ORIGINAL ARTICLE

Complexation study of dibenzo-18-crown-6 with UO_2^{2+} cation in binary mixed non-aqueous solutions

Fahimeh Razghandi · Gholamhossein Rounaghi · Roya Mohammadzadeh Kakhki

Abstract The complexation reaction of macrocyclic ligand, dibenzo-18-crown-6 (DB18C6) with UO_2^{2+} cation was studied in ethylacetate-1,2-dichloroethane (EtOAc/DCE), acetonitrile-1,2-dichloroethane (AN/DCE), methanol-1,2-dichloroethane (MeOH/DCE) and ethanol-1,2-dichloroethane (EtOH/DCE) binary solutions at different temperatures using the conductometric method. The conductance data show that the stoichiometry of the complex formed between DB18C6 and UO_2^{2+} cation is affected by the nature of the solvent systems. A non-linear behaviour was observed for changes of log K_f of $(DB18C6.UO_2)^{+2}$ complex versus the composition of the binary mixed solvents. The values of thermodynamic quantities (ΔS°_c, ΔH°_c) for formation of $(DB18C6.UO_2)^{+2}$ complex were obtained from temperature dependence of the stability constant using the van't Hoff plots. The results show that in most cases, the complex is enthalpy stabilized and in all cases entropy stabilized and both parameters are affected by the nature and composition of the mixed solvents. In addition, the complex formation between dicyclohexyl-18-crown-6 (DCH18C6) and UO_2^{2+} cation was studied in pure AN and the results were compared with those of the $(DB18C6.UO_2)^{+2}$ complex.

Keywords UO_2^{+2} cation · Dibenzo-18-crown-6 · Dicyclohexyl-18-crown-6 · Acetonitrile · Ethylacetate · Methanol · Ethanol · 1,2-Dichloroethane · Conductometry

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Introduction

Cyclic polyethers (crown ethers) are selective complexing agents for the cations [1–4]. They are utilized to extract cations from aqueous solutions into hydrophobic, nonpolar organic solvents [5–11] and to carry these cations selectively through solvent-polymeric [12] liquid membranes [13–15].

In the host–guest interaction, factors that are effective on the selectivity of any host species include the relative free energy of desolvation of the guest species and the free energy of organizing of the host into a suitable conformation with remote substitution for binding. It is known that solvation plays a major role in ion selectivity processes by influencing the stability and nature of host–guest complexes.

Solvation of macrocyclic polyethers in various solvent media is the result of the competition of solute–solute and solvent–solvent interactions and depends also on the conformational changes of the solute structure in solution. Crown ethers are flexible and their conformational changes sometimes occur with the nature and composition of the solvent systems.

Ion–solvent interactions play a very important role in the studies of stoichiometry, structure, and the stability of metal cation complexes with crown ethers. Knowledge of the ionophore solvation properties enables one to choose a suitable solvent for complexation studies and to obtain detailed information on the solvent effect. To control the chemical reactions in non-aqueous and mixed solvents, it is necessary to select an appropriate solvent [16]. This is a complicated problem because of an exceptionally great variety and specificity of chemical reactions in solutions. Recently, we have investigated the complexation processes of some of the crown ethers with various metal cations in pure and binary mixed organic solvents [17–19].

Uranium is at the heart of commercial nuclear power and is vital to the entire nuclear enterprise. Its presence and use worldwide has resulted in a vast literature, not only on uranium complexation and separations reactions, but also on all aspects of the uranium fuel cycle: mining and, milling; isotope enrichment; reactor fuel manufacturing; spent reactor fuel. The uranyl ion (UO_2^{2+}) is the most common uranium ion in aqueous media. Uranyl ion complexes extract readily into organic solvents. This is the basis of the widely used Purex Process for reprocessing spent nuclear reactor fuel reprocessing; and weapons production.

We would like to present in this paper, the results which are obtained from conductometric study of the complexation reaction of UO_2^{+2} cation and the macrocyclic ligand, dibenzo-18-crown-6 (DBH18C6) in ethylacetate-1,2-dichloroethane (EtOAc/DCE), acetonitrile-1,2-dichloroethane (AN/DCE), methanol-1,2-dichloroethane (MeOH/DCE) and ethanol-1,2-dichloroethane (EtOH/DCE) binary solutions and also in pure non-aqueous solvents at different temperatures. We also studied the complexation reaction of UO_2^{+2} cation with macrocyclic ligand, dicyclohexyl-18-crown-6, in pure acetonitrile.

Experimental

Reagents and solvents

Dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 (Fluka) and $UO_2(NO_3)_2 \cdot 6H2O$ (Riedel company) were used without further purification. The solvents: ethylacetate (Riedel), ethanol, acetonitrile, methanol and 1,2-dichloroethane all from Merck company were used with the highest purity.

Procedure

The stability constant and other thermodynamic parameters of $(DB18C6.UO_2)^{+2}$ complex were determined using a conductometric circuits (digital AMEL) thermostated at a given temperature. A solution of $UO_2 (NO_3)_2 \cdot 6H2O$ salt (1.0×10^{-4} M) was placed in a titration cell, and the conductance of the solution was measured. Then a step-by-step increase of the DCH18C6 solution prepared in the same solvent (2.0×10^{-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 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}. In each conductometric titration, the molar conductivity (Λ_m) of UO_2^{+2} cation, in the nonaqueous solvent containing the DB18C6

was obtained as a function of $[L]_t/[M]_t$, where $[L]_t$ and $[M]_t$ are the total concentrations of the ligand and cation, respectively and in each case, the Λ_m vs $[L]_t/[M]_t$ was plotted.

Result and discussions

Data analysis program

The 1:1 complexation of a metal cation, M^{n+}, with a crown ether (L) is represented by the following equilibrium:

$$M^{n+} + L \rightleftharpoons ML^{n+}. \tag{1}$$

The corresponding equilibrium constant, K_f, is given by:

$$K_f = [ML^{n+}]/[M^{n+}][L] \times f_{ML}^{n+}/ \cdot f_M^{n+} \cdot f_L, \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, $[L]$, and f represent the equilibrium molar concentration of the complex, free cation, free ligand and the activity coefficient of the species indicated, respectively.

Under the highly dilute conditions which we used in this investigation, the activity coefficient of the uncharged ligand, f_L can be reasonably assumed as unity [20, 21]. By using the Deby–Huckel limiting law [22], we can assume that the f_M^+, f_{ML}^+ values are unity in Eq. 2. Thus the complex formation constant in term of the molar conductance can be expressed as:

$$K_f = [ML^{n+}]/ [M^{n+}][L] = \Lambda_{M-}\Lambda_{obs}/\Lambda_{obs-}\Lambda_{ML[L]}, \tag{3}$$

where

$$[L] = C_L = C_M(\Lambda_{M-}\Lambda obs)/(\Lambda_{M-}\Lambda_{ML}). \tag{4}$$

Here Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal cation. The complex formation constant, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by computer fitting of Eqs. 3 and 4 to molar conductance as a function of ligand/metal cation mole ratio data, using a non-linear least-squares program GENPLOT[23]. All calculated stability constants are summarized in Table 1. The details of calculation of the stability constants of metal ion complexes by the conductometric method have been described elsewhere [24].

Effect of non-aqueous solvents on stability constant of $(DB18C6 \cdot UO_2)^{2+}$ complex

For determination of the stability constant of $(DB18C6 \cdot UO_2)^{2+}$ complex, Λ_m values versus $[L]_t/[M]_t$ were plotted.

Table 1 Log K_f values of $(DB18C6.UO_2)^{+2}$ complex in various solvent systems

Medium mol.% DCE	$\log K_f \pm (SD)$[a]			
	15 °C	25 °C	35 °C	45 °C
DCE-AN[b]				
100	d	d	d	d
75	c	c	c	c
50	3.48 ± 0.10	3.39 ± 0.10	3.67 ± 0.09	3.32 ± 0.06
25	2.75 ± 0.20	2.74 ± 0.10	2.73 ± 0.20	2.71 ± 0.20
0	2.70 ± 0.20	2.62 ± 0.08	2.70 ± 0.10	2.77 ± 0.09
DCE-MeOH[b]				
100	d	d	d	d
75	2.68 ± 0.1	2.70 ± 0.11	2.70 ± 0.16	2.69 ± 0.2
50	2.76 ± 0.09	2.69 ± 0.13	2.73 ± 0.12	2.73 ± 0.12
25	d	d	d	d
0	d	d	d	d
DCE-EtOH[b]				
100	d	d	d	d
75	3.24 ± 0.07	3.09 ± 0.07	3.07 ± 0.08	2.97 ± 0.10
50	3.14 ± 0.10	3.09 ± 0.06	3.24 ± 0.06	3.09 ± 0.07
25	2.73 ± 0.10	2.70 ± 0.10	2.94 ± 0.07	2.97 ± 0.10
0	d	d	d	d
DCE-EtOAc[b]				
100	d	d	d	d
75	3.19 ± 0.08	3.11 ± 0.06	3.18 ± 0.05	3.18 ± 0.06
50	3.84 ± 0.05	3.81 ± 0.03	3.77 ± 0.06	3.49 ± 0.06
25	4.19 ± 0.20	4.26 ± 0.10	4.01 ± 0.10	3.84 ± 0.10
0	4.40 ± 0.20	4.32 ± 0.20	4.28 ± 0.10	4.22 ± 0.09

[a] *SD* Standard deviation

[b] The composition of solvent systems is expressed in mol.% of each solvent

[c] The data cannot be fitted in equation

[d] The $UO_2(NO_3)_2 \cdot 6H_2O$ salt is not dissolved in these solvent systems

Examples of these plots in pure EtOAc and also in EtOAc-DCE binary solution (mol%EtOAc = 50) are shown in Figs. 1 and 2, respectively. The Λ_m value increases with an increase of $[L]_t/[M]_t$ at all temperatures, showing that addition of DB18C6 to UO_2^{2+} cation solution causes an increase in the molar conductivity which indicates that DB18C6 forms a complex with UO_2^{2+} cation and the complex is more mobile than the UO_2^{2+} cation. Similar behaviour was observed for the other solvent systems.

As evident from Fig. 1, the slope of the curves changes sharply at $[L]_t/[M]_t$ about 1, which is an evidence for formation of a stable 1:1 complex $(ML)^{2+}$, in pure EtOAc, but as shown in Fig. 2, a gradual increase in molar conductance of UO_2^{2+} cation is observed upon addition of the ligand in EtOAc/DCE binary system (mol.% EtOAc = 50), which does not show a considerable change in the curvature at a mole ratio of ca 1, therefore, a weaker complex is formed between UO_2^{2+} cation and DB18C6 in this binary solution.

It is seen from Table 1 that the sequence of the stability of $(DB18C6.UO_2)^{2+}$ complex in pure solvent systems at 25 °C decreases in order: EtOAc > AN. The $UO_2(NO_3)_2 \cdot 6H_2O$ salt is not dissolved in pure ethanol and methanol solvent systems. In the case of binary solvents, the stability constant of the complex at 25 °C decreases in order: DCE-EtOAc > DCE-AN > DCE-EtOH > DCE-MeOH.

In spite of the lower donor ability of acetonitrile (DN = 14) relative to EtOAc (DN = 17), the stability of $(DB18C6. UO_2)^{2+}$ complex is bigger in EtOAc with respect to AN. Although the solvation of the cation is an important factor in complexation reactions, solvation of the ligand and the resulting complex has also been documented to contribute to the overall free energy of complex formation, for example the interactions of crown ethers with solvent molecules can alter their conformation and affect their complexing ability. Thus, it is expected that a simple donor and acceptor approach to the complexation behaviour may not always apply.

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 behaviour observed in this solvent system is
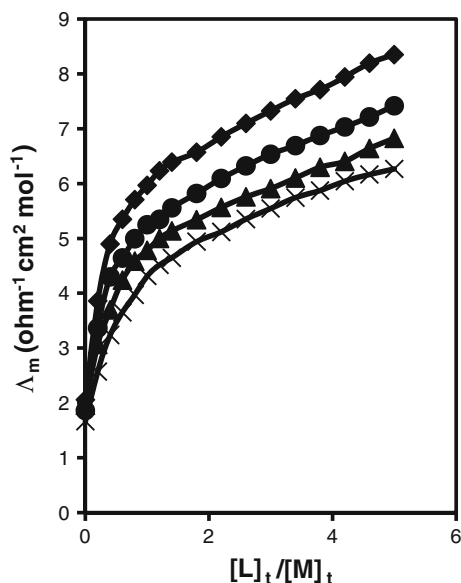
Fig. 1 Molar conductance-mole ratio plots for $(DB18C6 \cdot UO_2)^{2+}$ complex in pure EtOAc at different temperatures: (*filled diamond* 15 °C, *filled circle* 25 °C, *filled triangle* 35 °C, *times* 45 °C)
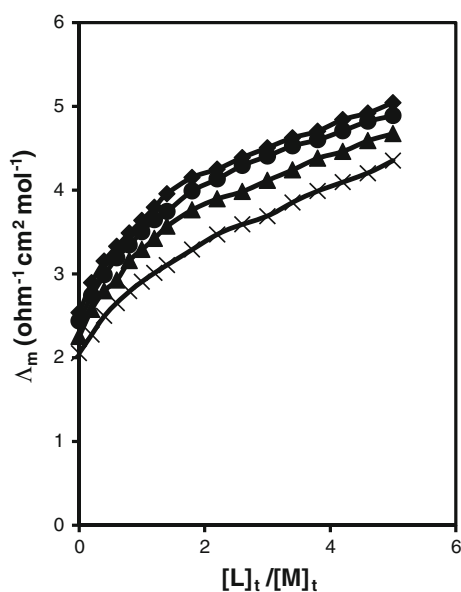

Fig. 2 Molar conductance-mole ratio plots for $(DB18C6 \cdot UO_2)^{2+}$ complex in EtOAc/DCE (mol%EtOAc = 50) binary system at different temperatures (*filled diamond* 15 °C, *filled circle* 25 °C, *filled triangle* 35 °C, *times* 45 °C)

probably due to the interactions between DB18C6 and the AN molecules which involves the hydrogen bonding between CH_3 protons of AN molecule and the oxygen atoms of the crown ether [25, 26].
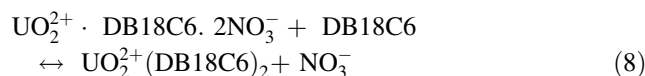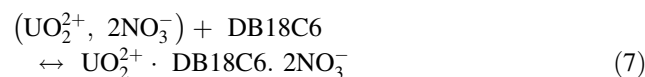
The role of solvent in complex formation reactions is convenient to discuss in terms of relationships between the excess stability constants of the complexes and the compositions of the mixed solvents [27].

$$\log K^{ex}_{[ML]}{}^{n+} = \log K^{exp}_{[ML]}{}^{n+} - \log K^{ad}_{[ML]}{}^{n+} \quad (5)$$

$$\log K^{ad}_{[ML]}{}^{n+} = \log K^{H2O}_{[ML]}{}^{n+} \\ + X_s/X_s^{max}(\log K^{s,max}_{[ML]}{}^{n+} \\ - \log K^{H2O}_{[ML]}{}^{n+}. \quad (6)$$

Here $K^{exp}_{[ML]}{}^{n+}$ is the experimental stability constant of complex in the mixture with the mole fraction X_s of nonaqueous solvent, $K^{ex}_{[ML]}{}^{n+}$ is the additive stability constant, $K^{H2O}_{[ML]}{}^{n+}$ is the stability constant of the complex in water, $K^{s,max}_{[ML]}{}^{n+}$ is the stability constant in the nonaqueous (mixed) solvent with the maximum fraction of nonaqueous component, and $X_s^{s,max}$ is the maximum mole fraction of the nonaqueous solvent in the mixture, where $K^{exp}_{[ML]}{}^{n+}$ was determined.

The results obtained for complexation process between the $UO_2{}^{2+}$ cation and DB18C6 show that the stoichiometry of the complex formed between the ligand and $UO_2{}^{2+}$ cation is effected by the nature of the solvent systems. As is evident from Fig. 3, in AN-DCE (mol.%AN = 25) binary system, addition of DB18C6 to a solution of the cation at different temperatures causes the molar conductivity to initially decrease until the molar ratio reaches to 1:1 and then to increase. Such behaviour may be described according to the following equilibria:

$$\begin{aligned}(UO_2^{2+},\ 2NO_3^-) + DB18C6 \\ \leftrightarrow UO_2^{2+} \cdot DB18C6.\ 2NO_3^-\end{aligned} \quad (7)$$

$$\begin{aligned}UO_2^{2+} \cdot DB18C6.\ 2NO_3^- + DB18C6 \\ \leftrightarrow UO_2^{2+}(DB18C6)_2 + NO_3^-\end{aligned} \quad (8)$$

It seems that the addition of the ligand to the cation solution results in the formation of a relatively stable 1:1 (ML) complex Eq. 7, which is present as an ion pair, then the addition of the second ligand to ion pair complex causes the formation of a stable 1:2 (ML₂) complex with a sandwich structure Eq. 8, which results in dissociation of the ion pair, therefore, the conductivity increases. The molecular structures of the 1:1 complex which is side way model and also the 1:2 complex which is a sandwich model are depicted in Ref. [9]. Indeed in contacts between the crown ether and the uranyl cation are hydrogen bonds from coordinated water molecules to the crown ether oxygens.

Effect of non-aqueous solvents on thermodynamic parameters of $(DB18C6 \cdot UO_2)^{2+}$ complex

The complexation process between a metal cation and a crown ether in a solvent can be considered to consist of the following steps:

1. Desolvation of the metal cation
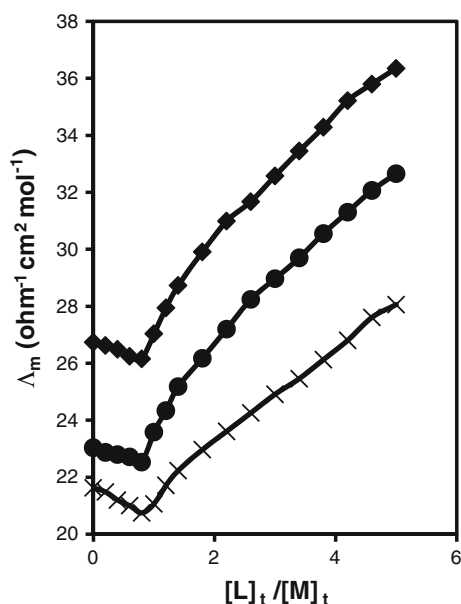2. Desolvation of the crown ether

Fig. 3 Molar conductance-mole ratio plots for $(DCH18C6·UO_2)^{2+}$ complex in AN/DCE (mol. %AN = 75) binery system at different temperatures (*filled square* 25 °C, *filled circle* 35 °C, *times* 45 °C)

3. Complexation between the metal ion and the crown ether
4. Solvation of the complex

Therefore, most reactions are accompanied by changes in the solvation shells of the reagents (liberation and replacement of solvent molecules and even increase in their number). The composition of the solvation shells of reagents in a binary solvent can considerably differ from the overall composition of the solution owing to selective solvation. The thermodynamic parameters must be evaluated to understand the factors governing the complexing ability and selectivity of the crown ethers.

The thermodynamic characteristics ($\Delta G°_C$, $\Delta H°_C$, and $\Delta S°_C$) of the complex formation, calculated from the temperature dependences of the stability constants, are given in Table 2. The Gibbs energy of the complex formation nonmonotonically varies with the composition of the binary organic solvents which indicates the interparticle interactions because of the entropy-enthalpy compensation [30]. Physically this means that the enthalpy and entropy components of the Gibbs energy directly reflect specifics of reagent-solvent interactions and characterize qualitative and quantitative distinctions of the systems and processes under comparison [28].

For all investigated systems, the van't Hoff plots of log K_f versus $1/T$ were constructed. The changes in standard enthalpy ($\Delta H°_C$) were obtained from the slope of the van't Hoff plots and the changes in standard entropy ($\Delta S°_C$) were

calculated from the relationship $\Delta G°_{C\ 298.15} = -RT\ln K_f = \Delta H°_C - 298.15\ \Delta S°_C$.

The results in Table 2, show that in most cases, the complex is enthalpy stabilized and in all cases entropy stabilized and both parameters are affected by the nature and composition of the mixed solvents. Since there are many factors which contribute to changes in complexation enthalpies and entropies, one should not expect a strict regularity between these parameters and the solvent composition of these binary mixtures of associated solvents.

The changes of log K_f of $(DB18C6.UO2)^{2+}$ complex versus the mole fraction of DCE in DCE-EtOAc binary system at different temperatures are shown in Fig. 4. As shown in this figure, the change of the stability constant (log K_f) of $(DB18C6.UO2)^{2+}$ complex with the composition of DCE-EtOAc binary solution is not linear. Similar behaviour was also observed in other binary solutions. This behaviour may be due to the preferential solvation of the cation, ligand, the resulting complex and even the counter ion in the binary mixed solvents. The interactions between the solvent molecules are also may be effective in this non-monotonic behaviour. In addition, the heteroselective solvation of the cation, anion and the ligand, and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in complexation process [29].

Effect of substituent on the crown ether ring on the complexation process

The complexation of DCH18C6 with UO_2^{2+} cation (Fig. 5, Scheme 1) was also studied in pure acetonitrile. The log K_f value of $(DCH18C6.UO_2)^{2+}$ complex at 25 °C was about (4.43 ± 0.10). The results show that the value of log K_f of $(DB18C6.UO_2)^{2+}$ complex (2.62 ± 0.08) is smaller than that of $(DC18C6.UO_2)^{2+}$ complex. Such a difference in the stability of these two complexes, reflects the electrostatic and steric effects of the side rings. The strength of C–O dipoles is affected by the nature of the substituent, and the ease of motion and attainable conformations of the polyether ring depend on the structure near the inter-ring bridges [30]. The aromatic ring lends rigidity to the ligand and withdraws electrons from the basic oxygen donor atoms, thus decreasing the strength of the metal cation–ligand interaction, or decreasing the stability of the complex.

Conclusion

In this work we investigated the complexation reaction of macrocyclic ligand, dibenzo-18-crown-6 (DB18C6) with UO_2^{2+} cation in ethylacetate-1,2-dichloroethane (EtOAc/DCE), acetonitrile-1,2-dichloroethane (AN/DCE), methanol-1,2- dichloroethane (MeOH/DCE) and ethanol-1,2-

**Table 2** Thermodynamic parameters for $(DB18C6 \cdot UO_2)^{+2}$ complex in various solvent systems

Medium mol.% DCE	$\Delta G_c^0 \pm SD^a$ (KJ mol^{-1})	$\Delta H_c^0 \pm SD^a$ (KJ mol^{-1})	$\Delta S_c^0 \pm SD^a$ (J mol^{-1} K^{-1})
DCE-AN[b]			
75	c	c	c
50	-19.35 ± 0.10	-9.21 ± 2.32	34.44 ± 7.18
25	-15.62 ± 0.45	-2.77 ± 4.01	43.09 ± 6.23
0	-14.96 ± 0.47	13.44 ± 8.26	95.20 ± 2.68
DCE-MeOH[b]			
75	15.42 ± 0.70	-7.79 ± 4.78	4.78 ± 1.55
50	15.37 ± 0.22	-2.72 ± 1.38	43.28 ± 4.65
DCE-EtOH[b]			
75	-17.68 ± 0.14	-14.67 ± 2.34	c
50	-17.65 ± 0.12	c	52.05 ± 6.00
25	-15.43 ± 0.49	c	c
DCE-EtOAc[b]			
75	7.71 ± 0.67	6.23 ± 3.23	80.63 ± 14.51
50	-21.76 ± 0.84	-7.56 ± 3.96	47.59 ± 1.33
25	-24.34 ± 0.57	-19.49 ± 3.46	12.82 ± 11.38
0	-24.66 ± 0.23	-9.93 ± 1.32	411.79 ± 4.31

[a] *SD* Standard deviation

[b] The composition of solvent systems is expressed in mol.% of each solvent

[c] With high uncertainty

Fig. 4 Change of the stability constant of $(DCH18C6 \cdot UO_2)^{2+}$ complex with the composition of the DCE/EtOAc (left) and EtOH/DCE (right) binary mixture at different temperatures (*filled diamond* 15 °C, *filled square* 25 °C, *filled triangle* 35 °C, *times* 45 °C)
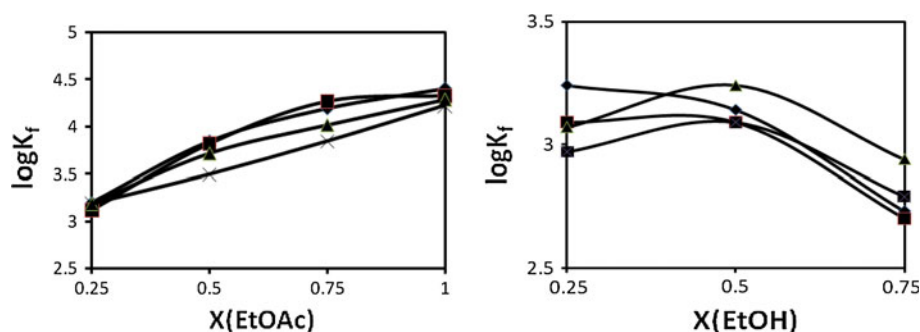
dichloroethane (EtOH/DCE) binary solutions at different temperatures using the conductometric method. The conductance data show that, the stoichiometry of the complex formed between DB18C6 and UO_2^{2+} cation is affected by the nature of the solvent systems. Also the sequence of the stability of $(DB18C6.UO_2)^{2+}$ complex in pure solvent systems at 25 °C decreases in order: EtOAc > AN and in the case of the binary solvent solutions, the stability constant at 25 °C decreases in order: DCE-EtOAc > DCE-AN > DCE-EtOH > DCE-MeOH. A non-linear behaviour was observed for changes of log K_f of $(DB18C6.UO_2)^{+2}$ complex versus the composition of the binary mixed solvents. The values of thermodynamic quantities (ΔS_c°, ΔH_c°) for formation of $(DB18C6.UO_2)^{+2}$ complex were also obtained. The results show that in most cases, the complex is enthalpy stabilized and in all cases entropy stabilized and both parameters are affected by the nature and composition of the mixed solvents. In addition, the complex formation between dicyclohexyl-18-crown-6 (DCH18C6) and UO_2^{2+} cation was studied in pure AN and
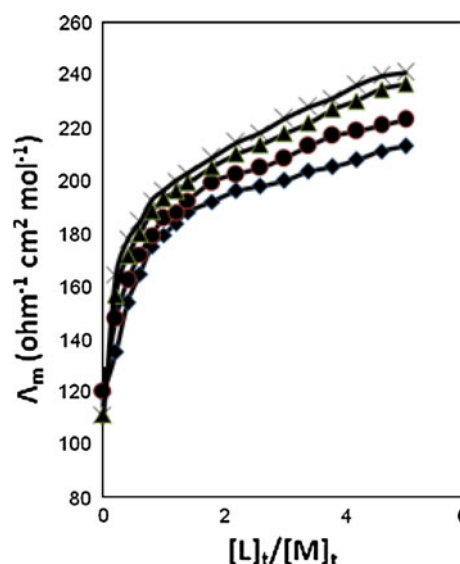
Fig. 5 Molar conductance-mole ratio plots for $(DCH18C6 \cdot UO_2)^{2+}$ complex in pure AN at different temperatures (*filled diamond* 15 °C, *filled circle* 25 °C, *filled triangle* 35 °C, *times* 45 °C)

Scheme 1 Structure of dibenzo-18-crown-6 (*left*) and dicyclohexyl-18-crown-6 (*right*)
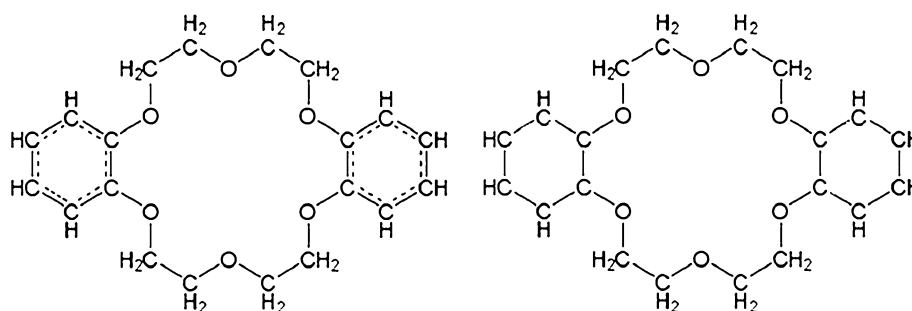
the results were compared with those of the $(DB18C6.UO_2)^{+2}$ complex.

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