**Solvents Influence On Thermodynamics Of Complexation Between
Dibenzo 18-Crown-6 With Tl^+ , Cs^+ And UO_2^{2+} Cations In Pure Acetonitrile,
Pure Dimethylesulfoxide And Acetonitrile-Dimethylesulfoxide Binary Mixtures
By Conductometric Method**

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Abstract

The stability constants of 1:1 (M-L) complexes of Dibenzo-18-crown-6 (DB18C6) with Tl^+ , Cs^+ and UO_2^{2+} cations have been determined conductometrically. The conductance data show that the stoichiometry of the complexes formed between the macrocyclic ligand and Tl^+ , Cs^+ and UO_2^{2+} cations is 1:1 (M:L). GENPLOT computer program used to find the stability constants of the complexes were obtained from fitting of molar conductivity curves. The selectivity order of DB18C6 for the metal cations changes with the nature and composition of the binary mixed solvent. We also determined the Gibbs standard free energies (ΔG^0), the standard enthalpy changes (ΔH^0) and standard entropy changes (ΔS^0) for formation of these complexes in acetonitrile – dimethylesulfoxide (AN-DMSO) binary mixtures for the complexation. The values of standard enthalpy changes (ΔH^0) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy (ΔS^0) were calculated from the relationship $\Delta G_{298.15}^0 = \Delta H^0 - 298.15 \Delta S^0$.

Keywords: thermodynamic parameters • conductometric method • stability constants • complexation

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Introduction

C. J. Pedersen discovered the macrocyclic ligand Dibenzo-18 crown 6 ether (DB18C6) in 1987[1] and observed that it forms very strong complexes with alkali and alkaline metal cations. The selectivity and stability of crown ethers complexes with cations are reliant on several factors like, cavity size of crown ether, the number and type of the donor atoms, the charge density and polarizability of the cation and cation diameter [2,3]. Crown ethers have been established to be highly selective complexing agents for many metal cations and can potentially be applied in their separation [4-7] and determination. Crown ethers have been used in different areas, such as organic synthesis [8], chemical analysis [9], in construction of ion selective electrodes [10,11], separation of metal cations [12,13].

To study the complex formation between macrocyclic ligands and different metal cations in solutions various techniques such as fluorescence spectroscopy [14], potentiometry [15], spectrophotometry [16], NMR spectrometry [17], conductometry [18], calorimetry [19] and polarography [20] have been used.

Experimental

Materials and procedure

Dibenzo-18-Crown-6 (Aldrich), Thallium nitrate TlNO_3 (Aldrich), cesium nitrate CsNO_3 (CDH) and uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (SRL) were used without further purification. Dimethylesulfoxide (DMSO) (Finar Chemicals) and Acetonitrile (AN) (Finar Chemicals) with the highest purity were used as solvents.

Following process was used to get formation constants of complexes: a cation salt solution (1.0×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, crown ether solution prepared in the same solvent (2.0×10^{-3} M) added step-by-step by a quick transfer to the titration cell using a micro burette. The same process was followed at 25 °C, 35 °C and 45

°C, and the conductivity data was used for the calculation of the formation constant of the complexes at the chosen temperatures.

Apparatus

A digital Metrohm (Herisau, Switzerland) conductivity apparatus, Model 856 used for conductance measurements, in a water-bath thermostated at constant temperature maintained within $\pm 0.01^\circ\text{C}$. A dip type 5-ring conductivity cell having a cell constant of 0.59 cm^{-1} was used. The cell constant of the conductivity cell was determined by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [21].

Result and Discussion

For the complexation of dibenzo-18-crown-6 with Ti^+ , Cs^+ and UO_2^{2+} cations in acetonitrile-dimethylethylsulfoxide (AN-DMSO) binary systems plot of molar conductivity versus the ligand to cation mole ratio were plotted at different temperatures. Molar conductance-mole ratio plots are shown in Figs. 1-5.

The stability constants of DB18C6 complexes with Ti^+ , Cs^+ and UO_2^{2+} cations at each temperature were calculated from variation of molar conductance as a function of $[\text{L}]/[\text{M}]$ molar ratio using a GENPLOT computer program [22]. The details of calculation of the stability constants of complexes by conductometric method have been explained in reference [23].

The stability constants ($\log K_f$) for DB18C6 – M^{n+} (M^{n+} : Ti^+ , Cs^+ and UO_2^{2+}) complexes in various solvent systems are listed in Table 1. The changes in standard enthalpy (ΔH^0) for the complexation reactions were determined from the slopes of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range is investigated, and the changes in standard entropy (ΔS^0) were calculated from the relationship $\Delta G^0_{298.15} = \Delta H^0 - 298.15 \Delta S^0$.

Figure 1. Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)-mole ratio plots for DB18C6 - Cs^+ complex in pure AN at various temperatures

Figure 2. Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)-mole ratio plots for DB18C6 - Tl^+ complex in AN-DMSO binary solutions (%AN = 75) at various temperatures

Figure 3. Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)-mole ratio plots for DB18C6 - Tl^+ complex in AN-DMSO binary solutions (%AN = 50) at various temperatures

Figure 4. Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)-mole ratio plots for DB18C6 - Tl^+ complex in AN-DMSO binary solutions (%AN = 25) at various temperatures

Figure 5. Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)-mole ratio plots for DB18C6 - UO_2^{2+} complex in pure DMSO at various temperatures

Table 1. Log K_f values of DB18C6- M^{n+} complex in AN-DMSO binary mixtures at different temperatures.

Complex	Solvent Medium	Log $K_f \pm SD^a$		
		298.15 K	308.15 K	318.15 K
DB18C6-Tl⁺	Pure AN	b	b	b
	75% AN-25% DMSO	4.32±0.07	4.30±0.03	4.28±0.04
	50% AN-50% DMSO	4.29±0.05	4.27±0.05	4.25±0.06
	25% AN-75% DMSO	4.26±0.03	4.24±0.06	4.22±0.04
	Pure DMSO	4.22±0.04	4.20±0.07	4.18±0.03
DB18C6-Cs⁺	Pure AN	4.29±0.05	4.26±0.05	4.23±0.05
	75% AN-25% DMSO	4.27±0.04	4.23±0.06	4.20±0.08
	50% AN-50% DMSO	4.25±0.06	4.20±0.08	4.16±0.04
	25% AN-75% DMSO	4.23±0.05	4.17±0.02	4.13±0.02
	Pure DMSO	4.20±0.04	4.15±0.05	4.10±0.03
DB18C6-UO₂²⁺	Pure AN	4.28±0.08	4.25±0.06	4.22±0.04
	75% AN-25% DMSO	4.26±0.03	4.22±0.04	4.19±0.06
	50% AN-50% DMSO	4.24±0.05	4.19±0.02	4.15±0.08
	25% AN-75% DMSO	4.22±0.05	4.16±0.03	4.12±0.04
	Pure DMSO	4.19±0.02	4.14±0.05	4.09±0.02

^aSD = standard deviation, b= salt not dissolved

A non-linear behavior is observed for the stability constants (log K_f) of these complexes with the composition of AN-DMSO binary system. For example, the variations of stability constant of (DB18C6- M^{n+}) complex with the composition of AN-DMSO binary system at different temperatures are shown in Fig. 6.

Figure 6. Change of the stability constant $\text{Log } K_f$ of (DB18C6- M^{n+}) complex with the composition of AN-DMSO binary systems at various temperatures

Figure 7. van't Hoff plots for the (DB18C6- M^{n+}) complex in AN-DMSO binary systems: (A = Pure AN, B = 25% DMSO, C = 50% DMSO, D = 75% DMSO and E = Pure DMSO).

From Table 1, in most cases, the stability constant ($\log K_f$) of (DB18C6- Tl^+) complexes increases with increasing the concentration of acetonitrile in AN–DMSO binary mixture. Solvents with high donor ability (high DN number), the stability constant of complex should decrease owing to competition between the ligand and the solvent molecules for the metal cation. In acetonitrile with a low Gutman Donor Number (DN = 14.1) [24], the solvation of the metal cations must be less than DMSO (DN = 29.8) [24] with a high solvating ability. The stability constant ($\log K_f$) of (DB18C6- Tl^+) complexes decrease with increasing the temperature in pure AN, AN–DMSO binary mixture and in pure DMSO, it indicates that process is exothermic process. It should be noted that somewhat lower dielectric constant of AN (38.0) in comparison with that of DMSO (46.45) would cause the electrostatic contribution to the bond formation to increase with increasing percentage of AN in the solvent mixture. The changes of the stability constant ($\log K_f$) for (DB18C6- M^{n+}) complexes versus the percentage of DMSO in AN–DMSO binary solution is not linear (Fig. 6).

Addition of the DB18C6 ligand to solutions of Cs^+ and UO_2^{2+} cations in pure AN at different temperatures shows that the molar conductivity values increase with increasing $[DB18C6]/[M^{n+}]$ mole ratio which indicates that the (DB18C6- M^{n+}) complexes in this solvent have higher mobility than free solvated Cs^+ and UO_2^{2+} cations. The slope of the corresponding molar conductivity versus $[L]/[M]$ mole ratio plots for strong complexes changes sharply at the point where the ligand to cation ratio is one, which is an evidence for formation of a relatively stable 1:1 complex. On the other hand, molar conductivity values decrease with increasing, when DB18C6 ligand was added to solution of Tl^+ , Cs^+ and UO_2^{2+} cations in all binary solvent systems and pure DMSO. This indicates that the complexes in these binary systems have lower mobility than the free solvated cations (Figs. 2-5). The results show, in all cases, DB18C6 ligand forms 1:1 complexes with Tl^+ , Cs^+ and UO_2^{2+} cations in pure AN, pure DMSO and AN–DMSO binary systems at different temperatures.

The selectivity order of DB18C6 ligand for the metal cations in pure AN, pure DMSO and in these binary solutions is: $Tl^+ > Cs^+ > UO_2^{2+}$. The selectivity and stability of crown ether complexes of metal cations depend on several factors like, the cavity size of the ligand, the hetero

atom character in the polyether ring, ring binding sites and the cation diameter and also the nature of the medium. The fitness of the metal cation to the cavity of a macrocyclic ligand is an important factor to explain the crown ether complexes selectivity. The ionic sizes of the Ti^+ (ionic radius = 1.50 Å) [24], Cs^+ (ionic radius = 1.70 Å) [24] and UO_2^{2+} (ionic radius = 0.99 Å) [24] ions are close to the size of the DB18C6 cavity (2.3–3.2 Å) [25], therefore, they form stable complexes with the ligand in these media. The Ti^+ ion forms the most stable complex with DB18C6 because its ionic diameter is very close to crown cavity. Plots of $\log K_f$ versus $1000/T$ in all cases were linear.

Table 2. Thermodynamic parameters for DB18C6- M^{n+} complexes in AN-DMSO binary systems at 298.15K

Complex	Solvent Medium	$\Delta G^\circ \pm \text{SD}^a$ (kJ.mol ⁻¹)	$\Delta H^\circ \pm \text{SD}^a$ (kJ.mol ⁻¹)	$\Delta S^\circ \pm \text{SD}^a$ (J.mol ⁻¹ K ⁻¹)
18C6- Ti^+	Pure AN	b	b	b
	75% AN-25% DMSO	-25.06±0.05	-3.62±0.08	70.54±5
	50% AN-50% DMSO	-24.91±0.03	-4.08±0.09	68.50±3
	25% AN-75% DMSO	-24.73±0.04	-3.98±0.07	68.28±4
	Pure DMSO	-24.49±0.06	-3.79±0.08	68.00±5
18C6- Cs^+	Pure AN	-24.88±0.05	-5.43±0.08	63.88±4
	75% AN-25% DMSO	-24.77±0.04	-6.26±0.06	60.70±6
	50% AN-50% DMSO	-24.65±0.04	-8.16±0.07	53.92±7
	25% AN-75% DMSO	-24.54±0.03	-9.08±0.05	50.44±4
	Pure DMSO	-24.36±0.07	-9.06±0.09	49.09±5
18C6- UO_2^{2+}	Pure AN	-24.84±0.04	-5.62±0.08	63.69±8
	75% AN-25% DMSO	-24.71±0.05	-6.35±0.09	60.20±7
	50% AN-50% DMSO	-24.59±0.04	-8.16±0.08	53.73±5
	25% AN-75% DMSO	-24.48±0.06	-9.08±0.07	50.24±8
	Pure DMSO	-24.32±0.03	-9.25±0.09	49.80±6

^aSD = standard deviation, b= salt not dissolved

The variation of $\log K_f$ of (DB18C6- Ti^+), (DB18C6- Cs^+) and (DB18C6- UO_2^{2+}) complexes vs. the ionic radii in pure AN, pure DMSO and various AN-DMSO binary mixtures is shown in Figure 7. As is seen, the order of stability of complexes formed between DB18C6 and these cations vary with the variation of volume of DMSO.

To understand the factors governing the complexing ability and selectivity of the crown ethers, the thermodynamic parameters must be evaluated. The thermodynamic parameters (ΔG° , ΔH° and

ΔS^0) of the complex formation, calculated from the temperature dependences of the stability constants, are given in Table 2. The Gibbs energy of the complex formation Nonmonotonically varies with the composition of the binary organic solvents which indicates the inter particle interactions because of the entropy-enthalpy compensation. The values of thermodynamic parameters (ΔH^0 and ΔS^0) for all of the complexes in AN– DMSO binary solutions are influenced by the solvent composition and in all cases, the complexes are enthalpy stabilized, but entropy destabilized. The results in Table 2, show that, the thermodynamic data show that in most cases, the complexation reactions between DB18C6 with Tl^+ , Cs^+ and UO_2^{2+} cations are exothermic. The values of thermodynamic parameters for complexation processes in binary mixed solvents are affected by the solvation capacity of the metal cations, the macrocyclic ligand and also the metal ion complexes which depends on the structural and energetic properties of the mixed solvents.

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