A Conductometric study of complexation reaction between dibenzyl-14-crown-4, with ZrO$^{2+}$ in some binary mixed non-aqueous solvents

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Abstract

In Some binary methanol mixtures, (MeOH), 1,2 dichloroethane (DCE), acetonitrile (AN), and tetrahydrofuran (THF), with dimethylformamide (DMF) at different temperatures using the conductometric process, the reaction of macrocyclic ligand to complexation, dibenzyl-14-crown-4 (DB14C4) with ZrO$^{2+}$ cation was examined. The conductance data show that in all solvent systems, the stoichiometry of the complex formed between (DB14C4) and ZrO$^{2+}$ cation is 1:1 (M:L). The stability order of (DB14C4.ZrO)$^{2+}$ complex in pure non-aqueous solvents was found to be: [AN], [DCE], [MeOH], [THF], [DMF]. A non-linear behaviour was observed improvements in log $K_f$ of (DB14C4.ZrO)$^{2+}$ complex or Binary mixed solvent composition, It Was clarified as to the Interactions with solvents and even solvents in terms of the hetero-selective solving of the ecosystem affected by complexation response. The obtained results show that the stability of (DB14C4.ZrO)$^{2+}$ complex is sensitive to the composition of the mixed solvent. The values of thermodynamic parameters ($\Delta H^\circ$ and $\Delta S^\circ$) for the formation of (DB14C4.ZrO)$^{2+}$ complex using van't Hoff maps, the stability constant was obtained from temperature dependence. The results show that in most cases, the (DB14C4.ZrO)$^{2+}$ complex is enthalpy destabilized but entropy balanced and the values and signs of thermodynamic parameters are often These are decided by nature and composition of the mixed solvents.

Keywords: Dibenzyl-14-crown-4; ZrO$^{2+}$cation;Mixed non-aqueous solvents; conductometry.

1. Introduction

Since the time Pedersen published the first report on crown compounds in 1967, [1] these compounds have been considered for a wide collection of applications including enzyme models, biophysics, and medicine [2]. Crown ethers are noted for their exceptional selectivity against different cations, making them perfect choices for the separation of desired cations.
metal ions from their Solvent separation and membrane conveying mixtures [3, 4]. Binding ability and crown ethers are selective to metal ions, depending on some factors: such as crown ether cavity size, metal ion length, atom type donor, crown ether conformation, solvent composition, etc. Solvent plays a significant function in the binding selectivity of the crown ethers for metal ions [5, 6]. And the Macrocyclic Polyethers synthesis and creating stable complexes between these ligands and different material cations were specified. And Crown ethers can bind guest molecules and metal cations because of the existence of their binding sites and the presence of a hydrophilic cavity delineated by a lipophilic envelope with a high-level quality specificity in 3-D cavities. A variety of physicochemical techniques such as calorimetry [7, 8], polarography [9], potentiometry [10, 11], NMR spectrometry [12, 13], and conductometry [14-16] have been used to study the complex creation of solutions between crown ethers and metal ions.

![Scheme1. Structure of Dibenzyl-14-crown-4 (DB14C4).](image)

Conductometry is a flexible and inexpensive tool for these investigations, between these different methods. The application of analytical techniques to the analysis of actinide compounds becomes ever more important. Chemistry of synchronization of the actinides is important for both fundamental and practical reasons and is different from that displayed by the elements located in the rest of the pieces table periodic. Further understanding of the factors influencing this behaviour that aid in the treatment of radioactive nuclear waste. Recent increases in the production of nuclear power, primarily based on uranium-based fuel, have resulted in the risk of releasing ultra-trace quantities of uranium in natural aquifers. ZrO$^{2+}$ as a heavy metal ion is considered to be nephrotoxic, and radiologically hazardous as a radionuclide. Although the total concentration of a particular uranium isotope determines the radiological effects, its chemical toxicity depends on the chemical type of its species that interacts with bio-molecules [17]. Uranium’s Capacity to create complexes was found in soil and the nuclear industry to clean up uranium pollution where chelating agents are specific constituents of fluids used to clean reactors [18]. The interaction between uranyl cation and several macrocyclic ligands has been analysed [19-21]. In the analysis underway, complexation of (Scheme 1) dibenzyl-14-crown-4 with uranyl (ZrO)${}^{2+}$ cation in acetonitrile–
methanol (AN–MeOH), acetonitrile -1,2 dichloroethane (AN - DCE), and acetonitrile–
dimethylformamide (AN–DMF), and acetonitrile-tetrahydrofuran (AN-THF) binary mixtures
of various temperatures. Use of a conductometric process to investigate the effect of solvent
properties and the composition of binary mixed solvents on the stability and stoichiometry of
complexes formed between solutions (ZrO)²⁺ and dibenzyl-14-crown-4.

2. Experimental
dibenzyl-14-crown-4 (Merck) and ZrO(NO₃)₂·6H₂O (Merck) were used without purification.
The solvents: acetonitrile, methanol, dimethylformamide, 1,2 dichloroethane, and
tetrahydrofuran all from Merck were used with the highest purity.

![Figure 1. Molar conductance-mole ratio plots for (DB14C4.ZrO)²⁺ in (AN–MeOH), binary
system (mol% AN=80.0) at different temperatures : (x: 15°C, ■: 25°C, △: 35°C, ◆: 45°C).](image)

The experimental method used to obtain the constant formation of (DB14C4.ZrO)²⁺ was as
follows: 20mL metal salt solution (1×10⁻⁴ mol. L⁻¹) was put in a titration cell, thermostated at
a specified temperature, and the solution's conductance was calculated. Then a step-by-step
increase of the crown ether solution (2 × 10⁻³ mol. L⁻¹) prepared in the same solvent was then
achieved by fast transfer to the titration cell using a micro-desktop, and the conductance of
the solution present in the cell was measured after each transfer at the desired temperature.
The conductivity measurements were performed in a Julabo (Model F12) water bath on a
Digital conductive Metrohm apparatus (Model 712), thermostat at a steady temperature held
inside ±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 (Conductance studies)
Changes of molar conductivity (m) versus the ligand to cation molar ratio ([L]t / [M]t) for complexation of (DB14C4) with ZrO\(^{2+}\) was measured in pure [AN], [DCE], [MeOH], [THF] and [DMF] and also in (AN–MeOH), (AN-DCE), (AN–DMF), and (AN-THF) binary systems at different temperatures. Two typical series of molar conductance values in the action of molar ratio in (AN–MeOH) binary mixture (mol% AN=80.0) and pure (AN) are shown in figures 1 and 2, respectively. Also, fitting.

![Figure 2](image_url)

Figure 2. Molar conductance-mole ratio plots for (DB14C4.ZrO)\(^{2+}\) in pure (AN) at different temperatures: (x:15°C, ■: 25°C, ∆:35°C, ▲:45°C)

The stability constant of (DB14C4.ZrO)\(^{2+}\) complex in different solvent mixtures. And experimental curves for (DB14C4ZrO)\(^{2+}\) in an acetonitrile–methanol binary system (mol% AN=80.0) at are shown in figure 3 (the fitting data are given in the appendix in Supplementary material). Constant stability of (DB14C4.ZrO)\(^{2+}\) at each temperature was calculated from the changes of the molar conductance in the action of [DB14C4] / [ZrO]\(^{2+}\) molar ratios using a GENPLOT computer program[22]. The details of the calculation of the stability constants of complexes by the conductometric method have been described [23]. The values of stability constant (logKf) for (DB14C4.ZrO)\(^{2+}\) in various solvent systems are listed in table 1. The 1:1 complexation.

the reaction of a metal cation, M\(^{n+}\), with a crown ether is expressed through the following equilibrium: M\(^{n+}\) + L ↔ ML\(^{n+}\) 

With equilibrium constant, Kf, given by

\[
K_f = \frac{[ML^{n+}] \cdot f_{ML}^{n+}}{[M^{n+}][L] \cdot f_{ML}^{n+} \cdot f_L}
\]
Where \([ML^{n+}]\), \([M^{n+}]\), 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 \(f_{ML^{n+}}/f_{M^{n+}}f_{L}\) is essentially the unity and, therefore, the equilibrium constants obtained in this study are thermodynamic. For all the structures under investigation, \(lnKf\)'s van’t Hoff plots versus \(1/T\) were built. Plots of \(lnKf\) versus \(1/T\) in all cases were linear. The changes in standard

\[
\Delta H^\circ = \text{enthalpy for complexation}
\]

were obtained from the slope of the van’t Hoff plots assuming that \(\Delta C_p\) is equal to zero over the entire temperature range tested. The changes in standard entropy \((\Delta S^\circ)\) were calculated from the relationship \(\Delta G^\circ,298:15 = \Delta H^\circ - 298.15 \Delta S^\circ\). The values of thermodynamic parameters are summarized in table 2. The changes of \(logKf\) of (DB14C4.ZrO)\(^{2+}\) provided the composition of the (AN–MeOH) and AN–DMF binary solutions at different temperatures are shown in figures 4 and 5, respectively.

4. Discussion

Addition of (DB14C4 to ZrO)\(^{2+}\) in an acetonitrile-methanol binary system (mol\% AN=80.0) at different temperatures results in a decrease in molar conductivity (figure 1), which indicates that (DB14C4.ZrO)\(^{2+}\) in this solution is less mobile than free solvated (ZrO)\(^{2+}\). According to Figure 1, The slope of corresponding molar conductivity versus \([L]/[M]\) plots shifts at the point where the ligand to cation mole ratio is around 1, which is proof of the formation of a fairly stable 1:1 [M:L] complex in solution. Similar behaviour was observed for (DB14C4.ZrO)\(^{2+}\) in all of the other pure and binary mixed solvent systems. The fitting and experimental curves for (DB14C4.ZrO)\(^{2+}\) in the acetonitrile-methanol binary system (mol
per cent AN=80.0) Explain the 1:1 [M: L] complexation model in Figure 3; The fitting and experimental results are very well agreed with.

Table 1. LogK, values of (DB14C4.ZrO2)2+ in AN–MeOH, AN–DMF, AN–DCE, and AN–THF binary mixtures at different temperatures.

| Medium            | LogK, ± SD* | 15°C | 25°C | 35°C | 45°C |
|-------------------|-------------|------|------|------|------|
| AN–MeOH           |             |      |      |      |      |
| Pure MeOH         |             |      |      |      |      |
| 60.0% MeOH –40.0% AN | 3.71 ± 0.04 | 3.83 ± 0.03 | 3.69 ± 0.03 | 3.56 ± 0.05 |
| 40.0% MeOH –60.0% AN | 3.41 ± 0.06 | 3.35 ± 0.04 | 3.23 ± 0.03 | 3.27 ± 0.16 |
| 20.0% MeOH –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          |             |      |      |      |      |
| 70.0% DMF–30.0% AN | 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–DCE            |             |      |      |      |      |
| 90.0% DCE–10.0% AN | 2.67 ± 0.02 | 2.70 ± 0.05 | 2.66 ± 0.02 | 2.66 ± 0.01 |
| 80.0% DCE–20.0% AN | 2.85 ± 0.06 | 2.83 ± 0.07 | 2.68 ± 0.02 | 2.54 ± 0.17 |
| 60.0% DCE–40.0% AN | 2.82 ± 0.07 | 2.81 ± 0.09 | 2.54 ± 0.15 | 2.83 ± 0.08 |
| 30.0% DCE–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–THF            |             |      |      |      |      |
| Pure THF          |             |      |      |      |      |
| 70.0% THF–30.0% AN | 2.70 ± 0.11 | 2.80 ± 0.09 | 2.83 ± 0.07 | 2.63 ± 0.03 |
| 40.0% THF–60.0% AN | 2.86 ± 0.12 | 2.49 ± 0.13 | 2.83 ± 0.08 | 2.54 ± 0.03 |
| 20.0% THF–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 |

*SD =Standard deviation.

bComposition of binary mixtures is expressed in mol% per cent for each solvent system.

cThe data cannot be fitted in the equation.

THF binary mixtures at different temperatures.
Experimental and fitting curves superimposed. In pure acetonitrile (Figure 2), the addition of (DB14C4 to ZrO)2+ at different temperatures results in an increase in molar conductivity which shows that the complex formed between DB14C4 and uranyl cation is more mobile than free solvated (ZrO)2+. It is interesting to note that as the (DB14C4.ZrO)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 (DB14C4) and (ZrO)2+ cation in pure (AN) at all temperatures, which is more mobile than free solvated (ZrO)2+, but further addition of the ligand results in the formation of a 1:2 [M:L2] 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 DB14C4 in this pure dipolar aprotic solvent at.

Table 2. Thermodynamic parameters for (DB14C4.ZrO2)2+ in (AN–MeOH), (AN–DMF), (AN–DCE), (AN–THF) binary mixtures.

| Medium          | $\Delta G^°_c \pm SD$ at 25°C (kJ mol$^{-1}$) | $\Delta H^°_c \pm SD$ (kJ mol$^{-1}$) | $\Delta S^°_c \pm SD$ (J mol$^{-1}$ K$^{-1}$) |
|-----------------|---------------------------------------------|--------------------------------------|---------------------------------------------|
| AN–MeOH         |                                             |                                      |                                             |
| 60.0% MeOH–40.0% AN$^b$ | 22 ± 0                                      | - 80 ± 35                            | c                                           |
| 40.0% MeOH–60.0% AN    | 19 ± 0                                      | - 35 ± 15                            | c                                           |
| 20.0% MeOH–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–DCE           |                                             |                                      |                                             |
| 90.0% DCE–10.0% AN$^b$ | 15 ± 0                                      | c                                    | 46 ± 5                                      |
| 80.0% DCE–20.0% AN    | 16 ± 0                                      | - 18 ± 4                             | c                                           |
| 60.0% DCE–40.0% AN    | 16 ± 0                                      | c                                    | c                                           |
| 30.0% DCE–70.0% AN    | 16 ± 0                                      | c                                    | c                                           |
| Pure AN          | 20 ± 0                                      | - 13 ± 2                             | 23 ± 6                                      |
| AN–THF           |                                             |                                      |                                             |
| 70.0% THF–30.0% AN$^b$ | 16 ± 0                                      | c                                    | c                                           |
| 40.0% THF–60.0% AN    | 14 ± 1                                      | c                                    | c                                           |
| 20.0% THF–80.0% AN    | 16 ± 0                                      | c                                    | c                                           |
| Pure AN          | 20 ± 0                                      | - 13 ± 2                             | 23 ± 6                                      |
SD=standard deviation.

Composition of binary mixtures is expressed in mol% per cent for each solvent system.

With high uncertainty.

all temperatures:

$$\text{ZrO}^{2+} + \text{DB14C4} \leftrightarrow (\text{DB14C4.ZrO})^{2+} \quad (I)$$

$$(\text{DB14C4.ZrO})^{2+} + \text{DB14C4} \leftrightarrow [(\text{DB14C4})_2 \cdot \text{ZrO}]^{2+} \quad (II)$$

The findings obtained in this investigation show that the existence of the solvent system will alter the stoichiometry of the crown ether-metal cation complexes [19, 20]. As obvious from Table 1, Constant stability of (DB14C4.ZrO)$^{2+}$ in the binary mixed solvents at is AN–MeOH, AN–DMF, AN–DCE, and AN–THF. This can be interpreted by considering the inherent relative solvating ability of the pure solvents which form the mixtures. AN with a high donor ability (DN=14.1) relative to MeOH (DN=20.0), DMF (DN=26.6), THF (DN=20.0), DCE (DN=0.0), can solvate the ZrO$^{2+}$ cation strongly and rival the Ligand.

![Graph showing changes of the stability constant of (DB14C4.ZrO)$^{2+}$ with the composition of the AN–MeOH binary mixture at different temperatures](image)

Figure 4. Changes of the stability constant of (DB14C4.ZrO)$^{2+}$ with the composition of the AN–MeOH binary mixture at different temperatures: (x:15°C, ■:25°C, △:35°C, □:45°C).
Figure 5. Changes of the stability constant of (DB14C4.ZrO)2+ with the composition of the AN-DMF binary mixture at different temperatures : (x: 15°C, ■: 25°C, Δ: 35°C, ◆: 45°C).

For this cation in the solution. Also, the higher dielectric constant of AN (ε = 36), DMF (ε = 36.7) compared with MeOH (ε = 32.6), DCE (ε = 10.4), THF (ε = 7.6), A decrease in the electrostatic interactions in the solution between dibenzyl-14-crown-4 and ZrO2+ may result. As seen from figures 4 and 5, changes of stability constant (logKf) of (DB14C4.ZrO)2+ with the composition of (AN-MeOH) and (AN-DMF) binary systems are not linear. Non-linear behaviour was also observed in all other binary solutions. This behaviour can be attributed to changes that occur in the solvent mixture structure and thus alter the solvation properties of cyclic polyether, cation, and even the resulting complex in these solvent mixtures. Besides, the stereoselective solvation of the cation and ligand and its changes with the composition of the mixed solvents in these binary mixed solution systems may be successful in the complexation reaction between uranyl cation and DB14C4. We studied interactions among some binary mixed solvents [24]. For example, mixing of DMF with AN induces the mutual destruction of dipolar structures of these dipolar aprotic liquids and releases the free dipoles [25].

As a result, strong dipolar interactions between AN and DMF molecules are expected. Also, there is an interaction between AN and MeOH molecules (K_{acc} = 1.23) via hydrogen bonding in their binary mixtures [26]. In this complexing method, preferential cation, anion and ligand solving with well-mixed solvent composition and temperature. The preferential solution of ions by one of the components of a mixed solvent system depends on two factors: the relative ability of the donor-acceptor member molecules against the ion and the interactions between
solvent molecules themselves. Solvent-solvent interactions can also substantially alter the solvent properties of the components in mixed solvents when the concentration of these is comparable to the concentration difference of solvent-ion interactions for both the components [27].

Thermodynamic data which are included in Table 2 reveals that in most cases (DB14C4.ZrO)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 ZrO2+ and DB14C4 is negligible; therefore, it seems that the complexation processes in some solvent systems are thermic. As the values of standard entropy (c) and standard enthalpy (c) for the formation of (DB14C4.ZrO)2+ in the solution vary with parameters for example changes in the flexibility of the macrocyclic ligand during intracy 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 [28-30]. The findings in this analysis suggest that thermodynamic parameters do not vary monotonically with the solvent composition (Table 2) due to variations in the contribution of important parameters such as solvation – a dissolving of the species involved in the reaction to the complexion (i.e., ZrO2+, DB14C4, the resulting complex and even NO3−), and also the conformational changes of the large macrocyclic ligand in binary solutions; thus, a monotonic relationship between those thermodynamic quantities and the solvent composition of binary mixed solutions should not be predicted. Somewhat similar thermodynamic behaviour has been observed for the complexation of DB14C4 with alkaline earth metal cations in AN–DMF binary mixture [31].

5. Conclusion
The results obtained for the complexation of ZrO2+ with DB14C4 in pure AN, MeOH, DMF, and THF and also in AN–MeOH, AN–DMF, AN–DCE, and AN–THF binary mixtures show that the stoichiometry, stability, and thermodynamics of complex formation The structure and composition of solvent systems shall be regulated by uranyl cation with a macrocyclic ligand. The conductance data show that in most cases DB14C4 forms a 1:1 [M: L] complex with ZrO2+. And the order of stability constant of (DB12C4.ZrO)2+ in the binary mixed solvents at 25˚C was found to be: AN–MeOH, AN–DMF, AN–DCE, and AN–THF. The findings show that solvents 'ability to contribute electrons and dielectric constant play a significant part in complexing. A non-linear relationship was observed between the stability constant of (DB14C4.ZrO)2+ and the composition of the binary solutions. Thermodynamic parameters do not vary monotonically with the solvent composition. Such actions are possible due to a change in binary solvent structure, as the medium's composition is varied. Complexation between ZrO2+ and DB14C4 is mainly stabilized by enthalpy and entropy, And The
Thermodynamic Principles quantities are affected by the existence and composition of the mixed solvents. The resolution of crown ethers is critical during the complexation process of macrocyclic ligands with metal cations, and the relative enthalpy and entropy changes can be better understood if ligand solvation is considered. Knowledge about the interaction of macrocyclic ligands with solvent is scarce, and additional ligand-solvent interaction studies are required to investigate the thermodynamic behaviour of the solution's macrocyclic complexes.

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