

Study of complex formation between 18-crown-6 and diaza-18-crown-6 with uranyl cation (UO_2^{2+}) in some binary mixed aqueous and non-aqueous solvents

M. Ansari Fard · G. H. Rounaghi · M. Chamsaz · K. Taheri

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Abstract The complexation reaction between UO_2^{2+} cation with macrocyclic ligand, 18-crown-6 (18C6), was studied in acetonitrile–methanol (AN–MeOH), nitromethane–methanol (NM–MeOH) and propylencarbonate–ethanol (PC–EtOH) binary mixed systems at 25 °C. In addition, the complexation process between UO_2^{2+} cation with diaza-18-crown-6 (DA18C6) was studied in acetonitrile–methanol (AN–MeOH), acetonitrile–ethanol (AN–EtOH), acetonitrile–ethylacetate (AN–EtOAc), methanol–water (MeOH– H_2O), ethanol–water (EtOH– H_2O), acetonitrile–water (AN– H_2O), dimethylformamide–methanol (DMF–MeOH), dimethylformamide–ethanol (DMF–EtOH), and dimethylformamide–ethylacetate (DMF–EtOAc) binary solutions at 25 °C using the conductometric method. The conductance data show that the stoichiometry of the complexes formed between (18C6) and (DA18C6) with UO_2^{2+} cation in most cases is 1:1 [M:L], but in some solvent 1:2 [M:L₂] complex is formed in solutions. The values of stability constants ($\log K_f$) of (18C6 · UO_2^{2+}) and (DA18C6 · UO_2^{2+}) complexes which were obtained from conductometric data, show that the nature and also the composition of the solvent systems are important factors that are effective on the stability and even the stoichiometry of the complexes formed in solutions. In all cases, a non-linear relationship is observed for the changes of stability constants ($\log K_f$) of the (18C6 · UO_2^{2+}) and (DA18C6 · UO_2^{2+}) complexes versus the composition of the binary mixed solvents. The stability order of

(18C6 · UO_2^{2+}) complex in pure studied solvents was found to be: EtOH > AN \approx NM > PC \approx MeOH, but in the case of (DA18C6 · UO_2^{2+}) complex it was : H_2O > MeOH > EtOH.

Keywords 18-Crown-6 · Diaza-18-crown-6 · UO_2^{2+} cation · Binary mixed aqueous and non-aqueous solvents · Conductometry

Introduction

The understanding of the metal–ion chemistry of macrocyclic ligands has important implications for a range of chemical and biochemical areas. Macrocyclic compounds are polydentate ligands containing their donor atoms attached to a cyclic backbone. The first report on the synthesis of macrocyclic compounds (crown ethers) was published in 1967 by Pedersen [1]. These synthetic macrocyclic ligands have been shown to form stable selective complexes with suitable cations in solutions [2]. Most of the applications of these macrocyclic ligands, are based on their complexing ability with different metal cations. Many researches have been carried out on a wide range of applications of these macrocyclic compounds in different areas such as construction of ion-selective electrode [3–5], separation of metal cations [6, 7], as stationary phase in chromatography columns [8–10], designing of chemical sensors [11], recognition of isomers [12] and chemical analysis [13].

Studies of crown ethers complexation with metal cations in different solvent systems, show that the understanding of the interaction between these macrocyclic ligands and the metal cations in solutions requires the study of various

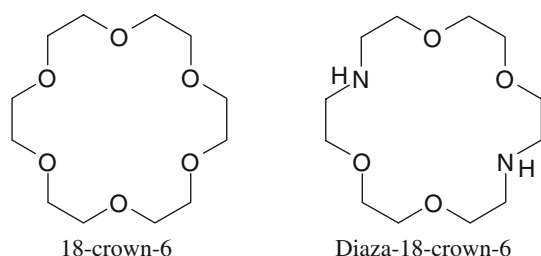
M. Ansari Fard · K. Taheri
Department of Chemistry, Faculty of Sciences,
The University of Sistan and Baluchestan, Zahedan, Iran

G. H. Rounaghi (✉) · M. Chamsaz
Department of Chemistry, Faculty of Sciences, Ferdowsi
University of Mashhad, Mashhad, Iran
e-mail: ghrounaghi@yahoo.com

parameters governing the complexation processes. The thermodynamic studies of such complexation reactions also result in a better understanding of high selectivity of these ligands towards different metal cations. Many investigators have studied the thermodynamics of solution of macrocyclic polyether complexes during the past two decades [14–17]. While the complexation of crown compounds with metal cations have been studied in aqueous solutions and in a wide variety of pure organic solvents [2], but a little attention has been paid to complexation of these macrocyclic ligands with metal cations in mixed binary solvents. The interaction between uranyl cation with several macrocyclic ligands has been studied [18–22].

Aza-crown ethers are suitable complexing agents for transition and heavy metal cations because when one or two oxygen donors in crown ethers are replaced by nitrogen atoms, the stability constants of complexes of the resulting aza-crown ethers with alkali and alkaline earth metal cations become smaller than those of the corresponding crown ethers. In contrast, the complexation abilities with transition metal cations and also heavy metal cations which belong to a class of soft acids, increase markedly to the same level as the corresponding acyclic amines [23].

In this research we studied the complexation of 18-crown-6 (Scheme 1) with uranyl (UO_2^{2+}) cation in methanol (MeOH), ethanol, (EtOH), acetonitrile (AN), nitromethane (NM), propylencarbonate (PC) and in their binary mixtures. We also studied the complexation process of diaza-18-crown-6 (Scheme 1) with uranyl (UO_2^{2+}) cation in water (H_2O), methanol (MeOH), ethanol (EtOH), dimethylformamide (DMF), ethylacetate (EtOAc), acetonitrile (AN) and in their binary mixture solutions at 25 °C using the conductometric method. The goal of the present work was investigation of the effect of the solvent properties and also the composition of the binary mixed solvents on the stoichiometry and the order of selectivity of 18C6 and DA18C6 for UO_2^{2+} in various solvent systems.



Scheme 1 Structure of the ligands

Experimental

Reagents and solvents

18C6 (MERCK) was recrystallized from acetonitrile (MERCK) and dried under vacuum for 72 h at room temperature. Diaza-18-crown-6 (MERCK) and uranyl nitrate hexahydrate (RIEDEL) were used without further purification. The solvents: acetonitrile, dimethylformamide, methanol, ethanol, ethylacetate, nitromethane and propylencarbonate, all from (MERCK), were used with the highest purity.

Apparatus

The conductance measurements were performed using a digital, WTW conductivity apparatus model LF2000 in a water bath thermostated with a constant temperature within ± 0.03 °C. 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 constants of $(18\text{C6} \cdot \text{UO}_2^{2+})$ and $(\text{DA}18\text{C6} \cdot \text{UO}_2^{2+})$ complexes was as follows: a solution of metal salt ($5 \times 10^{-4} \text{ M}$) 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 ($2 \times 10^{-2} \text{ M}$) to the titration cell using a microburette. The conductance of the solution in the cell was measured after each addition at 25 °C.

Results

The changes of molar conductance (Λ_m) versus the ligand to metal cation, $[\text{L}]_t/[\text{M}]_t$, for complexation of 18C6 and DA18C6 with UO_2^{2+} cation in various binary mixed solvents were studied at 25 °C. $[\text{L}]_t$ is the total concentration of the ligand and $[\text{M}]_t$ is the total concentration of uranyl UO_2^{2+} cation. Three typical series of molar conductance values as a function of ligand–metal cation mole ratios in H_2O –MeOH, H_2O –EtOH and AN–MeOH binary systems are shown in Figs. 1, 2 and 3, respectively. The stability constants of $(18\text{C6} \cdot \text{UO}_2^{2+})$ and $(\text{DA}18\text{C6} \cdot \text{UO}_2^{2+})$ complexes in various solvent systems at 25 °C was calculated from variation of molar conductance as a function of Ligand/Cation mole ratios using a GENPLOT computer

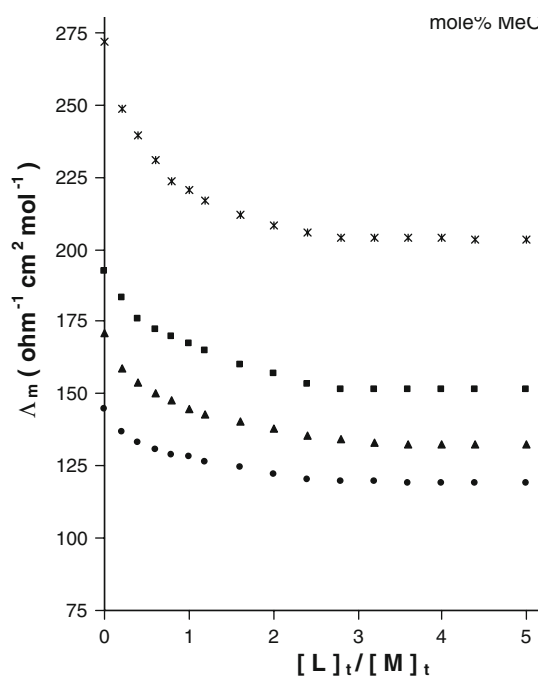


Fig. 1 Molar conductance–mole ratio plots for (DA18C6 · UO₂²⁺) complex in H₂O–MeOH binary systems at 25 °C

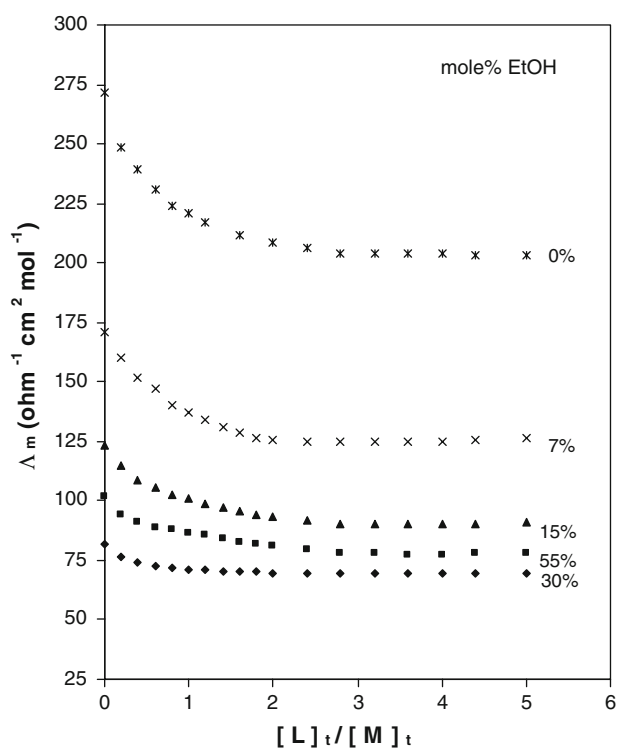


Fig. 2 Molar conductance–mole ratio plots for (DA18C6 · UO₂²⁺) complex in H₂O–EtOH binary systems at 25 °C

program [24]. The details of the calculation of the stability constants of complexes by conductometric method has been described in reference [25]. The values of stability

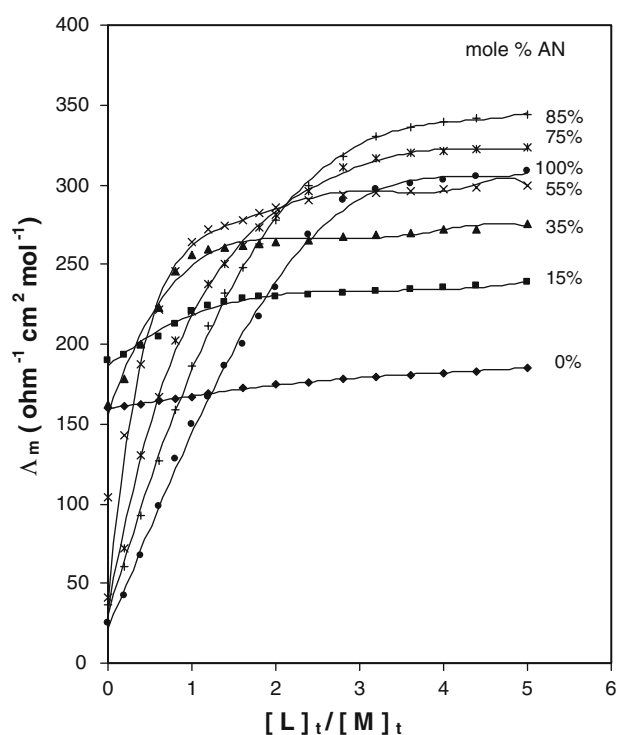


Fig. 3 Molar conductance–mole ratio plots for (DA18C6 · UO₂²⁺) complex in AN–MeOH binary systems at 25 °C

constants of (DA18C6 · UO₂²⁺) and (18C6 · UO₂²⁺) complexes in various solvent systems are listed in Tables 1 and 2, respectively. The changes of stability constant ($\log K_f$) of (18C6 · UO₂²⁺) complex with the composition of the PC–EtOH, AN–MeOH and NM–MeOH binary systems, as well as, the changes of stability constant ($\log K_f$) of (DA18C6 · UO₂²⁺) complex with the composition of the AN–MeOH, H₂O–AN, H₂O–MeOH and H₂O–EtOH binary solutions at 25 °C are shown in Figs. 4, 5, 6 and 7, respectively.

Discussion

As is evident from Figs. 1 and 2, addition of DA18C6 to uranyl cations in H₂O–MeOH and H₂O–EtOH binary solvent systems at 25 °C results in a decrease in molar conductivity which indicates that the (DA18C6 · UO₂²⁺) complex is less mobile than free solvated cation in these binary solvent systems. Similar behavior was observed for (DA18C6 · UO₂²⁺) complex in DMF–MeOH and in H₂O–AN binary solvent systems. But as seen in Fig. 3, addition of DA18C6 to uranyl cation in AN–MeOH binary solutions at 25 °C results in an increase in molar conductivity which indicates that the (DA18C6 · UO₂²⁺) complex in this solvent system is more mobile than free solvated cation. Similar behavior was observed for (DA18C6 · UO₂²⁺) complex in AN–EtOH, DMF–EtOAc and AN–EtOAc

Table 1 Log K_f values of (DA18C6 · UO₂²⁺) complex in different binary mixed solvents at 25 °C

Medium	Log $K_f \pm SD^a$	Medium	Log $K_f \pm SD^a$	Medium	Log $K_f \pm SD^a$
<i>AN–MeOH</i>		<i>H₂O–MeOH</i>		<i>DMF–MeOH</i>	
Pure AN	c	Pure H ₂ O	4.26 ± 0.15	Pure DMF	c
85% AN–15% MeOH ^b	c	90% H ₂ O–10% MeOH ^b	3.75 ± 0.09	85% DMF–15% MeOH ^b	>6
75% AN–25% MeOH	c	75% H ₂ O–25% MeOH	3.89 ± 0.12	65% DMF–35% MeOH	>6
55% AN–45% MeOH	4.58 ± 0.11	60% H ₂ O–40% MeOH	3.84 ± 0.13	45% DMF–55% MeOH	>6
35% AN–65% MeOH	4.85 ± 0.16	35% H ₂ O–65% MeOH	c	25% DMF–75% MeOH	>6
15% AN–85% MeOH	3.92 ± 0.10	25% H ₂ O–75% MeOH	c	10% DMF–90% MeOH	>6
Pure MeOH	2.72 ± 0.05	10% H ₂ O–90% MeOH	c	Pure MeOH	2.72 ± 0.05
		Pure MeOH	2.72 ± 0.05		
<i>AN–EtOH</i>		<i>H₂O–EtOH</i>		<i>DMF–EtOH</i>	
Pure AN	c	Pure H ₂ O	4.26 ± 0.15	Pure DMF	c
80% AN–20% EtOH	c	93% H ₂ O–7% EtOH	4.28 ± 0.07	80% DMF–20% EtOH	>6
60% AN–40% EtOH	c	85% H ₂ O–15% EtOH	3.97 ± 0.09	60% DMF–40% EtOH	>6
40% AN–60% EtOH	c	70% H ₂ O–30% EtOH	3.67 ± 0.11	40% DMF–60% EtOH	>6
20% AN–80% EtOH	c	45% H ₂ O–55% EtOH	4.76 ± 0.38	20% DMF–80% EtOH	>6
Pure EtOH	2.48 ± 0.13	30% H ₂ O–70% EtOH	c	Pure EtOH	2.48 ± 0.13
		15% H ₂ O–85% EtOH	c		
		7% H ₂ O–93% EtOH	c		
		Pure EtOH	2.48 ± 0.13		
<i>H₂O–AN</i>		<i>AN–EtOAc</i>		<i>DMF–EtOAc</i>	
Pure H ₂ O	4.26 ± 0.15	Pure AN	c	Pure DMF	c
90% H ₂ O–10% AN	3.82 ± 0.10	90% AN–10% EtOAc	c	80% DMF–20% EtOAc	2.46 ± 0.13
80% H ₂ O–20% AN	3.75 ± 0.16	75% AN–25% EtOAc	c	60% DMF–40% EtOAc	3.11 ± 0.03
65% H ₂ O–35% AN	c	55% AN–45% EtOAc	c	40% DMF–60% EtOAc	4.24 ± 0.04
40% H ₂ O–60% AN	c	35% AN–65% EtOAc	c	20% DMF–80% EtOAc	4.86 ± 0.10
20% H ₂ O–80% AN	4.31 ± 0.16	15% AN–85% EtOAc	c		
Pure AN	c				

^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**Table 2** Log K_f values of (18C6 · UO₂²⁺) complex in different binary mixed solvents at 25 °C

Medium	Log $K_f \pm SD^a$	Medium	Log $K_f \pm SD^a$	Medium	Log $K_f \pm SD^a$
<i>AN–MeOH</i>		<i>NM–MeOH</i>		<i>PC–EtOH</i>	
Pure AN	2.09 ± 0.26	Pure NM	2.09 ± 0.07	Pure PC	1.69 ± 0.12
75% AN–25% MeOH ^b	2.26 ± 0.11	85% NM–15% MeOH ^b	2.29 ± 0.06	75% PC–25% EtOH ^b	2.17 ± 0.14
55% AN–45% MeOH	3.08 ± 0.05	75% NM–25% MeOH	1.51 ± 0.08	50% PC–50% EtOH	1.57 ± 0.15
35% AN–65% MeOH	3.03 ± 0.11	55% NM–45% MeOH	1.92 ± 0.14	30% PC–70% EtOH	1.81 ± 0.24
15% AN–85% MeOH	1.88 ± 0.16	35% NM–65% MeOH	1.45 ± 0.14	15% PC–85% EtOH	1.76 ± 0.33
Pure MeOH	1.69 ± 0.33	15% NM–85% MeOH	1.68 ± 0.12	Pure EtOH	3.12 ± 0.04
		Pure MeOH	1.69 ± 0.33		

^a SD = Standard deviation^b The composition of binary solvents is expressed in mole% of each solvent

binary mixed solvents, as well as, for (18C6 · UO₂²⁺) complex in AN–MeOH, NM–MeOH and PC–EtOH binary solutions. These behaviors can be explained on the basis of

solvation sphere. It seems that the UO₂²⁺ cation is weakly solvated in H₂O–MeOH and H₂O–EtOH solvent systems. When this cation is complexed with crown ether, it

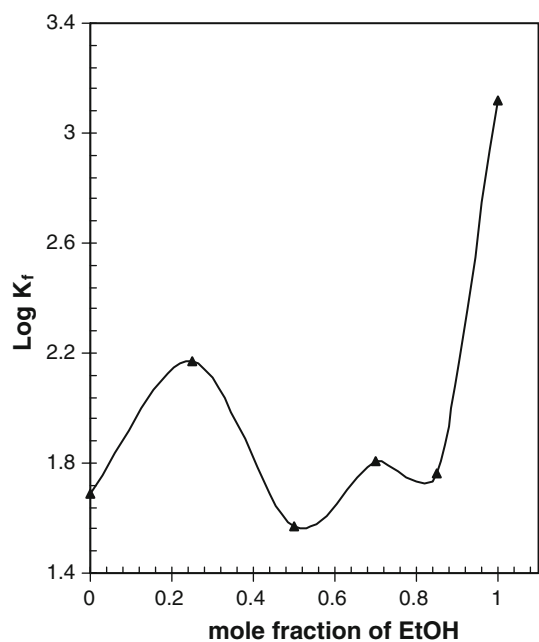


Fig. 4 Changes of stability constant ($\log K_f$) of $(18C6 \cdot UO_2^{2+})$ complex with the composition of PC–EtOH binary system at 25 °C

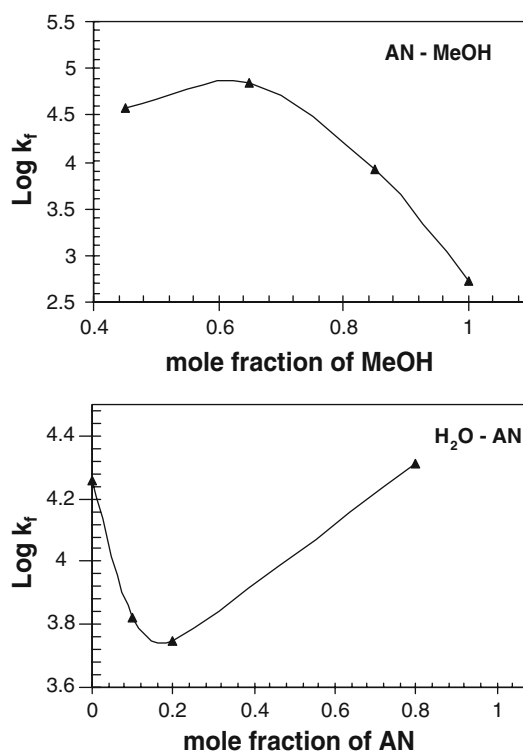


Fig. 6 Changes of stability constant ($\log K_f$) of $(DA18C6 \cdot UO_2^{2+})$ complex with the composition of AN–MeOH and H₂O–AN binary systems at 25 °C

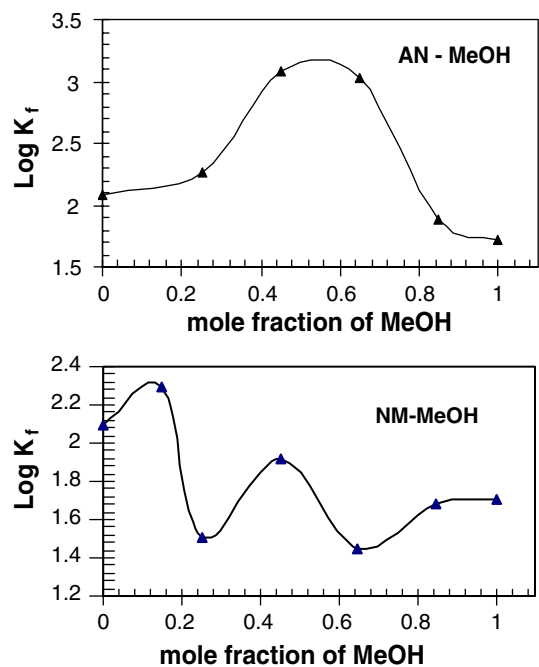


Fig. 5 Changes of stability constant ($\log K_f$) of $(18C6 \cdot UO_2^{2+})$ complex with the composition of AN–MeOH and NM–MeOH binary systems at 25 °C

becomes bulkier which results in a decrease in the molar conductivity of the solutions. On the other hand, it seems that the UO_2^{2+} cation is highly solvated in AN–MeOH binary solutions. However, upon complexation of UO_2^{2+} cation with DA18C6, the ligand molecule replaces the

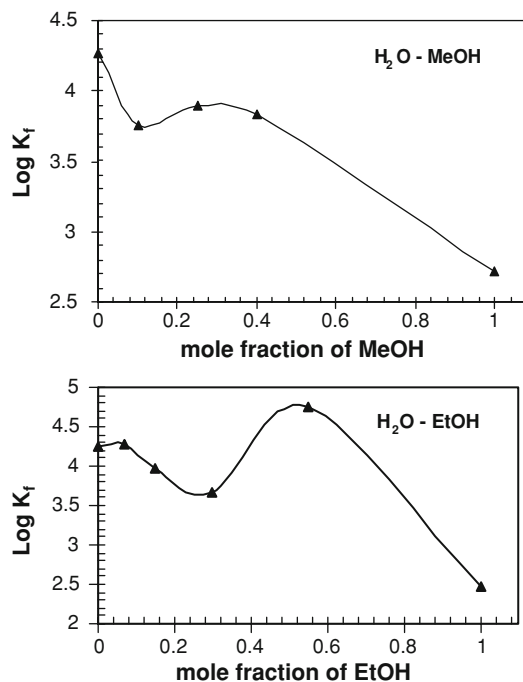


Fig. 7 Changes of stability constant ($\log K_f$) of $(DA18C6 \cdot UO_2^{2+})$ complex with the composition of H₂O–MeOH and H₂O–EtOH binary systems at 25 °C

solvation sheath around the cation and the moving entity becomes less bulky and more mobile and, therefore, the molar conductivity increases.

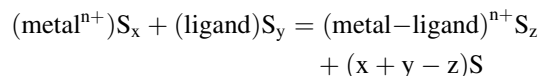
As is shown in Figs. 1 and 2, in all cases, the slope of corresponding molar conductivity versus Ligand/Cation mole ratio plots changes at the point where the ligand to cation mole ratio is about one which is an evidence for formation of a relatively stable 1:1 [M:L] complex between DA18C6 and UO_2^{2+} cation in these solutions. Similar behavior was observed for complexation of UO_2^{2+} cation with 18C6 in solutions. The spectroscopic study of uranyl crown ether complexes in non-aqueous solvents, has shown that the crown ethers with six oxygen atoms form inclusion complexes with uranyl ion in the center cavity, but aza crowns coordinate externally to the uranyl ion [26]. In the case of 18-crown-6 a complex with a high coordination symmetry is formed. The crystal structures of UO_2^{2+} complexes with DA18C6 have been studied and inclusion complexes are reported in which the linear uranyl moiety is included in to the macrocycle with hexagonal–bipyramidal coordination geometry [27].

As is obvious from Fig. 3, 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 at the point where the ligand to cation mole ratio is about one which is an evidence for formation of a 1:1 [M:L] complex between DA18C6 and UO_2^{2+} cation in these solutions, but it is interesting to note that in other compositions of this binary mixed solvent (mole% AN = 75, 85 and 100%), the slope of each curve changes at the point where $[\text{L}]_i/[\text{M}]_i$ is about two which is an evidence for formation of a 1:2 [M:L₂] complex between DA18C6 and UO_2^{2+} cation in these solutions. These results reveal that the stoichiometry of the complex formed between DA18C6 and UO_2^{2+} cation changes with the composition of AN–MeOH binary solutions. Similar results have been obtained for complexation of uranyl cation with diaza-15-crown-5 in AN–MeOH binary solvent systems [28], and also for complexation of Pb^{2+} cation with aza-18-crown-6 in DMSO– H_2O binary solutions [29]. The results obtained in this investigation indicate that the property and also the composition of the solvent system are affective factors on stoichiometry and stability of the complexes formed between DA18C6 and UO_2^{2+} cation in solutions.

As is evident from Table 1, the stability order of (DA18C6 · UO_2^{2+}) complex in pure studied solvents is: $\text{H}_2\text{O} > \text{MeOH} > \text{EtOH}$. Since the DA18C6 is probably strongly solvated in MeOH and EtOH solutions, therefore, the complex is more stable in water compared to these alcoholic solutions. The data in Table 2, show that the stability order of (18C6 · UO_2^{2+}) complex in pure organic solvents is: $\text{EtOH} > \text{AN} \approx \text{NM} > \text{PC} \approx \text{MeOH}$. It is

noticeable that the order of decreasing the stabilities of (DA18C6 · UO_2^{2+}) and (18C6 · UO_2^{2+}) complexes are not consistent with the order of donor ability of these pure organic solvents as expressed by the Gutmann donor number [30] (see Table 3). Similar results have been observed for (DA15C5 · UO_2^{2+}) complex in PC, H_2O , DMF and MeOH solvents [28]. 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 indicate that the donor ability of a solvent and, therefore, the cation solvation is not always a dominant factor in complexation processes and we should consider 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:



in which S is the solvent molecule, x, y and z are the solvation numbers of metal cation, ligand and the resulting complex, respectively. Therefore, the change of free energy of the solution, 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 to solvation of the metal cation, the solvation of the ligand and the resulting complex contribute to the overall free energy of complex formation in solutions [31].

The changes of stability constant ($\log K_f$) of (18C6 · UO_2^{2+}) complex versus the solvent composition, in PC–EtOH, AN–MeOH and NM–MeOH binary mixed solvents are shown in Figs. 4 and 5 and the changes of

Table 3 Donor number values for some of solvents

Solvent	Donor number (DN)
Nitromethane	2.7
Acetonitrile	14.1
Propylencarbonate	15.1
Etylacetate	17.1
Ethanol	19.1
Methanol	20.0
Dimethylformamide	26.6
Water	33.0

stability constant ($\log K_f$) of $(DA18C6 \cdot UO_2^{2+})$ complex versus the solvent composition in AN–MeOH, H_2O –AN, H_2O –MeOH and H_2O –EtOH are shown in Figs. 6 and 7. As illustrated in these figures, the changes in the stability constants ($\log K_f$) of $(18C6 \cdot UO_2^{2+})$ and $(DA18C6 \cdot UO_2^{2+})$ complexes 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 in PC–EtOH binary solutions, the stability constant of $(18C6 \cdot UO_2^{2+})$ complex initially increases until the mole fraction of ethanol reaches to about 0.2 and then decreases until the mole fraction of ethanol reaches to about 0.5, and again changes with the composition of the mixed binary system. Somewhat similar behavior has been observed for $(DA15C5 \cdot UO_2^{2+})$ complex in PC–EtOH binary solution [28]. A non-monotonic behavior has also been observed for complexation of some crown ethers and aza-crown ethers with various metal cations in AN–MeOH and H_2O –AN binary solutions [28, 32–34].

The non-linear behavior between the $\log K_f$ and the composition of the binary mixed solvents which is observed for complexation process between UO_2^{2+} cation with DA18C6 and 18C6, may be due to solvent–solvent interactions between 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 $(18C6 \cdot UO_2^{2+})$ and $(DA18C6 \cdot UO_2^{2+})$ complexes in solutions. In addition, the heteroselective solvation of the cation and the ligands and the character of its changes with the composition of the mixed solvents may be effective in complexation reactions between UO_2^{2+} cation and diaza-18-crown-6 and 18-crown-6 in these binary mixed solvents.

The interactions between some binary mixed solvents have been studied [35]. For example Parasad and co-workers have studied the interactions between acetonitrile and methanol molecules by excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) measurements at 303.15 K and they showed that these parameters become increasingly negative with increasing the strength of interactions between the component molecules [32]. It has also been shown that the change of viscosity of the binary mixtures of water with different alcohols versus their composition, passes through a maximum which indicates the strong interactions between the water and alcoholic molecules in these binary solutions [36].

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