Study of Complex Formation of Dibenzo-18-Crown-6 with Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ Cations in Acetonitrile–Dioxane Binary Solvent Mixtures

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Abstract The complexation reactions of dibenzo-18-crown-6 (DB18C6) with Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ cations were studied in acetonitrile–dioxane (AN–dioxane) binary solvent solutions at different temperatures by the conductometric method. The stability constants of the resulting 1:1 complexes were determined from computer fitting of the conductance–mole ratio data. The results show that dibenzo-18-crown-6 does not exhibit selectivity for the cation whose ionic size is closest to the cavity size of this macrocyclic ligand in AN–dioxane binary solvent solutions. A nonlinear relationship was observed between the stability constants (log$_{10}$ $K_f$) of these complexes with the composition of the AN–dioxane binary solvent. Values of thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$) for complexation reactions were obtained from the temperature dependence of the stability constants. The results show that the values along with the sign of these parameters are influenced by the nature and composition of the mixed solvent.

Keywords Dibenzo-18-crown-6 · Ce$^{3+}$ · Y$^{3+}$ · UO$_2^{2+}$ · Sr$^{2+}$ · Acetonitrile–dioxane · Conductometry

1 Introduction

Crown ethers have drawn much attention because of their ability to selectively bind various cations present in solutions [1, 2]. With this unique property, potential applications of crown ethers have been found in many diverse and practical areas. For example, crown ethers have been proposed as separating agents to sequester high-level nuclear waste [3], as ligating agents to transport ions through membranes [4], as phase transfer catalysts [5], or as probes to reveal the equilibrium structures and folding states of proteins [6]. In addition, crown ethers are model systems used to study the specificity of enzymes, molecular recognition processes in host-guest chemistry, and noncovalent interactions of multidentate ligands [2].
Complexation processes of macrocyclic receptors (crown ethers, cryptands, calixarenes and calixpyrroles) with guest species are strongly influenced by the nature of the solvent [7–10]. The influence of the solvent on a variety of chemical phenomena, including solubility, phase transfer, and chemical equilibria and kinetics are among the most important issues in molecular recognition processes [11, 12]. Thus, the solvent characteristics, which include properties such as the level of structure, polarity, hydrogen bond donor/acceptor ability, polarizability, acidity/basicity, hydrophobicity/hydrophilicity or other empirical parameters, mainly affect the interaction strength between the solvent molecules and the dissolved species [13, 14]. Recently, significant progress has been made in theoretical calculations of Gibbs energies of solvation [15]. The stability and selectivity of complex formation of crown ethers with cations are influenced by the interaction of the cation with the solvent as well as the crown ether. Thus, if the solvent medium is changed, a significant effect on the binding constant is observed especially where cations are strongly solvated in one solvent and not in another [16, 17].

The effect of solvent on the complexation of crown ethers with metal cations has been a subject of interest during recent years and has been studied by means of several different techniques [18–20]. We have recently reported the complexation behavior of certain metal cations with crown ethers in mixed solvent media [21–24]. It was of interest to us to study the influence of the cation nature and solvent properties on the interaction of metal ions with crown ethers.

In this work, we report the results of a conductometric study for the determination of the stoichiometry, stability and thermodynamic parameters of dibenzo-18-crown-6 (DB18C6) complexes with Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ cations in acetonitrile–dioxane binary solvents.

2 Experimental

2.1 Reagents and Apparatus

The ligand dibenzo-18-crown-6 (DB18C6, Merck) was of the highest purity available. The nitrate salts Ce(NO$_3$)$_3$·6H$_2$O (Merck), Y(NO$_3$)$_3$·6H$_2$O (Riedel), UO$_2$(NO$_3$)$_2$·6H$_2$O (Riedel) and Sr(NO$_3$)$_2$ (Merck) were used without any further purification except for vacuum drying over P$_2$O$_5$. The organic solvents acetonitrile (Merck) and dioxane (Merck) were used without further purification. Conductance measurements were carried out using a digital Metrohm conductivity meter (model 712) at a frequency of 1 kHz, with a specially designed water-jacketed cell (150 mL, pyrex) equipped with a magnetic stirrer, and connected to a thermostatted circulating water bath. Calibration of the conductometric cell was made with the use of an aqueous KCl solution and the cell constant was determined to be 0.75 cm$^{-1}$. Two platinum electrodes were placed in the measuring cell to which an alternating potential was applied. The temperature of the reaction was controlled using a thermostatted circulating water bath, with a precision of ±0.1 °C (Julabo, model F12), and equipped with a refrigeration unit. Other details concerning equipment are similar to those reported previously [25].

2.2 Procedure

Solutions having the same total salt concentration (1.25 × 10$^{-4}$ mol·L$^{-1}$) were used for preparing the crown ether solutions with concentrations of 6.25 × 10$^{-3}$ mol·L$^{-1}$. In such dilute solutions, in order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal ion concentration. In order to
determine the complex formation constants with the studied metal ions, a 20 mL sample of the desired salt solution was placed in the cell. The conductance of the solution was measured at each of the fixed temperatures. Then, a known amount of the macrocycle solution was added in a stepwise manner using a pre-calibrated micropipette. The conductivity of the solution was measured after stirring and temperature equilibration. This procedure was continued until the total concentration of the studied ligand was approximately five times higher than that of the metal cation. The conductance of the solution was measured after each transfer and the resulting data were used for the calculation of the stability constants of complexes in the AN–dioxane binary solvent mixtures.

3 Result and Discussion

3.1 Conductance Studies

In order to evaluate the influence of DB18C6 on the molar conductance of Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ cations in acetonitrile–dioxane (AN–dioxane) binary solvent mixtures, the conductivity at a constant salt concentration ($1.25 \times 10^{-4}$ mol·L$^{-1}$) was monitored while increasing the macrocycle concentration at each fixed temperature. The resulting molar conductances versus ligand/cation mole ratio plots for DB18C6 complexes with Ce$^{3+}$ and UO$_2^{2+}$ in AN–dioxane binary solutions, at each different temperature, are shown in Figs. 1 and 2, respectively.

**Fig. 1** Molar conductance against mole ratio plots for the (DB18C6·Ce)$^{3+}$ complex in the AN–dioxane (mol-% AN = 50%) binary solvent system at different temperatures: ■, 15°C; □, 25°C; ▲, 35°C; △, 45°C
As is seen from Fig. 1, addition of DB18C6 to Ce$^{3+}$ solutions in AN–dioxane (mol-% AN = 50%) binary solvents gives rise to a decrease in the molar conductivity with an increase in the ligand concentration at each different temperature, which indicates that the (DB18C6-Ce)$^{3+}$ complex in these solutions is less mobile than the free solvated Ce$^{3+}$ cation. Similar behavior was observed in most of the studied systems, but in the case of two AN–dioxane binary solvent solutions (mol-% AN = 10% and 25%), addition of DB18C6 to Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ solutions resulted in an increase in molar conductivity with an increase in the ligand concentration at the different temperatures (Fig. 2). This could be due to the lower mobility of the solvated cation and the occurrence of some ion pairing in the initial salt solutions. It should be noted that association into ion pairs was considered to be negligible at the highly dilute experimental concentrations used. Since the ligand concentration in solutions was also sufficiently low (<6.25 × 10$^{-3}$ mol·L$^{-1}$), we avoided corrections for viscosity changes.

In all cases, the slope of the corresponding molar conductivity versus [L]/[M] ratio plots changes at the point where the ligand-to-cation mole ratio is about 1, which is evidence for formation of a relatively stable 1:1 complex between DB18C6 and the studied cations. In most cases, the experimental molar conductances were also fitted well assuming only ML formation, which emphasizes the formation of a 1:1 (ligand to metal ion) complex.

A very different behavior was observed for complexation of Ce$^{3+}$ and Y$^{3+}$ cations with DB18C6 in pure acetonitrile. As is obvious from Fig. 3, addition of DB18C6 to Y$^{3+}$ solutions in pure AN causes the molar conductivity to decrease until the mole ratio reaches 1:1,
and then to increase. Such behavior may be described according to the following equilibria:

\[(Y^{3+}, NO_3^-) + \text{crown ether} \rightleftharpoons Y^{3+} \cdot (\text{crown ether}) \cdot NO_3^- \quad \text{(RI)}\]

\[Y^{3+} \cdot (\text{crown ether}) \cdot NO_3^- + \text{crown ether} \rightleftharpoons Y^{3+} \cdot (\text{crown ether})_2 + NO_3^- \quad \text{(RII)}\]

It is known that crown ethers are strong ion-pair separators [26]. It is believed that DB18C6 occupies only equatorial coordination sites of this metal ion and its axial sites are exposed to anion and solvent molecules. It seems that addition of the DB18C6 ligand to Y^{3+} solutions in pure AN results in the formation of a stable 1:1 complex which is present as an ion pair (RI). Further addition of the ligand to ion-pair complexes causes formation of a 1:2 (ML_2) complex with a sandwich structure, which decreases the space for diffusion and interaction of NO_3^- with Y^{3+}, resulting in dissociation of the ion pair (RII) and, therefore, the molar conductivity increases.

### 3.2 Theoretical Calculations of Complex Formation Constants

According to the mole ratio plots, in most cases the metal-ligand complexes have a 1:1 stoichiometry, and 1:1 binding of the metal ions with ligand can be expressed by the following equilibrium:

\[M^{n+} + L \rightleftharpoons ML^{n+}\]
The corresponding equilibrium constant, $K_f$, is given by:

$$
K_f = \frac{[\text{ML}^{n+}][\text{L}]}{[\text{M}^{n+}][\text{L}]}
$$

where $[\text{ML}^{n+}]$, $[\text{M}^{n+}]$, $[\text{L}]$ and $f$, represent the equilibrium molar concentrations of the complex, free cation, free ligand and the activity coefficient of the indicated species, respectively [19]. Under the highly dilute experimental conditions used in this study, the activity coefficient of the uncharged ligand, $f_L$, can reasonably be assumed to be unity [27]. The use of Debye-Hückel limiting law leads to the conclusion that, $f_M^{n+} \sim f_{\text{ML}}^{n+}$, therefore, the activity coefficient ratio in Eq. 2 can be canceled.

Mass balance equations of the ML type (Eqs. 3 and 4 used in computer program GENPLOT) need to be solved in order to obtain Eq. 5 for the free ligand concentration $[\text{L}]$.

$$
C_M = [\text{M}^{n+}] + [\text{ML}^{n+}]
$$

(3)

$$
C_L = [\text{L}^{n+}] + [\text{ML}^{n+}]
$$

(4)

Substitution of Eqs. 3 and 4 into Eq. 2 and rearrangement yields:

$$
K_f[L]^2 + \left\{1 + K_f(C_M - C_L)[L] - C_L = 0
$$

(5)

The complex formation constant in terms of the molar conductivity can be expressed as:

$$
K_f = \frac{[\text{ML}^{n+}]}{[\text{M}^{n+}][\text{L}]} = \frac{\Lambda_M - \Lambda_{\text{obs}}}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[L]}
$$

(6)

where

$$
[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_M - \Lambda_{\text{ML}})}
$$

(7)

Here, $\Lambda_M$ is the molar conductivity of the metal nitrate solution before addition of the ligand, $\Lambda_{\text{obs}}$ is the molar conductivity of the solution during titration, and $\Lambda_{\text{ML}}$ is the molar conductivity of the complexed ion. $C_L$ is the analytical concentration of the ligand added and $C_M$ is the analytical concentration of the metal nitrate. It is assumed that cation-anion association is negligible.

The stability constants of the complexes at each temperature were obtained from computer fitting of Eqs. 6 and 7 to the molar conductivity-mole ratio data using a non-linear least-squares program, GENPLOT [28]. The values of the stability constants ($\log_{10} K_f$) for (DB18C6-M$^{n+}$), (M$^{n+}$: Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$) complexes in acetonitrile–dioxane binary solvent mixtures, are listed in Table 1. The values of stability constants for (DB18C6-UO$_2$)$^{2+}$ and (DB18C6-Sr$^{2+}$) complexes in pure AN are in good agreement with those previously reported [29, 30].

3.3 Effect of Solvent Composition

As is seen from Fig. 4, the change of the stability constant ($\log_{10} K_f$) of the (DB18C6-Sr)$^{2+}$ complex with the composition of the AN–dioxane binary solvent system is not linear. A non-linear behavior was also observed for the other complexes. This behavior may be related to changes occurring in the structure of the solvent mixtures and, therefore, to changes in the solvation properties of the cyclic polyether, cation and even the resulting complex, in these
Table 1 Stability constant ($\log_{10} K_f$) values for the (DB18C6-Ce)${}^{3+}$, (DB18C6-Y)${}^{3+}$, (DB18C6-UO$_2$)${}^{2+}$ and (DB18C6-Sr)${}^{2+}$ complexes in AN–dioxane binary solvent solutions at different temperatures

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$^a$Standard deviations for all $\log_{10} K_f$ values are less than ($\pm 0.1$)

$^b$The salt is not completely dissolved

$^c$The data can not be fitted to equations

$^d$Reference [29]

$^e$Reference [30]

Solvent mixtures. These structural changes may result in changing of the interactions of these solvents with the solutes.

In addition, preferential solvation of the cation, anion and ligand, and their changes with the composition of the mixed solvents and temperature may effect the complexation processes. 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 towards the ion and the interactions between the 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 components [31].
The change of stability constants (log$_{10}K_f$) of (DB18C6-M$^{n+}$) (M$^{n+}$: Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$) complexes versus the ionic radii in AN–dioxane binary solvent systems is shown in Fig. 5. As is evident from Fig. 5, the order of selectivity of DB18C6 for these cations in AN-dioxane binary solvent solutions (mol-% AN = 10% and 25%) at 25°C is: Ce$^{3+}$ > Y$^{3+}$ > UO$_2^{2+}$ > Sr$^{2+}$. It is interesting to note that the selectivity order of the complexes in AN–dioxane binary mixtures with 50 mol-% of AN is Ce$^{3+}$ > UO$_2^{2+}$ > Sr$^{2+}$ > Y$^{3+}$, whereas in the case of 75 mol-% AN, the selectivity sequence changes to Ce$^{3+}$ > UO$_2^{2+}$ > Y$^{3+}$ > Sr$^{2+}$.

Crown ethers are characterized by the presence of a single hole [32] rather than a cavity. Cavity size, through the hole-size relationship, has generally been regarded as the prime parameter for selectivity. The hole-size concept states that when the diameter of the cation and the hole in the crown ether are the same size, the latter is selective for the former. However, this generalization does not really hold for all studied cases.

Although the size of Sr$^{2+}$ cation (radius 1.12 Å) is relatively close to the cavity size of DB18C6 (1.3–1.6 Å) [33] in comparison with the other cations, from these results it can be concluded that the DB18C6 macrocycle does not exhibit selectivity for this cation whose ionic size is closest to the cavity size of the ligand. On the other hand, the selection of solvents as mixture components, and their concentrations, may result in changes in the selectivity of the ligand for metal cations in solutions.

Certainly, the selectivity toward metal ions is also affected by other factors including the solvation energies of the species involved, ligand conformation before and after complexation, spatial arrangement of the donor atoms, molecular symmetry and the number and type of donor atoms in the polyether ring and so on [34, 35]. Therefore, the cavity-size effect is no longer the dominant factor in complexation reactions between DB18C6 and the studied cations in these solutions. It seems reasonable that the hole size concept would be most
valid for the most rigid ligand systems. A flexible ligand can accommodate a wider variety of cations than can a rigid one. In the case of flexible ligands such as crown ethers, other factors such as the cation’s solvation enthalpy and ligand conformations become important [23, 36]. The hole-size relationship is better represented by cryptands that are relatively rigid [36].

The stability constants of crown ether–cation complexes in solutions can be interpreted as representing the overall equilibrium constants of a series of reactions including: (i) partial or complete desolvation of the cation, (ii) partial or complete desolvation of the crown ether, (iii) conformational change of the crown ether, (iv) formation of a crown ether–cation complex, and (v) solvation of the resulting charged complex. As is evident, solvent molecules are directly involved in three of the five possible equilibria. Thus, it is expected that solvent properties such as dielectric constant, solvating ability and potential for hydrogen bonding will considerably affect the selectivity order of the formed complexes.

3.4 Thermodynamic Calculations

In order to have a better understanding of the thermodynamics of complexation reactions of the metal ions with the ligands, it is useful to determine the contributions of enthalpy and entropy of the reactions. The $\Delta H^\circ_c$ and $\Delta S^\circ_c$ values for complexation processes between DB18C6 and Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ cations in AN–dioxane binary solvent solutions were determined from the temperature dependence of the stability constants using van’t Hoff plots. The stability constants (log$_{10} K_f$) of all (DB18C6·M$^{n+}$) (M$^{n+}$: Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$) complexes in the binary solvent solutions at the studied temperatures are given in Table 1. In all cases, the plots of ln$K_f$ versus $1/T$ were linear, and a typical example of these plots is shown in Fig. 6 for the (DB18C6·Sr)$^{2+}$ complex in various solvent mixtures.
The values of standard enthalpies for complexation reactions were determined in the usual manner from the slope of the van’t Hoff plots assuming that $\Delta C_p^\circ$ is equal to zero over the investigated temperature range. The values of the standard entropies were calculated from the relationship: $\Delta G^\circ_{\text{f},298.15} = \Delta H^\circ_{\text{f}} - (298.15 \text{ K})\Delta S^\circ_{\text{f}}$. These results are summarized in Table 2.

The thermodynamic data given in Table 2 show that, depending on the solvent composition, the sign of the enthalpy values for formation of (DB18C6·Ce)$^3^+$, (DB18C6·Y)$^3^+$ and (DB18C6·UO$_2^+$)$^2^+$ complexes can be negative or positive, but in the case of the (DB18C6·Sr)$^2^+$ complex the values of enthalpies are negative. These results reveal that the complexation processes between DB18C6 and Ce$^3^+$, Y$^3^+$ and UO$_2^+$ cations are exothermic (favorable) or endothermic (unfavorable), depending on the composition of the solvent system. But, in the case of formation of the (DB18C6·Sr)$^2^+$ complex, the complexation reaction is exothermic (favorable) at all solvent compositions. The results in Table 1 show that in some of the solvent system compositions, the stability constants ($\log_{10} K_f$) do not change with the temperature and, therefore, the standard enthalpy changes are negligible; thus, the complexation reactions in these systems seems to be athermic.

The positive values of $\Delta S^\circ_{\text{f}}$ (Table 2) show that the complexation processes between Ce$^{3+}$, Y$^{3+}$ and UO$_2^{2+}$ cations with DB18C6 are entropy stabilized. However, negative $\Delta S^\circ_{\text{f}}$ values characterize the formation of the (DB18C6·Sr)$^{2+}$ complex. Hence, the (DB18C6·Sr)$^{2+}$ complex is destabilized from the entropic viewpoint. The two main factors that affect the $\Delta S^\circ_{\text{f}}$ values are (i) the loss of conformational entropy of ligand upon complexation, and (ii) randomness of solvent molecules in the bulk solvent after being released during desolvation of the metal cation and ligand. It has been reasonably assumed that the negative entropy changes upon complexation are related to a change in the conformational
monotonic behavior has also been observed between thermodynamic parameters of some of mixed and single parent solvates, may be responsible for this nonlinear behavior. A non-reactions, such as solvent-solvent interactions, heteroselective solvation, and formation of systems. Many factors which contribute to changes of enthalpy and entropy of complexation and the ligand, which depend on the structural and energetic properties of the mixed solvent systems. Many factors which contribute to changes of enthalpy and entropy of complexation reactions, such as solvent-solvent interactions, heteroselective solvation, and formation of mixed and single parent solvates, may be responsible for this nonlinear behavior. A non-monotonic behavior has also been observed between thermodynamic parameters of some of crown ether-metal ion complexes and the composition of binary solvent solutions [21–24].

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

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<td>$-18.51 \pm 4.35$</td>
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</table>

$^a$SD = standard deviation

$^b$Not reported since highly uncertain

Table 2 Thermodynamic parameters for the (DB18C6-Ce)$^{3+}$, (DB18C6-Y)$^{3+}$, (DB18C6-UO$_2^{2+}$) and (DB18C6-Sr)$^{2+}$ complexes in AN–dioxane binary solvent solutions

entropy of the ligand in going from a rather flexible structure in the free state to a rigid conformation in the complex [37], and the release of some solvent molecules after desolvation of cation and ligand may also contribute to the positive entropy values [38].

As is obvious from Table 2, the standard thermodynamic quantities ($\Delta H^0_{c}$, $\Delta S^0_{c}$) are quite sensitive to the nature and composition of the mixed solvent, and a non-monotonic behavior is observed between these thermodynamic functions and the composition of the acetonitrile–dioxane binary solvents. Changes of the enthalpy of the ligand by complexation are mainly due to changes of solvation, intermolecular ligand–ligand repulsion, the stacking of the aromatic residues, and steric deformation of the ligand induced by the bound metal ion [39]. It seems that the thermodynamics of complexation reactions between DB18C6 and Ce$^{3+}$, Y$^{3+}$, UO$_2^{2+}$ and Sr$^{2+}$ cations is affected by the solvation capacities of the metal cations and the ligand, which depend on the structural and energetic properties of the mixed solvent systems. Many factors which contribute to changes of enthalpy and entropy of complexation reactions, such as solvent-solvent interactions, heteroselective solvation, and formation of mixed and single parent solvates, may be responsible for this nonlinear behavior. A non-monotonic behavior has also been observed between thermodynamic parameters of some of crown ether-metal ion complexes and the composition of binary solvent solutions [21–24].

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References