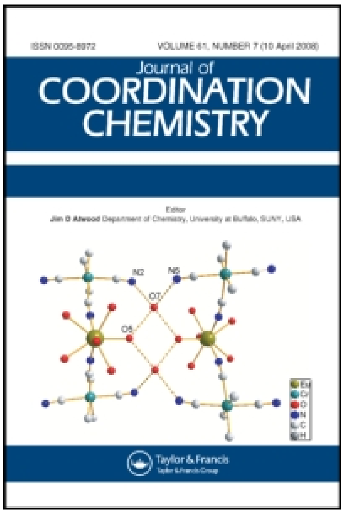


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Complexing ability of a macrocyclic ligand, dibenzo-24-crown-8, with UO_2^{2+} in some binary mixed non-aqueous solvents

Gholam Hossein Rounaghi[a]; Elahe Nazari[a]; Arezoo Ghaemi[b]; Massumeh Mohajeri[a]
[a] Department of Chemistry, Faculty of Sciences, Islamic Azad University, Mashhad Branch, Mashhad, Iran [b] Department of Chemistry, Islamic Azad University, Sciences and Research Branch, Ahvaz, Iran

First published on: 14 July 2010

To cite this Article Rounaghi, Gholam Hossein , Nazari, Elahe , Ghaemi, Arezoo and Mohajeri, Massumeh(2010) 'Complexing ability of a macrocyclic ligand, dibenzo-24-crown-8, with UO_2^{2+} in some binary mixed non-aqueous solvents', Journal of Coordination Chemistry, 63: 13, 2349 — 2359, First published on: 14 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.501863

URL: http://dx.doi.org/10.1080/00958972.2010.501863

Journal of Coordination Chemistry
Vol. 63, No. 13, 10 July 2010, 2349–2359

Complexing ability of a macrocyclic ligand, dibenzo-24-crown-8, with UO_2^{2+} in some binary mixed non-aqueous solvents

GHOLAM HOSSEIN ROUNAGHI*†, ELAHE NAZARI†,
AREZOO GHAEMI‡ and MASSUMEH MOHAJERI†

†Department of Chemistry, Faculty of Sciences, Islamic Azad University,
Mashhad Branch, Mashhad, Iran
‡Department of Chemistry, Islamic Azad University, Sciences and Research Branch,
Ahvaz, Iran

(*Received 24 January 2010; in final form 29 April 2010*)

Complexation between UO_2^{2+} and dibenzo-24-crown-8 (DB24C8) was studied in acetonitrile–ethylacetate (AN–EtOAc), acetonitrile–dimethylformamide (AN–DMF), acetonitrile–methanol (AN–MeOH), acetonitrile–ethanol (AN–EtOH), and acetonitrile–propanol (AN–PrOH) binary solutions at different temperatures using conductometry. The conductance data show that in most cases the stoichiometry of the complex formed between DB24C8 and UO_2^{2+} is 1 : 1 [M : L], but in pure EtOAc, a 1 : 2 [$M : L_2$] complex is formed in the solution. In all cases, except in pure EtOAc, addition of DB24C8 to UO_2^{2+} solutions causes a decrease in molar conductivity which indicates that the mobility of the complexed cation is lesser than that of the uncomplexed one. Non-linear behavior was observed for the changes of $\log K_f$ of $(DB24C8 \cdot UO_2)^{2+}$ *versus* the composition of the binary mixed solvents. The stability order of the complex in binary mixed solvents at 25°C was: AN–EtOAc > AN–PrOH ~ AN–EtOH ~ AN–MeOH > AN–DMF. The standard thermodynamic quantities (ΔH_c° and ΔS_c°) for the formation of $(DB24C8 \cdot UO_2)^{2+}$ were obtained from the temperature dependence of the stability constant using van't Hoff plots. The results show that in most cases complexation between UO_2^{2+} and DB24C8 is enthalpy and entropy stabilized and the values of these thermodynamic parameters are influenced by the nature and composition of the mixed solvents.

Keywords: Dibenzo-24-crown-8; UO_2^{2+} cation; Mixed non-aqueous solvents; Conductometry

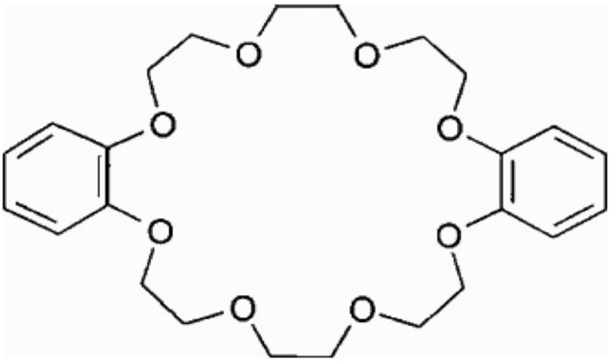
1. Introduction

In 1967, Pedersen [1] described the synthesis of macrocyclic polyethers and the formation of stable complexes between these ligands and various metal cations. Owing to the nature of their binding sites and the presence of a hydrophilic cavity delineated by a lipophilic envelope, crown ethers have the ability to bind guest molecules and metal cations with a high degree of specificity in 3-D cavities. A variety of physico-chemical techniques such as calorimetry [2, 3], polarography [4], potentiometry [5, 6], NMR spectrometry [7, 8], and conductometry [9–11] have been used to study the complex

---

*Corresponding author. Email: ghrounaghi@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.501863



Scheme 1. Structure of dibenzo-24-crown-8 (DB24C8).

formation between crown ethers and metal ions in solutions. Among these various methods, conductometry is a sensitive and inexpensive method for such investigations.

There is a growing interest in the application of computational methods toward the study of actinide compounds. Coordination chemistry of the actinides is important for both fundamental and practical reasons and is different from that displayed by the elements located in other parts of the periodic table. Better understanding of the factors that control this behavior will help work directed toward the treatment of radioactive nuclear wastes. Recent increase in nuclear power production, predominantly based on the uranium-based fuel, has led to the possibility of the release of ultra-trace amounts of uranium in natural aquifers. UO_2^{2+} is known to be nephrotoxic as a heavy metal ion and radiologically harmful as a radionuclide. Although radiological impact is determined by the total concentration of a particular uranium isotope, its chemical toxicity is dependent on the chemical form of its species that interacts with bio-molecules [12]. The ability of uranium to form complexes has been utilized for cleaning up uranium contamination in soils and in the nuclear industry where chelating agents are common constituents of fluids used to clean reactors [13]. The interaction between uranyl cation and several macrocyclic ligands have been studied [14–16].

In the present investigation, complexation of dibenzo-24-crown-8 (scheme 1) with uranyl (UO_2^{2+}) cation in acetonitrile–ethylacetate (AN–EtOAc), acetonitrile–dimethylformamide (AN–DMF), acetonitrile–methanol (AN–MeOH), acetonitrile–ethanol (AN–EtOH), and acetonitrile–propanol (AN–PrOH) binary solutions were studied at different temperatures using the conductometric method to investigate the effect of solvent properties and the composition of the binary mixed solvents on the stability and stoichiometry of the complexes formed between UO_2^{2+} and dibenzo-24-crown-8 in the solution.

2. Experimental

Dibenzo-24-crown-8 (Merck) and $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck) were used without purification. The solvents: acetonitrile, ethylacetate, dimethylformamide, methanol, ethanol, and propanol all from Merck were used with the highest purity.

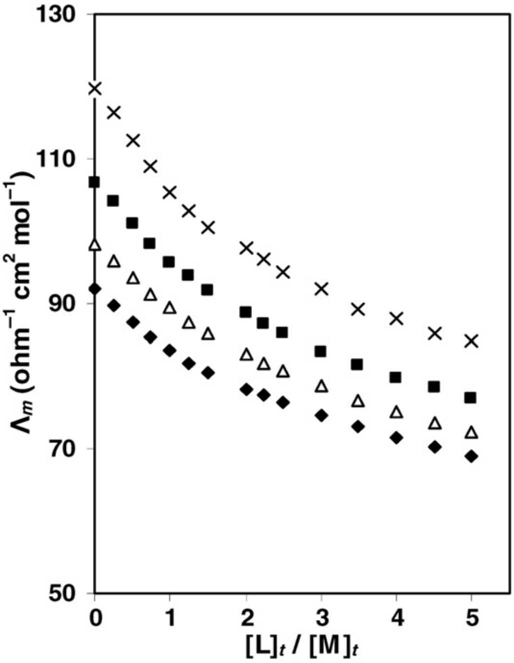


Figure 1. Molar conductance-mole ratio plots for $(DB24C8{\cdot}UO_2)^{2+}$ in AN–EtOAc binary system (mol% AN = 80.0) at different temperatures: (×: 15°C, ■: 25°C, △: 35°C, ◆: 45°C).

The experimental procedure used to obtain the formation constant of $(DB24C8 \cdot UO_2)^{+2}$ was as follows: 20 mL solution of metal salt (1×10^{-4} mol L^{-1}) was placed in a titration cell, thermostated at a given temperature, and the conductance of the solution was measured. Then a step-by-step increase of the crown ether solution (2×10^{-3} mol L^{-1}) prepared in the same solvent was carried out by rapid transfer 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 a digital Metrohm conductivity apparatus (Model 712) in a Julabo (Model F12) water bath, thermostated with a constant temperature maintained within ±0.1°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 0.866 cm^{-1} was used throughout the studies.

3. Results

Changes of molar conductivity (Λ_m) *versus* the ligand to cation molar ratio ($[L]_t/[M]_t$) for complexation of DB24C8 with UO_2^{2+} was measured in pure AN, EtOAc, DMF, and PrOH and also in AN–EtOAc, AN–DMF, AN–MeOH, AN–EtOH, and AN–PrOH binary systems at different temperatures. Two typical series of molar conductance values as a function of molar ratio in AN–EtOAc binary mixture (mol% AN = 80.0) and in pure EtOAc are shown in figures 1 and 2, respectively. In addition, the fitting

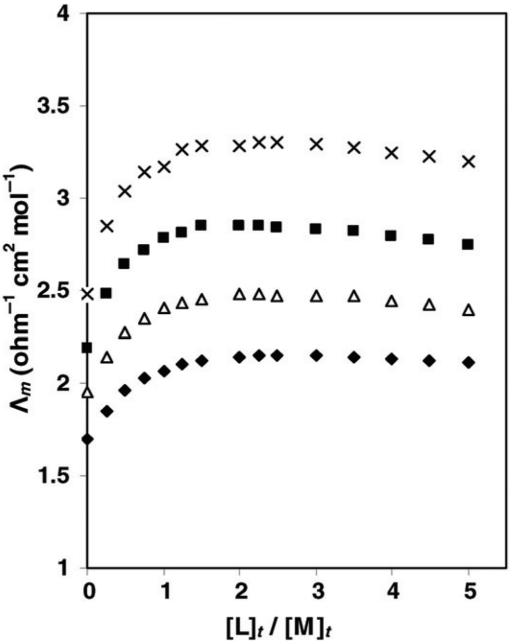


Figure 2. Molar conductance-mole ratio plots for $(DB24C8 \cdot UO_2)^{2+}$ in pure EtOAc at different temperatures: (×: 15°C, ■: 25°C, △: 35°C, ◆: 45°C).

and experimental curves for $(DB24C8 \cdot UO_2)^{2+}$ in acetonitrile–ethylacetate binary system (mol% AN = 80.0) at 25°C are shown in figure 3 (the fitting data are given in the appendix in Supplementary material).

The stability constant of $(DB24C8 \cdot UO_2)^{+2}$ at each temperature was calculated from the changes of the molar conductance as a function of $[DB24C8]/[UO_2^{2+}]$ molar ratios using a GENPLOT computer program [17]. The details of calculation of the stability constants of complexes by conductometric method have been described [18]. The values of stability constant ($\log K_f$) for $(DB24C8 \cdot UO_2)^{+2}$ in various solvent systems are listed in table 1. The 1 : 1 complexation reaction of a metal cation, M^{n+}, with a crown ether is represented by the following equilibrium:

$$M^{n+} + \mathrm{L} \longleftrightarrow \mathrm{ML}^{n+}$$

with equilibrium constant, K_f, given by

$$K_f = \frac{[\mathrm{ML}^{n+}] \cdot f_{\mathrm{ML}^{n+}}}{[\mathrm{M}^{n+}][\mathrm{L}] \cdot f_{\mathrm{ML}^{n+}} f_{\mathrm{L}}},$$

where $[\mathrm{ML}^{n+}]$, $[\mathrm{M}^{n+}]$, and [L] denote the molar concentrations of the complex, metal cation, and crown ether and "*f*" indicates the activity coefficient of the species indicated. Under the highly dilute conditions employed in these experiments, the $f_{\mathrm{ML}^{n+}}/f_{\mathrm{M}^{n+}} f_{\mathrm{L}}$ is essentially the unity and, therefore, the equilibrium constants obtained in this study are thermodynamic equilibrium constants.

The van't Hoff plots of $\ln K_f$ *versus* $1/T$ for all of the investigated systems were constructed. Plots of $\ln K_f$ *versus* $1/T$ in all cases were linear. The changes in standard

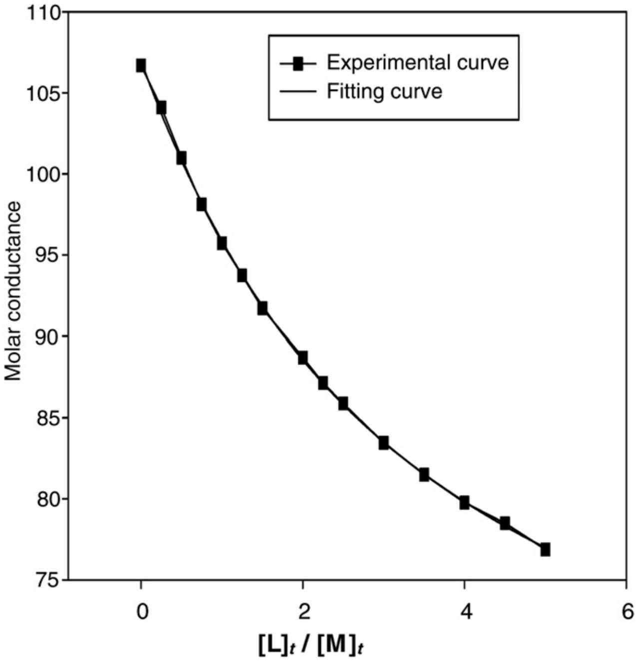


Figure 3. The fitting (–) and experimental (■) curves for $(DB24C8 \cdot UO_2)^{2+}$ in acetonitrile-ethylacetate binary system (mol% AN = 80.0) at 25°C.

enthalpy (ΔH_c°) for complexation were obtained from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. The values of thermodynamic parameters are summarized in table 2. The changes of $\log K_f$ of $(DB24C8 \cdot UO_2)^{+2}$ with the composition of the AN–EtOAc and AN–DMF binary solutions at different temperatures are shown in figures 4 and 5, respectively.

4. Discussion

Addition of DB24C8 to UO_2^{2+} in acetonitrile–ethylacetate binary system (mol% AN = 80.0) at different temperatures results in a decrease in molar conductivity (figure 1), which indicates that $(DB24C8 \cdot UO_2)^{2+}$ in this solution is less mobile than free solvated UO_2^{2+}. According to figure 1, the slope of the corresponding molar conductivity *versus* $[L]_t/[M]_t$ plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for the formation of a relatively stable 1 : 1 [M : L] complex in the solution. Similar behavior was observed for $(DB24C8 \cdot UO_2)^{2+}$ in all of the other pure and binary mixed solvent systems. In order to make more clear the 1 : 1 [M : L] complexation model, the fitting and experimental curves for $(DB24C8 \cdot UO_2)^{2+}$ in acetonitrile–ethylacetate binary system (mol% AN = 80.0) at 25°C are shown in figure 3; there is very good agreement between the fitting and experimental data with

Table 1. Log K_f values of $(\mathrm{DB24C8 \cdot UO_2})^{2+}$ in AN–EtOAc, AN–DMF, AN–MeOH, AN–EtOH, and AN–PrOH binary mixtures at different temperatures.

	Log $K_f \pm$ SD[a]			
Medium	15°C	25°C	35°C	45°C
AN–EtOAc				
Pure EtOAc	[c]	[c]	[c]	[c]
60.0%EtOAc–40.0%AN[b]	3.71 ± 0.04	3.83 ± 0.03	3.69 ± 0.03	3.56 ± 0.05
40.0%EtOAc–60.0%AN	3.41 ± 0.06	3.35 ± 0.04	3.23 ± 0.03	3.27 ± 0.16
20.0%EtOAc–80.0%AN	3.72 ± 0.04	3.61 ± 0.02	3.49 ± 0.01	3.56 ± 0.03
Pure AN	3.54 ± 0.07	3.50 ± 0.02	3.42 ± 0.02	3.32 ± 0.02
AN–DMF				
Pure DMF	2.54 ± 0.14	2.70 ± 0.07	3.20 ± 0.13	2.80 ± 0.05
70.0%DMF–30.0%AN[b]	2.80 ± 0.03	2.74 ± 0.03	2.80 ± 0.06	2.70 ± 0.01
40.0%DMF–60.0%AN	2.70 ± 0.03	2.70 ± 0.03	2.66 ± 0.01	2.65 ± 0.01
20.0%DMF–80.0%AN	2.83 ± 0.07	2.78 ± 0.09	2.71 ± 0.01	2.74 ± 0.13
Pure AN	3.54 ± 0.07	3.50 ± 0.02	3.42 ± 0.02	3.32 ± 0.02
AN–MeOH				
90.0%MeOH–10.0%AN[b]	2.67 ± 0.02	2.70 ± 0.05	2.66 ± 0.02	2.66 ± 0.01
80.0%MeOH–20.0%AN	2.85 ± 0.06	2.83 ± 0.07	2.68 ± 0.02	2.54 ± 0.17
60.0%MeOH–40.0%AN	2.82 ± 0.07	2.81 ± 0.09	2.54 ± 0.15	2.83 ± 0.08
30.0%MeOH–70.0%AN	2.82 ± 0.08	2.83 ± 0.07	2.78 ± 0.08	2.75 ± 0.09
Pure AN	3.54 ± 0.07	3.50 ± 0.02	3.42 ± 0.02	3.32 ± 0.02
AN–EtOH				
90.0%EtOH–10.0%AN[b]	2.68 ± 0.12	2.82 ± 0.08	2.68 ± 0.01	2.79 ± 0.10
70.0%EtOH–30.0%AN	2.36 ± 0.16	2.33 ± 0.16	2.55 ± 0.18	2.58 ± 0.13
50.0%EtOH–50.0%AN	2.55 ± 0.03	2.49 ± 0.03	2.25 ± 0.04	2.82 ± 0.10
30.0%EtOH–70.0%AN	2.70 ± 0.13	3.02 ± 0.06	2.88 ± 0.06	2.71 ± 0.13
Pure AN	3.54 ± 0.07	3.50 ± 0.02	3.42 ± 0.02	3.32 ± 0.02
AN–PrOH				
Pure PrOH	2.53 ± 0.06	2.06 ± 0.04	2.70 ± 0.15	2.70 ± 0.18
70.0%PrOH–30.0%AN[b]	2.70 ± 0.11	2.80 ± 0.09	2.83 ± 0.07	2.63 ± 0.03
40.0%PrOH–60.0%AN	2.86 ± 0.12	2.49 ± 0.13	2.83 ± 0.08	2.54 ± 0.03
20.0%PrOH–80.0%AN	3.05 ± 0.08	2.76 ± 0.05	2.77 ± 0.04	2.77 ± 0.18
Pure AN	3.54 ± 0.07	3.50 ± 0.02	3.42 ± 0.02	3.32 ± 0.02

[a] SD = standard deviation.

[b] Composition of binary mixtures is expressed in mol% for each solvent system.

[c] The data cannot be fitted in equation.

experimental and fitting curves superimposed. In pure ethylacetate (figure 2), the addition of DB24C8 to $\mathrm{UO_2^{2+}}$ at different temperatures results in an increase in molar conductivity which shows that the complex formed between DB24C8 and uranyl cation is more mobile than free solvated $\mathrm{UO_2^{2+}}$.

It is interesting to note that as the DB24C8/$\mathrm{UO_2^{2+}}$ mole ratio increases from 0 to 1 (figure 2), the molar conductivity increases sharply, then further addition of the ligand results in a gradual decrease in molar conductivity. It seems that at first a 1 : 1 [M : L] complex is formed between DB24C8 and $\mathrm{UO_2^{2+}}$ cation in pure EtOAc at all temperatures, which is more mobile than free solvated $\mathrm{UO_2^{2+}}$, but further addition of the ligand results in the formation of a 1 : 2 [$\mathrm{M : L_2}$] complex in the solution which is less mobile than the 1 : 1 complex. Therefore, we suggest the following mechanism for complexation between uranyl cation and DB24C8 in this pure dipolar aprotic solvent at

Table 2. Thermodynamic parameters for $(\mathrm{DB24C8\cdot UO_2})^{2+}$ in AN–EtOAc, AN–DMF, AN–MeOH, AN–EtOH, and AN–PrOH binary mixtures.

Medium	$-\Delta G^\circ_c$ ± SD[a] (25°C) (kJ mol^{-1})	ΔH°_c ± SD[a] (kJ mol^{-1})	ΔS°_c ± SD[a] (J mol^{-1} K^{-1})
AN–EtOAc			
60.0%EtOAc–40.0%AN[b]	22 ± 0	−80 ± 35	[c]
40.0%EtOAc–60.0%AN	19 ± 0	−35 ± 15	[c]
20.0%EtOAc–80.0%AN	21 ± 0	−11 ± 7	[c]
Pure AN	20 ± 0	−13 ± 2	23 ± 6
AN–DMF			
Pure DMF	15 ± 4	[c]	[c]
70.0%DMF–30.0%AN[b]	16 ± 0	−4 ± 3	38 ± 10
40.0%DMF–60.0%AN	15 ± 0	−3 ± 1	43 ± 3
20.0%DMF–80.0%AN	16 ± 0	−6 ± 3	34 ± 10
Pure AN	20 ± 0	−13 ± 2	23 ± 6
AN–MeOH			
90.0%MeOH–10.0%AN[b]	15 ± 0	[c]	46 ± 5
80.0%MeOH–20.0%AN	16 ± 0	−18 ± 4	[c]
60.0%MeOH–40.0%AN	16 ± 0	[c]	[c]
30.0%MeOH–70.0%AN	16 ± 0	[c]	[c]
Pure AN	20 ± 0	−13 ± 2	23 ± 6
AN–EtOH			
90.0%EtOH–10.0%AN[b]	16 ± 0	[c]	[c]
70.0%EtOH–30.0%AN	13 ± 1	[c]	[c]
50.0%EtOH–50.0%AN	14 ± 2	[c]	[c]
30.0%EtOH–70.0%AN	17 ± 0	[c]	[c]
Pure AN	20 ± 0	−13 ± 2	23 ± 6
AN–PrOH			
70.0%PrOH–30.0%AN[b]	16 ± 0	[c]	[c]
40.0%PrOH–60.0%AN	14 ± 1	[c]	[c]
20.0%PrOH–80.0%AN	16 ± 0	[c]	[c]
Pure AN	20 ± 0	−13 ± 2	23 ± 6

[a] SD = standard deviation.
[b] Composition of binary mixtures is expressed in mol% for each solvent system.
[c] With high uncertainty.

all temperatures:

$$\mathrm{UO_2^{2+} + DBC24C8 \longleftrightarrow (DB24C8\cdot UO_2)^{2+}} \tag{I}$$

$$\mathrm{(DB24C8\cdot UO_2)^{2+} + DB24C8 \longleftrightarrow [(DB24C8)_2\cdot UO_2]^{2+}} \tag{II}$$

The results obtained in this investigation show that the stoichiometry of the crown ether–metal cation complexes may be changed by the nature of the solvent system [14, 15].

As obvious from table 1, the stability constant of $(\mathrm{DB24C8\cdot UO_2})^{2+}$ in the binary mixed solvents at 25°C is: AN–EtOAc > AN–PrOH ~ AN–EtOH ~ AN–MeOH > AN–DMF. This can be interpreted by considering the inherent relative solvating ability of the pure solvents which form the mixtures. DMF with a high donor ability (DN = 26.6) relative to MeOH (DN = 20.0), EtOH (DN = 19), PrOH (DN = 18.0), and EtOAc (DN = 17.1) can solvate the $\mathrm{UO_2^{2+}}$ cation strongly and compete with the ligand

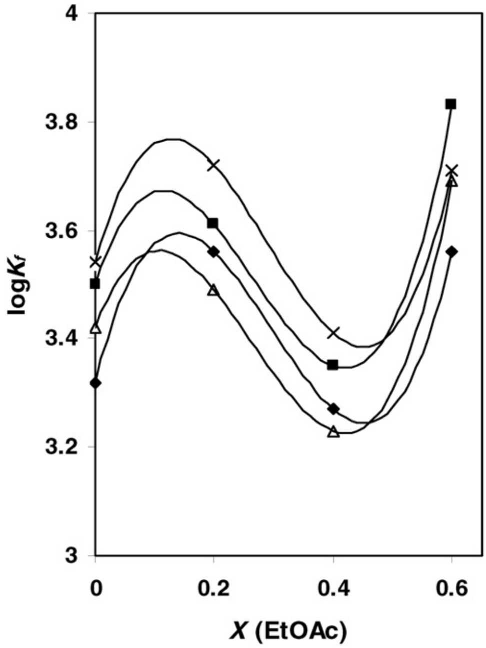


Figure 4. Changes of the stability constant of $(DB24C8{\cdot}UO_2)^{2+}$ with composition of the AN-EtOAc binary mixture at different temperatures: (×: 15°C, ■: 25°C, △: 35°C, ◆: 45°C).

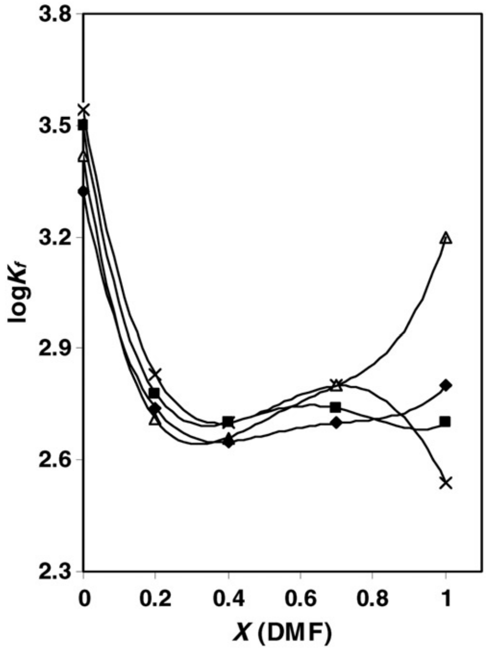


Figure 5. Changes of the stability constant of $(DB24C8{\cdot}UO_2)^{2+}$ with composition of the AN-DMF binary mixture at different temperatures: (×: 15°C, ■: 25°C, △: 35°C, ◆: 45°C).

for this cation in the solution. In addition, the higher dielectric constant of DMF ($\varepsilon = 36.7$) compared with MeOH ($\varepsilon = 32.6$), EtOH ($\varepsilon = 24.3$), PrOH ($\varepsilon = 20.1$), and EtOAc ($\varepsilon = 6.02$) could also lead to a decrease in electrostatic interactions between dibenzo-24-crown-8 and UO_2^{2+} in the solution.

As seen from figures 4 and 5, changes of stability constant ($\log K_f$) of $(DB24C8 \cdot UO_2)^{2+}$ with the composition of AN–EtOAc and AN–DMF binary systems are not linear. Non-linear behavior was also observed in all other binary solutions. This behavior may be related to the changes occurring in the structure of the solvent mixtures and, therefore, changing the solvation properties of the cyclic polyether, cation, and even the resulting complex in these solvent mixtures. In addition, the heteroselective solvation of the cation and the ligand and its changes with the composition of the mixed solvents may be effective in complexation reaction between uranyl cation and DB24C8 in these binary mixed solution systems.

Interactions between some binary mixed solvents have been studied [19]. For example, mixing of DMF with AN induces the mutual destruction of dipolar structures of these dipolar aprotic liquids and releases the free dipoles [20]. As a result, strong dipolar interactions between AN and DMF molecules are expected. In addition, there is an interaction between AN and MeOH molecules ($K_{\text{ass}} = 1.23$) *via* hydrogen bonding in their binary mixtures [21].

Preferential solvation of the cation, anion, and ligand with the composition of the mixed solvents and temperature may be effective in this complexation process. Preferential solvation of ions by one of the components of a mixed solvent system depends on two factors: the relative donor–acceptor abilities of the component molecules toward the ion and the interactions between solvent molecules themselves. The solvating properties of the components in mixed solvents can even be significantly modified by solvent–solvent interactions when the energy of the latter is comparable with the energy difference of solvent–ion interactions for both the components [22].

Thermodynamic data which are given in table 2 reveal that in most cases $(DB24C8 \cdot UO_2)^{2+}$ is both enthalpy and entropy stabilized, therefore, both of these thermodynamic quantities are driving forces for the formation of this complex in these solutions. As is obvious from table 2, in some cases the change in standard enthalpy for the complexation reaction between UO_2^{2+} and DB24C8 is negligible; therefore, it seems that the complexation processes in some solvent systems are athermic.

As the values of standard entropy (ΔS_c°) and standard enthalpy (ΔH_c°) for the formation of $(DB24C8 \cdot UO_2)^{2+}$ in the solution vary with parameters such as changes in the flexibility of the macrocyclic ligand during the complexation process, and also with the extent of cation–solvent, ligand–solvent, and complex–solvent interactions and even with the solvent–solvent interactions, these thermodynamic quantities change with the nature and composition of the solvent systems [23–25].

The results obtained in this study show that thermodynamic parameters do not vary monotonically with solvent composition (table 2) due to variations in the extent of the contribution of important parameters such as solvation–desolvation of the species involved in the complexation reaction (i.e., UO_2^{2+}, DB24C8, the resulting complex and even NO_3^-), and also the conformational changes of the large macrocyclic ligand in the binary solutions; therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition of the binary mixed solutions. Somewhat similar thermodynamic behavior has been observed for the complexation of DB24C8 with alkaline earth metal cations in AN–DMF binary mixture [26].

5. Conclusion

The results obtained for the complexation of UO_2^{2+} with DB24C8 in pure AN, EtOAc, DMF, and PrOH and also in AN–EtOAc, AN–DMF, AN–MeOH, AN–EtOH, and AN–PrOH binary mixtures show that the stoichiometry, stability, and thermodynamics of complex formation between uranyl cation with the macrocyclic ligand are governed by the nature and composition of solvent systems. The conductance data show that in most cases DB24C8 forms a 1 : 1 [M : L] complex with UO_2^{2+}, but in pure EtOAc, a 1 : 2 [M : L_2] complex is formed in the solution. The order of stability constant of $(DB24C8 \cdot UO_2)^{2+}$ in the binary mixed solvents at 25°C was found to be: AN–EtOAc > AN–PrOH ~ AN–EtOH ~ AN–MeOH > AN–DMF. The results show that the electron donor ability and the dielectric constant of the solvents play an important role in complexation. A non-linear relationship was observed between the stability constant of $(DB24C8 \cdot UO_2)^{+2}$ and the composition of the binary solutions. Thermodynamic parameters do not vary monotonically with the solvent composition. These behaviors are probably due to a change in the structure of the binary solvents as the composition of the medium is varied. In most cases, complexation between UO_2^{2+} and DB24C8 is enthalpy and entropy stabilized and the values of these thermodynamic quantities are affected by the nature and composition of the mixed solvents. The solvation of crown ethers is of importance during the complexation process of macrocyclic ligands with the metal cations, and the relative enthalpy and entropy changes can be better understood if ligand solvation is taken into consideration. Information on the interaction of macrocyclic ligands with solvent is sparse, and additional studies on the ligand–solvent interaction are necessary to investigate the thermodynamic behavior of macrocyclic complexes in the solution.

Acknowledgment

We gratefully acknowledge the support of this work by Islamic Azad University, Mashhad Branch, Mashhad, Iran.

References

[1] C.J. Pedersen. *J. Am. Chem. Soc.*, **89**, 2495 (1967).
[2] J.D. Lamb, R.M. Izatt, C.S. Swain, J.J. Christensen. *J. Am. Chem. Soc.*, **102**, 475 (1980).
[3] A. Gherrou, H.J. Buschmann, E. Schollmeyer. *Thermochim. Acta*, **425**, 1 (2005).
[4] M. Chamsaz, G.H. Rounaghi, M.R. Sovizi. *Russ. J. Inorg. Chem.*, **50**, 413 (2005).
[5] K. Yoshihiro, U. Jun, K. Shoichi, T. Yasuyuki. *J. Mol. Liquids*, **123**, 29 (2006).
[6] G.W. Gokel, D.M. Goli, C. Minganti, L. Echegoyen. *J. Am. Chem. Soc.*, **105**, 6786 (1983).
[7] P. Radosław, S. Grzegorz, B. Bogumil, B. Franz. *J. Mol. Struct.*, **749**, 128 (2005).
[8] G.H. Rounaghi, A.I. Popov. *J. Inorg. Chim. Acta*, **114**, 145 (1986).

[9] G.H. Rounaghi, A. Ghaemi. *Russ. J. Inorg. Chem.*, **54**, 1921 (2009).
[10] G.H. Rounaghi, E. Razavipanah. *J. Inclusion Phenom. Macrocyclic Chem.*, **61**, 313 (2008).
[11] G. Cihan, S. Umit, O. Nalan, B. Ismet, C. Umit, B. Mustafa. *Dyes Pigm.*, **71**, 161 (2006).
[12] S.J. Markich. *Sci. World J.*, **2**, 707 (2002).
[13] R.M. Sellers. *Radiat. Phys. Chem.*, **21**, 295 (1983).
[14] M. Ansari Fard, G.H. Rounaghi, M. Chamsaz, K. Taheri. *J. Inclusion Phenom. Macrocyclic Chem.*, **64**, 49 (2009).
[15] M. Ansari Fard, G.H. Rounaghi, M. Chamsaz, K. Taheri. *Asian J. Chem.*, **21**, 2799 (2009).
[16] G.H. Rounaghi, R. Mohammad Zade Kakhki. *J. Inclusion Phenom. Macrocyclic Chem.*, **63**, 117 (2009).
[17] Genplot. *A Data Analysis and Graphical Plotting Program for Scientist and Engineers*, Computer Graphic Service, Ltd., Ithaca, New York, USA (1989).
[18] G.H. Rounaghi, Z. Eshaghi, E. Ghiamati. *Talanta*, **44**, 275 (1997).
[19] A. Ali, S. Hydar, A.K. Nain. *J. Mol. Liq.*, **79**, 89 (1999).
[20] G.H. Rounaghi, M.H. Arbab Zavvar, K. Badiee, F. Boosaidi, M.S. Kazemi. *J. Inclusion Phenom. Macrocyclic Chem.*, **59**, 363 (2007).
[21] G.A. Krestov, N.P. Novosyolov, I.S. Perelygin. *Ionic Solvation*, Ellis Horwood, New York (1994).
[22] J. Szymańska-Cybulska, E. Kamieńska-Piotrowicz. *J. Solution Chem.*, **35**, 1631 (2006).
[23] G.H. Rounaghi, S. Tarahomi, M. Mohajeri. *J. Inclusion Phenom. Macrocyclic Chem.*, **63**, 319 (2009).
[24] G.H. Rounagh, N. Khazaee, K.R. Sanavi. *Polish J. Chem.*, **79**, 1143 (2005).
[25] G.H. Rounaghi, R. Sanavi Khoshnood, M.H. Arbab Zavvar. *J. Inclusion Phenom. Macrocyclic Chem.*, **54**, 247 (2006).
[26] G.H. Rounaghi, E. Esmaily Shahri, A. Soleimani. *J. Chinese Chem. Soc.*, **51**, 923 (2004).