

Thermodynamic study of complex formation between dibenzo-18-crown-6 and UO_2^{2+} cation in different non-aqueous binary solutions

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Abstract In the present work the complexation process between UO_2^{2+} cation and the macrocyclic ligand, dibenzo-18-crown-6 (DB18C6) was studied in ethylacetate–dimethyl formamide (EtOAc/DMF), ethylacetate–acetonitrile (EtOAc/AN), and ethylacetate–tetrahydrofuran (EtOAc/THF) and ethylacetate–propylencarbonate (EtOAc/PC) binary solutions at different temperatures using the conductometric method. The results show that the stoichiometry of the (DB18C6 · UO_2^{2+}) complex in all binary mixed solvents is 1:1. A non-linear behavior was observed for changes of $\log K_f$ of this complex versus the composition of the binary mixed solvents. The stability constant of (DB18C6 · UO_2^{2+}) complex in various neat solvents at 25 °C decreases in order: THF > EtOAc > PC > AN > DMF, and in the binary solvents at 25 °C is: THF–EtOAc > PC–EtOAc > DMF–EtOAc \approx AN–EtOAc. The values of thermodynamic quantities (ΔH°_c , ΔS°_c) for formation of this complex in the different binary solutions were obtained from temperature dependence of its stability constant and the results show that the thermodynamics of complexation reaction between UO_2^{2+} cation and DB18C6 is affected strongly by the nature and composition of the mixed solvents.

Keywords Dibenzo-18-Crown-6 · UO_2^{2+} cation · Mixed non-aqueous solvents · Conductometry

Introduction

Crown ethers are macrocyclic polyethers whose structure exhibits a conformation with a so-called hole capable of trapping cations by coordination with lone pair of electrons on the oxygen atoms. The ability of these compounds to form stable complexes with cations has spurred interest in these compounds. They are a special type of polydentate ligand in which the ligating atoms lie approximately in a plane about the central metal atom, and the remainder of the molecule lies in a “crown” arrangement. All of the oxygen atoms of the polyether “point” inward toward the metal cation, and these macrocyclic ligands have the unusual property of the forming stable complexes with alkali metal ions. This exceptional stability is related to the cavity size of the ligand, with different cavity sizes favoring specific alkali metal ions. A variety of physico-chemical techniques such as calorimetry [1, 2], polarography [3], potentiometry [4, 5], NMR spectrometry [6, 7] and conductometry [8, 9] have been used to study the complex formation between crown ethers and various metal ions in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

It is not surprising that the crown ether ligands have been considered as potential extractant for actinide and lanthanide ions. Reddy et al. reported an increase of both the extractability and selectivity for the extraction of Nd(III), Eu(III) and Tm(III) with acylpyrazolones, 18C6, DCH18C6, or DB18C6 [10]. A review of crown ether containing extraction systems has recently been published [11].

A key chemical process in the nuclear industry is the extraction and purification of uranium in the initial production of fuel for nuclear reactors and in the reprocessing of spent nuclear fuel. Uranyl can easily form complexes

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with various types of ligands, e.g., inorganic ligands, small organic ligands or macrocyclic ligands like crown ethers. Several studies have been carried out to enhance the selectivity in the separation of lanthanides and actinides elements in the extraction systems based on the size-fitting effect of the crown ethers [12–16].

In the 1980s, Lagrange et al. pioneered the study of complex formation of uranyl with crown ethers and azacrowns in water, acetonitrile and propylencarbonate [17, 18]. These last two solvents exhibit good solvating properties to promote the inclusion of uranyl in a macrocyclic ligand: their dielectric constants are high enough to provide dissociation of strong electrolytes and yet metallic cations are less solvated by these organic solvents.

In these complexation processes, solvent plays a critical role in local structure optimization and complex stabilization. Solvents are known to have a profound effect on the stability of supramolecular complexes. So that the stability constants (K_f) of such complexes can vary over many order of magnitudes with the nature of medium. The orders of stabilities of the metal ion complexes do not at all conform to usual expectations, based e.g., on solvent polarities. It has also been shown that the stability and selectivity of crown ether–metal cation complexes vary drastically with the nature and composition of some the binary mixed non-aqueous solvents [19–23].

One of our main research interests is the influence of solvent properties on the thermodynamics of complexation reactions of macrocyclic ligands with different metal cations. In the present paper, we report the results which are obtained from conductometric study of the complexation reaction of UO_2^{2+} cation with macrocyclic ligand, dibenzo-18-crown-6, in ethylacetate–dimethylformamide (EtOAc/DMF), ethylacetate–acetonitrile (EtOAc/AN) and ethylacetate–tetrahydrofuran (EtOAc/THF) and ethylacetate–propylencarbonate (EtOAc/PC) binary solutions at different temperatures.

Experimental

Dibenzo-18-crown-6 (Fluka) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Riedel company) were used without further purification. The solvents: ethylacetate (Riedel) and dimethylformamide, acetonitrile, tetrahydrofuran and propylencarbonate all from Merck company were used with the highest purity. The experimental procedure for study of the complexation process is as follows: a solution of metal salt (1×10^{-4} M) 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 prepared in the same solvent (2×10^{-3} M) was carried out by a 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 using a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature which maintained within ± 0.03 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The cell constant was 0.73 cm^{-1} .

Results

The changes of molar conductivity (Λ_m) versus the ligand to the cation molar ratio ($[\text{UO}_2^{2+}]/[\text{DB18C6}]$), for complexation of DB18C6 with UO_2^{2+} cation was measured in pure EtOAc, DMF, PC, THF, AN and also in EtOAc–DMF, EtOAc–PC, EtOAc–THF and EtOAc–AN binary systems at different temperatures. Two typical series of molar conductance values as a function of ($[\text{UO}_2^{2+}]/[\text{DB18C6}]$) mole ratio in pure EtOAc and pure THF are shown in Figs. 1 and 2, respectively. The stability constants of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex at each temperature were calculated from changes of the molar conductance as a function of $[\text{UO}_2^{2+}]/[\text{DB18C6}]$ molar ratios using a GENPLOT computer program [24]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference [25]. The values of stability constants ($\log K_f$) for $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in various solvent systems are listed in Table 1. Assuming that the activity coefficients of the cation and the complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, ΔG_c° . The vant Hoff plots of $\ln K_f$ versus $1/T$ for all of the investigated systems were constructed. A typical example of these plots is shown in Fig. 3. The changes in standard enthalpy (ΔH_c°) for complexation reactions were obtained from the slope of the vant 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 $\Delta G_c^\circ, 298.15 = \Delta H_c^\circ - 298.15 \Delta S_c^\circ$. The results are summarized in Table 2. The changes of $\log K_f$ of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex versus the mole fraction of EtOAc in EtOAc–DMF and EtOAc–AN binary systems at different temperatures are shown in Figs. 4 and 5.

Discussion

As is obvious from Figs. 1 and 2, addition of DB18C6 ligand to UO_2^{2+} solution, in pure ethylacetate and pure THF at different temperatures, shows an increase in molar

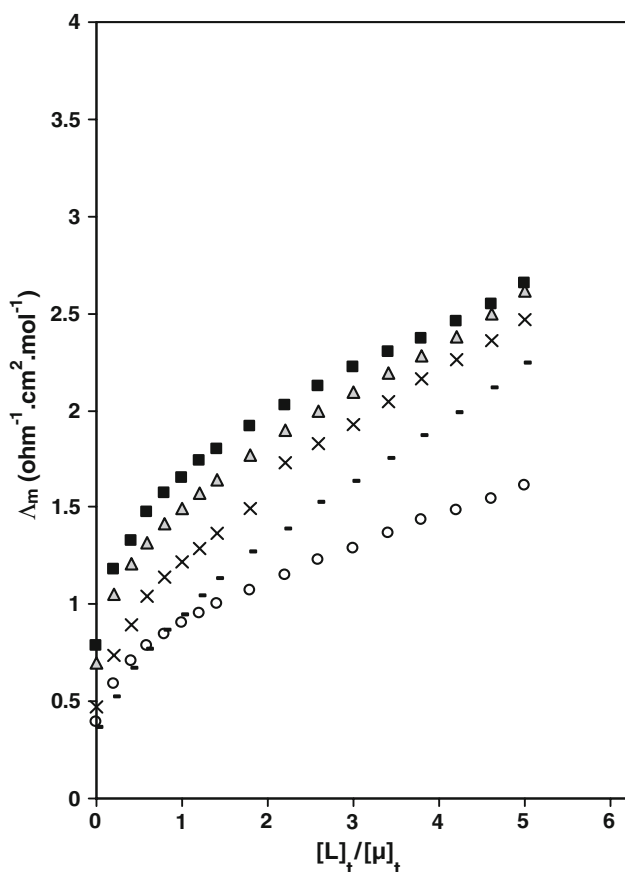


Fig. 1 Molar conductance–mole ratio plots for $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in pure ethylacetate at different temperatures ($\circ = 15^\circ\text{C}$, $\blacksquare = 25^\circ\text{C}$, $\blacktriangle = 35^\circ\text{C}$, $\times = 45^\circ\text{C}$, $- = 55^\circ\text{C}$)

conductivity with an increase in ligand concentration. This indicates that the $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in pure EtOAc and pure THF is more mobile than free solvated UO_2^{2+} cation. Similar behavior was observed in all other solution systems. It is evident from Figs. 1 and 2 that the slope of the corresponding molar conductivity versus $[\text{DB18C6}]/[\text{UO}_2]^{2+}$ mole ratio changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex between dibenzo-18-crown-6 and UO_2^{2+} in these solvents. It is obvious from these Figures that as the temperature increases, the curvature of the plots of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex decreases, which is an evidence for formation of a weaker complex at high temperatures. Therefore, the complexation process between DB18C6 and uranyl cation is exothermic.

The thermodynamic parameters (ΔH°_c , ΔS°_c) for complex formation are given in Table 2. As expected, the values of thermodynamic quantities depend strongly on nature and composition of the mixed solvents used in this investigation. Since the values of standard entropy (ΔS°_c)

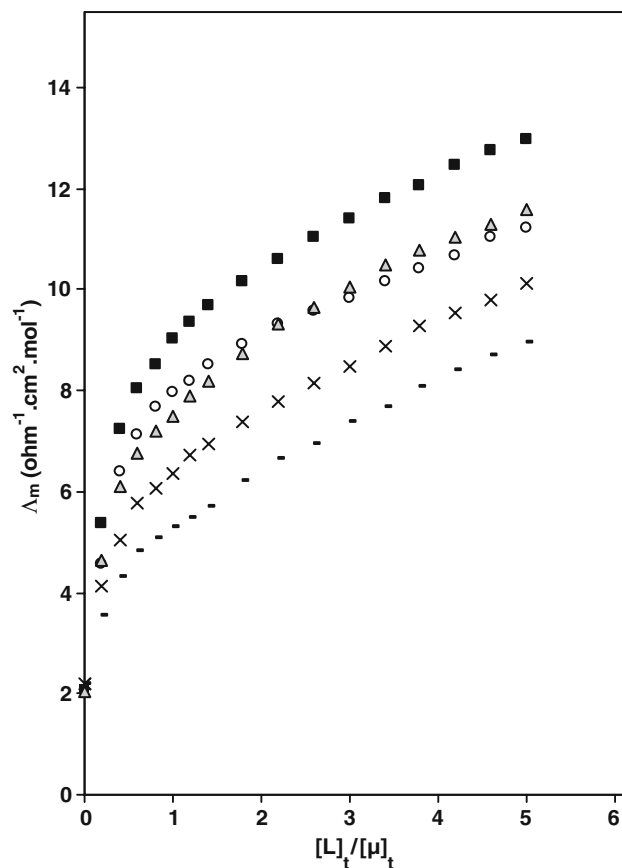


Fig. 2 Molar conductance–mole ratio plots for $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in pure THF at different temperatures ($\circ = 15^\circ\text{C}$, $\blacksquare = 25^\circ\text{C}$, $\blacktriangle = 35^\circ\text{C}$, $\times = 45^\circ\text{C}$, $- = 55^\circ\text{C}$)

and standard enthalpy (ΔH°_c) for formation of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in solution, vary with different 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, therefore, as is evident in Table 2, these thermodynamic quantities change with the nature and composition of the used solvent systems.

The experimental results show that in some cases, the change in standard enthalpy for the complexation reaction between UO_2^{2+} cation and DB18C6 is negligible; therefore, it seems that the complexation processes in some solvent systems are probably athermic. But in the case of most binary solutions, the complexation reaction is exothermic.

As is obvious from Figs. 4 and 5, the change in the stability constant ($\log K_f$) of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex versus the composition of these binary systems at various temperatures is not monotonic. Somewhat similar behavior was observed in other binary solutions. The non-monotonic

Table 1 $\log K_f$ values of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in EtOAc–THF, EtOAc–PC, EtOAc–DMF and EtOAc–AN binary mixtures at different temperatures ($^{\circ}\text{C}$)

Medium mol. % EtOAc	$\log K_f (\pm\text{SD})^a$				
	15 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	35 $^{\circ}\text{C}$	45 $^{\circ}\text{C}$	55 $^{\circ}\text{C}$
EtOAc–THF ^b					
100	3.57 \pm 0.10	3.78 \pm 0.11	3.55 \pm 0.12	3.43 \pm 0.08	3.16 \pm 0.08
75	4.24 \pm 0.17	4.52 \pm 0.17	4.22 \pm 0.18	3.91 \pm 0.11	3.43 \pm 0.18
50	4.55 \pm 0.22	4.58 \pm 0.26	4.30 \pm 0.19	4.04 \pm 0.18	3.40 \pm 0.20
25	4.30 \pm 0.19	4.60 \pm 0.18	4.31 \pm 0.19	3.91 \pm 0.11	3.51 \pm 0.20
0	4.59 \pm 0.20	4.44 \pm 0.18	4.20 \pm 0.15	4.00 \pm 0.14	3.76 \pm 0.15
EtOAc–PC ^b					
100	3.57 \pm 0.10	3.78 \pm 0.11	3.55 \pm 0.12	3.43 \pm 0.08	3.16 \pm 0.08
75	2.89 \pm 0.06	2.89 \pm 0.05	2.74 \pm 0.06	2.52 \pm 0.08	2.48 \pm 0.09
50	3.00 \pm 0.05	2.90 \pm 0.08	2.80 \pm 0.09	2.79 \pm 0.08	2.84 \pm 0.06
25	2.94 \pm 0.08	3.04 \pm 0.07	2.78 \pm 0.06	2.61 \pm 0.07	2.48 \pm 0.06
0	3.03 \pm 0.06	3.02 \pm 0.06	2.89 \pm 0.06	2.74 \pm 0.06	2.78 \pm 0.13
EtOAc–DMF ^b					
100	3.57 \pm 0.10	3.78 \pm 0.11	3.55 \pm 0.12	3.43 \pm 0.08	3.16 \pm 0.08
75	3.35 \pm 0.06	3.11 \pm 0.06	2.79 \pm 0.09	2.85 \pm 0.08	2.78 \pm 0.10
50	2.62 \pm 0.04	2.59 \pm 0.04	2.78 \pm 0.08	2.79 \pm 0.09	2.58 \pm 0.27
25	2.72 \pm 0.12	2.72 \pm 0.12	2.76 \pm 0.10	2.74 \pm 0.10	2.68 \pm 0.15
0	2.68 \pm 0.14	2.68 \pm 0.14	2.66 \pm 0.16	2.67 \pm 0.15	2.69 \pm 0.14
EtOAc–AN ^b					
100	3.57 \pm 0.10	3.78 \pm 0.11	3.55 \pm 0.12	3.43 \pm 0.08	3.16 \pm 0.08
75	2.72 \pm 0.18	2.79 \pm 0.10	3.00 \pm 0.05	2.74 \pm 0.05	2.78 \pm 0.13
50	2.91 \pm 0.11	2.74 \pm 0.12	2.74 \pm 0.12	2.62 \pm 0.21	2.64 \pm 0.09
25	2.95 \pm 0.16	2.57 \pm 0.24	2.58 \pm 0.24	2.67 \pm 0.21	2.72 \pm 0.14
0	3.26 \pm 0.07	3.31 \pm 0.06	3.15 \pm 0.11	2.90 \pm 0.08	3.07 \pm 0.09

^a Standard deviation^b The composition of solvent systems is expressed in mol % of each solvent

behavior which is observed for changes of the stability constant ($\log K_f$) of complex versus the composition of the binary solutions is probably due to a change in the structure of the binary solvents as the composition of the medium is varied. In addition, the heteroselective solvation of cation and the ligand and also the formation of mixed solvates may be effective in complexation process.

As is obvious from Table 1, the stability constant of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in various pure solvents at 25 $^{\circ}\text{C}$ decreases in order: THF > EtOAc > PC > AN > DMF, and in the case of binary solvents at 25 $^{\circ}\text{C}$ is: THF–EtOAc > PC–EtOAc > DMF–EtOAc \approx AN–EtOAc. In spite of medium donor ability of acetonitrile (DN = 14), the stability of the $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in pure AN and AN–EtOAc binary solutions is lower than most of other solvent systems. Dibenzo-18-crown-6 (DB18C6) is a fairly rigid, electron rich, bowl-like host and, therefore, suitable for the complexation of cationic, aromatic, organic guests via stacking and charge transfer interactions, as well as, via hydrogen bonding. It has been reported that the acetonitrile molecules interact

strongly with the crown ether molecules. Therefore, the behavior observed in these two solvent systems is probably due to the interactions between DB18C6 and the AN molecules which involves the hydrogen bonding between CH_3 protons and the AN involves oxygen of crown [7, 26]. A relatively weak $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex is formed in pure DMF and EtOAc/DMF binary solutions. This behavior reflects a strong cation solvation by dimethylformamide molecules. Dimethylformamide with a high donor ability (DN = 24) can solvate the UO_2^{2+} cation strongly and compete with the ligand for UO_2^{2+} cation. The results obtained in the case of THF (DN = 20), EtOAc (DN = 17), PC (DN = 15) and their binary solutions cannot only interpreted on the base of their donor ability and we should consider the other chemical and physical properties of these organic solvents such as acceptor ability, dielectric constant, dipole moment and even the size and the shape of the solvent molecules which are effective in the complexation process between the DB18C6 and UO_2^{2+} cation in these pure solvents and their binary mixtures.

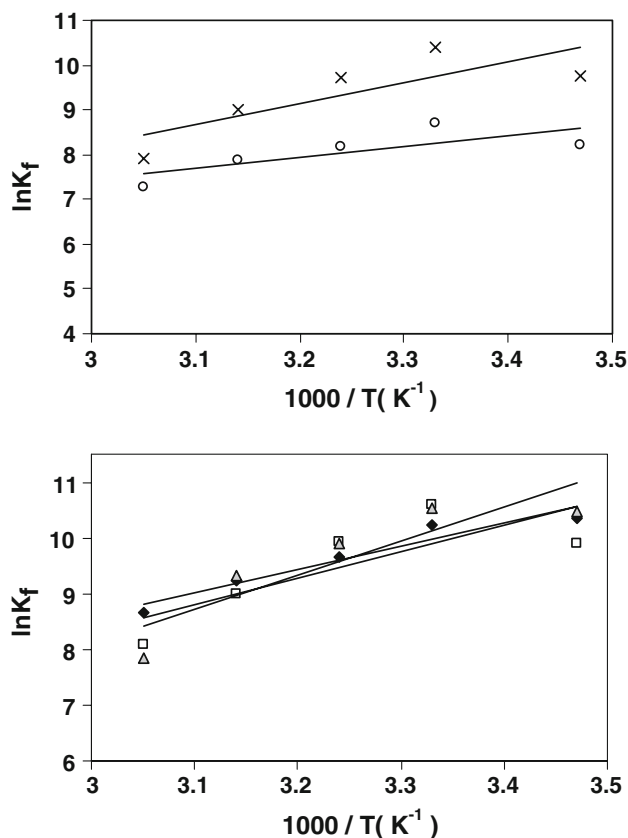


Fig. 3 van't Hoff plots for $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in EtOAc–THF binary systems (mol% EtOAc: $\blacklozenge = 0$, $\square = 25.0$, $\blacktriangle = 50.0$, $\times = 75.0$, $\circ = 100$)

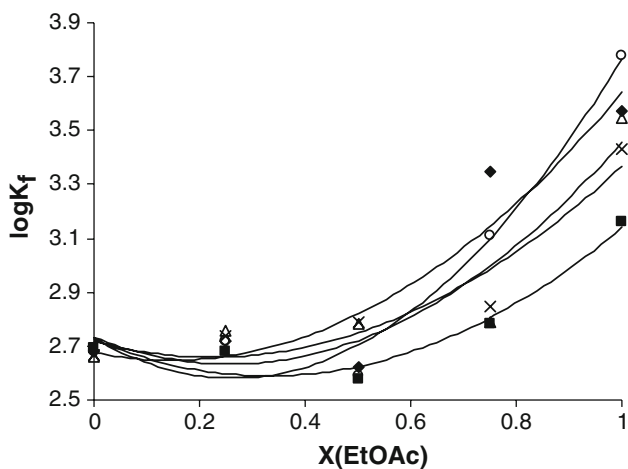


Fig. 4 Changes of stability constant of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex with the composition of the EtOAc–DMF binary system at different temperatures ($\blacklozenge = 15\text{ }^\circ\text{C}$, $\circ = 25\text{ }^\circ\text{C}$, $\triangle = 35\text{ }^\circ\text{C}$, $\times = 45\text{ }^\circ\text{C}$, $\square = 55\text{ }^\circ\text{C}$)

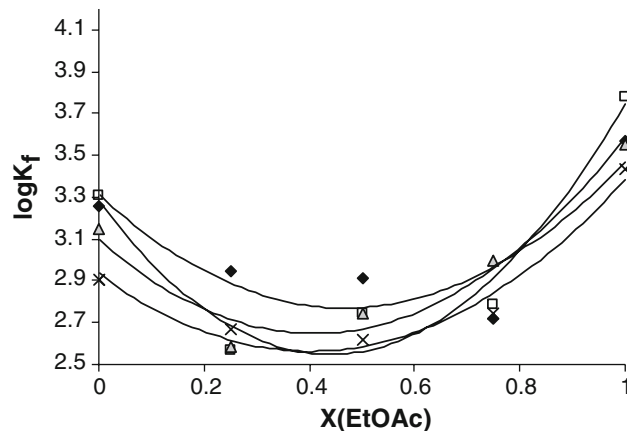


Fig. 5 Changes of stability constant of $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex with the composition of the EtOAc–AN binary system at different temperatures ($\blacklozenge = 15\text{ }^\circ\text{C}$, $\circ = 25\text{ }^\circ\text{C}$, $\triangle = 35\text{ }^\circ\text{C}$, $\times = 45\text{ }^\circ\text{C}$, $\square = 55\text{ }^\circ\text{C}$)

Table 2 Thermodynamic parameters for $(\text{DB18C6} \cdot \text{UO}_2)^{2+}$ complex in EtOAc–THF, EtOAc–PC, EtOAc–DMF and EtOAc–AN binary mixtures

Medium mol. % EtOAc	$-\Delta G_c^\circ (25\text{ }^\circ\text{C})$ (KJ mol ⁻¹)	$-\Delta H_c^\circ$ (KJ mol ⁻¹)	ΔS_c° , (J mol ⁻¹ K ⁻¹)
EtOAc–THF^b			
100	21.6 ± 0.6	a	a
75	26 ± 1	40 ± 17	a
50	26 ± 1	50 ± 13	a
25	26 ± 1	40.2 ± 5	a
0	25 ± 1	a	a
EtOAc–PC^b			
100	21.6 ± 0.6	a	a
75	2.63 ± 0.3	21 ± 4	-63 ± 12
50	2.64 ± 0.4	8 ± 4	a
25	2.76 ± 0.4	25 ± 6	-74 ± 19
0	2.7 ± 0.3	14 ± 3	-38 ± 10
EtOAc–DMF^b			
100	21.6 ± 0.6	a	a
75	17.7 ± 0.3	-8 ± 2	a
50	14.8 ± 0.2	a	a
25	15.5 ± 0.7	a	51 ± 10
0	15.3 ± 0.8	a	51 ± 13
EtOAc–AN^b			
100	21.6 ± 0.6	a	a
75	15.9 ± 0.6	a	66 ± 20
50	15.7 ± 0.7	a	43 ± 13
25	15 ± 2	a	a
0	18.9 ± 0.4	3 ± 1	53 ± 3

^a The data are estimated with high uncertainties

^b The composition of solvent systems is expressed in mol% of each solvent

References

- Gherrou, A., Buschmann, H.-J., Schollmeyer, E.: Complex formation of crown ethers and cryptands with Ba²⁺ in the biphasic system chloroform/water studied by titration calorimetry. *Thermochim. Acta.* **425**, 1–5 (2005). doi:10.1016/S0040-6031(03)00369-1
- Nadezhda, L., Volkova, Elena V., Parfenyuk: Selective interactions of 18-crown-6 with D-glucose and D-galactose in aqueous solutions: titration calorimetry, densimetry, viscosimetry. *Thermochim. Acta.* **435**, 108–112 (2005). doi:10.1016/j.tca.2005.05.002
- Rounaghi, G.H., Chamsaz, M., Nezhadali, A.: A Conductometric study of complexation reactions between Dibenzo-18-Crown-6 (DB18C6) with Cu²⁺, Zn²⁺, Tl⁺ and Cd²⁺ metal cations in dimethylsulfoxide–ethylacetate binary mixtures. *J. Incl. Phenom. Macro.* **43**, 231 (2002). doi:10.1023/A:1021283200802
- Thaler, A., Cox, B.G., Schneider, H.: Stability constants of aza-oxa-crown ether complexes with silver(I) in nonaqueous polar solvents. *Inorg. Chim. Acta.* **351**, 123–132 (2003). doi:10.1016/S0020-1693(03)00193-2
- Yoshihiro, K., Jun, U., Shoichi, K., Yasuyuki, T.: On the difference between ion-pair formation constants of crown ether-complex ions with picrate ion in water determined by solvent extraction and by potentiometry. *J. Mol. Liquids.* **123**, 29–37 (2006). doi:10.1016/j.molliq.2005.05.003
- Radosław, P., Grzegorz, S., Bogumił, B., Franz, B.: NMR, FT-IR and ESI-MS study of new lasalocid ester with 2-(hydroxymethyl)-12-crown-4 and its complexes with monovalent cations. *J. Mol. Struct.* **749**, 128–137 (2005). doi:10.1016/j.molstruc.2005.03.039
- Mosier-Boss, P.A.: Spectroscopic studies of the interaction between crown ethers and organic nitriles. *Spectrochimica. Acta. Part A.* **61**, 527–534 (2005)
- Cihan, G., Umit, S., Nalan, O., Ismet, B., Umit, C., Mustafa, B.: The synthesis and complexation study of some novel 3-methoxyphenyl chromenone crown ethers using conductometry. *Dyes Pigments* **71**, 161–167 (2006). doi:10.1016/j.dyepig.2005.06.021
- Saziye, A., Cihan, G., Umit, C., Baki, C., Mustafa, B.: The synthesis and complexation study of some coumestan and coumestan analog derivatives of crown ethers using conductometry. *Dyes Pigments* **65**, 197–204 (2005). doi:10.1016/j.dyepig.2004.07.011
- Pavitrana, R., Luxmi Varma, R., Reddy, M.L.P.: Synergistic solvent extraction of trivalent lanthanoids with mixtures of 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone and crown ethers. *Solv. Extr. Ion. Exch.* **21**, 797–813 (2003). doi:10.1081/SEI-120025924
- Bond, A.H., Dietz, M.L., Chiarizia, R.: Incorporating size selectivity into synergistic solvent extraction: a review of crown ether-containing systems. *Ind. Eng. Chem. Res.* **39**, 3442–3464 (2000). doi:10.1021/ie000356j
- Nash, K.L.: A review of the basic chemistry and recent developments in trivalent f-element separations. *Solv. Extr. Ion. Exch.* **11**, 729–768 (1993). doi:10.1080/07366299308918184
- Dukov, I.L.: Synergistic extraction of lanthanides with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one and benzo-15-crown-5. *Solv. Extr. Ion. Exch.* **10**, 637–653 (1992). doi:10.1080/07366299208918126
- Aly, H.F., Khalifa, S.M., Navratil, J.D., Saba, M.T.: Extraction of some lanthanides and actinides by 15-crown-5 thenoyltrifluoroacetone mixture in chloroform. *Solv. Extr. Ion. Exch.* **3**, 623 (1985). doi:10.1080/07366298508918531
- Habib-ur, R., Akbar, A., Chaudhary, J.A., Shafaat, A.: Synergistic extraction of Nd(III), Tb(III) and Lu(III) ions with a mixture of picrolonic acid and benzo-15-crown-5 in chloroform. *Radiochim. Acta.* **94**, 475–480 (2006). doi:10.1524/ract.2006.94.8.475
- Yoshihiro M., Yoshihiro K., Takaumi K., Zenko Y.: Steric effect of β-diketone in synergistic extraction of actinide(III) and lanthanide(III) with β-diketone + 18-crown-6 ether/1,2-dichloroethane. *J. Alloy. Comp.* **271–273**, 790–793 (1998). doi:10.1016/S0925–8388(98)00209-6
- Lagrange, J., Metabanzoulou, J.P., Fux, P., Lagrange, P.: Complexation of the uranyl ion by crown ethers, diaza-crown ethers and analogous acyclic ligands in solution. *Polyhedron.* **8**, 2251–2254 (1989). doi:10.1016/S0277-5387(00)81251-6
- Fux, P., Lagrange, J., Lagrange, P.: Kinetics and mechanisms of complex formation of uranyl ion with 18-crown-6 and diaza-18-crown-6 ligands in propylene carbonate. *J. Am. Chem. Soc.* **107**, 5927–5931 (1985). doi:10.1021/ja00307a017
- Rounaghi, G.H., Khazaei, N., Sanavi, R.K.: Study of complex formation between 18-crown-6 with Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ cations in some binary mixed non-aqueous solvents using the conductometric method. *Pol. J. Chem.* **79**, 1143–1153 (2005)
- Rounaghi, G.H., Mofazzeli, F.: Study of complex formation between dicyclohexano-18-crown-6 (DCH18C6) with Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ cations in methanol–water binary mixtures using conductometric method. *J. Incl. Phenom. Macrocycl. Chem.* **51**, 205–210 (2005). doi:10.1007/s10847-004-5691-z
- Rounaghi, G.H., Sanavi, R.K., Arbab Zavvar, M.: Study of complex formation between N-phenylaza-15-crown-5 with Mg²⁺, Ca²⁺, Ag⁺ and Cd²⁺ metal cations in some binary mixed aqueous and non-aqueous solvents using the conductometric method. *J. Incl. Phenom. Macrocycl. Chem.* **54**, 247–252 (2006). doi:10.1007/s10847-005-8380-7
- Rounaghi, G.H., Masroomnia, M., Ghaemi, A., Rahchamani, H.A.: Thermodynamic behaviour of complexation process between 15-crown-5 with Li⁺, Na⁺ and K⁺ cations in acetonitrile–water and 1-propanol–water binary media. *Asian. J. Chem.* **19**, 1679–1686 (2007)
- Rounaghi, G.H., Zavar, M.H., Mohammad Zadeh Kakhki, R.: Thermodynamic behavior of complexation process between dibenzo-18-crown-6 and K⁺, Ag⁺, NH₄⁺, and Hg²⁺ cations in ethylacetate–dimethylformamide binary media. *Russ. J. Coord. Chem.* **34**, 167–171 (2008)
- Genplot Computer Graphic Service. U.S.A (1989)
- Rounaghi, G.H., Eshaghi, Z., Ghiamati, E.: Thermodynamic study of complex formation between 18-crown-6 and potassium ion in some binary non-aqueous solvents using a conductometric method. *Talanta.* **44**, 275–282 (1997). doi:10.1016/S0039-9140(96)02045-0
- Grootenhuis, P.D.J., Kollman, P.A.: Crown ether-neutral molecule interactions studied by molecular mechanics, normal mode analysis, and free energy perturbation calculations near quantitative agreement between theory and experimental binding free energies. *J. Am. Chem. Soc.* **111**, 4046–4051 (1989). doi:10.1021/ja00193a042