}/C_{Tl^+} curves in acetone solution.

Fig. 3. Molar conductance vs. C_{crown}/C_{Ag^+} curves in acetone solution.
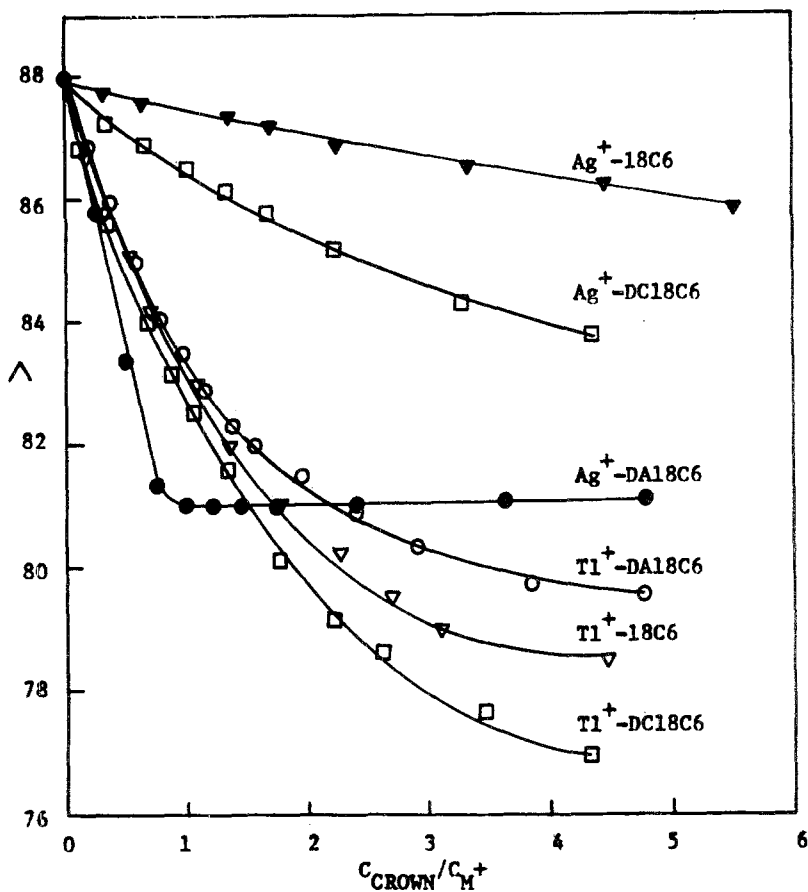
Fig. 4. Molar conductance vs. C_{crown}/C_{M^+} curves for different Tl^+–crown and Ag^+–crown systems in dimethylformamide solution.

macrocyclic ligands for the cation resulting in weak Ag^+–crown ether interactions. Thus it is not surprising to observe no significant change in the conductance of silver perchlorate solution in AN during the titration with crowns.

In all other cases studied, however, addition of crown ethers to the metal ion solutions causes a rather large and continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the complexed cations compared to the free ones. As can be seen from Figures 1–4, in some metal ion–ligand systems such as Tl^+–18C6, Tl^+–DC18C6, Tl^+–DA18C6, Ag^+–DC18C6 and Ag^+–DA18C6, in all three solvents used, the slope of the corresponding molar conductance-mole ratio plots changes sharply at the point where the ligand to cation mole ratio is one and further addition of the ligand causes no significant change in the molar conductance. Such a conductance behavior is indicative of the formation of a fairly stable 1 : 1 complex in solution. In the other cases, the observed gradual decrease in molar
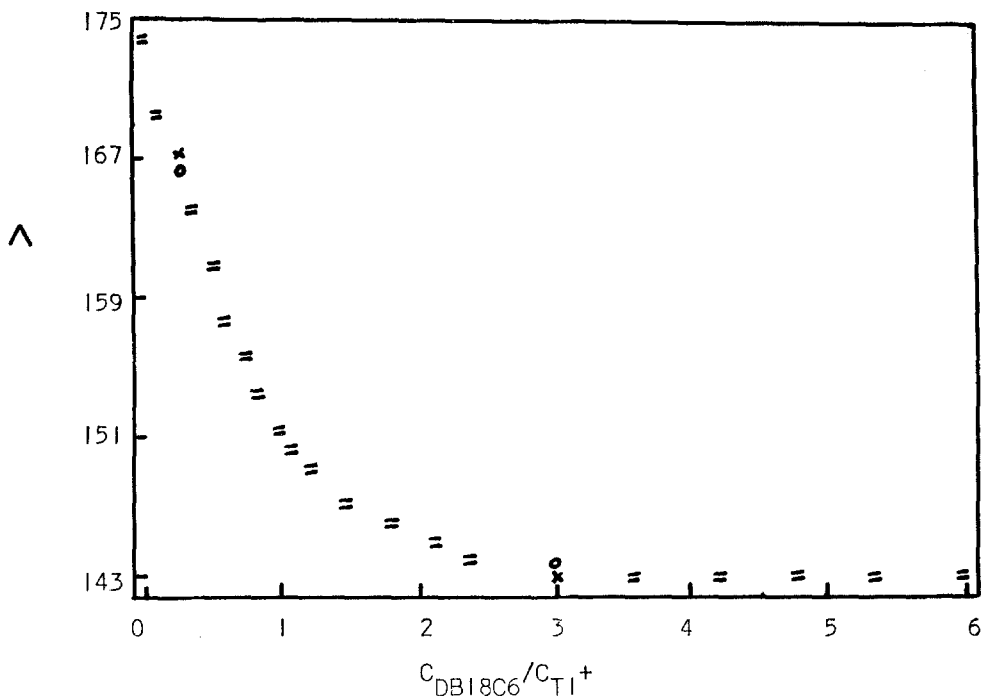
Fig. 5. Computer fit of molar conductance–mole ratio data for Tl$^+$–DB18C6 system in acetonitrile solution: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

conductance of salt solutions does not exhibit any significant change in slope at a mole ratio of about one and, in some cases, the mole ratio plots would not tend to level off even at mole ratios of 6, emphasising the formation of weaker 1 : 1 complexes.

The stability constants of the resulting 1 : 1 complexes were determined by the computer fitting of Equations (3) and (5) to the molar conductance–mole ratio data. A sample computer fit of the resulting mole ratio data is shown in Figure 5. The assumed 1 : 1 stoichiometry for the resulting complexes seems reasonable in the light of the fair agreement between the observed and calculated molar conductances.

It should be noticed that, in the procedure for the calculation of stability constants, the ion pairing between Tl$^+$ and Ag$^+$ ions and the bulky ClO$_4^-$ anion was not considered under the highly dilute experimental conditions used (1.0×10^{-4} M). Furthermore, since the concentration of crown ethers was kept below 1.0×10^{-3} M during the conductometric titrations, the corrections for viscosity changes were also neglected. All the calculated formation constants are summarized in Table I. The previously reported stability constants are also included. Comparison of the values obtained in this study with those reported in the literature (and obtained by different

TABLE 1. Stability constants of Tl$^+$ and Ag$^+$ complexes with different crown ethers in acetonitrile, acetone and dimethylformamide solutions at 25°C.

Crown ether	log K_f				
	Tl$^+$			Ag$^+$	
	AN	AC	DMF	AC	DMF
12C4	4.01 ± 0.02	3.12 ± 0.13	–	–	–
B15C5	4.21 ± 0.04	2.90 ± 0.12	< 2	3.50 ± 0.03	< 2
18C6	5.39 ± 0.07	4.99 ± 0.14	3.75 ± 0.03	4.79 ± 0.09	2.64 ± 0.25
	5.81[a]	> 5[b]	3.73[c]		
DB18C6	4.87 ± 0.02	4.73 ± 0.11	< 2	4.52 ± 0.02	< 2
	4.90[b]				
DC18C6	> 6.5	6.23 ± 0.21	3.52 ± 0.03	5.38 ± 0.14	3.03 ± 0.06
	7.40[d]		3.30[e]		
DA18C6	> 6.5	> 6.5	3.83 ± 0.03	> 6.5	> 6.5
	7.0[a]	> 5.5[a]	3.55[b]		9.91[f]
DB21C7	5.28 ± 0.04	5.07 ± 0.08	–	3.15 ± 0.02	< 2
	> 5[g]	4.71[g]		2.93[h]	
DB24C8	5.13 ± 0.06	4.90 ± 0.07	–	4.20 ± 0.11	< 2
	4.80[d]	4.15[d]			1.55[h]
DB30C10	5.66 ± 0.22	5.39 ± 0.12	–	3.53 ± 0.14	< 2
	5.60[d]				1.60[h]

[a] Ref. 34. [b] Ref. 35. [c] Ref. 37. [d] Ref. 36. [e] Ref. 39. [f] Ref. 38. [g] Ref. 13. [h] Ref. 24.

techniques) in most cases show a satisfactory agreement.

Table I immediately shows that the nature of solvents plays a very fundamental role in the complexation reactions. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents, as expressed by the Gutmann donor number (DN) [25]. Acetonitrile is the solvent with a lower donicity $(DN = 14.1)$ than acetone $(DN = 17.0)$ and dimethylformamide $(DN = 26.6)$ and, therefore, shows less competition with the crown ethers for Tl$^+$ ion which in turn results in the more stable Tl$^+$–crown complexes in the series. A similar solvent effect is also observed for Ag$^+$–crown ether complexes in AC and DMF solutions. However, the silver perchlorate–AN system shows an exceptional behavior, as discussed in the previous paragraphs. The same kind of solvent effect on the complexation of different metal ions with macrocyclic ligands has been reported previously [10,13,17,26,27].

As can be seen from Table I, in all three solvents used, the stabilities of Tl$^+$ complexes with different crown ethers vary in the order DA18C6 > DC18C6 > DB30C10 > 18C6 > DB21C7 > DB24C8 > DB18C6 > B15C5 > 12C4, while those of Ag$^+$ complexes in AC and DMF solutions decrease in the order DA18C6 DC18C6 > 18C6 > DB18C6 > DB24C8 > DB30C10 ≈ B15C5 > DB21C7.

It is well known that the relative size of the cation to crown ether cavity plays an important role in the stability and selectivity of the resulting complexes [2,3]. From the results, it is obvious that the ionic sizes of Ag^+ (2.3 Å) and, especially, Tl^+ (3.0 Å) [9] match best the cavity size of 18C6 (2.3–3.2 Å) [28] so that the resulting complexes with this ligand and its diaza- and dicyclohexyl substituents are the most stable one in the series. However, the Tl^+ ion seems to have a better fit for the cavity of 18-crowns and, therefore, forms more stable complexes with these ligands than the Ag^+ ion. On the other hand, the cavities of 12C4 and B15C5 are too small for both cations resulting in much less stable complexes than with 18-crowns. However, because of a better size matching, the Ag^+–B15C5 complex is more stable than Tl^+–B15C5 in acetone solution.

Comparison of the data given in Table I reveals that among the 18-crowns used, where the ring frame remains the same, the stabilities of the resulting complexes with both Tl^+ and Ag^+ ions vary in the order DA18C6 > DC18C6 > 18C6 > DB18C6. The substitution of two oxygen atoms by two nitrogens in the 18C6 macrocyclic ring increases the stability of the complexes significantly. These results are not unexpected since both Tl^+ and Ag^+ ions as soft acids [8] would interact more strongly with nitrogen atoms of the ring as soft bases. Also the presence of two cyclohexyl groups on 18C6 can pump electrons into the ligand ring and thus increase the basicity of the donating oxygen atoms, while the flexibility of the macrocycle remains more or less the same as 18C6. Thus it is not unexpected to observe increased stability of the DC18C6 complexes compared with 18C6.

The effect of substitution of two benzo groups on the 18C6 ring is to markedly lower the stability of Tl^+ and Ag^+ complexes. It should be noticed that the introduction of two electron withdrawing benzo groups reduces the donicity of oxygen atoms in the ring and hence reduces the cation-crown interactions. On the other hand, DB18C6 is a more rigid molecule than 18C6, so that the existence of two bulky benzo groups on the ring of 18C6 would prevent the macrocyclic molecule wrapping itself around the cation. Combination of these two factors causes a drastic decrease in the stability of Tl^+ and Ag^+ complexes with DB18C6 in comparison with corresponding 18C6 complexes.

It should be noted, however, that the 'ion-in-the-hole' model [2] has limited usefulness in predicting the stability of the metal ion complexes with large crown ethers (i.e. larger than 18C6). It is well known that large crown ethers are flexible enough to twist around a cation of suitable size (e.g. K^+ ion with DB30C10) and form a three-dimensional 'wrap around' structure in which all oxygen atoms of the ring participate in bond formation [10,13,17,26,29–32].

The data obtained in this study show that the stability of large crown complexes with Tl^+ ion vary in the order DB30C10 > DB21C7 > DB24C8, while that of Ag^+– large crown complexes decrease in the order DB24C8 > DB30C10 > DB21C7. In the case of thallium complexes, the cation is such that it can neither have a comfortable fit inside the cavity of DB21C7 and DB24C8 nor form a proper 'wrap around' complex with these macrocycles, resulting in weak complexes. However,

Tl$^+$ ion seem to have a proper size to form a stable 'wrap around' complex with the large flexible DB30C10 molecule in which all ten oxygen atoms may participate in bond formation with the central cation [17,33]. It is interesting to note that, the resulting Tl$^+$–DB30C10 complex is even more stable than Tl$^+$–18C6 in AN and AC solutions.

On the other hand, in the case of Ag$^+$–DB30C10, with the cationic size smaller than the cavity size of the twisted ligand, although the ligand can still form the 'wrap around' structure, the oxygen atoms of the ring will have to be in close proximity and, therefore, the resulting repulsive forces will weaken the complex. The case of Ag$^+$–DB21C7 is even worse; the resulting complex could have neither a suitable 'ion-in-the-hole' position, nor a complete 'wrap around' structure and, hence, the resulting complex is the weakest in the series. The ionic size of Ag$^+$ seems to be suitable to form a stable three-dimensional structure with DB24C8. Evidence for the formation of such a 'wrap around' complex between Na$^+$ ion, with about the same ionic size as Ag$^+$ ion, has been reported in the literature [13,40].

Acknowledgement

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