Asian Journal of Chemistry Vol. 19, No. 2 (2007), 929-936

Solvent Influence Upon Complex Formation Between Dibenzo-18-Crown-6 and Cd^{2+}, Cu^{2+}, Tl^{+} and Zn^{2+} Cations in Dimethylsulfoxide-Methanol Binary Mixtures

GHOLAM HOSSEIN ROUNAGHI* and NOORANI GAMIL GEREY
Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad
Mashhad, Iran
E-mail: ghrounaghi@yahoo.com

The complexation reactions between Cd^{2+}, Cu^{2+}, Tl^{+} and Zn^{2+} cations with dibenzo-18-crown-6 (DB18C6) were studied in DMSO-MeOH binary mixtures at different temperatures using conductometric method. In all cases, DB18C6 froms 1:1 complexes with Cd^{2+}, Cu^{2+}, Tl^{+} and Zn^{2+} cations. With the exception of Tl^{+} cation in pure methanol, addition of DB18C6 to the cations solutions causes a continous increase in the molar conductivity which indicates that the mobility of the complexed cations is more than the uncomplexed ones. The values of stability constants of the complexes which were determined from conductometric plots using the GENPLOT computer program, show that the stability of the complexes is affected by the nature and composition of the mixed solvents. A non-linear behaviour was observed between the log K_f and the composition of the mixed solvents for all of the complexes. The selectivity of DB18C6 for Cu^{2+}, Cd^{2+}, Tl^{+} and Zn^{2+} is sensitive to the solvent composition and in some cases the order of selectivity is reversed in certain compositions of the mixed solvent systems. The selectivity of DB18C6 for the cations in pure MeOH is : $Tl^{+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$. The values of thermodynamic parameters (ΔS_c°, ΔH_c°) for formation of $(DB18C6)Cd^{2+}$, $(DB18C6)Cu^{2+}$, $(DB18Cd)Tl^{+}$ and $(DB18C6)Zn^{2+}$ complexes were obtained from temperature dependence of the formation constants of the complexes using the van't Hoff plots. The obtained results show that in most cases, the complexation reactions between DB18C6 and these heavy metal cations are enthalpy destabilized but entropy stabilized.

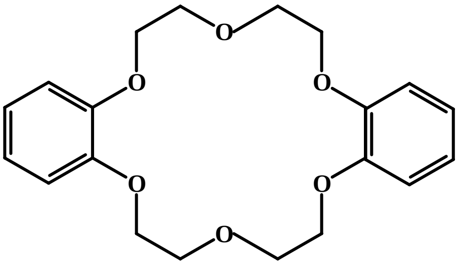
Key Words: Dibenzo-18-crown-6, Cd^{2+}, Cu^{2+}, Tl^{+}, Zn^{2+}, DMSO-CH_3OH binary mixtures, Conductometry.

INTRODUCTION

The first macrocyclic polyethers were reported by Kuttrinjhaus in 1937. However, the importance of these compounds began from 1967 with the synthesis of dibenzo-18-crown-6 (DB18C6) by Pedersen and the observation that this compound and its homologues form very strong complexes with alkali and alkaline earth metal cations[1]. The values of stability constants, as well as the values of enthalpy changes (ΔH_c°), entroply changes (ΔS_c°) and the heat capacity changes (ΔC_p) of various crown ether complexes are summarized in two reviews by Christensen *et.al*[2,3]. Naturally occuring macrocycles were shown to be capable of actively transport the metal cations across the biological memberanes. Macrocyclic crown ethers which are similar to antibiotic ligands can be used as models for investigation of ion transport through membranes in biological systems . Studies of crown ether complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent system[4,5].

A number of physico-chemical techniques such as potentiometry[6], calorimetry[7], conductometry[8-12], polarography[13-16], NMR spectrometry[17-19], spectrophotometry[20,21] and ion exchange membrane[22] have been used to study the complexation reactions between crown ethers with different metal cations in solutions. Most of these techniques still have problems, *i.e.*, measurements are carried out in non-ideal solutions in which the association between the metal cations and anions is fairly large. Therefore, it is difficult to determine accurate complex formation constant under such conditions.The advantage of conductometry is that measurements can be carried out with high precision at extremely low solution concentrations, where the intractions between cations and anions are known to be very small. In addition, conductometry is a highly sensitive and inexpensive technique with a simple experimental arrangement.

In this paper, the results of thermodynamic study for complexation reactions between DB18C6 (Fig. 1) with Cd^{2+}, Cu^{2+}, Tl^{+} and Zn^{2+} cations in DMSO-MeOH binary mixtures at different temperatures using conductometric method is reported.



Dibenzo-18-Crown-6

Fig. 1.

EXPERIMENTAL

DB18C6 (Fluka), copper nitrate, zinc nitrate, thalium nitrate and cadmium nitrate (all from Merck) were used without further purification.

The solvents: dimethyl sulfoxide and methanol (both from Merck) were used with the highest purity.

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water bath thermostated within ± 0.03ºC. 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 0.79 cm^{-1} was used throughout the studies.

The experimental procedure to obtain the formation constants of complexes is as follow: a solution of the corresponding metal salt (5×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase in the crown ether concentration was performed by rapid transfer of crown ether solutions prepared in the same solvent (5×10^{-3} M) to the titration cell using a microburet and the conductance of the solution in the cell was measured after each addition at the desired temperature.

RESULTS AND DISCUSSION

The variations of molar conductance (Δ_m) *vs.* the ligand to the cation molar ratios ([L]/[M]) for complexation of DB18C6 with Cd^{2+}, Cu^{2+}, Tl^+ and Zn^{2+} in DMSO-MeOH binary systems were studied at different temperatures. The changes of Ω_m *vs.* ligand/metal cation mole ratios ([L]/[M]) for $(DB18C6)Cd^{2+}$ in DMSO-MeOH binary mixture and for $(DB18C6)Tl^+$ in pure MeOH are shown in Figs. 2 and 3, respectively.

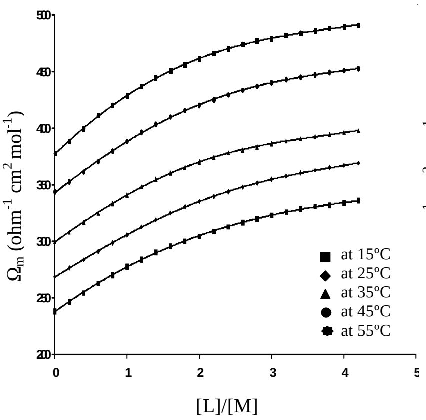


Fig.2. Molar conductance-mole ratio plots for $(DB18C6)Cd^{2+}$ complex in DMSO-MeOH (mol % MeOH = 75) binary mixture at different temperatures

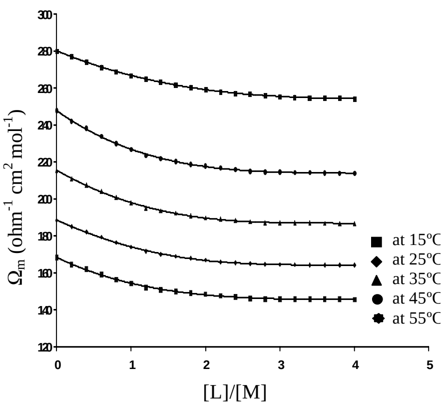


Fig. 3 Molar conductance-mole ratio plots for $(DB18C6)Tl^+$ complex in pure MeOH at different temperatures

The stability constants of DB18C6 crown ether complexes at each temperature were calculated from changes of molar conductance as a function of ligand/cation mole ratios using a GENPLOT computer program[23]. The details of calculation of the stability constants of complexes by conductometric method has been described elsewhere[13]. The stability constants (log K_f) for DB18C6-M^{n+} (M^{n+} = Cd^{2+}, Cu^{2+}, Tl^+ or Zn^{2+}) complexes in various solvent systems are listed in Table-1. Assuming that the activity coefficients of cation and complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale. The changes of standard enthalpy (ΔH_c°) for the complexation reactions were determined from the slope of the van't Hoff plots and the changes in the standard entropy (ΔS_c°) were calculated from the relationship $(\Delta G_c^\circ)_{298.15} = \Delta H_c^\circ - 298.15\ \Delta S_c^\circ$. The thermodynamic data are summarized in Table-2.

TABLE-1

log K_f VALUES OF (DB18C6)Cd^{2+}, (DB18C6)Cu^{2+}, (DB18C6)Tl^+ AND (DB18C6)Zn^{2+} COMPLEXES IN DMSO-MeOH BINARY MIXTURES AT DIFFERENT TEMPERATURES

Medium[a]	log K_f ± SD[b] (ºC)				
	15	25	35	45	55
(DB18C6)Cu^{2+}					
100 % DMSO	2.93 ± 0.03	3.00 ± 0.03	3.06 ± 0.02	3.08 ± 0.03	3.03 ± 0.03
25 % MeOH-75 % DMSO	2.89 ± 0.04	2.89 ± 0.04	2.95 ± 0.04	3.00 ± 0.03	3.04 ± 0.03
50 % MeOH-50 % DMSO	2.76 ± 0.04	2.80 ± 0.04	2.89 ± 0.04	2.92 ± 0.04	2.96 ± 0.04
75 % MeOH-25 % DMSO	2.88 ± 0.04	3.20 ± 0.03	3.10 ± 0.03	3.02 ± 0.02	2.83 ± 0.04
100 % MeOH	2.73 ± 0.03	2.88 ± 0.04	2.88 ± 0.04	2.87 ± 0.06	2.83± 0.06
(DB18C6)Cd^{2+}					
100 % DMSO	2.99 ± 0.02	2.92 ± 0.01	2.92 ± 0.01	2.93 ± 0.01	2.95 ± 0.01
25 % MeOH-75 % DMSO	2.98 ± 0.02	3.03 ± 0.01	3.04 ± 0.01	2.97 ± 0.01	3.08 ± 0.01
50 % MeOH-50 % DMSO	2.96 ± 0.04	3.04 ± 0.03	3.09 ± 0.02	3.08 ± 0.03	3.00 ± 0.01
75 % MeOH-25 % DMSO	2.96 ± 0.02	2.86 ± 0.03	3.09 ± 0.03	3.04 ± 0.03	3.09 ± 0.02
100 % MeOH	2.81 ± 0.02	2.91 ± 0.02	3.00 ± 0.02	2.96 ± 0.03	2.76 ± 0.03
(DB18C6)Tl^+					
100 % DMSO	3.17 ± 0.02	3.17 ± 0.01	3.21 ± 0.02	3.11 ± 0.02	3.05 ± 0.02
25 % MeOH-75 % DMSO	3.13 ± 0.01	3.18 ± 0.01	3.14 ± 0.01	3.16 ± 0.02	3.22 ± 0.02
50 % MeOH-50 % DMSO	3.24 ± 0.02	3.21 ± 0.01	3.33 ± 0.02	3.29 ± 0.02	3.42 ± 0.01
75 % MeOH-25 % DMSO	3.24 ± 0.03	3.33 ± 0.04	3.33 ± 0.02	3.30 ± 0.02	3.01 ± 0.01
100 % MeOH	3.75 ± 0.04	3.70 ± 0.04	3.75 ± 0.04	3.76 ± 0.03	3.39 ± 0.03
(DB18C6)Zn^{2+}					
100 % DMSO	3.24 ± 0.02	2.94 ± 0.04	3.00 ± 0.04	3.03 ± 0.04	3.10 ± 0.03
25 % MeOH-75 % DMSO	2.77 ± 0.03	2.71 ± 0.03	2.75 ± 0.04	2.97 ± 0.03	2.95 ± 0.03
50 % MeOH-50 % DMSO	2.94 ± 0.04	2.85 ± 0.05	2.89 ± 0.04	2.91 ± 0.03	3.04 ± 0.03
75 % MeOH-25 % DMSO	2.83 ± 0.04	2.87 ± 0.04	2.86 ± 0.04	2.88 ± 0.04	2.76 ± 0.04
100 % MeOH	2.70 ± 0.04	2.75 ± 0.04	2.81 ± 0.04	2.79 ± 0.04	2.75 ± 0.03

a) The composition of the mixed solvents is expressed in mole % of each solvent

b) SD = Standard deviation

The changes of log K_f *vs.* the mole fraction of MeOH for (DB18C6)Cu^{2+} complex in DMSO-MeOH binary systems at different temperatures are shown in Fig.4. Somewhat similar behaviour was observed for (DB18C6)Cd^{2+}, (DB18C6)Tl^+ and (DB18C6)Zn^{2+} complexes in these binary mixed solvents. The changes of log K_f for these complexes *vs.* the cationic radii in various DMSO-MeOH binary systems are shown in Fig.5.

TABLE-2
THERMODYNAMIC PARAMETERS FOR (DB18C6)Cd^{2+}, (DB18C6)Cu^{2+}, (DB18C6)Tl^{+} AND (DB18C6)Zn^{2+} COMPLEXES IN DMSO-MeOH BINARY MIXTURES

Medium[a]	log $K_f \pm SD^b$ (25ºC)	$\Delta G_c^o \pm SD^b$ (KJ mol^{-1})	$\Delta G_c^o \pm SD^b$ (KJ mol^{-1})	$\Delta G_c^o \pm SD^b$ (J mol^{-1} k^{-1})
(DB18C6)Cu^{2+}				
100% DMSO	3.00 ± 0.03	17.13 ± 0.07	8.8 ± 0.5	87.0 ± 2.0
25% MeOH-75% DMSO	2.89 ± 0.04	16.50 ± 0.10	7.8 ± 0.1	81.5 ± 0.2
50% MeOH-50% DMSO	2.80 ± 0.04	16.00 ± 0.20	9.3 ± 0.1	85.0 ± 1.0
75% MeOH-25% DMSO	3.20 ± 0.03	18.27 ± 0.05	-2.2 ± 2 1	-13.0 ± 3.0
100% MeOH	2.88 ± 0.04	16.40 ± 0.10	-2.5 ± 0.2	46.6 ± 0.6
(DB18C6)Cd^{2+}				
100% DMSO	2.92 ± 0.01	16.68 ± 0.03	1.7 ± 0.1	61.6 ± 0.3
25% MeOH-75% DMSO	3.03 ± 0.01	17.27 ± 0.02	4.1 ± 0.1	71.7 ± 0.3
50% MeOH-50% DMSO	3.04 ± 0.03	17.31 ± 0.07	11.3 ± 0.6	96.0 ± 2.0
75% MeOH-25% DMSO	2.86 ± 0.03	16.30 ± 0.10	11.3 ± 0.6	93.0 ± 2.0
100% MeOH	2.91 ± 0.02	16.60 ± 0.06	9.8 ± 0.4	88.0 ± 1.0
(DB18C6)Tl^{+}				
100% DMSO	3.17 ± 0.01	18.07 ± 0.02	-5.1 ± 0.3	44.0 ± 1.0
25% MeOH-75% DMSO	3.18 ± 0.01	18.14 ± 0.02	2.9 ± 0.2	70.6 ± 0.7
50% MeOH-50% DMSO	3.21 ± 0.01	18.30 ± 0.02	7.9 ± 0.4	88.0 ± 1.0
75% MeOH-25% DMSO	3.33 ± 0.04	18.98 ± 0.05	3.0 ± 0.2	73.7 ± 0.6
100% MeOH	3.70 ± 0.04	21.13 ± 0.02	1.4 ± 0.2	75.6 ± 0.7
(DB18C6)Zn^{2+}				
100% DMSO	2.94 ± 0.04	16.8 ± 0.1	9.5 ± 0.6	88.0 ± 2.0
25% MeOH-75% DMSO	2.71 ± 0.03	15.5 ± 0.1	11.2 ± 0.6	90.0 ± 2.0
50% MeOH-50% DMSO	2.85 ± 0.05	16.2 ± 0.2	11.2 ± 0.6	92.0 ± 2.0
75% MeOH-25% DMSO	2.87 ± 0.04	16.4 ± 0.1	2.6 ± 0.1	63.7 ± 0.2
100% MeOH	2.75 ± 0.04	15.7 ± 0.2	5.9 ± 0.3	72.4 ± 0.8

a) The composition of the mixed solvents is expressed in mole % of each solvent
b) SD=Standard deviation

It is evident from Fig. 2 that addition of DB18C6 to Cd^{2+} solutions in DMSO-MeOH binary mixture at various temperatures causes an increase in the molar conductivity which indicates that the (DB18C6)Cd^{2+} complex is more mobile than the corresponding solvated cation. Similar behaviour was observed for Cu^{2+}, Tl^{+} and Zn^{2+} cations in various solvent systems. However, as seen from Fig. 3, addition of DB18C6 to Tl^{+} cation in pure MeOH at different temperatures, results in a decrease in molar conductivity which shows that the (DB18C6)Tl^{+} complex in pure methanol is less mobile than free solvated Tl^{+} cation.

As shown in Fig. 4, a non-linear behaviour is observed between the stability constant (log K_f) of (DB18C6)Cu^{2+} complex *vs.* the composition of DMSO-MeOH binary mixture at different temperatures. Somewhat similar behaviour was observed for other complexes. The non-linear behaviour is observed for these studied systems may be related to the solvent-solvent interactions between DMSO and MeOH molecules and therefore, changing the solvation number of the cations, ligand, the resulting complexes and even the preferential solvation of the ligand in these binary mixed solvents. The MeOH and DMSO solvents are dipolar liquids with large dipole moments. Thus mixing of DMSO with MeOH will induce the mutual destruction of dipolar structures of the component liquids and releasing the free dipoles. Therefore, the strong dipolar interactions between MeOH and DMSO result in changing the structural and energetic properties of the mixed solvent with the composition.

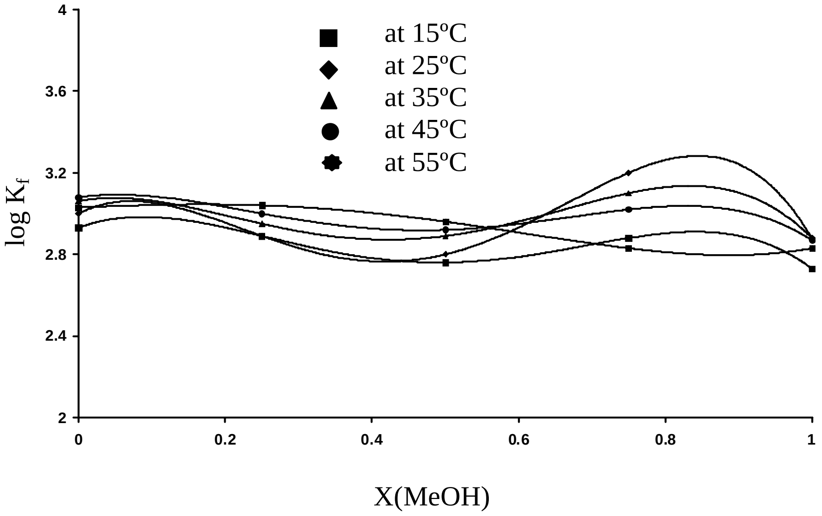


Fig. 4. Variation of stability constant (log K_f) of (DB18C6) Cu^{2+} complex with the composition of the DMSO-MeOH binary systems at different temperatures

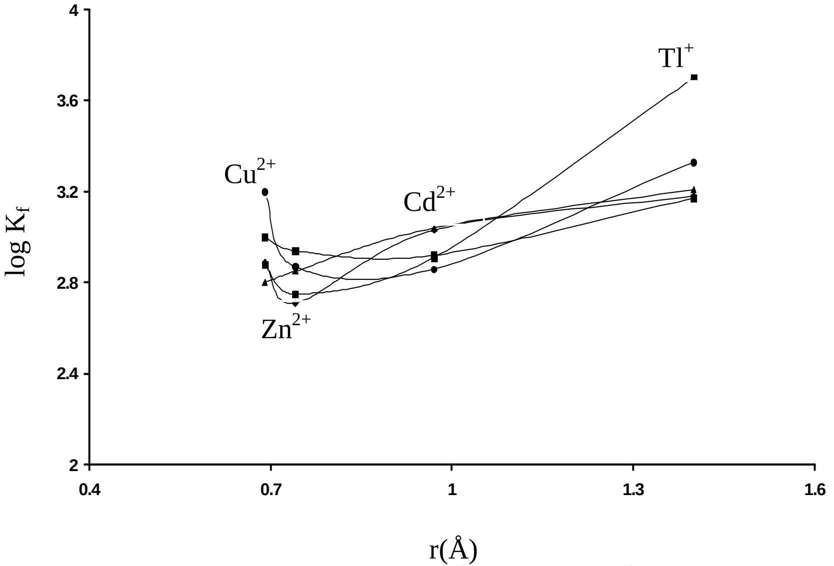


Fig. 5. Variation of log K_f for (DB18C6)Cu^{2+}, (DB18C6)Cd^{2+}, (DB18C6)Tl^+ and (DB18C6)Zn^{2+} complexes *vs.* cationic radii in various solvent systems at 25ºC

The solvation of crown ethers is of great importance during the complexation process of these compounds with the metal cations. In DMSO-MeOH binary mixtures, the preferential solvation of DB18C6 may depend on the structural and energetic properties of the mixtures which varies with the solvent composition.

The variations of stability constants (log K_f) of $(DB18C6)Cd^{2+}$, $(DB18C6)Cu^{2+}$, $(DB18C6)Tl^{+}$ and $(DB18C6)Zn^{2+}$ complexes *vs.* the ionic radii in various compositions of DMSO-MeOH binary solutions are shown in Fig. 5. As is evident from this figure, in most cases the selectivity of DB18C6 for the studied metal cations is $Tl^{+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$. Some reversals in selectivity are observed in certain compositions of the mixed solvents. 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 and the number of the heteroatoms in the polyether ring, the spatial distribution of the ring sites and the cation diameter[25]. The fitness of the size of the cations into the crown ether cavity is an important factor to explain the selectivity of the crown compounds towards the metal cations. In seems that the selectivity order of DB18C6 which is observed for these heavy metal cations is due to the relative size of the metal cations and the cavity size of the polyether ring. The ionic radii of the above cations vary in the order: $Tl^{+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$. The Tl^{+} cation with a large ionic size can attian a more convenient fit condition than the other three cations for the ligand's cavity. Since the Cu^{2+} and Zn^{2+} cations are too small for the ligand's hole, they form the least stable complexes compared with the Cd^{2+} and Tl^{+} cations.

The data in Table-2 show that in most cases, the complexation reactions between DB18C6 and the studied heavy metal cations in DMSO-MeOH binary solutions are enthalpy destabilized but entropy stabilized, and both of these parameters are influenced by the solvent and vary with the solvent composition. It seems reasonable to assume that the positive values of ΔS_c° observed for complexation reactions is due to additional solvent molecules which may be released from the solvation shell of the cations and the ligand upon complexation process.

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(*Received*: 25 May 2005; *Accepted*: 30 June 2006) AJC-5035