



Conductance Study of the Thermodynamics of Binding of Some Macrocyclic Polyethers with Tl^+ Ion in Dimethylformamide-Acetonitrile Mixtures

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(Received: 22 March 2002; in final form 19 July 2002)

Key words: Tl^+ complexes, crown ethers, conductance, stability, enthalpy, entropy, mixed solvent

Abstract

The complexation reactions between Tl^+ ion and dibenzo-30-crown-10 (DB30C10), dibenzo-24-crown-8 (DB24C8), dibenzo-21-crown-7 (DB21C7), and aza-18-crown-6 (A18C6) were studied in different dimethylformamide-acetonitrile mixtures at various temperatures. The formation constants of the resulting 1 : 1 complexes were determined from the molar conductance-mole ratio data and found to vary in the order $A18C6 > DB30C10 > DB21C7 > DB24C8$. The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constants.

Introduction

It is well known that several factors influence the formation of crown ether complexes of metal ions in solution [1–3]. The most emphasized factor is the crown's cavity size-cation diameter ratio although its importance has been questioned in the case of large crown ethers [1, 2]. Actually, large crown ethers (i.e. larger than 18-crown-6) possess highly flexible geometries in solution, and adapt their conformations for optimum complexation of guest cations. Thus, evidence for the formation of tridimensional 'wrap-around' complexes between large crown ethers and some alkali metal ions both in the solid state [4, 5] and in solution [6–9] have been reported in the literature. Other important factors include the number and the nature of heteroatoms 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 [1–3, 7,9].

It was of interest to us to study the influence of cation size (and nature) and solvent properties on the interactions of metal ions with large crown ethers [7, 10–13]. Due to the special importance of Tl^+ as a polarizable soft cation in biological and environmental processes [14, 15], we decided to study the thermodynamics of complexation of Tl^+ ion with aza-18-crown-6 (A18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8), and dibenzo-30-crown-10 (DB30C10) in binary dimethylform-

amide (DMF)-acetonitrile (AN) mixtures. The structures of the ligands are shown in Figure 1.

Experimental

Reagent-grade thallium nitrate, DB21C7 and A18C6 (Fluka) were of the highest purity available and used as received. Reagent-grade DMF and AN (both from Merck) were purified and dried as described elsewhere [16]. The conductivities of the solvents were less than $1.0 \times 10^{-7} \text{ S-cm}^{-1}$. All the DMF-AN mixtures were prepared by weight. Crown ethers DB24C8 and DB30C10, both from (Fluka), were purified and dried using the previously reported methods [9, 11, 12].

Conductance measurements were carried out with a Metrohm 712 conductometer. A dip-type conductivity cell made of platinum black was used. The cell constant at the different temperatures used was determined by measuring the conductivity of a $1 \times 10^{-2} \text{ mol-dm}^{-3}$ solution of analytical-grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures have been reported in the literature [17]. In all measurements, the cell was thermostated at the desired temperature $\pm 0.03 \text{ }^\circ\text{C}$ using a MLW thermostat-circulator water bath.

In a typical experiment 10 mL of a desired thallium nitrate solution ($1.0 \times 10^{-4} \text{ M}$) was placed in the titration cell, thermostated to the desired temperature and the conductance of solution was measured. Then, a known amount of the concentrated crown ether solution 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.

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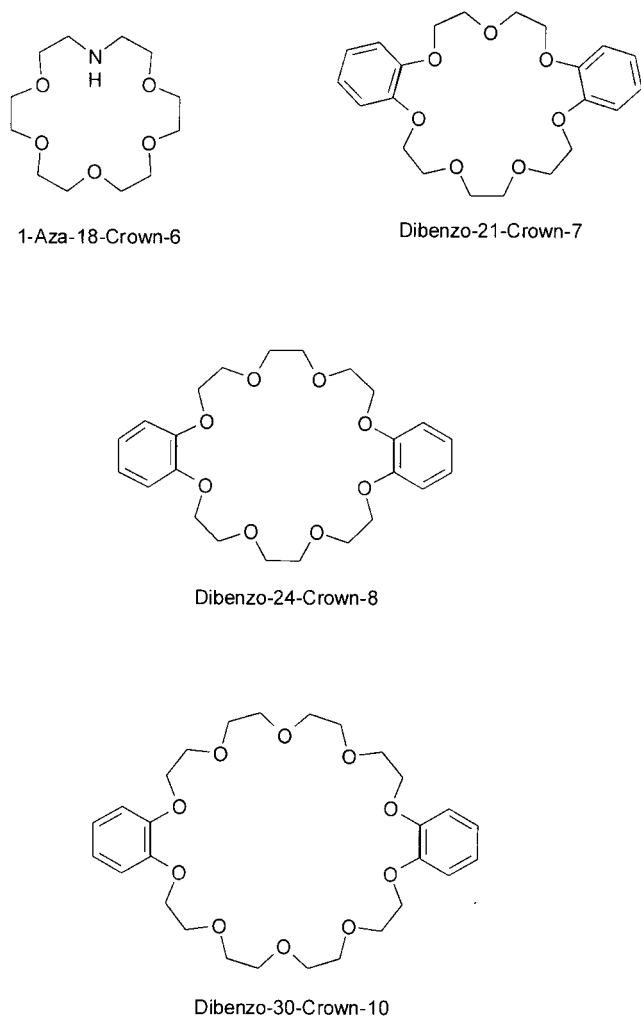


Figure 1. Structures of the macrocyclic ligands used.

Results and discussion

The molar conductance, Λ , of TlNO_3 (1.0×10^{-4} M) in four different DMF-AN mixtures was monitored as a function of crown ether to metal ion mole ratio at various temperatures. The resulting molar conductance vs. crown/cation mole ratio plots at 15.0, 25.0, 35.0 and 45.0 °C are shown in Figures 2 and 3. In every case, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates that the complexed thallium is less mobile than the corresponding solvated Tl^+ ion.

As can be seen from Figures 2 and 3, in some cases such as the complexation of Tl^+ ion with A18C6, addition of the ligand to the metal 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. However, in the case of the other crown ethers used, the decrease in molar conductance of the thallium nitrate solution upon addition of the macrocycles exhibit neither any considerable change in the slope at the mole ratio of about one, nor any tendency for leveling off even at a mole ratio of 3, emphasizing the formation of weaker complexes.

By comparison of the molar conductance-mole ratio plot for all Tl^+ -A18C6 systems obtained at different temperat-

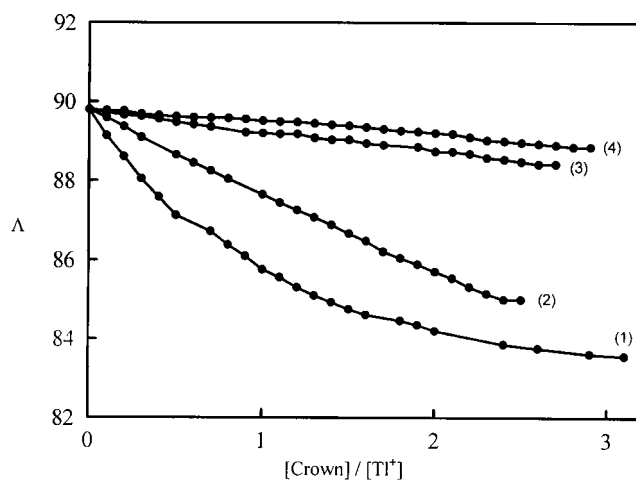


Figure 2. Molar conductance vs. $[\text{crown}]/[\text{Tl}^+]$ for various crown- Tl^+ systems in 60% DMF: (1) A18C6; (2) DB30C10; (3) DB21C7; (4) DB24C8.

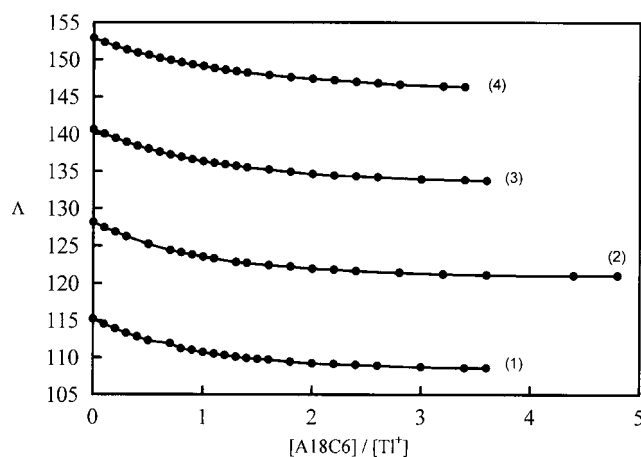


Figure 3. Molar conductance vs. $[\text{A18C6}]/[\text{Tl}^+]$ plots in 80% DMF at different temperatures: (1) 15 °C; (2) 25 °C; (3) 35 °C; (4) 45 °C.

ures (Figure 3), two trends were observed which deserve attention. First, as expected, the corresponding molar conductance increased rapidly with temperature, due to the decreased viscosity of the solvent and, consequently, the enhanced mobility of the charged species present. Secondly, for each cation used, the curvature of the corresponding mole ratio plot decreased with increasing temperature, indicating the formation of weaker complexes at elevated temperatures.

The 1 : 1 complexation of Tl^+ ion with various crown ethers can be expressed by the following equilibrium



The corresponding equilibrium constant, K_f is given by

$$K_f = \frac{[MC^+]}{[M^+][C]} \times \frac{f(MC^+)}{f(M^+)f(C)}, \quad (2)$$

where $[MC^+]$, $[M^+]$, $[C]$ and f represent the equilibrium molar concentrations of the complex, free cation, free ligand and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, the activity

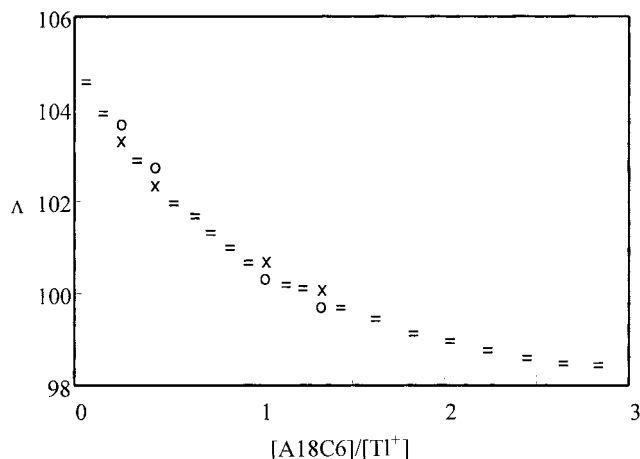


Figure 4. Computer fit of the molar conductance-mole ratio data for the A18C6-Tl⁺ system in 100% DMF at 25 °C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

coefficient of uncharged macrocycle, $f(C)$, can be reasonably assumed as unity [18, 19]. The use of the Debye-Hückel limiting law [20], leads to the conclusion that $f(M^+) \sim f(MC^+)$, so the activity coefficients in Equation (2) cancel.

The complex formation constant in terms of the molar conductances, Λ , can be expressed as [21, 22]

$$K_f = \frac{[MC^+]}{[M^+][C]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{MC})[C]}, \quad (3)$$

where

$$[C] = C_C - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{MC})}. \quad (4)$$

Here, Λ_M is the molar conductance of the metal ion before addition of ligand, Λ_{MC} the molar conductance of the complexed ion, Λ_{obs} the molar conductance of the solution during titration, C_C the analytical concentration of the macrocycle added and C_M the analytical concentration of the salt. The complex formation constant, K_f , and the molar conductance of the complex, Λ_{MC} , were evaluated by computer fitting of Equations (3) and (4) to the molar conductance-mole ratio data using a non-linear least-squares program KINFIT [23]. Sample computer fits of the mole ratio data for the Tl⁺-A18C6 system are shown in Figure 4. Our assumption of 1:1 stoichiometry for the resulting complexes of Tl⁺ ion was further supported by excellent agreement between the observed and calculated molar conductances in the process of computer fitting of the mole ratio data. It is noteworthy that, in the process of calculation of formation constants, the association between Tl⁺ and NO₃⁻ ions was considered negligible under the highly dilute experimental conditions used (1.0×10^{-4} M) [24]. Since the concentration of macrocycles was kept below 5.0×10^{-4} M during the experiments, correction for the viscosity changes was also neglected.

In order to have a better understanding of the thermodynamics of the complexation reactions of Tl⁺ ion with the crown ethers used it is useful to consider the enthalpic and

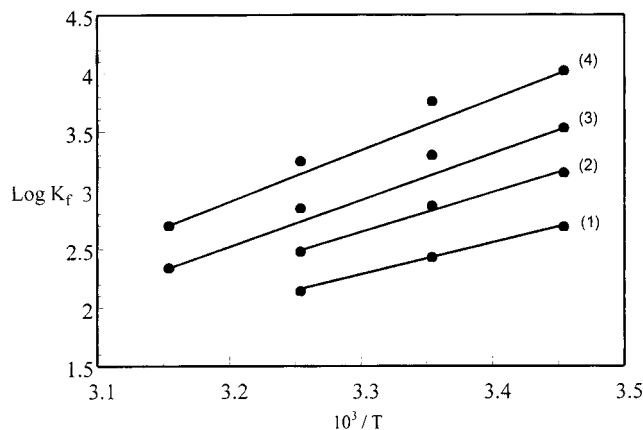


Figure 5. $\log K_f$ vs. $1/T$ for the 1:1 complexation of Tl⁺ with DB30C10 in different DMF-AN solvents: (1) pure DMF; (2) 80% DMF; (3) 60% DMF; (4) 40% DMF.

entropic contributions to these reactions. The ΔH° and ΔS° values for the complexation reactions were evaluated from the corresponding $\log K_f$ and temperature data by applying a linear least-squares analysis according to the equation:

$$2.303 \log K_f = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (5)$$

Plots of $\log K_f$ vs. $1/T$ for the different Tl⁺ macrocycle systems were linear for all cases studied (Figure 5). The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots and the results are also included in Table 1.

The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the Tl⁺ – macrocycle complexation reactions studied. In all cases, the stability of the resulting complexes increases rapidly with increasing weight percent of AN in the solvent mixture. It is known that the solvating ability of the solvent, as expressed by the Gutmann donor number [25], plays an important role in different complexation reactions [26–35]. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents. Acetonitrile has a lower donicity (DN = 14.1) than dimethylformamide (DN = 26.6) and, therefore, shows less competition with the crown ether for Tl⁺ ion which in turn results in the more stable Tl⁺ – crown complexes. Thus, it is not unexpected to observe that addition of acetonitrile to DMF will increase the stability of the complexes.

From the data given in Table 1 it is immediately obvious that, in all the solvent mixtures used, the Tl⁺ complex with A18C6 is much more stable than that with the dibenzo-substituted large crown ethers used. It is well known that the substitution of one of the oxygen atoms in the 18C6 macrocyclic ring with NH groups increases the stability of Tl⁺ complexes significantly. The thallium ion, as a soft acid, would interact more strongly with the donating soft bases, the nitrogen atom, as compared to the interaction with the oxygen atoms as hard bases [36]. On the other hand, the addition of two benzo groups to the macrocyclic ring lowers the stability of the Tl⁺ complexes markedly. This beha-

Table 1. Formation constant values of Tl^+ -ion complexes with several crown ethers in various DMF-AN mixtures at different temperatures^a

Crown ether	wt% DMF in solvent mixture ^b	$\log K_f$				ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
		15 °C	25 °C	35 °C	45 °C		
DB24C8	100	<2	<2	<2	<2	–	–
	80	2.36 ± 0.05	2.17 ± 0.13	<2	<2	–6	–13.7
	60	3.07 ± 0.04	2.65 ± 0.05	2.27 ± 0.25	<2	–68 ± 0.4	–177 ± 1
	40	3.22 ± 0.03	2.89 ± 0.10	2.70 ± 0.10	2.39 ± 0.08	–47 ± 2	–101 ± 7
DB21C7	100	2.70 ± 0.13	2.42 ± 0.09	<2	<2	–7.8	–18.9
	80	2.83 ± 0.06	2.55 ± 0.09	2.13 ± 0.20	<2	–59 ± 5	–151 ± 19
	60	3.18 ± 0.04	2.84 ± 0.04	2.65 ± 0.06	2.38 ± 0.14	–45 ± 2	–97 ± 7
	40	3.54 ± 0.02	3.29 ± 0.02	3.05 ± 0.04	2.69 ± 0.09	–48 ± 3	–101 ± 10
DB30C10	100	2.74 ± 0.04	2.48 ± 0.07	2.19 ± 0.18	<2	–46 ± 1	–109 ± 5
	80	3.17 ± 0.04	2.92 ± 0.06	2.53 ± 0.11	<2	–54 ± 5	–127 ± 18
	60	3.58 ± 0.03	3.35 ± 0.03	2.90 ± 0.03	2.39 ± 0.15	–70 ± 6	–173 < 22
	40	4.06 ± 0.04	3.81 ± 0.03	3.30 ± 0.04	2.75 ± 0.12	–77 ± 7	–189 < 24
A18C6	100	4.40 ± 0.01	4.30 ± 0.01	3.99 ± 0.01	3.89 ± 0.01	–32 ± 3	–27 ± 12
	80	4.61 ± 0.02	4.52 ± 0.01	4.36 ± 0.01	4.18 ± 0.01	–25 ± 2	0.9 ± 7.2
	60	4.91 ± 0.02	4.82 ± 0.02	4.74 ± 0.02	4.67 ± 0.02	–14 ± 0.1	45 ± 0.6
	40	6.15 ± 0.15	5.97 ± 0.17	5.80 ± 0.08	–	–29.7 ± 0.06	14.5 ± 0.2

^a The error associated with all thermodynamic parameters are given as ± SD.

^b The corresponding mole fractions DMF (XDMF) in the solvent mixtures are: 100%, 1.00; 80%, 0.69; 60%, 0.46; 40%, 0.27.

avior 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, thus, the decreased stability of the Tl^+ -dibenzocrowns in comparison with the Tl^+ -A18C6 is not surprising.

Comparison of the data given in Table 1 indicates that the stability of the Tl^+ complexes with the dibenzocrowns used varies in the order DB30C10 > DB21C7 > DB24C8. Although DB21C7 with a cavity size of 3.4–4.3 Å [37] provides the best fitting condition for Tl^+ ion (with an ionic size of 3.08 Å) [38], its Tl^+ complex is less stable than that with DB30C10 with the largest cavity size in the series. However, the ion-in the hole model [1] has limited usefulness in predicting the stability of the metal ion complexes of large crown ethers such as DB30C10. The increased number of ring atoms as well as the increased flexibility of the macrocyclic molecule make it difficult to define a fixed cavity diameter for the ligand. Actually, it has been shown that large crown ethers such as DB30C10 can twist around a cation of suitable size (such as K^+ , ionic size 2.86 Å) to form a tridimensional ‘wrap around’ complex in which all oxygen atoms of the ring participate in the bond formation with the central cation [4, 6, 7, 39]. Thallium ion, with about the same ionic size as the potassium ion, seems to fit properly inside the twisted DB30C10 molecule to form a rather stable ‘wrap around’ complex. DB24C8 falls between the above two cases (i.e., DB30C10 and DB21C7) and it is probable that a two-dimensional complex is formed in which only a part of the donor sites are bound to the Tl^+ ion. Thus the resulting complex would be the least stable of the four.

The thermodynamic data in Table 1 reveal that, in all cases, the complexes are enthalpy stabilized. However, depending on the nature of the macrocycle and the solvent composition, some of the complexes are entropy destabil-

ized and some are entropy stabilized. A similar behavior of the entropy of the complexation of different macrocyclic complexes has been frequently reported in the literature [1, 2]. This is due to variation in the extent of the contribution of such important parameters as solvation-desolvation of the species involved in the complexation reaction (i.e. Tl^+ ion, macrocycle and the resulting complex) as well as the conformational change of the macrocyclic crown ethers from a rather flexible structure in the free state to a rigid conformation in the complexed form.

Table 1 shows that, as expected, for all the Tl^+ -crown systems studied, the thermodynamic data vary significantly with the solvent properties [1, 2, 21]. However, in all cases, the observed increase (or decrease, depending on the nature of the macrocycle) in the ΔH° value upon addition of AN to the solvent mixture will be compensated by an increase (or decrease) in the corresponding ΔS° value. The existence of such a compensating effect between ΔH° and ΔS° values, which has been frequently reported for a variety of metal-ligand systems [18, 21, 25, 41–43], would cause the overall change in the ΔG° value of the complex to be smaller than might be expected from the change in either ΔH° or ΔS° independently.

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