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Therodynamic Studies on Complexation of Cu^{2+}, Ag^{+} and Tl^{+} Metal Cations with 4′,4″,(5″)-di*tert*-butyldibenzyl-18-crown-6 in Acetonitrile-Dimethylformamide Binary Solutions

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log K_f, ΔH° and ΔS° values are reported for the complexation reactions of Cu^{2+}, Ag^{+} and Tl^{+} metal cations with macrocyclic ligand, 4′,4″,(5″)-di*tert*-butyldibenzyl-18-crown-6 (DTDB18C6) in acetonitrile-dimethylformamide binary solutions (AN-DMF) at different temperatures, using conductometric method. The conductance data show that in most cases, the stoichiometry of the complexes formed between DTDB18C6 and these metal cations is 1:1 (M:L). The values of log K_f of the complexes are sensitive to the solvent composition and it was found that the stability sequences of the complexes are changed with the composition of acetonitrile-dimethylformamide binary solution, and in some cases, the stability order is changed with the composition of the binary solution. The values of the thermodynamic quantities (ΔH_c°, ΔS_c°) for formation of (DTDB18C6-Cu^{2+}), (DTDB18C6-Ag^{+}) and (DTDB18C6-Tl^{+}) complexes were obtained from the temperature dependence of the stability constants and the results show that in most solution systems, the complexes are enthalpy stabilized but entropy destabilized.

Key Words: 4′,4″,(5″)-Di*tert*-butyldibenzyl-18-crown-6, Cu^{2+}, Ag^{+} and Tl^{+} cations, Acetonitrile-dimethylformamide binary mixture, Conductometry.

INTRODUCTION

The discovery of complexing properties of macrocyclic polyetheres (crown ethers) by Pedersen[1] has sparked a wide range of activity in the fields ranging from synthesis of compounds to various analytical applications[2-4]. An important property of crown ethers is their ability in formation of stable complexes with metal ions. In a typical complex, the metal ion occupies a site in the center of the crown ether with ligating donor atoms from the ring providing a full or partial inner coordination sphere for the metal ion. The studies of macrocyclic polyethers, mainly deal with the stability and selectivity of metal ion complexes of crown compounds[5,6], and also with the kinetics and thermodynamic of complex formation in pure solvents[7,8], but the complexation behaviour of crown compounds with metal cations has been studied to a very lesser extent in mixed non-aqueous solutions[9-12]. Macrocyclic crown ethers which are similar to antibiotic ligands can be used as models for investigation of ion trasport through membranes in biological systems[13], as stationary phase in chromatography[14], in the design of fiber optic chemical sensors[15] and as selective bulk liquid membrane for transport of metal cations[16].

A large number of physico-chemical techniques such as potentiometry[17], calorimetry[18], conductometry[19,20], NMR spectroscopy[21], spectrophotometry[22] and polarography[23] have been used for study of complexation reactions between crown ethers with different metal cations in solutions. These ligands have also many potential applications as ion selective electrodes, neutral carriers in PVC electrode membrane, phase transfer catalysts for organic reactions, anion activator and ion transport carriers through liquid membranes.

The goal of the peresent investigation is to study the effect of nature of the cation, especially the solvent properties on the stability, selectivity and of thermodynamic parameters of 4′,4″,(5″)-di*tert*-butyldibenzyl-18-crown-6 (DTDB18C6) complexes with Cu^{2+}, Ag^+ and Tl^+ metal cations in AN-DMF binary system using the conductometric technique.

EXPERIMENTAL

4′,4″,(5″)-Di*tert*-butyldibenzyl-18-crown-6 (Fluka) (**Scheme-I**), thallium(I) nitrate (Prolabo), silver(I) nitrate (Merck) and mercury(II) nitrate (Merck) were used without further purification. The solvents:acetonitrile (Merck), dimethylformamide (Merck) were used with the highest purity. The experimental procedure to obtain the formation constants of complexes was as follows :a solution of metal salt (5×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then step-by-step increase in the crown ether concentration was carried out by a rapid transfer from crown ether solution prepared in the same solvent (2.5×10^{-2} M) to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

The conductance measurements were performed on digital Metrohm conductivity apparatus (Model 712) in a water bath Julabo (Model F12) thermostated with a constant temperature maintained within ± 0.01 ºC. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 1.25 cm^{-1} was used throughout the studies.

RESULTS AND DISCUSSION

The changes of molar conductance (Λ_m) *versus* the ligand to the cation molar ratio ($[L]_t/[M]_t$) for complexation of (DTDB18C6) with Cu^{2+}, Ag^+ and Tl^+ metal cations in AN-DMF binary systems were studied at different temperatures. $[L]_t$ is the total concentration of the ligand and $[M]_t$ is the total concentration of the cation.Two typical series of molar conductance values as a function of ligand/metal cation mole ratios in an AN-DMF binary system and also in pure DMF are shown in Figs. 1 and 2, respectively.

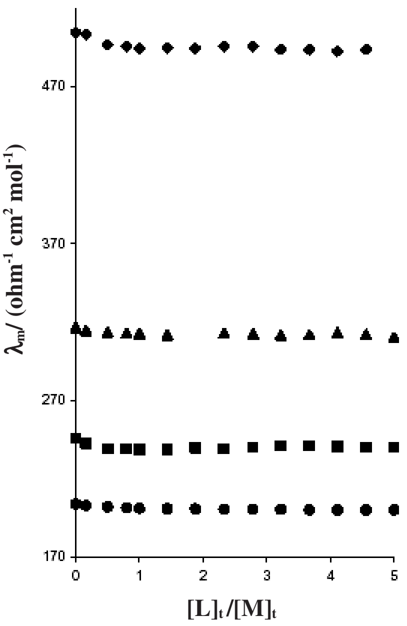


Fig. 1

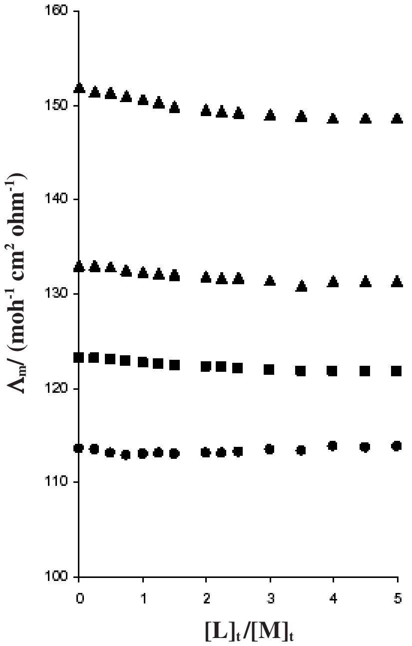


Fig. 2.

Fig. 1. Molar conductance-mole ratio plots for ($DTDB18C6-Cu^{2+}$) complex in ANDMF binary solution(mole % AN = 85.7) solution at different temperatures (ºC): (●) 45, (■) 35, (▲) 25, (◆) 15

Fig. 2. Molar conductance-mole ratio plots for ($DTDB18C6-Tl^+$) complex in pure DMF at different temperatures (C): (●) 45, (■) 35, (▲) 25, (◆) 15

As seen in Figs. 1 and 2, addition of DTDB18C6 to copper and thallium ions in pure DMF at different temperatures results in a decrease in molar conductivity which indicates that the ($DTDB18C6-Cu^{2+}$) and ($DTDB18C6-Tl^+$) complexes in these solutions are less mobile than free solvated Cu^{2+} and Tl^+ cations.

The slope of the corresponding molar conductivity *versus* ligand/metal cation mole ratio plots in all cases changes at the point where the ligand to cation mole ratio is about 1 which is an evidence for formation of a relatively stable 1:1 [L:M] complexes between DTDB18C6 and these metal cations. It is evident from Figs. 1 and 2, that the curvature of the plots of the (DTDB18C6-Cu^{2+}), (DTDB18C6-Ag^{+}) and (DTDB18C6-Tl^{+}) complexes decreases as the temperature increases, which is an evidence for formation of weaker complexes at higher temperatures. Therefore, the complexation reactions between Cu^{2+}, Ag^{+} and Tl^{+} metal cations with DTDB18C6 in these solvent system are exothermic.

The stability constants of the crown ether complexes at each temperature were calculated from the variation of the molar conductance as a function of ligand/metal cation mole ratios by using a GENPLOT computer program[24]. The details of the calculation of the stability cosntants of complexes by the conductometric method has been described elsewhere[19]. The values of the stability constants (log K_f) for the DTDB18C6-M^{n+} (M^{n+} = Cu^{2+}, Ag^{+}, Tl^{+}) complexes in various solvent systems are listed in Table-1.

TABLE-1
log K_f VALUES OF (DTDB18C6-Cu^{2+}), (DTDB18C6-Ag^{+}) AND (DTDB18C6-Tl^{+}) COMPLEXES IN AN-DMF BINARY MIXTURES AT DIFFERENT TEMPERATURES

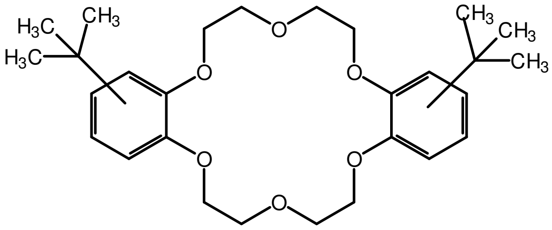
Meidum	log K_f ± SD[a]			
	15 °C	25 °C	35 °C	45 °C
DTDB18C6-Cu^{2+}				
Pure AN	3.10±0.02	2.38±0.06	2.50±0.08	1.96±0.10
85.7 % AN-14.3 % DMF[c]	3.90±0.06	3.69±0.01	2.47±0.07	1.40±0.10
69.3 % AN-30.7 % DMF	3.15±0.60	3.50±1.07	3.07±0.13	2.68±0.08
27.3 % AN-72.7 % DMF	1.91±0.10	2.79±0.29	4.16±0.60	3.58±0.03
Pure DMF	1.97±0.08	2.33±0.14	2.36±0.20	3.39±0.20
DTDB18C6-Ag^{+}				
Pure AN	1.30±0.09	3.18±0.15	2.82±0.20	3.12±0.20
85.7 % AN-14.3 % DMF[c]	3.40±0.10	3.16±0.20	2.86±0.10	3.18±0.10
69.3 % AN-30.7 % DMF	3.47±0.06	2.18±0.13	2.56±0.14	1.47±0.15
50.0 % AN-50.0 % DMF	3.49±0.07	3.15±0.09	2.97±0.03	2.81±0.06
27.3 % AN-72.7 % DMF	3.23±0.09	2.86±0.10	3.16±0.12	2.00±0.10
Pure DMF	2.40±0.28	2.70±0.20	2.82±0.20	3.37±0.10
DTDB18C6-Tl^{+}				
Pure AN	d	d	d	d
90.2 % AN-9.8 % DMF	3.36±0.20	2.34±0.30	3.40±0.10	3.00±0.03
69.3 % AN-30.7 % DMF	3.14±0.09	3.08±0.20	3.03±0.09	2.08±0.10
50.0 % AN-50.0 % DMF	3.13±0.02	3.08±0.06	1.89±0.05	1.71±0.03
27.3 % AN-72.7 % DMF	2.02±0.15	2.60±0.08	2.14±0.16	2.36±0.10
Pure DMF	2.40 ±0.08	2.30±0.23	4.34±0.20	3.10±0.15

a) SD = standard deviation.

b) The concentration of each metal cation was 5.0×10^{-4} M.

c) Composition of binary mixtures is expressed in mole % for each solvent system.

d) The metal salts are not soluble.



4′,4″,(5″)-Di*tert*-butyldibenzyl-18-crown-6

As is evident from Fig. 3, the changes of the stability constant (log K_f) of (DTDB18C6-Tl^+) complex *vs.* the composition of acetonitrile-dimethylformamide binary solution at different temperatures is not monotonic. Some what similar behaviour was observed for other complexes. The non-linear behaviour is observed for these complexation systems in AN-DMF binary mixtures is probably due to heteroselective solvation of metal cations and also the ligand or it may be due some kinds of solvent-solvent interactions between the two solvents which result in changing the structure of the solvents when they are mixed with each other.

Assuming that the activity coefficients of the cation and complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, $\Delta G^\circ c$. The van't Hoff plots of log K_f *versus* 1/T for all of the investigated systems were constructed.

The changes in the standard enthalpy ($\Delta H^\circ c$) for the complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy ($\Delta S^\circ c$) were calculated from the relationship $\Delta G^\circ c$, 298.15 = $\Delta H^\circ c - 298.15\ \Delta S^\circ c$. The thermodynamic data are summarized in Table-2. The changes of log K_f of (DTDB18C6-Tl^+) complex *versus* the mole fraction of acetonitrile in AN-DMF binary system at different temperatures are shown in Fig. 3.

The data in Table-2, shows that the calculated thermodynamic quantities ($\Delta H^\circ c$ and $\Delta S^\circ c$) for complexation reactions between DTDB18C6 with Cu^{2+}, Ag^+ and Tl^+ metal cations in acetonitrile-dimethylformamide binary solutions are influenced by the nature of solvent and vary with the solvent composition. In most cases, positive values of $\Delta S^\circ c$ characterize the formation of these complexes. It seems reasonable to assume that the increase in entropy on complexation process is due to additional solvent molecules which may be released from the solvation shell of the cations and the ligand upon complexation.

As shown in Table-2, a non-linear behaviour is observed for variations of $\Delta H^\circ c$ and $\Delta S^\circ c$ values for the complexation reactions with the composition of acetonitrile-dimethylformamide binary solutions. Since there are many

TABLE-2
THERMODYNAMIC PARAMETERS FOR (DTDB18C6-Ag^{+}), (DTDB18C6-Cu^{2+}) AND (DTDB18C6-Tl^{+}) COMPLEXES IN AN-DMF BINARY MIXTURES

Medium	$-\Delta G^{o}c_{(25)} \pm SD^{a}$ (KJ/mol)	$-\Delta H^{o}c \pm SD$ (KJ/mol)	$-\Delta S^{o}c \pm SD$ (J/mol K)
DTDB18C6-Cu^{2+}			
Pure AN	13.60±0.10	-51.50±0.01	-127.10±0.30
85.7 % AN-14.3 % DMF[c]	22.30±0.10	-95.11±0.09	-244.33±0.45
69.3 % AN-30.7 % DMF	19.98±0.08	-27.44±0.10	-25.01±0.42
27.3 % AN-72.7 % DMF	15.86±0.02	50.70±0.09	223.35±0.30
Pure DMF	13.38±0.12	64.85±0.09	262.52±0.50
DTDB18C6-Ag^{+}			
Pure AN	18.09±0.06	85.72±0.03	348.35±0.02
85.7 % AN-14.3 % DMF[c]	18.02±0.04	-18.87±0.02	2.85.00±0.15
69.3 % AN-30.7 % DMF	12.44±0.06	-87.30±0.03	-251.19±0.20
50.0 % AN-50.0 % DMF	17.85±0.03	-35.75±0.03	-60.06±0.14
27.3 % AN-72.7 % DMF	16.36±0.01	-47.88±0.02	-105.77±0.06
Pure DMF	15.39±0.02	48.22±0.01	213.39±0.06
DTDB18C6-Tl^{+}			
Pure AN	d	d	d
90.2 % AN-9.8 % DMF	13.35±0.06	-9.47±0.03	13.02±0.20
69.3 % AN-30.7 % DMF	17.60±0.01	-46.56±0.07	-97.18±0.02
50.0 % AN-50.0 % DMF	15.09±0.01	-78.73±0.10	-213.55±0.03
27.3 % AN-72.7 % DMF	14.87±0.05	-10.80±0.07	13.62±0.20
Pure DMF	13.11±0.10	74.83±0.08	295.10±0.40

a) SD = standard deviation.
b) The concentration of each metal cation was 5.0×10^{-4} M.
c) Composition of binary mixtures is expressed in mole % for each solvent system.
d) The metal salts are not soluble.

factors which contribute to changes in complexation enthalpies and entropies, one should not expect a strict regularity between these thermodynamic quantities and the composition of the mixed solvents.The acetonitrile and dimethylformamide both are dipolar aprotic liquids with large but nearly equal dipole moments[25]. Thus mixing of dimethylformamide with acetonitrile will induce the mutual destruction of dipolar structures of component liquids and releasing the free dipoles. As a result, strong dipolar intractions will exist between these two dipolar aprotic solvents when they mixed with each other.

The stability and selectivity of crown ether complexes with metal cations depend on several factors. These include the cavity size of the ligand, the character of heteroatoms in the polyether ring, spatial distribution of ring binding sites and the cation diameter[26]. The fitness of the metal cations into the cavity size of a macrocyclic compound is an important factor to explain the crown ether complexes selectivity.

The changes of log K_f for formation of (DTDB18C6-Ag^+), (DTDB18C6-Cu^{2+}) and (DTDB18C6-Tl^+) complexes *vs.* ionic radii of the metal cations in pure dimethylformamide and in acetonitrile-dimethylformamide binary mixtures at 25 °C is shown in Fig. 4. As shown in this figure, the sequence of stability of complexes of these heavy metal cations with DTDB18C6 ligand in pure dimethylformamide is $Ag^+ > Cu^{2+} > Tl^+$, but in the case of another binary solution of acetonitrile and dimethylformamide (mol % AN = 69.3), the stability order of complexes changes to: $Cu^{2+} > Tl^+ > Ag^+$. It seems that in most cases, the Ag^+ cation forms the most stable complex with DTDB18C6 because its ionic size (2.30 Å) is close to the size of the ligand's cavity (2.3-3.2 Å) and therefore, it can attain a more convenient fit condition than the other metal cations. In addition, the silver ion may also interact with the π-electrons of the aromatic systems present in the macrocyclic ligand[27]. The result obtained in this study show that the selectivity of the macrocyclic ligands for metal cations may change with the composition of the mixed solvents.

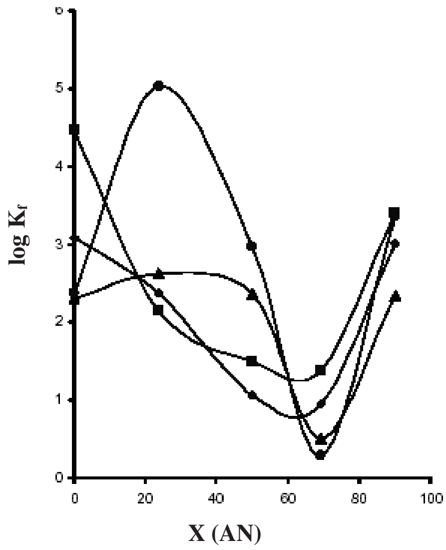


Fig. 3

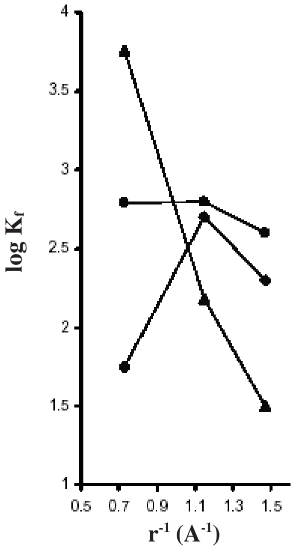


Fig. 4

Fig. 3. Changes of formation constant (log K_f) of (DTDB18C6-Tl^+) complex with the composition of AN-DMF binary system at different temperature (ºC): (●) 45, (■) 35, (▲) 25, (◆) 15

Fig. 4. Changes of log K_f for (DTDB18C6-Cu^{2+}), (DTDB18C6-Ag^+) and (DTDB18C6-Tl^+) complexes *versus* ionic radii in various solvent systems at 25 ºC : (▲) mole % AN = 69.3, (●) mole % AN = 27.3, (■) pure AN

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