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Study of Complex Formation Between Diaza-15-Crown-5 with Uranyl Cation in Some Binary Mixed Aqueous and Non-Aqueous Solvents

MOHAMMAD ANSARIFARD†, GHOLAM HOSSEIN ROUNAGHI*, MAHMOOD CHAMSAZ
and KHALILOLLAH TAHERI†
Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
E-mail: ghrounaghi@yahoo.com; mohammad_ansarifard@yahoo.com

The complexation reaction between UO_2^{2+} cation with diaza-15-crown-5 (DA15C5) was studied in acetonitrile-methanol (AN-MeOH), acetonitrile-ethanol (AN-EtOH), water-methanol (H_2O-MeOH), water-ethanol (H_2O-EtOH), dimethyl formamide-ethanol (DMF-EtOH), dimethyl formamide-ethyl acetate (DMF-EtOAc), propylene carbonate-methanol (PC-MeOH), propylene carbonate-ethanol (PC-EtOH) and dimethyl formamide-propylene carbonate (DMF-PC) binary mixtures at 25 ºC using the conductometric method. The conductance data show that the stoichiometry of the complexes formed between DA15C5 and UO_2^{2+} cation in most cases is 1:1 [M:L], but in some solvent systems also a 1:2 [$M:L_2$] complex is formed in solution. The results obtained in this study show that the mechanism of complex formation reactions between the macrocyclic ligands and the metal cations may change with the nature and even the composition of the mixed binary solvents. The values of stability constant of ($DA15C5.UO_2^{2+}$) complex which were obtained from conductometric data, show that the stability of the complex is affected by the nature and also the composition of the solvent system and in all cases, a non-linear behaviour is observed for the variation of log K_f of the ($DA15C5.UO_2^{2+}$) complex *versus* the composition of the binary mixed solvents. The stability order of ($DA15C5.UO_2^{2+}$) complex in pure studied solvents was found to be: PC > H_2O > DMF ≈ MeOH.

Key Words: Diaza-15-crown-5, UO_2^{2+} cation, Binary mixture solvents, Conductometry.

INTRODUCTION

Since the first publication on the synthesis of crown ethers in 1967 by Pedersen[1], many investigations have been carried out on applications of this compounds in several varieties of areas, such as: chemical analysis[2], organic synthesis[3], in construction of ion-selective electrodes[4,5], separation of metal ions[6,7], as solid phase in chromatography column[8], in the design of fiber optic chemical sensors[9] and in ion exchange membranes[10]. Most of applications of crown compounds are based on

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†Department of Chemistry,Faculty of Sciences, Sistan and Baluchestan University, Zahedan, Iran.

their ability to form stable complexes with various metal cations such as: alkali, alkaline earth and some of transition and heavy metal cations. Because macrocyclic crown ethers are similar to antibiotic ligands, therfore, they can also be used as models for investigation of ion transport through membranes in biological systems[11].

Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters and even the mechanism of the complexation processes are affected by the nature and composition of the solvent system[12,13].

While the complexation of crown ethers with metal ions have been studied in aqueous solutions and in a wide variety of organic solvents[14], but the data available for complexation of crown ethers with metal ions in mixed binary solvent systems, are scarce. When one or two of the oxygen donors in 15-crown-5 or 18-crown-6 are replaced with nitrogen atoms, the stability constants of the complexes of the resulting aza-crown ethers with alkali and alkaline earth metal ions become smaller than those of the corresponding crown ethers. In constract, the complexation abilities with transition metal ions and also heavy metal ions which belong to a class of soft acids, increase markedly the same level as the corresponding acyclic amines. Therefore, aza-crown ethers are suitable complexing agents for transition and heavy metal ions[15]. In order to achieve appropriate solvent properties, one often must use mixtures of two solvents. Mixed solvents play important roles in modern electrochemistry[16].

Various physico-chemical techniques such as: spectrophotometry[17,18], NMR spectrometry[19], polarography[20,21], potentiometry[22] and conductometry[23,24] have been used to study the complex formation between macrocyclic polyethers (crown ethers) and various metal cations in solutions. Among the various methods, the conductometric tehnique is highly sensitive and inexpensive with a simple experimental arrangement. In addition, in this method, the measurments can be carried out at low solution concentrations, where the interactions between the cations and anions are to be small.

In present investigation, the complexation of diaza-15-crown-5 (DA15C5) with uranyl (UO_2^{2+}) cation in water (H_2O), methanol (MeOH), ethanol (EtOH), dimethyl formamide (DMF), propylene carbonate (PC), ethyl acetate (EtOAc), acetonitrile (AN) and in their binary mixtures were studied at 25 ºC using the conductometric method in order to investigate the effect of nature of the solvent properties and the composition of the binary mixed solvents on the stability and stoichiometry of the complexes formed between UO_2^{2+} cation and diaza-15-crown-5 in solution.

EXPERIMENTAL

Diaza-15-crown-5 (Merck) and uranyl nitrate hexahydrate (Riedel) were used without further purification. The solvents: acetonitrile, dimethyl formamide, ethanol, methanol, ethyl acetate, propylene carbonate, all from Merck, were used with the highest purity.

The conductance measurements were performed using a digital, WTW conductivity apparatus model LF 2000 in a water bath thermostated with a constant temperature within ± 0.03 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 0.958 cm^{-1} was used throughout the studies.

Method: The experimental procedure to obtain the stability constant of $(DA15C5.UO_2^{2+})$ complex was as follows: a solution of metal salt $(5 \times 10^{-4}$ 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 from crown ether solutions prepared in the same solvent $(2 \times 10^{-2}$ M) to the titration cell using a microburette. The conductance of the solution in the cell was measured after each addition at the desired temperature.

RESULTS AND DISCUSSION

The changes of molar conductance (Λ_m) *versus* the ligand to metal cation mole ratios, $[L]_t/[M]_t$, for complexation of DA15C5 with UO_2^{2+} cation in various binary mixed solvents were studied at 25 ºC. $[L]_t$ is the total concentration of DA15C5 and $[M]_t$ is the total concentration of uranyl cation (UO_2^{2+}). Three typical series of molar conductance values as a function of ligand-metal cation mole ratios in AN-MeOH, DMF-EtOAc and AN-EtOH binary systems are shown in Figs. 1-3, respectively. The stability constant of $(DA15C5.UO_2^{2+})$ complex in various solvent systems at 25 ºC was calculated from variation of molar conductance as a function of DA15C5/ UO_2^{2+} mole ratios using a GENPLOT computer program[25]. The details of the calculation of the stability constants of complexes by conductometric method has been described elsewhere[26]. The values of stability constant of the $(DA15C5.UO_2^{2+})$ complex in various solvent systems are listed in Table-1. The changes of stability constant $(\log K_f)$ of $(DA15C5.UO_2^{2+})$ complex with the composition of the PC-EtOH, DMF-EtOAc and AN-MeOH binary systems at 25 ºC are shown in Figs. 4 and 5.

As evident from Figs. 1-3, addition of DA15C5 to uranyl cation solutions in AN-MeOH, DMF-EtOAc and AN-EtOH binary solvent systems at 25 ºC results in an increases in molar conductivity which indicates that the $(DA15C5.UO_2^{2+})$ complex is more mobile than free solvated UO_2^{2+} cation in these binary solvent systems.

It is clear from Fig. 1 that in three AN-MeOH binary systems (mole % AN = 15, 35 and 55 %), the slope of the corresponding molar conductivity *versus* ligand/cation mole ratio plots changes sharply at the point where the ligand to cation mole ratio is about 1 which is an evidence for formation of relatively a stable 1:1 [M:L] complex between DA15C5 and UO_2^{2+} cation in these solutions, but in other compositions of this binary solvent (mole % AN = 75, 85 and 100 %), the slope of each curves changes at the point where $[L]_t/[M]_t$ is about 2 which shows the formation of a 1:2 $[M:L_2]$ complex between DA15C5 and UO_2^{2+} cation in these solutions. These results reveal that the stoichiometry of the complexes formed between DA15C5 and uranyl cation changes with the composition of AN-MeOH binary solutions. Similar results have been obtained for complexation of Pb^{2+} cation with aza-18-crown-6 in $DMSO-H_2O$ binary system[27].

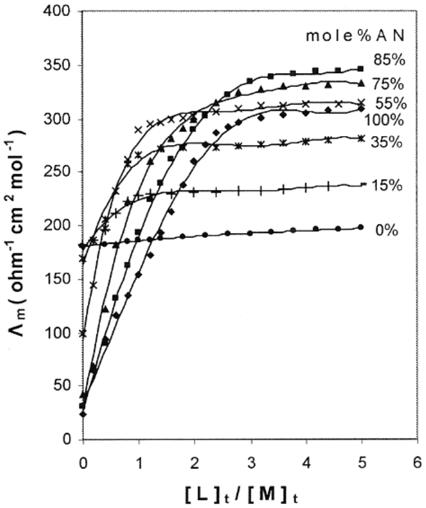

Fig. 1. Molar conductance-mole ratio plots for ($DA15C5.UO_2^{2+}$) complex in AN-MeOH binary systems at 25 °C

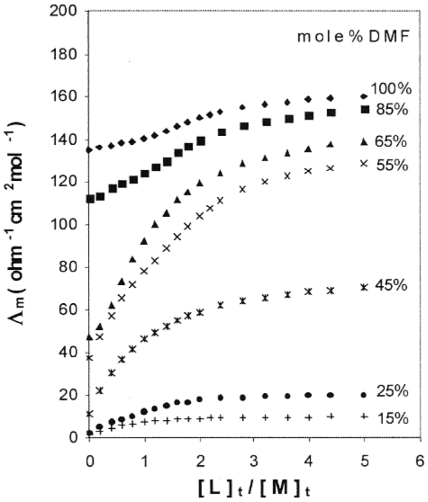

Fig. 2. Molar conductance-mole ratio plots for ($DA15C5.UO_2^{2+}$) complex in DMF-EtOAc binary systems at 25 °C

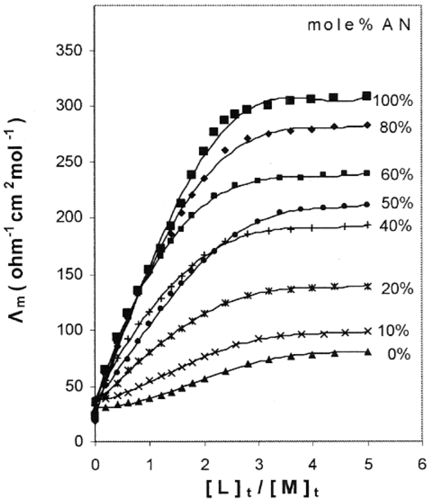

Fig. 3. Molar conductance-mole ratio plots for ($DA15C5.UO_2^{2+}$) complex in AN-EtOH binary systems at 25 °C

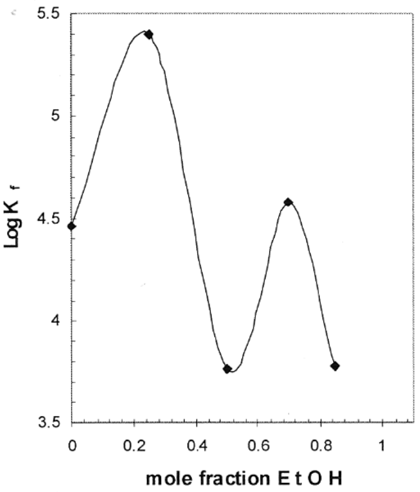

Fig. 4. Changes of stability constant (log K_f) of ($DA15C5.UO_2^{2+}$) complex with the composition of PC-EtOH binary system at 25 °C

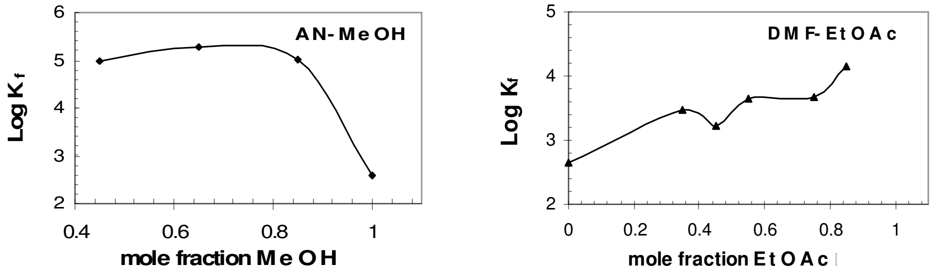

Fig. 5. Changes of stability constant (log K_f) of ($DA15C5.UO_2^{2+}$) complex with the composition of DMF-EtOAc and AN-MeOH binary systems at 25 ºC

As obvious from Fig. 2, in the case of DMF-EtOAc binary system, the slope of each molar conductivity curve changes at the point where $[L]_t/[M_t$ is about 1 which is an evidence for formation of relatively a stable 1:1 [M:L] complex between DA15C5 and UO_2^{2+} cation in this binary system, but as is obvious from Fig. 3, in AN-EtOH binary system, the slope of each curve changes at the point where $[L]_t/[M]_t$ is about 2, which is an evidence for formation of a 1:2 [M:L_2] complex between DA15C5 and UO_2^{2+} cation in this binary system. The results obtained in this work reveals that the property and also the composition of the solvent system are affective factors on stoichiometry and stability of the complexes formed between DA15C5 and uranyl cation.

As illustrated in Table-1, the stability order of ($DA15C5.UO_2^{2+}$) complex in pure studied solvents is: PC > H_2O > DMF ≈ MeOH. It is noticable that the order of decreasing the stability of ($DA15C5.UO_2^{2+}$) complex is not consistent with the order of donor ability of these pure solvents as expressed by the Gutmann donor number[28], because the sequence of the donor number for these solvents is: H_2O (DN = 33) > DMF (DN = 24) > MeOH (DN = 20) > PC (DN = 15.1).

Although the solvating ability of a solvent as expressed by the Gutmann donor number, plays a fundamental role in complexation reactions between metal cations and macrocyclic ligands and a solvent with a high donor number can compete strongly with the ligand for the cation, but the results obtained in this investigation, reveal that the donor ability of a solvent and, therefore, the cation solvation is not always a dominant factor in complexation processes and considering the solvation of the ligand, the resulting complex and even the solvation of counter ion in solutions.

The complexation reaction between a metal cation with a ligand in solution which is an exchange process can be written as:

$$(\text{metal}^{n+})S_x + (\text{ligand})S_y = (\text{metal-ligand})^{n+}S_z + (x + y - z)S$$

in which S is the solvent molecule, x, y, z, are the solvation numbers of metal cation, ligand and the resulting complex, respectively. Therefore, the change of free energy of this reaction, depends on the difference in affinity of ligand and solvent for the metal cation and also the difference in affinity of the metal cation and solvent molecules for the ligand. In addition, the solvation of the resulting complex is effective in the free energy of complexation process. Therefore, in addition of solvation of the metal cation, the solvation of the ligand and the resulting complex contribute to the overal free energy of complex formation in solutions[29]. As evident from Table-1, in DMF-EtOAc binary mixtures in most cases, as the concentration of EtOAc increases, the stability of (DA15C5.UO_2^{2+}) complex increases. Since the donor ability of DMF (DN = 24.0) is higher than of EtOAc (DN = 17.1), therefore, the stability of the complex increases with increasing the concentration of EtOAc in DMF-EtOAc binary solution.

TABLE-1
log K_f VALUES OF (DA15C5.UO_2^{2+}) COMPLEX IN BINARY
MIXTURES SOLVENTS AT 25 °C

Medium	log K_f ± SD[a]	Medium	log K_f ± SD[a]	Medium	log K_f ± SD[a]
AN-EtOH		**AN-MeOH**		**H_2O-MeOH**	
Pure AN	c	Pure AN	c	Pure H_2O	4.17±0.11
80%AN-20%EtOH[b]	c	85%AN-15%MeOH[b]	c	90%H_2O-10%MeOH[b]	3.94±0.19
60%AN-40%EtOH	c	75%AN-25%MeOH	c	75%H_2O-25%MeOH	3.99±0.19
50%AN-50%EtOH	c	55%AN-45%MeOH	4.99±0.16	60%H_2O-40%MeOH	c
40%AN-60%EtOH	c	35%AN-65%MeOH	5.29±0.27	35%H_2O-65%MeOH	c
20%AN-80%EtOH	c	15%AN-85%MeOH	5.01±0.28	15%H_2O-85%MeOH	c
10%AN-90%EtOH	c	Pure MeOH	2.60±0.06	Pure MeOH	2.60±0.06
Pure EtOH	c				
H_2O-EtOH		**DMF-EtOAc**		**DMF-EtOH**	
Pure H_2O	4.17±0.11	Pure DMF	2.66±0.16	Pure DMF	2.66±0.16
93%H_2O-7%EtOH	c	85%DMF-15%EtOAc	2.86±0.10	75%DMF-25%EtOH	c
85%H_2O-15%EtOH	c	65%DMF-35%EtOAc	3.47±0.05	55%DMF-45%EtOH	c
70%H_2O-30%EtOH	c	55%DMF-45%EtOAc	3.22±0.03	35%DMF-65%EtOH	c
45%H_2O-55%EtOH	c	45%DMF-55%EtOAc	3.64±0.03	15%DMF-85%EtOH	c
15%H_2O-85%EtOH	c	25%DMF-75%EtOAc	3.68±0.04	Pure EtOH	c
Pure EtOH	c	15%DMF-85%EtOAc	4.14±0.03		
PC-MeOH		**PC-EtOH**		**DMF-PC**	
Pure PC	4.46±0.07	Pure PC	4.46 ± 0.07	Pure DMF	2.66±0.16
65%PC-35%MeOH	c	75%PC-25%EtOH	5.40 ± 0.15	80%DMF-20%PC	c
40%PC-60%MeOH	c	50%PC-50%EtOH	3.76 ± 0.10	60%DMF-40%PC	c
25%PC-75%MeOH	c	30%PC-70%EtOH	4.58 ± 0.12	40%DMF-60%PC	2.82±0.15
10%PC-90%MeOH	c	15%PC-85%EtOH	3.78 ± 0.04	20%DMF-80%PC	2.67±0.11
Pure MeOH	2.60±0.06	Pure EtOH	c	Pure PC	4.46±0.07

(a) SD = Standard deviation; (b) The composition of binary solvents is expressed in mole% of each solvent; (c) Data can not be fitted in equation.

The changes of stability constant of (DA15C5.UO_2^{2+}) complex *versus* the solvent composition in, PC-EtOH, DMF-EtOAc and AN-MeOH binary mixed systems, are shown in Figs. 4 and 5. As seen in these Figures, the changes in the stability constant (log K_f) of (DA15C5.UO_2^{2+}) complex *versus* the composition of the mixed solvents certainly are not monotonic. For instance, as is evident in Fig. 4, when the concentration of ethanol increases, the stability constant of (DA15C5.UO_2^{2+}) complex initially increases until the mole fraction of ethanol reaches to about 0.2 in PC-EtOH binary systems and then decreases rapidly until the mole fraction of ethanol is reached to about 0.5 and again changes with the composition of the mixed binary systems.

Somewhat similar behaviours have been observed for some of the complexation reactions of crown ethers and aza-crown ethers with metal cations in various binary mixed solvent systems[30,31].

An anomalous behaviour also is observed for changes of stability constant (log K_f) of ($DA15C5.UO_2^{2+}$) complex with the composition of dimethyl formamide-ethyl acetate binary solution (Fig. 5). Somewhat similar behaviour has been observed for ($18C6.Pb^{2+}$) complex in DMF-EtOAc binary mixture[32].

The non-linear behaviour between the log K_f and the composition of the binary mixed non-aqueous solvents which is observed for complexation process between UO_2^{2+} cation and diaza-15-crown-5, may be due to solvent-solvent intractions between the two constituent solvent molecules which result in changing the structure of the solvent systems with their composition and, therefore, changing the solvation numbers of the cation, ligand and even the ($DA15C5.UO_2^{2+}$) complex in solutions. In addition, the heteroselective solvation of the cation and ligand and the character of its changes with the composition of the mixed solvents may be affective in complexation reactions between UO_2^{2+} cation and diaza-15-crown-5 in these binary mixed solvents.

In the case of AN-MeOH binary system (Fig. 5), as the concentration of methanol increases, the stability constant of ($DA15C5.UO_2^{2+}$) complex initially increases until the mole fraction of methanol reaches about 0.65 and then decreases. A non-linear behaviour has also been observed in the case of ($15C5.Mg^{2+}$)complex in AN-MeOH binary mixture[33]. It seems that the interactions between acetonitrile and methanol molecules are responsible for non-monotonic relationship between the log K_f of ($DA15C5.UO_2^{2+}$) complex and the composition of acetonitrile-methanol binary mixture. Prasad and co-workers[34] have studied the interactions between acetonitrile and methanol molecules by excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) measurments at 303.15 K and they showed that these parameters become increasingly negative with increasing strength of intraction between the component molecules. In addition, it has been shown that there is an interaction between acetonitrile and methanol molecules ($K_{ass} = 1.23$) *via* hydrogen bonding in their binary mixtures[35].

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