Complexation thermodynamics of UO_2^{2+}/diglycolamide complex in a room temperature ionic liquid: A study by optical spectroscopy and microcalorimetry

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ABSTRACT

Complexation thermodynamics of UO_2^{2+} and a series of *N,N,N',N'*-tetraalkyl diglycolamide (T*R*DGA) ligands having alkyl chains $-CH_3$ to $-C_6H_{13}$ were investigated in an ionic liquid (IL). The complexation constant for UO_2^{2+}/DGA complex increased linearly with increasing alkyl chain length of DGA from tetramethyl ($\log\beta_1 = 4.52$, $\log\beta_2 = 8.01$) to tetrahexyl ($\log\beta_1 = 5.62$, $\log\beta_2 = 10.3$). There were two types of species recorded in the calorimetric titration for all the four ligands, one having endothermic complexation, and other exothermic. This observation was in contrast with those observed for aqueous medium, where both the stepwise complexation enthalpies were endothermic. The structural feature indicated the formation of $[UO_2L_2]^{2+}$ type of complex without water or Tf_2N^- anion in the primary coordination sphere of the uranyl cation.

1. Introduction

In the recent past, room-temperature ionic liquids (IL) have gained the status of "designer" solvents, where the properties of the solvent can be tailored through the judicious choice of their cationic and anionic components [1]. With imidazolium-based cations and hydrophobic anions, such as bis(trifluoromethane sulfonyl)amide, ILs are immiscible in water with desired physicochemical properties (e.g., viscosity [2]) and, therefore, have been widely studied in the separation of metal ions from aqueous solutions [3–5]. One of the first papers in the area of metal ion separation by Dai *et al.* reported about 10^5 times enhancement in metal ion extraction when an IL was used in place of a molecular diluent [6]. This was subsequently attributed to a unique mechanism commonly seen in IL medium, referred to as 'cation exchange' mechanism, where the cationic species of the metal-ligand species is transferred into the IL phase with a simultaneous transfer of the cationic part of IL phase into the aqueous phase [3,4]. Similar results were also reported when DGA (diglycolamide) ligands were employed for the extraction of several actinide ions [7,8]. However, the enhancement in the extraction of UO_2^{2+} ion was much lower as compared to those observed for Am^{3+} and Pu^{4+} ions. Studies on complexation of UO_2^{2+} ion with CMPO (octyl-phenyl-*N,N*-diisobutyl carbamoylmethyl phosphine oxide) in IL medium

have also shown very interesting complexation features [9]. It has been shown that the complexation of UO_2^{2+} with CMPO in dry and wet-IL (IL saturated with water) yielded quite different thermodynamic parameters. In dry-IL, the UO_2^{2+}/CMPO complex was stronger, and complex formation was driven by negative enthalpies. In wet-IL, on the other hand, the complexation was relatively weak and entropy driven. Such features can be attributed to different solvation behaviour of the metal ions and the ligands by the ILs, and strong electrostatic effect of the complexing medium [10].

In our earlier communication, we reported for the first time the structural features of $UO_2(TMDGA)_2 \cdot (Tf_2N)_2$ complex (TMDGA = *N,N,N',N'*-tetramethyl diglycolamide) that was isolated from the IL medium by single crystal XRD [11]. In this communication, we are reporting the detail complexation thermodynamics of UO_2^{2+} cation with a series of four DGA ligands in IL, viz. *N,N,N',N'*-tetramethyl DGA (TMDGA), *N,N,N',N'*-tetraethyl DGA (TEDGA), *N,N,N',N'*-tetrabutyl DGA (TBDGA), and *N,N,N',N'*-tetrahexyl DGA (THDGA). The study includes the spectrophotometric titration of UO_2^{2+} ions with DGA ligands, including the direct determination of enthalpy of complexation (Δ_rH) by microcalorimetry. Choice of the lower alkyl chain family of DGAs ($R = C_1 - C_6$) were based on their well understood aqueous complexation behavior with actinyl ions [12–14], with a curiosity to understand the difference

in their complexation behaviour in aqueous and IL media. 1-butyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide (Bumim·Tf$_2$N) was the choice of IL in this work due to its favourable viscosity for conducting the spectrophotometric and calorimetric titrations.

2. Experimental

N,N,N′,N′-tetraalkyl diglycolamide (TRDGA, Fig. 1) was synthesized by reacting diglycolyl chloride with the respective dialkyl amine, as reported earlier [15]. The materials were characterized by ^{1}H NMR, FT-IR and mass spectrometry. The IL, Bumim·Tf$_2$N (Fig. 1), having purity > 99%, was procured from Iolitec, Germany. No attempt was made to dry the IL and it was used as received. The water content of the IL was about 1000 ppm as estimated by Karl Fischer titration, which was in agreement with the earlier report [16]. Trifluoromethane sulfonimide or tri-flimide (HTf$_2$N) was procured from Sigma Aldrich. UO$_2$(Tf$_2$N)$_2$ salt was prepared by reaction of uranium trioxide with HTf$_2$N as per the procedures described earlier [11]. A stock uranium solution in Bumim·Tf$_2$N was prepared by dissolving the appropriate amount of the UO$_2$(Tf$_2$N)$_2$ salt, and its concentration was confirmed by volumetric titration using the Davies-Gray method [17].

Absorption spectra of UO$_2^{2+}$ in IL were recorded in the wavelength region 370–510 nm (0.1 nm interval) on a double beam Jasco V-530 spectrophotometer using 10 mm path length quartz cells. The initial concentration of UO$_2^{2+}$ in the cell was ~ 20 mmol/L. In each titration, appropriate aliquots of the titrant solution (100 mmol/L DGA solution in Bumim·Tf$_2$N) were added into the cell and mixed thoroughly for about 5 min before recording the spectrum. This mixing time was found sufficient for completion of the complexation reaction (see ESI). Usually, a set of 20–25 spectra were recorded in each titration, and the spectra were analyzed for calculation of the formation constants of the complexes using the HypSpec® program [18].

Microcalorimetric titrations were carried out in an isothermal titration calorimeter (TAM-III, Thermometric AB, Sweden) as per the details described earlier [19]. All calorimetric titrations were performed at 25 °C. The reaction cup containing 2.7 mL of the UO$_2$(Tf$_2$N)$_2$ solution in Bumim·Tf$_2$N was stirred with a gold propeller maintained at 100 rpm. The ligand solution (titrant) was added stepwise to the reaction vessel through a Hamilton 500 μL syringe in small lots (15 μL per addition). About 30 injections were made in each set of titrations. The heat of reaction obtained during the titration was corrected for dilution heats measured in blank experiment separately. For each blank experiment, dilution heat measurements were carried out by using the identical procedure as in the main experiment, except the metal ion being absent in the titrand. Enthalpy of the reaction was then calculated using HypDeltaH® program [20] employing the logβ values obtained by spectrophotometry. Details about the calibration of the instruments and calculation of the enthalpy of complexation are given in the ESI.

3. Results and discussion
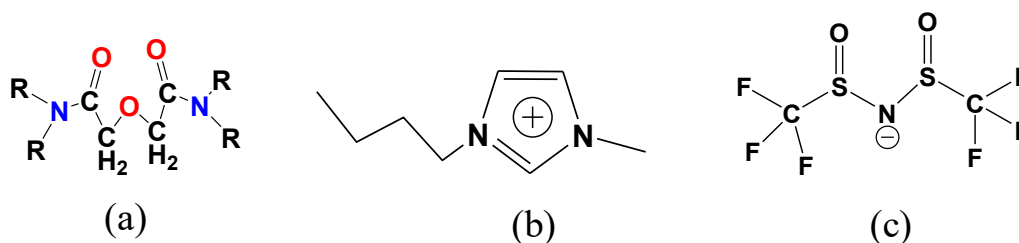
Fig. 2 represents the spectrophotometric titration of UO$_2^{2+}$ ions with the TRDGA ligands in Bumim·Tf$_2$N. Several bands in the absorbance spectra of bare UO$_2^{2+}$ ions (392 nm, 405 nm, 417 nm and 429 nm) were noted, which were identical to those recorded in the aqueous perchlorate medium [12]. The spectral features in the absorption spectra corresponded to the hydrated uranyl ions with five water molecules in the equatorial plane. Our observation was in line with the earlier report which indicated that the penta-hydrated uranyl cation exists even in dry ILs with a water content below 100 ppm [21]. Absorbance spectra of the uranyl ion in 'dry' and 'wet' ILs have been reported to be identical [9]. Based on these observations, it can be confidently stated that the main species present in this work is [UO$_2$(H$_2$O)$_5$]$^{2+}$, where five H$_2$O molecules are bound in the equatorial plane of the central metal atom as the IL used in this work was not dried and contained about 1000 ppm water. During the titration of UO$_2^{2+}$ ions with DGA, gradual changes in the absorption spectra were observed (Fig. 2), indicating the gradual complexation of uranyl cations with the ligands. As the ratio of ligand-to-metal concentration (L/M) increased, formation of two new absorption bands with peak maxima at 463 nm and 479 nm was clearly observed which indicated the gradual complexation of uranyl cations with DGA ligands. These changes primarily arise due to the symmetry change in the primary coordination sphere of the uranyl cation as the H$_2$O molecules are replaced with the complexing ligand.

Titration was continued till the ligand-to-metal molar concentration ratio reached to 4, and the complexation was complete and only dilution of the spectra was noticed as there was no further complexation after the addition of fresh aliquots of the ligands. The spectra were analyzed and fitting to the HypSpec® program [18], and the best fit of the data were obtained with the assumption of the formation of two successive complexes, viz., [UO$_2$L]$^{2+}$ and [UO$_2$L$_2$]$^{2+}$, where L = DGA ligands. The calculated stepwise formation constant (log K) for the formation of [UO$_2$L]$^{2+}$ and [UO$_2$L$_2$]$^{2+}$ are summarized in Table 1. Formation of [UO$_2$L$_2$]$^{2+}$ as the limiting species was in accordance to the solid complex of UO$_2^{2+}$/TMDGA obtained in the aqueous medium, where it has been confirmed that the two DGA ligands are indeed occupying the six equatorial positions of the UO$_2^{2+}$ cation in a tridentate fashion [12]. Identical structure was also confirmed on the solid UO$_2^{2+}$/TMDGA complex isolated from IL medium [11]. Similar cationic species of UO$_2^{2+}$/DGA complex was observed in liquid–liquid extraction of uranium with TODGA in Bumim·Tf$_2$N as well [22]. In an independent study with tetramethyl DGA and tetrabutyl DGA, Shen *et al.* demonstrated the formation of [UO$_2$L$_2$]$^{2+}$ cationic species by distribution ratio measurements in IL medium [23]. Recently, Wei *et al.* also reported the formation of [UO$_2$L$_2$]$^{2+}$ cationic species in their solvent extraction studies with *N,N*-dimethyl-*N',N'*-dioctyl diglycolamide dissolved in Bumim·Tf$_2$N [24]. Boltoeva *et al.* reported a more systematic investigation on the speciation of UO$_2^{2+}$/TODGA extracted complex in pure Bumim·Tf$_2$N, pure DCE (dichloroethane) and in their mixtures [22]. Their studies by UV–Vis spectrophotometry and EAXFS indicated the extraction of [UO$_2$(TODGA)$_2$]$^{2+}$ species from 1 to 5 M HNO$_3$ into the Bumim·Tf$_2$N medium. Their studies also confirmed that the two DGA ligands in the complex occupy the six equatorial positions of the UO$_2^{2+}$ cation in a tridentate fashion, and the nitrate ions are present in the outer sphere of the complex. In light of these reports on the UO$_2^{2+}$/DGA
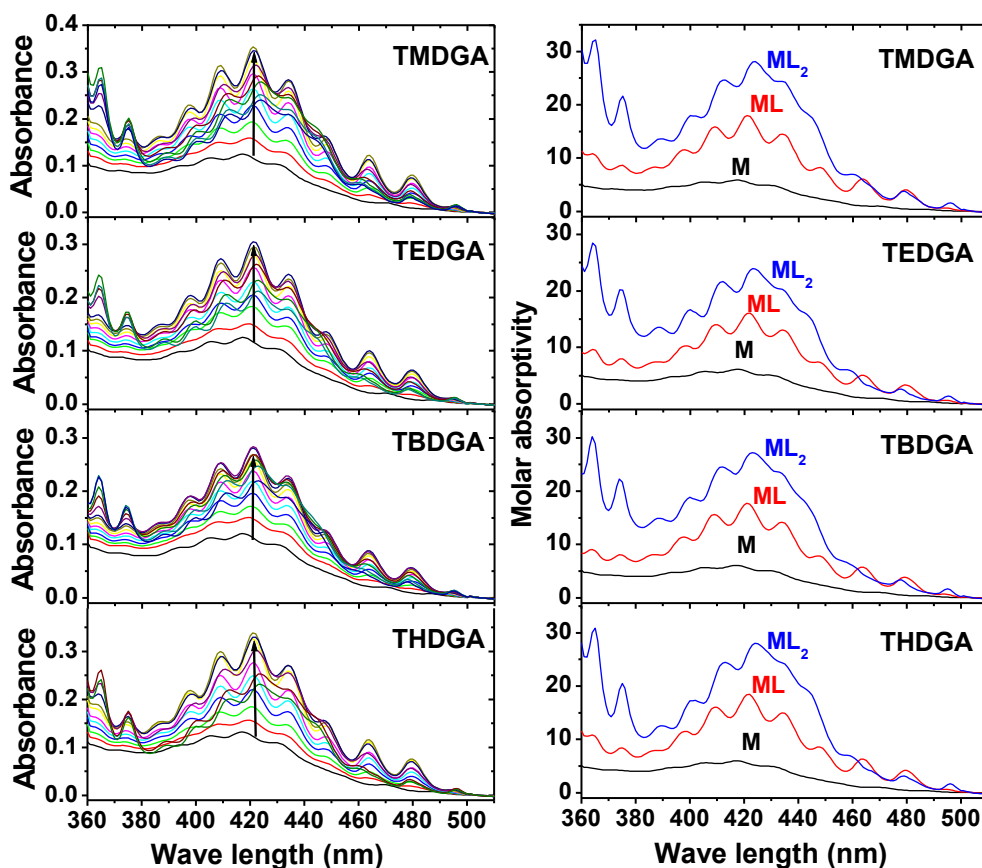

Fig. 1. (a) Molecular structure of TRDGA. TMDGA: R = − CH$_3$, TEDGA: R = − C$_2$H$_5$, TBDGA: R = − C$_4$H$_9$, THDGA: R = − C$_6$H$_{13}$. (b) Structure of the cation, and (c) anion of 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide (Bumim·Tf$_2$N).
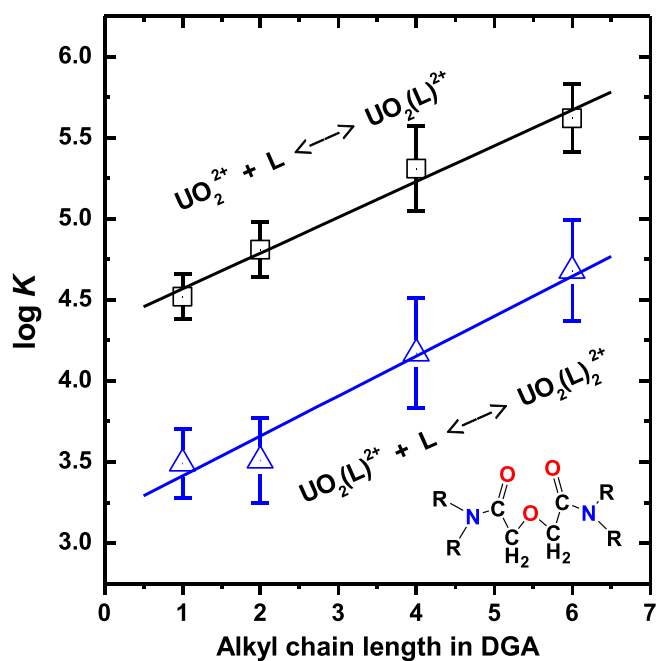
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Fig. 3. Effect of alkyl chain length of DGA ligands on stability constant of their complexes.

other exothermic heat (positive peaks). For TMDGA, the first complex ML was formed with an endothermic complexation enthalpy of 14.3 kJ/mol, while the second ML_2 complex was formed with an exothermic enthalpy of -2.4 kJ/mol (Table 1). This observation is in contrast with the reported complexation enthalpies measured in aqueous medium

where the formation of both complexes is by endothermic complexation reaction. This feature is attributed to different solvation behaviour of the UO_2^{2+} ions and the DGA ligand by the ILs *vis-a-vis* those seen in the aqueous medium [12]. From the calculated enthalpy of reaction ($\Delta_r H$), the value of entropy change during the complexation was calculated based on the following relationship: $\Delta_r G = -RT \ln\beta$, *and* $\Delta_r G = \Delta_r H - T\Delta_r S$, where β is the overall formation constant. From the earlier discussion, it is clear that the UO_2^{2+} ions present in Bumim·Tf$_2$N (which contains about 1 mol/L water) was hydrated, and the complexation proceeded by the replacement of H_2O molecules from the primary co-ordination sphere. In such cases, the complexation shall be driven by the large positive entropy contributions. As evident from Table 1, large positive entropy changes of 135 J/mol/K, and 58 J/mol/K for TMDGA are suggest that the complexation proceeds by the replacement of H_2O molecules from the hydrated $[UO_2(H_2O)_5]^{2+}$ species.

After understanding the complexation thermodynamics between the UO_2^{2+} ions and DGA ligands, it was of interest to gain insight into the structural features of the complex. The solid complex of UO_2^{2+} with the methyl derivative of DGA (TMDGA) has confirmed that the two DGA molecules occupied the equatorial positions of the uranyl cation *via* three donor '*O*' atoms without any water or nitrate ion in the complex [12]. In earlier communication, we reported for the first time the structral features of UO_2^{2+}/TMDGA complex by isolating it as a single crystal from IL medium [11]. The crystal structure data implied an identical nature of the UO_2^{2+}/TMDGA complex irrespective of their complexing media. All the bond lengths and the angles were almost identical, confirming that the nature and the structure of the complex formed in aqueous medium or IL medium are identical. This observation supports the earlier work on the complexation of uranyl ion with dipicolinamide, where it was confirmed that the nature of complex extracted in the IL phase was independent of the type of the anion of the IL phase (e.g., Bumim·Tf$_2$N or Bumim·PF$_6$) [28]. Similarly, UV–Vis and EXAFS studies also confirmed that the nature of UO_2^{2+}/DGA complex extracted
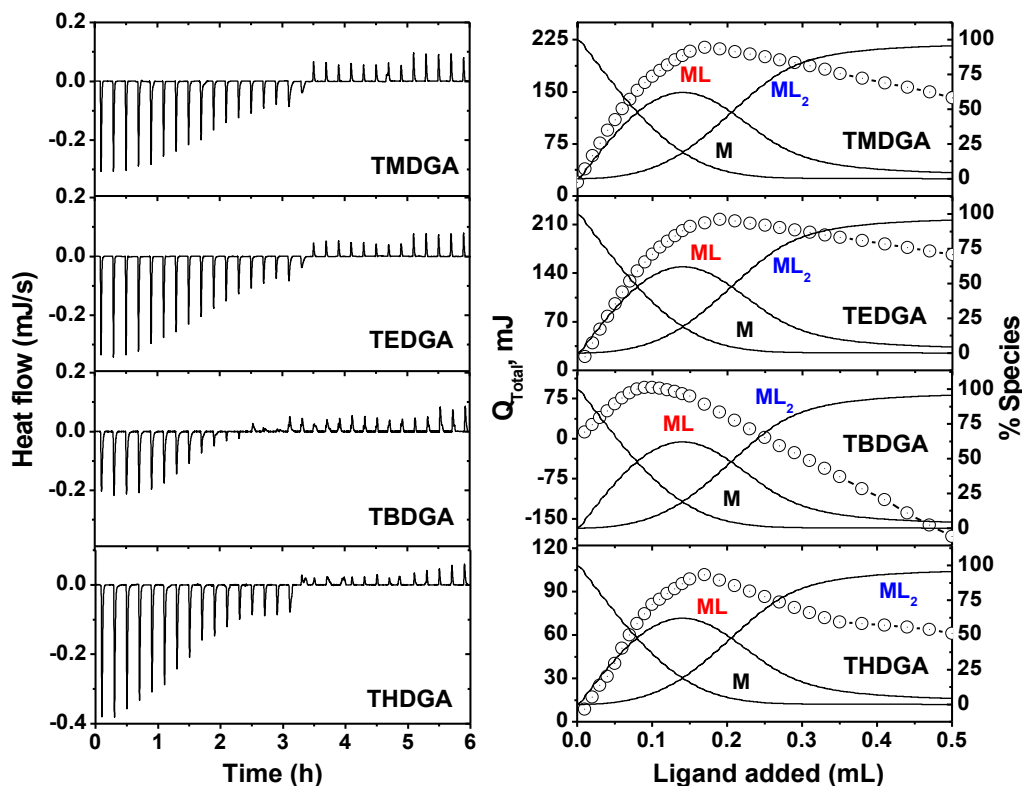

Fig. 4. Calorimetric titration of UO_2^{2+} at 25 °C. Left: titration thermogram that is uncorrected for dilution heat. Right: Accumulated reaction heat and ML speciation (M = UO_2^{2+}, L = DGA) as a function of titrant added. o -experimental; — fit. Initial cup solution: 5.0 mmol/L $UO_2(Tf_2N)_2$ (2.7 mL); Titrant: 100 mmol/L DGA; Medium: Bumim·Tf$_2$N.

in IL phase was independent of the aqueous phase nitrate ion concentration [24]. As observed from the crystallographic data from the IL phase, and from the aqueous perchlorate phase, the overall charge on the UO_2^{2+}/DGA complex is indeed balanced by the anions (NO_3^-, ClO_4^-, Tf_2N^- or PF_6^- anions) present in the outer sphere of the complex. Apart from UO_2^{2+} ion, a detailed structural investigation on the PuO_2^{2+}/TMDGA complex by UV–Vis spectroscopy and crystallography also gave identical structure to those observed for UO_2^{2+}/TMDGA complex [13]. Similar to UO_2^{2+}, it was shown that PuO_2^{2+} also formed a perfect centrosymmetric complex with two TMDGA coordinating in a tridentate fashion with perchlorate anion occupying the outer sphere position. In yest another paper, the authors reported similar centrosymmetric complex with two TMDGA with the penta-valent neptunyl cation (NpO_2^+) [14].

Boltoeva *et al.* also investigated the speciation of UO_2^{2+}/TODGA complex extracted in Bumim·Tf_2N [22]. Their studies by UV–Vis spectroscopy and EAXFS confirmed the extraction of $[UO_2(TODGA)_2]^{2+}$ species without any nitrate or Tf_2N^- anions in the complex. A similar study by Yuan *et al.* also confirmed that the structural features of uranyl complex with substituted dipicolinamide remains identical when the complex is either in solution phase (Bumim·Tf_2N) or crystallized in molecular solvents (methanol or acetone) after isolation from IL phase [28].

4. Conclusions

In this work, we report the complexation thermodynamics of uranyl-diglycolamide complex in ionic liquid medium. Optical absorption spectroscopy investigation confirmed the formation of two successive complexes, $[UO_2L]^{2+}$ and $[UO_2L_2]^{2+}$ where L = TRDGA. The stability constant of UO_2^{2+}/TRDGA complex increased linearly with increasing the alkyl chain length of DGA from methyl to the n-hexyl group. The UO_2^{2+}/DGA complexation was driven by exothermic enthalpy changes and large positive entropy changes. The structural feature indicated the formation of $[UO_2L_2]^{2+}$ type of complex without water or Tf_2N^- anion in the primary coordination sphere of the uranyl cation. Though the DGA ligand formed several orders of magnitude stronger complex with UO_2^{2+} cations in IL medium, the size, nature and structural features of the complex is exactly same to those of analogous complex obtained in the aqueous medium.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.115820.

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