Uranyl Species in 1-Ethyl-3-methylimidazolium Nitrate ([EMI][NO₃]) Solution of $[EMI]_2[UO_2(NO_3)_4]$: First Spectrophotometric Evidence for Existence of $[UO_2(NO_3)_4]^{2-1}$

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In order to examine chemical forms of uranyl species in nitrate-based ionic liquid (IL), we have performed spectrophotometric experiments for [EMI][NO₃] (EMI: 1-ethyl-3-methyl-imidazolium) and CH₃CN solution of [EMI]₂[UO₂(NO₃)₄]. As a result, it was found that in CH₃CN solution uranyl species exist as $[UO_2(NO_3)_3]^-$, that with an increase in $[NO_3]^-$ the $[UO_2(NO_3)_4]^{2-}$ species is formed, and that uranyl species in neat [EMI][NO₃] exist as $[UO_2(NO_3)_4]^{2-}$. This is the first spectrophotometric evidence for formation of $[UO_2(NO_3)_4]^{2-}$ in IL.

For the last decade, ionic liquids (ILs) have widely attracted attention in various industries as an alternative to conventional organic solvents. This is due to their unique properties such as thermal stability, nonflammability, high ionic conductivity, low vapor pressure, wide electrochemical potential windows, and so on.^{1–5} In the nuclear industry, ILs have been also noted as media for radioactive waste treatment and the reprocessing of spent nuclear fuels, i.e., as alternative media to organic solvents for liquid-liquid extraction and to molten salts for pyro-reprocessing.^{6,7} As a part of basic studies on application of ILs to the nuclear industry, the structures of uranyl species in ILs, the dissolution properties of uranium oxides (UO₂ and U₃O₈) into ILs, the extraction behavior of uranyl species from aqueous solutions to IL phases, electrochemical properties of uranyl species in ILs, and properties of actinoid species except for U in ILs have been studied extensively.8-19

In structural studies on uranyl species in ILs, uranyl chloride species have been reported to exist as [UO₂Cl₄]²⁻ in ILs containing a relatively large amount of Cl^{-, 20-24} However, properties of uranyl nitrate species in ILs have not been clarified sufficiently in spite of large amounts of data on uranyl nitrato complexes in aqueous and nonaqueous solutions.²⁵⁻³⁷ Neutral uranyl nitrato complexes, [UO₂(NO₃)₂(L)₂] (L: oxygen donor unidentate ligands), have been known to exist in nonaqueous solvents in a form similar to the typical unanyl nitrato complexes in the solid state.^{31–34,38–40} And also it has been reported that the 1:3 complex, $[UO_2(NO_3)_3]^-$, is formed as a limiting complex in aqueous and nonaqueous solutions containing UO_2^{2+} and NO_3^{-} with the ratio of $[NO_3^-]/[UO_2^{2+}] \ge 3.^{25,34-37}$ As far as we know. only Ryan has reported that the 1:4 complex, $[UO_2(NO_3)_4]^{2-}$, is formed in CH₃NO₂ solution and that the formation constant for $[UO_2(NO_3)_3]^- + NO_3^- = [UO_2(NO_3)_4]^{2-}$ is $4.7 \pm 0.17 M^{-1}$ (M = mol dm⁻³).²⁶ Similarly, the limiting uranyl nitrato complexes in ILs have been reported to be the 1:3 complex, [UO₂(NO₃)₃]^{-.35,41,42} Nockemann et al. have measured UV-vis absorption and magnetic circular dichroism spectra of solutions prepared by dissolving UO₂(NO₃)₂.6H₂O and Bu₄NNO₃ (Bu₄N

tetrabutylammonium, $[NO_3^-]/[UO_2^{2+}] = 4)$ into $[BMI][Tf_2N]$ or [BMP][Tf₂N] (BMI: 1-butyl-3-methylimidazolium, BMP: Nbutyl-N-methylpyrrolidinium, and Tf₂N: bis(trifluoromethylsulfonyl)imide) and proposed the formation of $[UO_2(NO_3)_3]^-$ in both ILs.⁴¹ This proposal was supported by EXAFS study of a [BMI][Tf₂N] solution of UO₂(NO₃)₂·6H₂O and Bu₄NNO₃ $([NO_3^{-}]/[UO_2^{2+}] = 4)$ ³⁵ Furthermore, Billard et al. have also reported that the dominant uranyl species in a [BMI][Tf₂N] solution of UO₂(Tf₂N)₂ and [BMI][NO₃] is [UO₂(NO₃)₃]⁻ under the condition of $[NO_3^{-1}]/[UO_2^{2+1}] > 3$ based on UV-vis absorption spectra.⁴² However, recently Gaillard et al. have shown that the 1:4 complex, $[UO_2(NO_3)_4]^{2-}$, is formed in [BMI][NO₃] solution dissolved UO₂(NO₃)₂.6H₂O or UO₂(Tf₂N)₂ based on EXAFS study and proposed that the equatorial plane of uranyl moiety is coordinated by two bidentate and two unidentate nitrate groups.43 Unfortunately, in their study, the anionic component of IL is different from that (Tf₂N) of uranyl compound, and the aqua complex was used. This results in uncertainty of the interpretation of structures of uranyl species in [BMI][NO₃].

In the present study, in order to prevent such ambiguity, we have studied the structure of uranyl species in $[EMI][NO_3]$ solution of $[EMI]_2[UO_2(NO_3)_4]$ by using spectrophotometry and by comparing the same uranyl compound dissolved in CH₃CN.

[EMI][NO₃] was prepared by mixing [EMI][Br] dissolved in H₂O-CH₃CN (Kanto Chemical Co., Ltd.,) with an aqueous solution containing AgNO₃ (Kanto Chemical) equivalent to [Br⁻] for 12h at room temperature, followed by removal of AgBr by filtration and evaporation of H₂O and CH₃CN using a rotary evaporator. The resulting [EMI][NO₃] was dissolved in the H₂O-CH₃CN mixture and mixed with activated charcoal. After stirring for 1 h, the activated charcoal was filtered off using a membrane filter (ADVANTEC H010A025A). This procedure was repeated three times, followed by removal of solvent (H₂O and CH₃CN) using a rotary evaporator. The synthesis of [EMI]₂[UO₂(NO₃)₄] was carried out by adding AgNO₃ (fourfold concentration of $[UO_2^{2+}]$) to CH₃CN solutions of $[EMI]_2$ -[UO₂Cl₄] synthesized by the literature method,⁴⁴ followed by filtration to remove AgCl and evaporation of CH₃CN. The synthesis of [EMI]₂[UO₂(NO₃)₄] was confirmed by comparing the peak area of -C₂H₅ signal in ¹HNMR spectrum of D₂O solution of [EMI]₂[UO₂(NO₃)₄] at an appropriate concentration to that of a -CH₃ signal of external standard solution (D₂O solution containing CH₃CN). The [DMI]₂[UO₂(NO₃)₄] (DMI: 1,3-dimethylimidazolium) crystals were also prepared using the literature method.⁴⁵ The structure and spectrophotometric data of $[DMI]_2[UO_2(NO_3)_4]^{45}$ were used to examine the chemical form of uranyl species in [EMI][NO₃] dissolved [EMI]₂[UO₂(NO₃)₄].



Figure 1. UV-vis absorption spectra of $[EMI][NO_3]$ solutions dissolved $[EMI]_2[UO_2(NO_3)_4]$ (a) or $UO_2(NO_3)_2 \cdot 6H_2O$ (b). [U(VI)] = 24 mM. Temp.: 50 °C.



Figure 2. Changes in UV–vis absorption spectra with the addition of $[EMI][NO_3]$ (a: 0, b: 0.050, c: 0.10, d: 0.20, e: 0.50, and f: 1.5 M) to an CH₃CN solution of $[EMI]_2[UO_2(NO_3)_4]$ (24 mM). Temp.: 50 °C.

UV-vis absorption spectra of [EMI][NO₃] solution of [EMI]₂[UO₂(NO₃)₄] or UO₂(NO₃)₂·6H₂O ([UO₂²⁺] = 2.4 × 10^{-2} M) were measured at 50 °C using a SHIMADZU UV-3150 spectrophotometer and are shown in Figure 1. These spectra are found to be consistent with each other and show a broad band with a maximum around 430 nm (ε = 43 M⁻¹ cm⁻¹). They are similar to that of [(C₂H₅)₄N]₂[UO₂(NO₃)₄] reported by Ryan (maximum band: 433 nm, ε : 46 M⁻¹ cm⁻¹).²⁶ This suggests that the uranyl species in [EMI][NO₃] exist as [UO₂(NO₃)₄]²⁻.

We also measured the changes of UV–vis absorption spectra with the addition of [EMI][NO₃] (0, 0.050, 0.10, 0.20, 0.50, and 1.5 M) to an CH₃CN solution of [EMI]₂[UO₂(NO₃)₄] ([UO₂²⁺] = 2.4×10^{-2} M) at 50 °C. The results are shown in Figure 2. As seen from this figure, the absorbance increases with the appearance of isosbestic points at 465 and 469 nm, and the absorption spectrum for the system containing low [NO₃⁻] is almost consistent with the typical absorption spectra for



Figure 3. Molar absorption coefficients of $[UO_2(NO_3)_3]^-$ (a) and $[UO_2(NO_3)_4]^{2-}$ (b) obtained by HypSpec analyses.

 $[UO_2(NO_3)_3]^-$ in aqueous, nonaqueous, and IL solutions reported previously.^{25,26,34-36,41} These phenomena are consistent with the absorption spectral changes observed in CH₃NO₂ solutions containing $[(C_2H_5)_4N][UO_2(NO_3)_3]$ (0.0177 M) and $(C_2H_5)_4NNO_3$ (0.000, 0.0972, 0.194, 0.486, and 1.58 M), in which the isosbestic points were observed at 465.5 and 470.0 nm.²⁶ This strongly supports that the uranyl species in CH₃CN solution of $[EMI]_2[UO_2(NO_3)_4]$ exist as $[UO_2(NO_3)_3]^$ and that the $[UO_2(NO_3)_4]^{2-}$ species is formed with increasing $[NO_3^-]$; that is, the following equilibrium reaction exists in this system.

$$[UO_2(NO_3)_3] + NO_3^{-} \stackrel{K}{=} [UO_2(NO_3)_4]^{2-}$$
(1)

The *K* and ε values corresponding to $[UO_2(NO_3)_3]^-$ and $[UO_2(NO_3)_4]^{2-}$ species were determined by means of SQUAD method (software: HypSpec).⁴⁶ The obtained *K* value is $3.85 \pm 0.01 \text{ M}^{-1}$ at 50 °C, which is in fair agreement with the result reported by Ryan, $4.74 \pm 0.17 \text{ M}^{-1}$. Figure 3 shows the obtained absorption spectra of $[UO_2(NO_3)_3]^-$ and $[UO_2(NO_3)_4]^{2-}$ species. The former is consistent with the typical absorption spectrum of $[UO_2(NO_3)_3]^-$ reported in previous studies. The latter is the first data on the absorption spectrum of $[UO_2(NO_3)_4]^{2-}$ in IL.

Furthermore, similar phenomena to the absorption spectral changes shown in Figure 2 were also observed in an CH₃CN solution system of [DMI][NO₃] and [DMI]₂[UO₂(NO₃)₄] as shown in Figure 4. The absorbance is found to increase with the appearance of isosbestic points at 465 and 469 nm. This indicates that the equilibrium reaction shown by eq 1 occurs in this system and suggests that the [UO₂(NO₃)₄]²⁻ species is formed in the neat [DMI][NO₃]. The *K* value for this system was roughly estimated to be 8.8 M^{-1} from a plot of [U][NO₃⁻]/(*Abs* - ε_3 [U]) against [NO₃⁻] based on the following equation,

$$[U][NO_3^-]/(Abs - \varepsilon_3[U])$$

= [NO_3^-]/(\varepsilon_4 - \varepsilon_3) + 1/{K(\varepsilon_4 - \varepsilon_3)} (2)

where *Abs*, ε_3 , ε_4 , and [U] are absorbance at a peak band (467 nm), the molar absorptivity of $[UO_2(NO_3)_3]^-$ and $[UO_2(NO_3)_4]^{2-}$ species at 467 nm, and the concentration of U(VI) (24 mM), respectively.



Figure 4. Changes in UV–vis absorption spectra with the addition of $[DMI][NO_3]$ (a: 0, b: 0.012, and c: 0.063 M) to CH₃CN dissolved $[DMI]_2[UO_2(NO_3)_4]$ (24 mM). Temp.: 50 °C.

The *K* value for the CH₃CN solution of $[DMI]_2[UO_2(NO_3)_4]$ is larger than that of $[EMI]_2[UO_2(NO_3)_4]$. This means that the $[UO_2(NO_3)_4]^{2-}$ species is formed more stably in CH₃CN solution of $[DMI]_2[UO_2(NO_3)_4]$. This is supported by the facts that the $[DMI]_2[UO_2(NO_3)_4]$ complex is deposited as crystals, whereas the $[EMI]_2[UO_2(NO_3)_4]$ complex is not crystallized.

Furthermore, the absorption spectrum in the vicinity of 375 to 410 nm in Figure 4a is different from that in Figure 3a in spite of the existence of the same uranyl species, $[UO_2(NO_3)_3]^-$. This is presumed to be due to effect of the cationic components (EMI and DMI).

From only data on UV–vis absorption spectra, it is difficult to decide the coordination mode of NO_3^{-1} in $[UO_2(NO_3)_4]^{2-1}$ in $[EMI][NO_3]$ or $[DMI][NO_3]$. However, based on the crystal data on $[DMI]_2[UO_2(NO_3)_4]$ that the uranyl equatorial plane is coordinated by two unidentate and two bidentate nitrate groups,⁴⁵ it can be proposed that the $[UO_2(NO_3)_4]^{2-1}$ species in $[EMI][NO_3]$ or $[DMI][NO_3]$ exists as the species with the similar structure to that in $[DMI]_2[UO_2(NO_3)_4]$ crystal. The detailed structural analyses using EXAFS are in progress.

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