Journal of Inclusion Phenomena and Macrocyclic Chemistry **39:** 109–113, 2001.

Conductance Study of the Thermodynamics of Tl^+ ion Complexes with Different 18-Membered Crown Ethers in Binary Dimethylformamide-Acetonitrile Mixtures [*]

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(Received: 20 December 1999; in final form: 15 April 2000)

Key words: Tl^+-18-crown ether complexation, conductance, stability, thermodynamics, mixed solvent

Abstract

A conductance study of the interaction between Tl^+ ion and 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), benzo-18-crown-6 (B18C6), diaza-18-crown-6 (DA18C6), dibenzyldiaza-18-crown-6 (DBzDA18C6) and hexaaza-18-crown-6 (HA18C6) in dimethylformamide-acetonitrile mixtures was carried out 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 HA18C6 > DA18C6 > DBzDA18C6 > 18C6 > DC18C6 > B18C6. The enthalpy and entropy of the complexation reactions were determined from the temperature dependence of the formation constants.

Introduction

The synthesis of macrocyclic crown ethers [1], and the discovery of their ability to form stable and selective inclusion complexes with a variety of metal ions have led to an extensive study of these ligands and their complexes [2–4]. The thermodynamics of complexation of crown ethers have been mainly studied with alkali and alkaline earth cations in water and in various nonaqueous solvents [2, 3]. However, in comparison with numerous literature reports on alkali- and alkaline earth-crown complexes, the systematic investigation of the thermodynamics of transition and heavy metal ion complexes with macrocyclic ligands in various solvents have received much less attention.

The monovalent thallium ion is a polarizable soft ion [5] with an ionic radius of 1.49 Å [6] which has been suggested as a probe for potassium ion in biological systems [7, 8]. It can substitute for K^+ in activation of some important enzymes such as ATPase [9] and pyruvate kinase [10]. Thus, information about the stability and selectivity of Tl^+ complexes with macrocyclic ligands are of special interest in this respect. It is well known that the topological features of the macrocyclic crown ethers involving the cavity size, the nature and number of donor atoms in the ring and the type of substituents on the ligand, as well as the nature of solvent play important roles in both the selectivity and stability of the resulting macrocycle-metal ion complexes [2, 3]. Since the ionic size of Tl^+ ion matches best the cavity of 18-crowns (2.8-3.2 Å) [11], in this work, we decided to study the influence of different substituents on the 18-crown-6 macrocyclic ring and the solvent properties on the thermodynamics of the corresponding thallium ion complexes.

In recent years, we have employed conductance measurements as a sensitive and powerful technique to study the complexation of macrocyclic ligands with different cations in a variety of nonaqueous and mixed solvents [12–20]. In this paper we report a conductance study of the thermodynamics of Tl^+ ion complexes with 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), benzo-18-crown-6 (B18C6), diaza-18-crown-6 (DA18C6), dibenzyldiaza-18-crown-6 (DBzDA18C6) and hexaaza-18-crown-6 (HA18C6) in binary dimethylformamide (DMF)-acetonitrile (AN) mixtures. The structures of the crown ethers used are shown in Figure 1.

Experimental

Reagent-grade thallium nitrate, HA18C6 and DBzDA18C6 (all from Fluka) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. 18C6, DC18C6, B18C6 and DA18C6 (all from Fluka) were purified and dried by the previously reported methods [20]. Reagent-grade DMF and AN (both from Merck) were purified and dried as described elsewhere [21]. The conductivities of the solvents were less than 1.0×10^{-7} S cm^{-1}. All the DMF-AN mixtures were prepared by weight.

Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type conductivity cell made of platinum black was used. The cell constant at the different temperatures used was determined by measuring

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[*] **Supplementary Data** relevant to this article have been deposited with the British Library as Supplementary Publication No. 82286 (7 pages).

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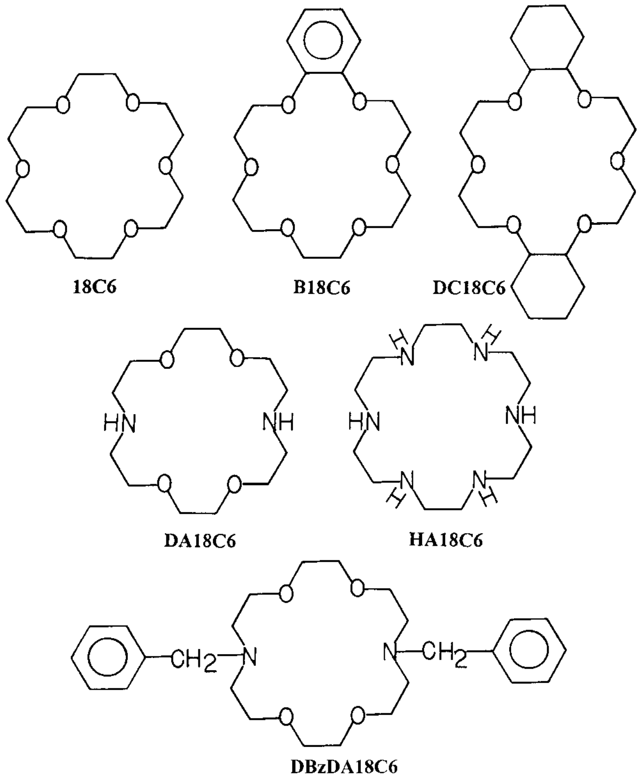

Figure 1. Structures of the macrocyclic ligands.

the conductivity of a 0.010 M 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 [22]. The corresponding cell constant at 5.0, 15.0, 25.0, 35.0 and 45.0 °C were 0.840, 0.834, 0.832, 0.829 and 0.820 cm^{-1}, respectively. In all measurements, the cell was thermostated at the desired temperature ± 0.03 °C using a MLW thermostat. Errors associated with the measured conductivities were estimated to be at the most 1.5%.

In a typical experiment, 10 mL of the desired thallium nitrate solution (1.00×10^{-4} M) was placed in the titration cell, thermostated to the desired temperature and the conductance of the 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.

The formation constants, K_f, and the limiting molar conductances, Λ_o, of the resulting 1 : 1 complexes between the macrocycles used and Tl^+ ion in different DMF-AN mixtures at various temperatures were calculated by fitting the observed molar conductances Λ_{obs} at various macrocycle/Tl^+ mole ratios to the previously derived equations [23] which express the Λ_{obs} as a function of the free and complexed metal ions and the formation constant by using a nonlinear least-squares program KINFIT [24]. The details are described elsewhere [12–20].

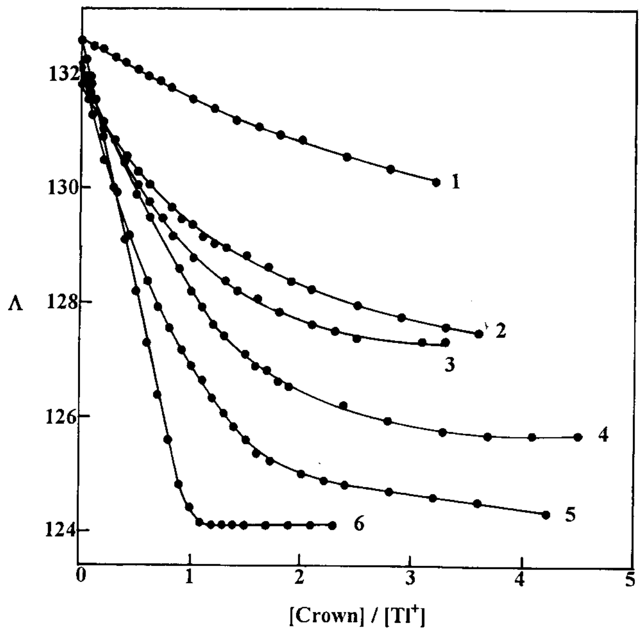

Figure 2. Molar conductance vs [crown]/[Tl^+] for various crown-Tl^+ systems in 60% DMF: (1) B18C6; (2) 18C6; (3) DA18C6; (4) DC18C6; (5) DBzDA18C6; (6) HA18C6.

Results and discussion

The molar conductance of TlNO_3 (1.00×10^{-4} M) in four different DMF-AN mixtures was monitored as a function of 18-crown to metal ion mole ratio at various temperatures. Some of the resulting molar conductance vs. macrocycle/Tl^+ mole ratio plots are shown in Figures 2 and 3. In all cases, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior shows that the complexed thallium is less mobile than the solvated Tl^+ ion. As seen from Figures 2 and 3, in some cases such as the complexation of Tl^+ ion with HA18C6, addition of the ligand to a metal ion 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 some other cases such as the Tl^+-B18C6 system, although the molar conductance does not show any tendency for leveling off even at a molar ratio of about 4, the corresponding mole ratio data show a considerable change in their slopes at a mole ratio of about one, emphasizing the formation of some weaker 1 : 1 complexes.

In order to have a clearer picture of the thermodynamics of the complexation of Tl^+ with the 18-crown macrocycles used, it is useful to investigate the enthalpic and entropic contributions to these reactions. The $\Delta H°$ and $\Delta S°$ of the complexation reactions in different DMF-AN mixtures were evaluated from the temperature dependence of the formation constants by applying a linear least-squares analysis according to the equation:

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

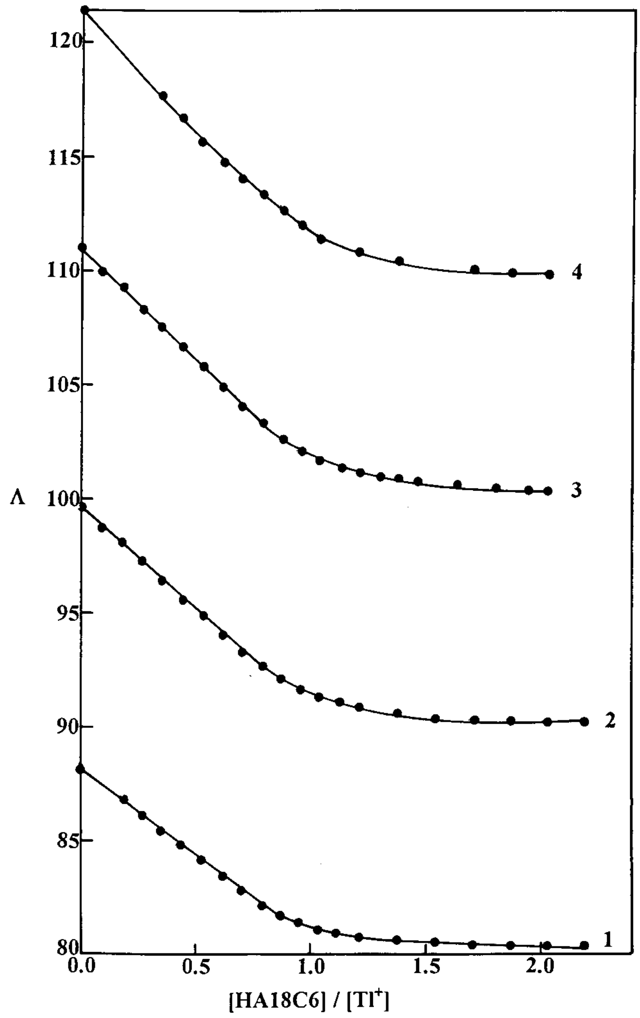

Figure 3. Molar conductance vs [HA18C6]/[Tl$^+$] plots in 100% DMF at different temperatures: (1) 15 °C; (2) 25 °C; 35 °C; (4) 45 °C.

The formation constants of all Tl$^+$-18-crown complexes in different solvent mixtures at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data, are summarized in Table 1.

The formation constants for the Tl$^+$ complexes with aza-substituted crown ethers in the solvent mixtures of higher AN content are not reported, mainly due to the high values of their formation constants (i.e., $K_f > 10^6$) which cannot be accurately evaluated by the curve fitting program KINFIT [13, 25]. A sample computer fit of the mole ratio data is shown in Figure 4. Our assumption of 1 : 1 stoichiometry seems reasonable in the light of the fair agreement between the observed and calculated molar conductances. It is noteworthy that, in the process of calculation of formation constants, the association between Tl$^+$ and NO_3^- ions was considered negligible, under the highly dilute experimental conditions used (1.0×10^{-4} M) [26]. 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 accordance with Equation (1), the plot of $\log K_f$ vs. $1/T$ for different Tl$^+$-macrocycle complexes was linear for all cases studied. The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively. The resulting ΔH° and $\Delta S°$ values are also included in Table 2.

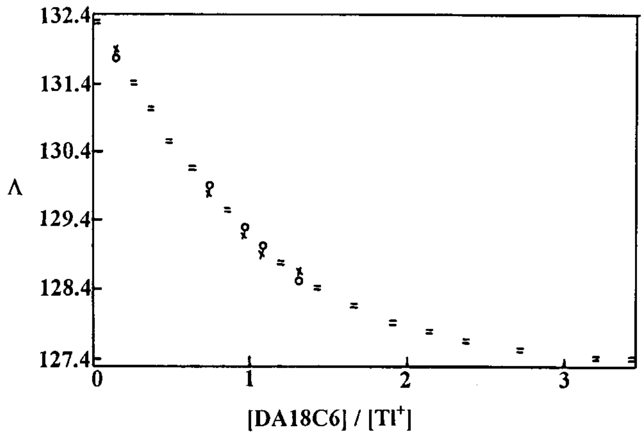

Figure 4. Computer fit of the molar conductance-mole ratio data for the DA18C6-Tl$^+$ system at 25 °C in 60% DMF; (×) experimental point; (○) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the Tl$^+$-18-crown 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 [27], plays an important role in different complexation reactions [12–21, 25]. There is actually an inverse relationship between the stability of the complexes and the solvating ability of the solvents. DMF is a solvent of high solvating ability (DN = 26.6) 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 DMF will increase the stability of the complexes.

Comparison of the data given in Table 1 reveals that the stability of the resulting Tl$^+$-macrocycle complexes varies in the order HA18C6 > DA18C6 > DBzDA18C6 > 18C6 > DC18C6 > B18C6. The results indicate that among different 18-membered crown ether derivatives used, where the ring frame remains the same, the Tl$^+$ ion interaction as well as the thermodynamic parameters depends significantly on the nature of the substituents on the ring, which control both the electron-pair donicity and the flexibility of the ligand molecules, and the nature of donating atoms, as well as the properties of the solvent mixtures used.

The substitution of all or some 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 atoms, as compared to the interaction with the oxygen atoms as hard bases [5]. On the other hand, the increased stability of the Tl$^+$ complex with DA18C6 over that with DBzDA18C6 originates from its favorable entropic term. The highly negative $\Delta S°$ values obtained from the Tl$^+$-DBzDA18C6 system seem to reflect a pronounced

Table 1. Formation constants and enthalpy and entropy values for different Tl^+-18-crown-6 complexes in various DMF-AN mixtures[a]

Crown ether	wt% DMF in solvent mixture[b]	log K_f					ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
		5 ° C	15 °C	25 °C	35 ° C	45 ° C		
18C6	100	–	3.98 ± 0.06	3.82 ± 0.02	3.66 ± 0.02	3.34 ± 0.06	−27.2 ± 0.4	−18 ± 1
	80	–	4.05 ± 0.05	3.87 ± 0.04	3.71 ± 0.04	3.60 ± 0.04	−26 ± 1	−15 ± 3
	60	–	4.21 ± 0.02	4.07 ± 0.04	3.93 ± 0.03	3.87 ± 0.05	−20 ± 1	9 ± 5
	40	4.80 ± 0.06	4.73 ± 0.04	4.60 ± 0.04	–	- -	−17 ± 2	33 ± 8
DC18C6	100	–	3.68 ± 0.02	3.53 ± 0.03	3.32 ± 0.03	3.21 ± 0.02	−28 ± 1	−28 ± 5
	80	–	3.96 ± 0.07	3.79 ± 0.03	3.60 ± 0.02	3.46 ± 0.02	−29.6 ± 0.7	−27 ± 2
	60	–	4.69 ± 0.03	4.49 ± 0.04	4.38 ± 0.03	4.25 ± 0.03	−25 ± 1	2 ± 5
	40	5.36 ± 0.07	5.20 ± 0.04	5.03 ± 0.05	4.74 ± 0.03	–	−33 ± 3	−16 ± 10
B18C6	100	–	2.87 ± 0.03	2.76 ± 0.08	2.58 ± 0.10	–	−25 ± 3	−30 ± 9
	80	–	3.20 ± 0.04	3.03 ± 0.08	2.85 ± 0.07	- -	−30 ± 1	−42 ± 5
	60	–	3.43 ± 0.04	3.27 ± 0.07	3.10 ± 0.06	2.83 ± 0.11	−35 ± 3	−53 ± 9
	40	–	4.00 ± 0.06	3.73 ± 0.06	3.52 ± 0.06	- -	−41 ± 1	−65 ± 5
DA18C6	100	–	4.06 ± 0.04	4.00 ± 0.02	3.89 ± 0.04	3.83 ± 0.03	−14 ± 1	29 ± 3
	80	–	4.31 ± 0.03	4.20 ± 0.04	4.10 ± 0.04	4.06 ± 0.03	−15 ± 1	30 ± 4
	60	5.00 ± 0.05	4.84 ± 0.04	4.77 ± 0.04	4.69 ± 0.05	–	−21 ± 1	21 ± 10
DBzDA18C6	100	–	3.82 ± 0.2	3.51 ± 0.03	3.28 ± 0.04	–	−44 ± 2	−81 ± 5
	80	–	4.16 ± 0.03	3.94 ± 0.03	3.64 ± 0.03	3.35 ± 0.04	−48 ± 2	−86 ± 7
	60	–	4.89 ± 0.06	4.55 ± 0.04	4.27 ± 0.04	4.06 ± 0.03	−49 ± 2	−76 ± 6
HA18C6	100	–	5.56 ± 0.09	5.48 ± 0.09	5.35 ± 0.09	5.23 ± 0.08	−20 ± 1	39 ± 4
	80	–	6.31 ± 0.18	6.14 ± 0.16	6.06 ± 0.15	5.87 ± 0.16	−24 ± 2	36 ± 6
	60	–		> 6.5	> 6.5	> 6.5	–	–

[a] The errors associated with all thermodynamic parameters are given as ± SD.

[b] The corresponding mole fractions of DMF (X_{DMF}) in the solvent mixtures are: 100%, 1.00; 80%, 0.69; 60%, 0.46; 40%, 0.27.

decreased in flexibility of the DBzDA18C6 molecule upon complexation with Tl^+ ion. This is possible only if the two benzyl arms of the ligand participate (from the top and bottom) in complex formation with the cation located inside its macrocyclic cavity [2–4]. Therefore, the stability constant of the N-substituted macrocycle-Tl^+ complexes is in the order HA18C6 > DA18C6 > DBzDA18C6.

As also seen, the substitution of cyclohexyl or benzo groups on the 18C6 ring will result in diminished stability of the resulting Tl^+ complexes. In the case of DC18C6, this is due to the reduced flexibility of the macrocyclic ring, which prevents the ligand wrapping itself around the central Tl^+ ion, resulting in some decreased stability of the resulting complex, as compared with that of 18C6. This is reflected in more positive ΔS° values for the Tl^+-18C6 complex, in most solvent mixtures, in comparison with the Tl^+-DC18C6 system. It is interesting to note that by increasing the %wt of acetonitrile in the mixed solvent (Table 1, DMF %wt of 60 and 40) the Tl^+-DC18C6 complex is more stable than Tl^+-18C6. This is most probably due to the rather strong interaction between 18-crown-6 and acetonitrile [29, 30]. In the case of B18C6, the observed pronounced decrease in the stability of the resulting Tl^+ complex may be attributed to some combination of the decreased ligand flexibility and the electron-withdrawing effect of the benzo group, which weaken the electron-donor ability of the oxygen atoms, resulting in much weaker metal ion interaction [2, 13]. Thus, the stability sequence is 18C6 > DC18C6 > B18C6.

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 destabilized 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 [2, 3]. 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 [25].

Table 1 shows that, as expected, for the case of all Tl^+-18-crown systems studied, the thermodynamic data vary significantly with the solvent properties [2, 3, 15, 16, 20, 25]. 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 [15, 16, 31–35], 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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