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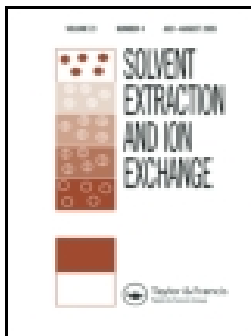
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Extraction of Uranium(VI) from Nitric Acid Solutions Using *N,N*-Dihexyloctanamide in Ionic Liquids: Solvent Extraction and Spectroscopic Studies

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ABSTRACT

Liquid-liquid extraction studies of uranium(VI) were carried out from nitric acid medium using di-*n*-hexyloctanamide (DHOA) in several room-temperature ionic liquids (RTIL). The extraction of the metal ion as a function of nitric acid concentration showed different trends based on the alkyl substituents of the RTIL. While the D_U values decreased with increasing HNO_3 concentration with $[C_4mim][NTf_2]$ and $[C_6mim][NTf_2]$, an opposite trend was seen with $[C_8mim][NTf_2]$. This suggested that while a cation-exchange mechanism is operative with the former diluents, an ion-pair mechanism is prevalent for the latter. The extracted species were found to contain about 3 and 2 molecules of DHOA from the feed solution containing 0.01 M and 4 M HNO_3 , respectively, which was arrived at from the ligand-concentration-variation experiments. Recycling studies were also performed by carrying out stripping and radiolytic stability studies. The nature of the extracted species as ascertained from the UV-visible spectrophotometry studies indicated similarity between the extracts obtained in RTIL medium, which were entirely different from that observed with *n*-dodecane as the diluent.

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#. Deceased

1. INTRODUCTION

Tri-*n*-butyl phosphate (TBP) has been one of the most versatile extractants being used at various stages of the nuclear fuel cycle, the most prominent being in the PUREX (plutonium uranium reduction extraction) process for the reprocessing of spent nuclear fuel.^[1] However, several limitations of TBP such as the generation of large volumes of secondary wastes, significant water solubility, difficulty in stripping due to the degradation products such as MBP (mono-*n*-butyl phosphoric acid) and DBP (di-*n*-butyl phosphoric acid), etc., have made dialkyl amides as possible 'green' alternatives, due to their complete incinerability and innocuous nature of their degradation products, to TBP.^[2,3] Among the dialkyl amides, di-*n*-hexyl octanamide (DHOA, Fig. 1) has been found to be particularly interesting due to its favorable extraction properties vis-à-vis TBP and several recent countercurrent extraction studies underline its potential^[4-6].

The extraction efficiency of organic ligands has been shown to be enhanced manifold when room-temperature ionic liquids (RTILs),^[7-11] which are solvents with negligible vapor pressure, nonflammable properties, and tendency to remain in the liquid phase over a wide range of temperature,^[12-15] have been used as the diluents in place of the conventional diluents such as *n*-dodecane.^[16,17] The extraction of actinide ions such as uranium(VI) has been investigated using TBP in RTILs, and an unusual cation-exchange mechanism has been proposed for the transfer of the actinide ion into the ionic liquid phase with a simultaneous partitioning of the cationic part of the IL, namely $C_n\text{mim}^+$, into the aqueous phase.^[18] There is no report, however, on the extraction behavior of any metal ion, particularly the actinides, with DHOA in RTILs. Yet, it is expected that the mechanism of extraction could be similar to that observed with TBP, lack of literature makes it rather difficult to confirm this, as there have also been reports on the similarity in the extraction behavior of ionic liquids and molecular diluents for the extraction of uranium(VI).^[19] It was, therefore, of interest to investigate the extraction behavior of actinide ions from nitric acid medium using DHOA in RTILs.

The present work deals with the extraction of uranium(VI) from nitric acid feed conditions using DHOA in three commercially available RTILs, viz. $[C_n\text{mim}][\text{NTf}_2]$ ($n = 4, 6,$ and 8). In addition to the effects of equilibration time and feed acidity, the stoichiometry of the complexes, the thermodynamic parameters, and the radiolytic stability are also studied. To our knowledge, this is the first ever report on the extraction of an actinide ion using DHOA in ionic liquids. This paper also gives a comparative account of the extraction of the metal ion with DHOA vis-à-vis TBP. We have also made an attempt to understand the nature of the extracted species by UV-visible spectrophotometric analysis of the uranium(VI) complexes with DHOA in ionic liquids.

2. Experimental

2.1 Reagents

2.1.1. DHOA and room temperature ionic liquids

DHOA was received from Heavy Water Plant, Tuticorin, India and was used after ascertaining the purity by elemental analyzer, IR, NMR, MS, and distribution measurements as described in a previous paper.^[31] *n*-Dodecane (AR grade), procured from Lancaster, UK and the ionic liquids [C_{*n*}mim][NTf₂] (*n* = 4, 6, 8) (>99%) purchased from IoliTech, Germany were used as received. Desired weights of DHOA were dissolved (by simple mixing) in either the ionic liquids or *n*-dodecane to yield 1.1 M solutions.

2.1.2. Radiotracers

Purified ²³³U was used from laboratory stock solution for the extraction experiments. The purification was carried out by an anion-exchange separation method to eliminate the daughter products of ²³²U and was found by α spectrometry to be free from ²²⁸Th and its daughter products.^[20] Natural-uranium stock solution (prepared from uranyl nitrate hexahydrate in nitric acid medium) was used for the UV-visible spectrophotometric studies.

2.2 Instruments

The density and viscosity of the samples were measured simultaneously using a Stabinger Viscometer (Model No. SVM 3000) from Anton Paar, Austria. These measurements were made at different temperatures in the range 298–318K. The relative uncertainty in these measurements was within $\pm 2\%$. All the measurements were carried out at least in triplicate, and the deviation from the mean of the measured values was within $\pm 5\%$. Absorption spectra were recorded by use of a UV-vis spectrophotometer (JASCO V-530). Radioactivity assay (for ²³³U) was obtained on an alpha liquid scintillation counting system (Hydex, Finland) using dioxane-based cocktail (Sisco Research Laboratory, Mumbai).

2.3 Distribution studies

Equal volumes of DHOA solutions in RTILs (or in *n*-dodecane) and aqueous phases were equilibrated at room temperature ($24 \pm 1^\circ\text{C}$) for two hours (except for the kinetics experiments). The two phases were then separated by centrifugation, and equal volumes (usually 100 μL) from both phases were drawn for radioactivity counting. The organic phases were lighter as compared to the aqueous phases in case of *n*-dodecane for all nitric acid concentrations. Conversely, the aqueous phases were lighter when ionic liquids were used as the diluent. The appearance of emulsion in case of ionic liquids at certain aqueous phase acidities was eliminated by centrifugation. The distribution ratio of uranium (D_U) is defined as the ratio of concentration of metal ions (expressed in terms of radioactivity) in the organic phase to that in the aqueous phase. The measurement of radioactivity was carried out by liquid scintillation counting (alpha emitters) and by gamma ray counting as mentioned above. The material balance and reproducibility of the data were within acceptable error limits ($\pm 5\%$). Uranium extraction with the RTILs alone (no

DHOA was added) was found to be negligible at lower acidities (0.01 and 1 M HNO₃). However, 2–3 % U extraction was observed at 4 M HNO₃ using the RTILs alone.

2.4 Irradiation experiments

The radiolytic degradation studies were carried out by exposing the DHOA solutions in the appropriate ionic liquid taken in glass vials using a ⁶⁰Co irradiation source at a dose rate of 1.6 kGy/h.

2.5 NMR determination of aqueous NTf₂⁻ and C_nmim⁺ solubilities

We adapted a published procedure^[21] to determine the concentrations of NTf₂⁻ and C_nmim⁺ ions in the aqueous phase using a 400 MHz NMR spectrometer available at Grenoble University, so the protocol is identical to that described previously.^[22] In such experiments, where deuterated solvents and solutes were used, a phase inversion was observed for $n = 8$ above 5 M DNO₃. The detection limit for both ions is equal to 2 mM and uncertainties are in the range of 10% (cations) and 5% (anions). C_nmim⁺ solubility values were above the detection limit for all ILs investigated and over the whole acidic range, and so were data for NTf₂⁻ in the case of $n = 4$. By contrast, for $n = 6$ and 8, NTf₂⁻ values were below the detection limit for most of the HNO₃ range investigated.

3. Results and Discussion

3.1 Viscosity and density measurements

The extraction kinetics during hydrometallurgical operations is frequently guided by the viscosity and density differences of the organic and the aqueous phases. RTILs are known to have significantly greater viscosities as compared to the molecular diluents like *n*-dodecane and require extended durations for attaining equilibrium distribution ratios. It is well known that the viscosity is a consequence of the self-association of the molecules due to inter-molecular bonding properties because of dipole-dipole interactions. It was, therefore, of interest to compare the densities and viscosities of 1.1 M DHOA solutions in RTILs and in *n*-dodecane.

Table 1 gives the densities and viscosities of all four organic phases, composed of *n*-dodecane or the three investigated ILs, in which 1.1 M DHOA has been dissolved, together with densities and viscosities in the absence of DHOA at 298 K. The table shows that the addition of 1.1 M DHOA increases both the density and the viscosity of *n*-dodecane at 298 K, while it decreases these parameter values for the three IL phases of this work. Table 1 also shows that the density and viscosity values for these four organic phases decrease with increasing temperature (298–318 K). It is worth noting that, at a given temperature, the density values follow the order: [C₄mim][NTf₂] > [C₆mim][NTf₂] > [C₈mim][NTf₂] >> *n*-dodecane. On the other hand, the viscosity values show an opposite trend for RTILs: [C₄mim][NTf₂] < [C₆mim][NTf₂] < [C₈mim][NTf₂]. The viscosity of *n*-dodecane + 1.1 M DHOA at 298 K was only 16 times lower than that observed with [C₄mim][NTf₂] + 1.1 M DHOA, while this factor amounts to ca. 46 in the absence of DHOA. Such variations along the imidazolium series are obviously related to the alkyl chain length. Activation energies for viscous flow of these solvents were determined from

the viscosity measurements at different temperatures in the range of (298–318 K) and using the following empirical equation:^[23]

$$\ln \eta = \ln A + E / RT \quad (1)$$

where η is the viscosity (mPa s), A is a system specific constant, E is the activation energy (kJ mol^{-1}) for viscous flow, R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and T is the absolute temperature (K). The values of E were determined from the slope analysis using Eq. (1) after plotting $\ln \eta$ versus $1/T$.

Table 2 shows marginal increase in the viscosity activation energy with chain length of alkyl group from C_4 to C_8 . The viscosity activation energy for different 1.1 M DHOA solutions followed the order n -dodecane \ll $[\text{C}_4\text{mim}][\text{NTf}_2] < [\text{C}_6\text{mim}][\text{NTf}_2] < [\text{C}_8\text{mim}][\text{NTf}_2]$, and the IL + 1.1 M DHOA phase values are approximately double of the value obtained for 1.1 M DHOA/ n -dodecane system, which is due to the increased self-association in RTIL.

3.2 Solvent extraction studies employing ionic liquids

3.2.1 Extraction kinetics in RTIL

Our viscosity and density measurement studies showed large differences in these values for 1.1 M DHOA solutions in n -dodecane vs those in the RTILs. Extraction kinetics is expected to be significantly influenced by the viscosity and density of the solvent system. It is well known that the mass-transfer rates depend not only on the globule diameter of the dispersed organic phase, but also on the diffusion coefficients (from the surface to the bulk of the globule). As both these factors are dependent on the viscosity of the medium, one would expect slower kinetics in the RTIL. In this context, it was important to evaluate U(VI) extraction kinetics using the dialkylamide in the ionic liquid $[\text{C}_n\text{mim}][\text{NTf}_2]$ media as the solvents. The studies showed that, while 30 min were sufficient for attaining equilibrium in case of $[\text{C}_4\text{mim}][\text{NTf}_2]$, as indicated from the plateau in the D_U values obtained as a function of equilibration time while using 0.01 M HNO_3 as the aqueous phase (**Figure 2**), about 90 and 120 min were needed to obtain equilibrium D_U values for $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$, respectively, suggesting that the viscosity of the ionic liquids plays a role in the metal ion extraction rates, which are lower in the presently studied RTIL based solvent systems as compared to molecular diluents.^[24] Analogous slow attainment of equilibrium is reported in the literature for some ionic liquid based solvent systems used for actinide^[24] or lanthanide^[25] extraction. In all experiments to follow, a contact time of 120 min was used.

3.2.2 Evaluation of DHOA in different ionic liquids for U(VI) extraction

1.1 M solutions of DHOA in $[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$, and $[\text{C}_8\text{mim}][\text{NTf}_2]$ were evaluated for U(VI) extraction from aqueous phases, with acid concentrations in the range of 0.01 M to 8 M HNO_3 . The results are displayed in Fig. 3, together with extraction results for n -dodecane + 1.1 M DHOA. Table 3 lists some D_U values and also includes published data for a

few analogous extraction systems using TBP as the extractant. Comparison of these values shows that DHOA/[C₄mim][NTf₂] is a superior extracting solvent to TBP/[C₄mim][NTf₂] or TBP/[C₅mim][NTf₂] at 0.01 M HNO₃ but is significantly less efficient at 4 M HNO₃. On the other hand, DHOA/[C₆mim][NTf₂] and DHOA/[C₈mim][NTf₂] are poor extracting phases as compared to TBP/[C₄mim][NTf₂] at both 0.01 M HNO₃ and 4 M HNO₃. DHOA/*n*-dodecane is the worst extracting phase at 0.01 M HNO₃ and the best one at 4 M HNO₃.

The results of Giridhar et al.^[16] indicated a significantly higher D_U value (~25) from 4 M HNO₃ using 1.1 M TBP in [C₄mim][PF₆] as compared to the reported D_U values of 9 with 1.1 M TBP in [C₄mim][NTf₂] at 4 M HNO₃ by Billard et al.^[27] and ~8 with 1.2 M TBP in [C₅mim][NTf₂] (at 4 M HNO₃) by Dietz and Stepinski.^[18] In addition to the influence of slight changes in the alkyl chain length on the imidazolium cation (from 4 to 5) and in the TBP concentration (from 1.1 M to 1.2 M) from one experiment to the other, we think that this difference in the D values is mainly due to the change in the IL anion, from PF₆⁻ for the work of Giridhar^[16] to NTf₂⁻ for the other two works.^[17,27] In a separate study, Giridhar et al. reported a D_U value of ca. 6 under identical conditions (i.e., with 1.1 M TBP in [C₄mim][NTf₂] at 4 M HNO₃),^[28] which is close to the values of Billard and Dietz in the same IL (see Table 3). Therefore, depending on the extraction system, both the cation and the anion of the IL can have a significant impact on the D_U values.

Even though [C₄mim][NTf₂] was a better performing extraction medium at lower acidity, all the above-mentioned RTILs were evaluated for uranium extraction in the subsequent experiments to get more insight into the extraction mechanism. Indeed, our data indicate a strong impact of the IL diluent and acidity on the trends. As for the latter parameter, we make a clear distinction between the data obtained at low and high acidities. The value at which the nitric acid concentration changes from “low” to “high” depends on the specific IL (see Fig. 3): 2 M for [C₄mim][NTf₂], 1 M for [C₆mim][NTf₂], and 0.5 M for [C₈mim][NTf₂]. Below 0.5 M HNO₃ (see also Table 3), the D_U values followed the trend [C₄mim][NTf₂] > [C₆mim][NTf₂] > [C₈mim][NTf₂], which is similar to the order of aqueous solubilities of the cations in the ionic liquids.^[29] This behavior is a well-known phenomenon for IL extraction systems regardless of the metal or extracting agent. For example, it has been observed in earlier reports on extraction studies of Eu(III) using CMPO + TBP in [C_{*n*}mim][NTf₂] (*n* = 4, 6, 8)^[30] or Am(III) using tripodal diglycolamide (T-DGA) and TODGA in [C_{*n*}mim][NTf₂] (*n* = 4, 6, 8).^[24] In these two works, however, the decrease in the D values as a function of *n* was observed in the whole range of acidity, from 0.01 M up to 7 M^[24] or from 1 M to 5 M.^[30] These authors have ascribed this behavior to the decreased hydrophilicity of imidazolium cation with increased alkyl chain length of the ionic liquid,^[29] in relation with a cation exchange mechanism, which is an explanation that has been also proposed for the extraction of Sr(II) using crown ethers in [C₅mim][NTf₂]^[31] or Eu(III) using malonamides in [C₄mim][NTf₂].^[32] All D_U values are identical at 1 M HNO₃, which we assume to be merely a coincidence. On the other hand, above 2 M HNO₃, the D_U values followed the trend [C₄mim][NTf₂] < [C₆mim][NTf₂] < [C₈mim][NTf₂], which is exactly

the opposite of the trend seen at lower HNO_3 concentrations. These features are surprisingly different from those seen in case of TBP as the extractant for which the D_U values at higher HNO_3 concentrations are not dependent on the cation nature.^[28] To the best of our knowledge, the impact of the IL's cation nature onto D_U at very high acidic values has not yet been reported. Conversely, focusing on the effect of acid concentration, Figure 3 evidences two types of D_U features. For $[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$, and $[\text{C}_8\text{mim}][\text{NTf}_2]$, it shows a decrease in the D_U values with increased nitric acid concentration up to 2 M, 1 M, and 0.5 M HNO_3 , respectively, beyond which D_U increases, these D_U variations following the classical boomerang shape.^[33] Finally, the D_U values increased with nitric acid concentration in the nonpolar molecular diluent, *n*-dodecane. At this point, we would like to stress that, as all three ILs studied here involve the same anion (NTf_2^-), any possible dependence on the IL anion structure cannot be observed in our work, but this does not mean such dependence does not exist.

3.2.3 Nature of the extracted species

3.2.3.1 Slope analysis method

In a nonpolar diluent, viz. *n*-dodecane, DHOA is reported to form di-solvated extracted species for U(VI) extraction from nitric acid medium.^[24,34] An attempt was made to find out the number of DHOA molecules involved in the extracted species at low (0.01 M HNO_3) as well as at high (4 M HNO_3) acidity for these ionic liquids. To this end, DHOA concentration was varied from 0.05 M to 1.1 M in all the three RTILs, and the results are presented in Figs. 4 and 5. For both the acidities, the slopes were closer to 2, indicating the extraction of species bearing 1:2 (M:L) species as usually observed in molecular solvents. While in case of 0.01 M HNO_3 , where the possibility of cation-exchange mechanism (vide infra) was high in view of the extraction pattern (Fig. 3), species of the type $\text{UO}_2(\text{NO}_3)_x\text{L}_3^{(2-x)+}$ (where $x = 0$ or 1) are expected to be extracted, the species of the type $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$ is proposed for 4 M HNO_3 as the feed, where an ion pair or solvation mechanism may appear to be operative (vide supra). Though the slopes (Fig. 5) are closer to two for $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$, a lower slope is obtained in the case of $[\text{C}_4\text{mim}][\text{NTf}_2]$ as the diluent, which may be attributed to the extraction of a mixture of species with partial contribution of a species like $\text{UO}_2(\text{NO}_3)_2 \cdot \text{L}$.

3.2.3.2 UV-VIS spectrophotometric studies on U(VI) extraction

UV-visible spectroscopy of the loaded organic phase samples was used to compare the signatures of the extracted species of U(VI) by DHOA in RTILs as well as in *n*-dodecane as the diluents, at low and high HNO_3 values (0.01 M and 4 M, respectively). However, the extracts obtained in $[\text{C}_8\text{mim}][\text{NTf}_2]$ and *n*-dodecane while using 0.01 M HNO_3 as the aqueous phase were not studied due to relatively inefficient extraction of the metal ion. The data show that the uranyl cation complexed by DHOA is extracted into the two ionic liquid media, viz. $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{NTf}_2]$ in a similar fashion when extracts made from 0.01 M HNO_3 were investigated (Fig. 6). Because of the similarity between our data in Fig. 6 and the absorption spectrum of $\text{UO}_2(\text{NTf}_2)_2$ salt dissolved in dry $[\text{C}_4\text{mim}][\text{NTf}_2]$,^[35] we infer the absence

of nitrate ions in the extracted species (0.01 M HNO₃). However, comparison with our data should be made with caution, because of the use of DHOA and of water-saturated IL in our case, while in a previous study^[35] the IL was dry and did not contain any ligand. The spectral data also suggest similar extracted species as prepared from 4 M HNO₃ feeds (Fig. 7), but the absorption spectra of U(VI) were markedly different from those obtained at 0.01 M HNO₃, which is in line with the change in the D_U vs HNO₃ features. The introduction of nitrate ions in the first coordination sphere of U(VI) dissolved in [C₄mim][NTf₂], in the absence of any ligand, has been proved to induce striking changes in the UV-vis spectrum of U(VI), with the appearance of bands at 425, 438, 453, 467, and 486 nm.^[36] Again, comparison with our data, obtained for water-saturated ILs and in the presence of DHOA, should be considered with care, for the same reasons as above. Moreover, the number of nitrate ions present in the uranyl coordination sphere is difficult to ascertain by simply considering the shape and peak positions in the UV-vis spectral data. As already shown in other studies both in neat [C₄mim][NTf₂]^[35] and in water,^[37] addition of one, two, or three nitrate ions to the uranyl coordination sphere only induces changes in the relative intensities of the absorption bands without causing any significant shift. However, the absorption spectra obtained in *n*-dodecane look similar. As already discussed above, in *n*-dodecane, the stoichiometry of the extracted species is well-known and corresponds to two nitrate ions. We, thus conclude from Fig. 7 that the extracted complexes in all three ILs at 4 M HNO₃ contain UO₂(NO₃)₂(DHOA)₂ species arising out of a solvation mechanism similar to that seen in case of *n*-dodecane as the diluent. The proposed structure of the extracted complex is shown in Fig. 8, where the nitrate ions are coordinating in a bidentate manner while the two DHOA molecules bond as monodentate ligands.

3.2.4 Proposed extraction mechanism

On the basis of the UV-vis spectrophotometric data, and taking advantage of the previous studies,^[17] we suggest that at low acidities the extraction behavior is explained in terms of the double cation-exchange mechanism as shown in Eq. (2):^[9,10]

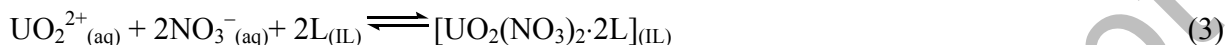


where L = DHOA. Subscripts 'aq' and 'IL' refer to aqueous and ionic liquid phases, respectively.

Equation (2) is in qualitative agreement with the main experimental observations discussed above. First, the extracted species does not contain nitrate ions, as suggested by our UV-vis spectral data. Second, the U(VI) extraction is concomitant with the transfer of the IL cation to the aqueous phase, so D_U would depend on IL cation solubilities, which is experimentally observed. Previous studies have shown that IL cation solubilities are highly dependent on the composition (HNO₃, HCl, HClO₄, etc.) and concentration of the acid used,^[38] and also strongly depend on the nature of the ligand.^[17,39] It was therefore necessary to estimate the C_{*n*}mim⁺ solubilities under the chemical conditions of this study. Our data show (Fig. 9) that

in the presence of 1.1 M DHOA, the IL cation solubility increases in the order $C_4\text{mim}^+ > C_6\text{mim}^+ > C_8\text{mim}^+$ in the entire acidity range (0.1 M–7 M HNO_3). Therefore, an increase in n , the alkyl chain length of the IL cation, induces a decrease in D_U .

We also suggest that at higher nitric acid concentrations, the extraction mechanism switches from cation exchange given by Eq. (2) to ion pair formation (solvation mechanism):



Once again, this extraction model qualitatively agrees with the UV-vis spectral data. However, the increase in D_U with increasing HNO_3 concentrations as given by Eq. (3) cannot explain the D_U dependence on the alkyl chain length (beyond 1 M HNO_3 concentration) in the IL cation as illustrated in Fig. 3. One can suggest that the extraction of the relatively nonpolar complexes $[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}]_{(\text{IL})}$ depends on the dielectric constant (ϵ) of the ionic liquids^[25] and $[\text{C}_8\text{mim}][\text{NTf}_2]$ with an ϵ value of 6.5 D acts as a better extracting medium as compared to $[\text{C}_6\text{mim}][\text{NTf}_2]$ ($\epsilon = 7.0$ D), which in turn is a better medium than $[\text{C}_4\text{mim}][\text{NTf}_2]$ ($\epsilon = 9.4$ D). The mass-action laws corresponding to Eqs. 2 and 3 for $n = 4$, together with mass-balance equations for all species allow to express the distribution ratio, D_U , as a function of controlled chemical parameters, (initial concentrations of acid, uranium, ligand, etc.) and as a function of the (unknown) equilibrium constants of Eqs. 2 and 3. Because the ligand concentration is fixed in these experiments, it is implicitly included in the constants so these are conditional ones. Some additional reasonable assumptions were considered in order to get a tractable expression for D_U as follows: nitrate/U(VI) complexation in the aqueous phase according to published equilibrium values, negligible DHOA protonation, as already discussed^[22] and polynomial empirical variations of $C_4\text{mim}^+$ as a function of HNO_3 (see solid line in Fig. 9). Then, fitting attempts have been performed by minimizing (least-square adjustment in a dedicated Fortran routine) the difference between the experimental D_U values and the theoretical D_U expression. Fitting results are shown in Fig. 10, and good agreement is supporting the above hypotheses.

3.2.5 Studies on recycling of the solvent system

3.2.5.1 Stripping studies

Usually, U(VI) is stripped from the DHOA extract by lowering the acidity of the aqueous phase to ca. 0.01 M.^[24,34] However, as the forward extraction into the RTIL phase remains efficient even at low acidities, this common approach cannot be used. Aqueous complexing agents have been used by many researchers in analogous studies with good results, and we used this alternative approach.^[40] Stripping studies were carried out using 1 M Na_2CO_3 and 0.05 M EDTA in 1 M guanidine carbonate aqueous solution, and the results are presented in Table 4. In view of differences in the nature of the extracted species, the stripping data involved U(VI) extracts in DHOA (in the three RTILs) from both 0.01 M and 4 M HNO_3 as the raffinate. As shown in the

table, the stripping was efficient with both of the strippant solutions in a single contact for a volume ratio of 1, and quantitative stripping (>99.9%) was possible after 2–3 contacts.

3.2.5.2 Radiolytic degradation studies

Most of the applications of the solvent systems containing DHOA as the extractant involve the recovery of U from radioactive feeds. This implies that there can be significant exposure of the solvent system to radiation and hence, it was imperative to carry out studies on the radiolytic stability of the various RTIL based solvent systems. Allen et al.,^[41] reported poor stability of the RTIL based solvents, while some recent reports indicate reasonably good stability of these solvent systems if properly designed.^[42] The present studies indicated two interesting features. Firstly, the extraction of the metal ion showed marginal increase with the dose when the solvent system did not contain DHOA and the amount of U extracted was insignificant in all the cases. On the other hand, the solvent containing a mixture of DHOA and RTILs showed significant decrease in the D_U values with increasing dose (Table 5). Interestingly, the extent of radiolytic degradation was comparable for $[C_6mim][NTf_2]$ and $[C_8mim][NTf_2]$, while it was lower when $[C_4mim][NTf_2]$ was used as the diluent, and only 13% decrease in the D_U value was seen after exposure to 1 M Gy dose. This suggests that, although $[C_4mim][NTf_2]$ has limitation as a diluent due to its significant aqueous solubility, it may be considered as a better extraction medium in high radiation fields.

4. CONCLUSIONS

The extraction of uranium(VI) from nitric acid feed solutions using DHOA in three RTILs demonstrated a reversal of the extraction trends from $[C_4mim][NTf_2] > [C_6mim][NTf_2] > [C_8mim][NTf_2]$ observed at 0.01 M HNO_3 to $[C_8mim][NTf_2] > [C_6mim][NTf_2] > [C_4mim][NTf_2]$ observed at 4 M HNO_3 . These extraction studies indicate the cation-exchange mechanism for $[C_4mim][NTf_2]$ and $[C_6mim][NTf_2]$ and to a much lesser extent for $[C_8mim][NTf_2]$ at lower HNO_3 concentrations. This mechanism changes to the ion-pair extraction mechanism at higher HNO_3 concentrations. The stoichiometry of the extracted species was found to be $UO_2(DHOA)_2^{2+}$ at 0.01 M HNO_3 , which changed to $UO_2(NO_3)_2 \cdot 2DHOA$ at 4 M HNO_3 . Stripping studies using complexing agents such as carbonate and EDTA showed good recovery of the extracted uranyl ion from the ionic IL phase. The radiolytic stability of these IL based systems was also satisfactory, as only marginal decrease in U extraction was seen after exposure to 1 MGy dose. On the other hand, the radiolytic degradation of DHOA in *n*-dodecane has been more severe,^[43] suggesting IL based solvents can be used for a longer period of time, making such a process, if employed, more sustainable.

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References

1. Swanson, J.L. PUREX Process Flowsheets. In: "Science and Technology of Tributyl Phosphate," Schulz, W.W.; Burger, L.L.; Navratil, J.D.; Bender, K.P., eds.; CRC Press Inc.: Boca Raton, **1984**.
2. Gasparini, G.M.; Grossi, G. Long chain disubstituted aliphatic amides as extracting agents in industrial applications of solvent extraction. *Solvent Extr. Ion Exch.*, **1986**, *4*, 1233.
3. Manchanda, V.K.; Pathak, P.N. Amides and diamides as promising extractants in the back end of the nuclear fuel cycle: An overview. *Sep. Purif. Technol.* **2004**, *35*, 85.
4. Pathak, P.N. *N,N*-Dialkyl amides as extractants for spent fuel reprocessing: An overview. *J. Radioanal. Nucl. Chem.* **2014**, *300*, 7.
5. Kumari, N.; Prabhu, D.R.; Kanekar, A.S.; Pathak, P.N. Validation of solvent extraction scheme for the reprocessing of advanced heavy water reactor spent fuel using *N,N*-dihexyloctanamide as extractant. *Ind. Eng. Chem. Res.*, **2012**, *51*, 14535-14542.
6. Pathak, P.N.; Prabhu, D.R.; Kumari, N.; Kanekar, A.S.; Manchanda, V.K. Evaluation of *N,N*-dihexyloctanamide as an alternative extractant for spent fuel reprocessing: Batch and mixer settler studies. *Desal. Wat. Treat.*, **2012**, *38*, 40-45.
7. Dai, S.; Barnes, C.E.; Ju, Y.H. Solvent extraction of strontium nitrate by crown ether using room-temperature ionic liquids. *J. Chem. Soc., Dalton Trans.*, **1999**, 1201-1202.
8. Visser, A.E.; Rogers, R.D. Room-temperature ionic liquids: New solvents for f-element separations and associated solution chemistry. *J. Solid State Chem.*, **2003**, *171*, 109-113.
9. Sun, X.; Luo, H.; Dai, S. Ionic liquids based extraction: a promising strategy for the advanced nuclear fuel cycle. *Chem. Rev.* **2012**, *112*, 2100-2128.
10. Billard, I. Ionic liquids: new hopes for efficient lanthanide/actinide extraction and separation? In *Handbook on the Physics and Chemistry of Rare Earths*; Elsevier: The Netherlands, **2013**, Vol. 43, Chapter 256, p. 213-273.
11. Mohapatra, P.K. Actinide Ion Extraction Using Room Temperature Ionic Liquids: Opportunities and Challenges for Nuclear Fuel Cycle Applications. *Dalton Trans.* **2017**, *46*, 1730-1747.
12. Freemantle, M. An Introduction to Ionic liquids, RSC Publishing, London, **2010**.
13. Seddon, K.R. Ionic liquids: A taste of the future. *Nat. Mater.*, **2003**, *2*, 363-365.
14. Huddleston, J.G.; Willauer, H.D.; Swatloski, R.P.; Visser, A.E.; Rogers, R.D. Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction. *Chem. Commun.* **1998**, 1765-1766.

15. Binnemans, K. Lanthanides and actinides in ionic liquids. *Chem. Rev.* **2007**, *107*, 2592–2614.
16. Giridhar, P.; Venkatesan, K.A.; Srinivasan, T.G.; Vasudeva Rao, P.R. Extraction of uranium(VI) from nitric acid medium by 1.1 M tri-*n*-butylphosphate in ionic liquid diluent. *J. Radioanal. Nucl. Chem.*, **2005**, *265*, 31–38.
17. Gaillard, C.; M. Boltoeva, M.; Billard, I.; Georg, S.; Mazan, V.; Ouadi, A.; Ternova, D.; Hennig, C. Insights into the Mechanism of Extraction of Uranium (VI) from Nitric Acid Solution into an Ionic Liquid by using Trin-butyl phosphate. *ChemPhysChem*, **2015**, *16*, 2653–2662.
18. Dietz, M.L.; Stepinski, D.C. Anion concentration-dependent partitioning mechanism in the extraction of uranium into roomtemperature ionic liquids. *Talanta*, **2008**, *75*, 598–603.
19. Cocalia, V.A.; Jensen, M.P.; Holbrey, J.D.; Spear, S.K.; Stepinski, D.C.; Rogers, R.D. Identical extraction behavior and coordination of trivalent or hexavalent f-element cations using ionic liquid and molecular solvents. *Dalton Trans.* **2005**, 1966–1971.
20. Rattan, S.S.; Reddy, A.V.R.; Mallapurkar, V.S.; Singh, R.J.; Prakash, S. A method for the simultaneous estimation of ^{228}Th and ^{229}Th . *J. Radioanal. Chem.* **1981**, *67*, 95–98.
21. Mazan, V.; Billard, I.; Papaiconomou, N. Experimental connections between aqueous–aqueous and aqueous–ionic liquid biphasic systems. *RSC Advances* **2014**, *4*, 13371–13384.
22. Ternova, D.; Boltoeva, M.; Cointeaux, L.; Gaillard, C.; Kalchenko, V.; Mazan, V.; Miroshnichenko, S.; Mohapatra, P.K.; Ouadi, A.; Papaiconomou, N.; Petrova, M.; Billard, I. Dramatic changes in the solubilities of ions induced by ligand addition in biphasic system $\text{D}_2\text{O}/\text{DNO}_3//[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$: A phenomenological study. *J. Phys. Chem. B.*, **2016**, *120*, 7502–7510.
23. Fang, S.; Zhao, C.; He, C. H. Density and viscosity of binary mixtures of tri-*n*-butyl phosphate + cyclohexane, + *n*-heptane at $T = (288.15, 303.15, \text{ and } 308.15) \text{ K}$. *J. Chem. Eng. Data*, **2008**, *53*, 2244–2246.
24. Gupta, K.K.; Manchanda, V.K.; Subramanian, M.S.; Singh, R.K. Solvent extraction studies on U(VI), Pu(IV) and fission products using N,N,-dihexyloctanamide. *Solvent Extr. Ion Exch.*, **2000**, *18*, 273–292.
25. Sengupta, A.; Mohapatra, P.K.; Iqbal, M.; Verboom, W.; Huskens, J.; Godbole, S.V. Extraction of Am(III) using novel solvent systems containing a tripodaldiglycolamide ligand in room temperature ionic liquids: a ‘green’ approach for radioactive waste processing. *RSC Advances*, **2012**, *2*, 7492–7500.
26. Sypula, M.; Ouadi, A.; Gaillard, C.; Billard, I. Kinetics of metal extraction in ionic liquids: $\text{Eu}^{3+}/\text{HNO}_3//\text{TODGA}/[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ as a case study. *RSC Advances*, **2013**, *3*, 10736–10744.
27. Billard, I.; Ouadi, A.; Jobin, E.; Champion, J.; Gaillard, C.; Georg, S. Understanding the extraction mechanism in ionic liquids: $\text{UO}_2^{2+}/\text{HNO}_3/\text{TBP}/\text{C}_4\text{-mimTf}_2\text{N}$ as a case study. *Solvent Extr. Ion Exch.*, **2011**, *29*, 577–601.

28. Giridhar, P.; Venkatesan, K.A.; Subramaniam, S.; Srinivasar, T.G.; Vasudeva Rao, P.R. Extraction of uranium (VI) by 1.1 M tri-n-butylphosphate/ionic liquid and the feasibility of recovery by direct electrodeposition from organic phase. *J. Alloys Compounds*, **2008**, *448*, 104–108.
29. Toh, S.L.I.; McFarlane, J.; Tsouris, C.; DePaoli, D.W.; Luo, H.; Dai, S. Room-Temperature ionic liquids in liquid-liquid extraction: Effects of solubility in aqueous solutions on surface properties. *Solvent Extr. Ion Exch.*, **2006**, *24*, 33–56.
30. Rout, A.; Venkatesan, K.A.; Srinivasan, T.G.; Vasudeva Rao, P.R. Room temperature ionic liquid diluent for the extraction of Eu(III) using TRUEX extractants. *J. Radioanal. Nucl. Chem.*, **2011**, *290*, 215–219.
31. Jensen, M.P.; Dzielawa, J.A.; Rickert, P.; Dietz, M.L. EXAFS investigations of the mechanism of facilitated ion transfer into a room-temperature ionic liquid. *J. Am. Chem. Soc.*, **2002**, *124*, 10664–10665.
32. Bonnaffé-Moity, M.; Ouadi, A.; Mazan, V.; Miroshnichenko, S.; Ternova, D.; Georg, S.; Sypula, M.; Gaillard, C.; Billard, I. Comparison of uranyl extraction mechanisms in an ionic liquid by use of malonamide or malonamide-functionalized ionic liquid. *Dalton Trans.*, **2012**, *41*, 7526–7536.
33. Patil, C.B.; Mohapatra, P.K.; Singh, R.R.; Gurba, P.B.; Janardan, P.; Changrani, R.D.; Manchanda, V.K. Transport of uranium from nitric acid solution by non-dispersive solvent extraction using a hollow fibre contactor. *Radiochim. Acta* **2006**, *94*, 331–334.
34. Georg, S.; Billard, I.; Ouadi, A.; Gaillard, C.; Petitjean, L.; Picquet, M.; Solov'ev, V. Determination of successive complexation constants in an ionic liquid: complexation of UO_2^{2+} with NO_3^- in $\text{C}_4\text{mimTf}_2\text{N}$ studied by UV-vis spectroscopy. *J. Phys. Chem. B* **2010**, *114*, 4276–4282.
35. Servaes, K.; Hennig, C.; Billard, I.; Gaillard, C.; Binnemans, K.; Gorller-Walrand, C.; Van Deun, R. Speciation of uranyl nitrate complexes in acetonitrile and in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Eur. J. Inorg. Chem.* **2007**, 5120–5126.
36. Ikeda-Ohno, A.; Hennig, C.; Tsushima, S.; Scheinost, A.C.; Bernhard, G.; Yaita, T. Speciation and structural study of U(IV) and -(VI) in perchloric and nitric acid solutions. *Inorg. Chem.* **2009**, *48*, 7201–7210.
37. Atanassova, M.; Mazan, V.; Billard, I. Modulating the solubilities of ionic liquid components in aqueous-ionic liquid biphasic systems: A Q-NMR investigation. *ChemPhysChem*, **2015**, *16*, 1703–1711.
38. Gaillard, C.; Mazan, V.; Georg, S.; Klimchuk, O.; Sypula, M.; Billard, I.; Schurhammer, R.; Wipff, G. Acid extraction to a hydrophobic ionic liquid: The role of added tributylphosphate investigated by experiments and simulations. *PhysChemChemPhys* **2012**, *14*, 5187–5199.

39. Rickert, P.G.; Stepinski, D.C.; Rausch, D.J.; Bergeron, R.M.; Jakab, S.; Dietz, M.L. Solute-induced dissolution of hydrophobic ionic liquids in water. *Talanta* **2007**, *72*, 315–320.
40. Nakashima, K.; Kubota, F.; Maruyama, T.; Goto, M. Feasibility of Ionic Liquids as Alternative Separation Media for Industrial Solvent Extraction Processes. *Ind. Eng. Chem. Res.* **2005**, *44*, 4368–4372.
41. Allen, D.; Baston, G.; Bradley, A.E.; Gorman, T.; Haile, A.; Hamblett, I.; Hatter, J.E.; Healey, M.J.F.; Hodgson, B.; Lewin, R.; Lovell, K.V.; Newton, B.; Pitner, W.R.; Rooney, D.W.; Sanders, D.; Seddon, K.R.; Simsand, H.E.; Thied, R.C. An investigation of the radiochemical stability of ionic liquids. *Green Chemistry*, **2002**, *4*, 152–158.
42. Shkrob, I.A.; Marin, T.W.; Chemerisov, S.D.; Hatcher, J.; Wishart, J.F. Towards radiation-resistant ionic liquids. Radiation stability of sulfonyl imide anions. *J. Phys. Chem. B* **2012**, *116*, 9043–9055.
43. Parikh, K.J.; Pathak, P.N.; Misra, S.K.; Tripathi, S.C.; Dakshinamoorthy, A.; Manchanda, V.K. Radiolytic Degradation Studies on *N,N*-dihexyloctanamide (DHOA) under PUREX Process Conditions. *Solvent Extr. Ion Exch.*, **2009**, *27*, 244–257.

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Table 1: Density and viscosity measurements of 1.1 M DHOA solutions in RTILs and *n*-dodecane. Literature values for the four diluents in the absence of DHOA at 298 K are given inside parentheses.

Density (g cm^{-3}) measurements at different temperatures (K)			
Diluent	298 K	308 K	318 K
<i>n</i> -dodecane	0.800 ± 0.001 (0.7455)	0.793 ± 0.001	0.786 ± 0.001
[C ₄ mim][NTf ₂]	1.207 ± 0.001 (1.43)	1.201 ± 0.001	1.193 ± 0.001
[C ₆ mim][NTf ₂]	1.165 ± 0.001 (1.37)	1.158 ± 0.001	1.151 ± 0.001
[C ₈ mim][NTf ₂]	1.152 ± 0.001 (1.32)	1.135 ± 0.001	1.128 ± 0.001
Viscosity (mPa s) measurements at different temperatures (K)			
Diluent	298 K	308 K	318 K
<i>n</i> -dodecane	3.167 ± 0.009 (1.34 cP)	2.482 ± 0.009	2.005 ± 0.001
[C ₄ mim][NTf ₂]	51.100 ± 0.011 (61 cP)	33.353 ± 0.010	22.991 ± 0.004
[C ₆ mim][NTf ₂]	60.738 ± 0.062 (68 cP)	38.812 ± 0.015	26.323 ± 0.179
[C ₈ mim][NTf ₂]	71.211 ± 0.008 (104 cP)	44.672 ± 0.112	29.896 ± 0.020

Table 2: Activation energy of 1.1 M DHOA solutions in different ionic liquids and *n*-dodecane

Solvent	E (kJ mol⁻¹)Mean
1.1 M DHOA in [C ₄ mim][NTf ₂]	31.47 (±0.65)
1.1 M DHOA in [C ₆ mim][NTf ₂]	32.95 (±0.74)
1.1 M DHOA in [C ₈ mim][NTf ₂]	34.21 (±0.83)
1.1 M DHOA in <i>n</i> -dodecane	17.39 (±0.35)

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Table 3: Comparative extraction data of U with DHOA and TBP in various RTILs.

Solvent system	[HNO ₃], M	D_U	Ref.
1.1 M DHOA in [C ₄ mim][NTf ₂]	0.01	28.7±2.2	This work
	4	0.72 ± 0.01	This work
1.1 M DHOA in [C ₆ mim][NTf ₂]	0.01	7.82 ± 0.44	This work
	4	2.34 ± 0.03	This work
1.1 M DHOA in [C ₈ mim][NTf ₂]	0.01	1.27 ±0.01	This work
	4	5.23 ±0.10	This work
1.1 M TBP in [C ₄ mim][NTf ₂]	4	9	27
1.2 M TBP in [C ₅ mim][NTf ₂]	4	~8	18
	0.01	~10	
1.1 M TBP in [C ₄ mim][NTf ₂]	4	~6	28
	0.01	~16	
1.1 M TBP in [C ₄ mim][PF ₆]	4	~25	16
	0.01	~0	

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Table 4: Stripping performance of complexing agents for U back-extraction from the ionic liquid extracts containing DHOA. Volume ratio = 1. $T = 25^{\circ}\text{C}$.

Ionic liquid	Feed acidity used for U extraction	Strippant	% U stripping
[C ₄ mim][NTf ₂]	0.01 M	1 M Na ₂ CO ₃	99.1 ± 0.2
		0.05 M EDTA in 1 M GC	98.1 ± 0.8
	4 M	1 M Na ₂ CO ₃	100 ± 0.2
		0.05 M EDTA in 1 M GC	99.5 ± 0.1
[C ₆ mim][NTf ₂]	0.01 M	1 M Na ₂ CO ₃	98.9 ± 0.2
		0.05 M EDTA in 1 M GC	98.8 ± 0.7
	4 M	1 M Na ₂ CO ₃	96.8 ± 2.4
		0.05 M EDTA in 1 M GC	98.1 ± 0.3
[C ₈ mim][NTf ₂]	4 M	1 M Na ₂ CO ₃	98.8 ± 0.3
		0.05 M EDTA in 1 M GC	98.4 ± 0.8

* GC = guanidine carbonate

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Table 5: Distribution ratios using irradiated pure RTILs and 1.1 M DHOA solutions in RTILs; $[\text{HNO}_3] = 4 \text{ M}$; $T = 25^\circ\text{C}$.

Absorbed dose, kGy	Sample	D_U
0	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.02 ± 0.00
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.03 ± 0.00
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	0.03 ± 0.00
	1.1 M DHOA/ $[\text{C}_4\text{mim}][\text{NTf}_2]$	1.45 ± 0.09
	1.1 M DHOA/ $[\text{C}_6\text{mim}][\text{NTf}_2]$	3.72 ± 0.15
	1.1 M DHOA/ $[\text{C}_8\text{mim}][\text{NTf}_2]$	5.32 ± 0.31
650	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.02 ± 0.01
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.04 ± 0.01
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	0.05 ± 0.01
	1.1 M DHOA/ $[\text{C}_4\text{mim}][\text{NTf}_2]$	1.43 ± 0.02
	1.1 M DHOA/ $[\text{C}_6\text{mim}][\text{NTf}_2]$	2.66 ± 0.14
	1.1 M DHOA/ $[\text{C}_8\text{mim}][\text{NTf}_2]$	3.91 ± 0.14
1000	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.04 ± 0.01
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.06 ± 0.01
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	0.08 ± 0.01
	1.1 M DHOA/ $[\text{C}_4\text{mim}][\text{NTf}_2]$	1.21 ± 0.01
	1.1 M DHOA/ $[\text{C}_6\text{mim}][\text{NTf}_2]$	2.42 ± 0.05
	1.1 M DHOA/ $[\text{C}_8\text{mim}][\text{NTf}_2]$	3.58 ± 0.08

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Figure 1: Structural formula of DHOA.

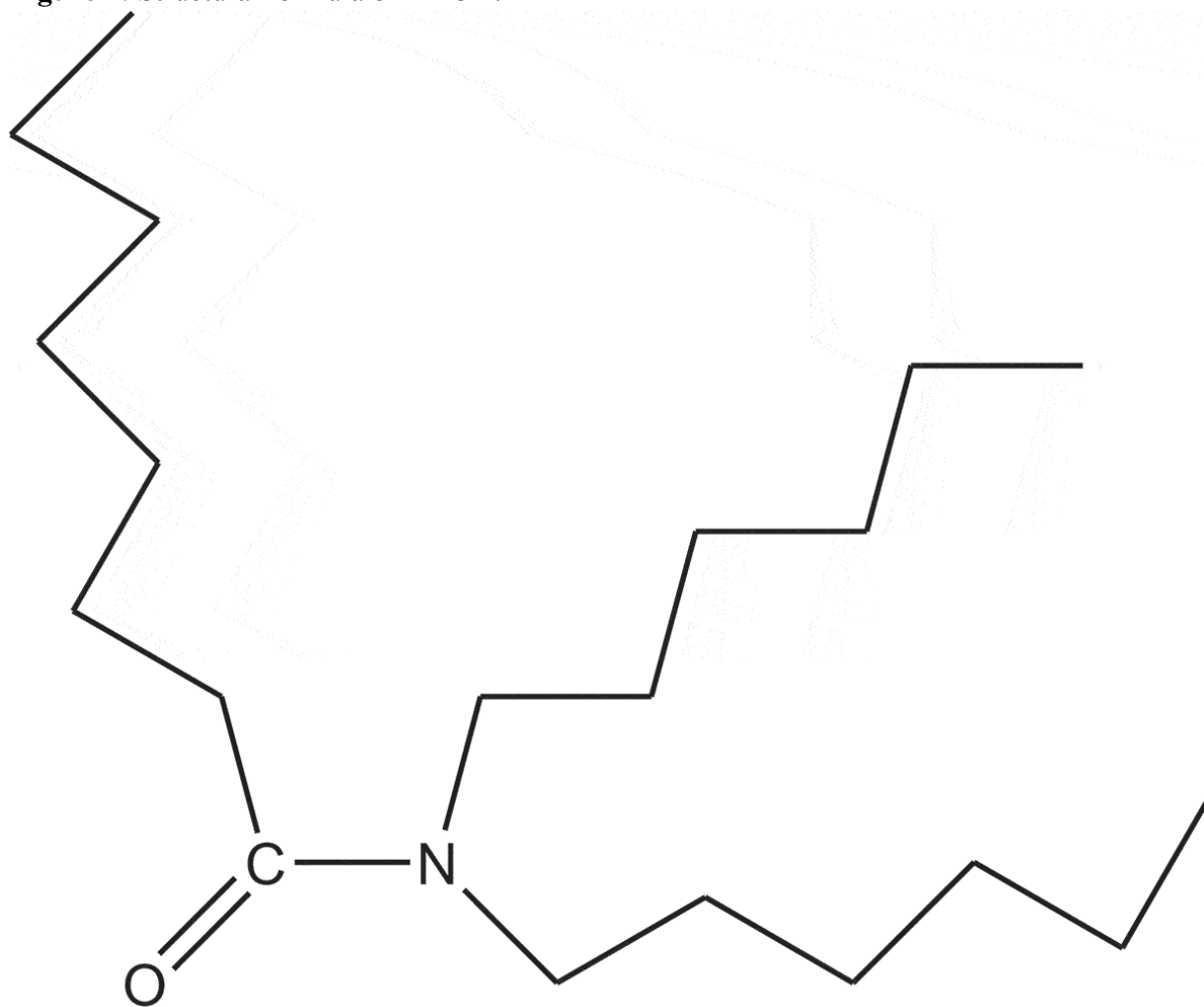


Figure 2: Variation of D_U with time of equilibration in ionic liquid medium. Aqueous phase: 4 M HNO_3 . $T = 25^\circ\text{C}$. $\text{O/A} = 1$.

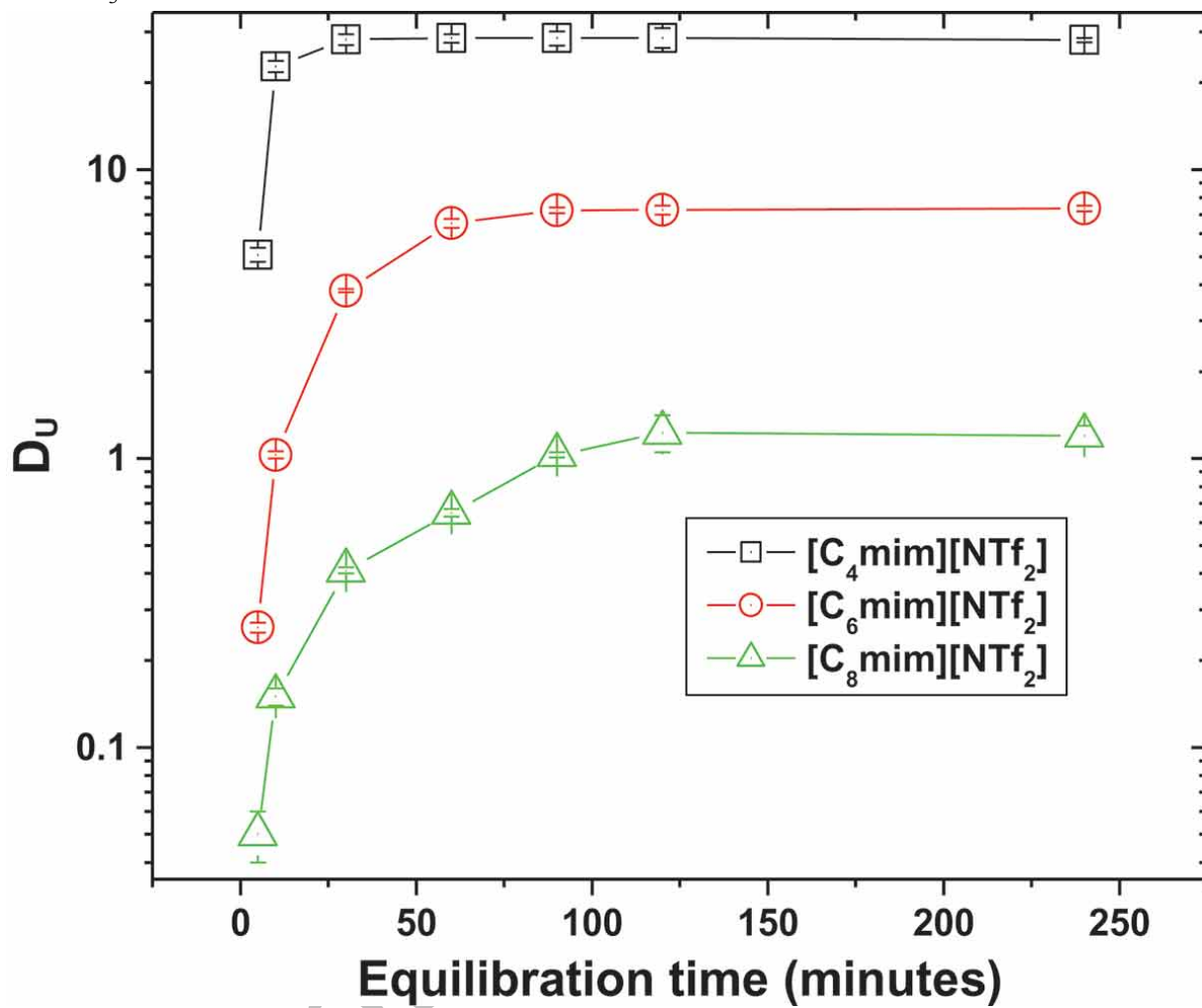
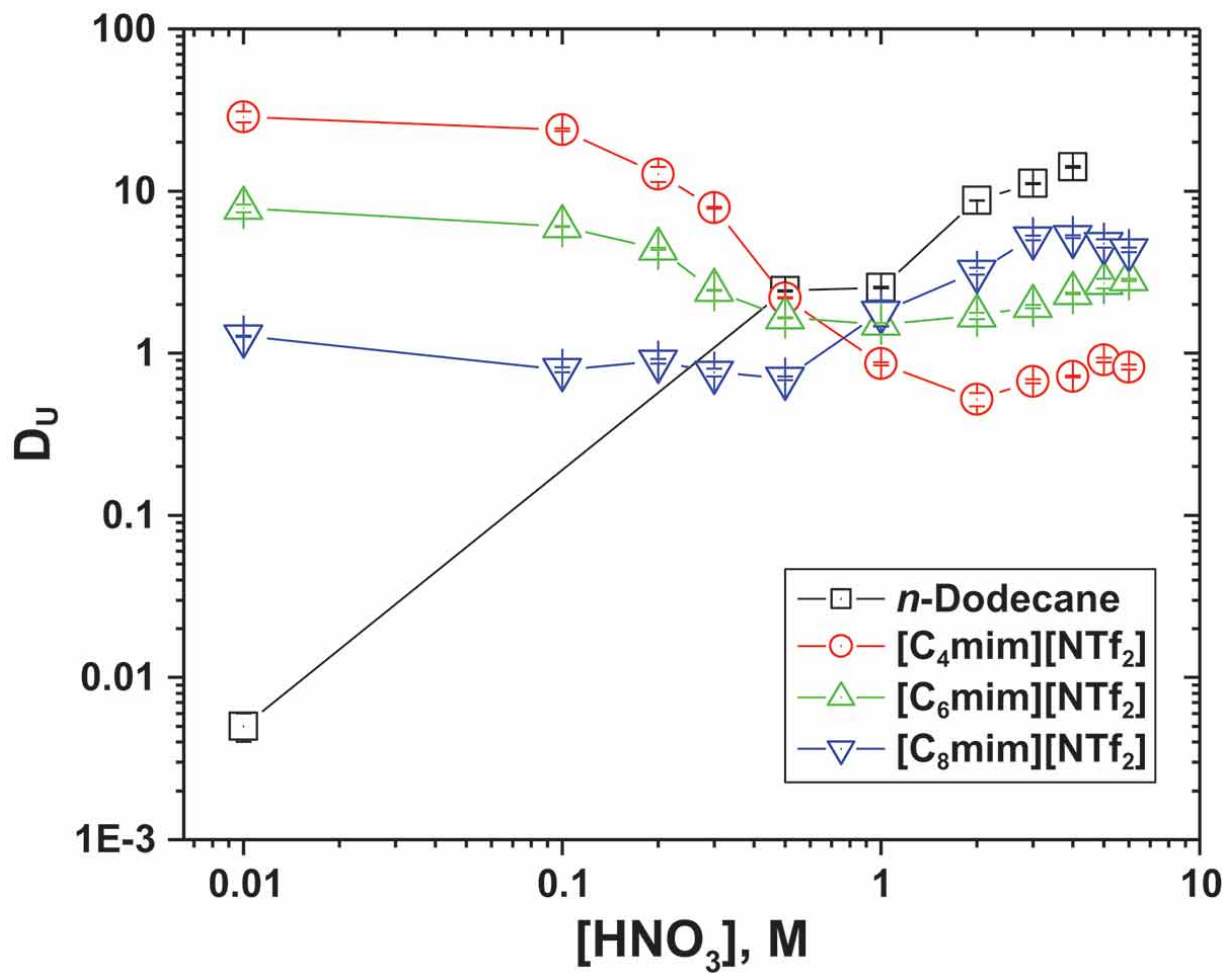


Figure 3: Variation of D_U ($\sim 10^{-5}$ M ^{233}U) with aqueous phase acidity. Organic phase: 1.1 M DHOA in different diluents. O/A = 1. $T = 25^\circ\text{C}$. Equilibration time: 2 h for ionic liquids, 1 h for n -dodecane.



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Figure 4: Variation of D_U with DHOA concentration in RTILs. Aqueous phase: $\sim 10^{-5}$ M ^{233}U in 0.01 M HNO_3 . O/A = 1. Equilibration time: 2 h. $T = 25^\circ\text{C}$.

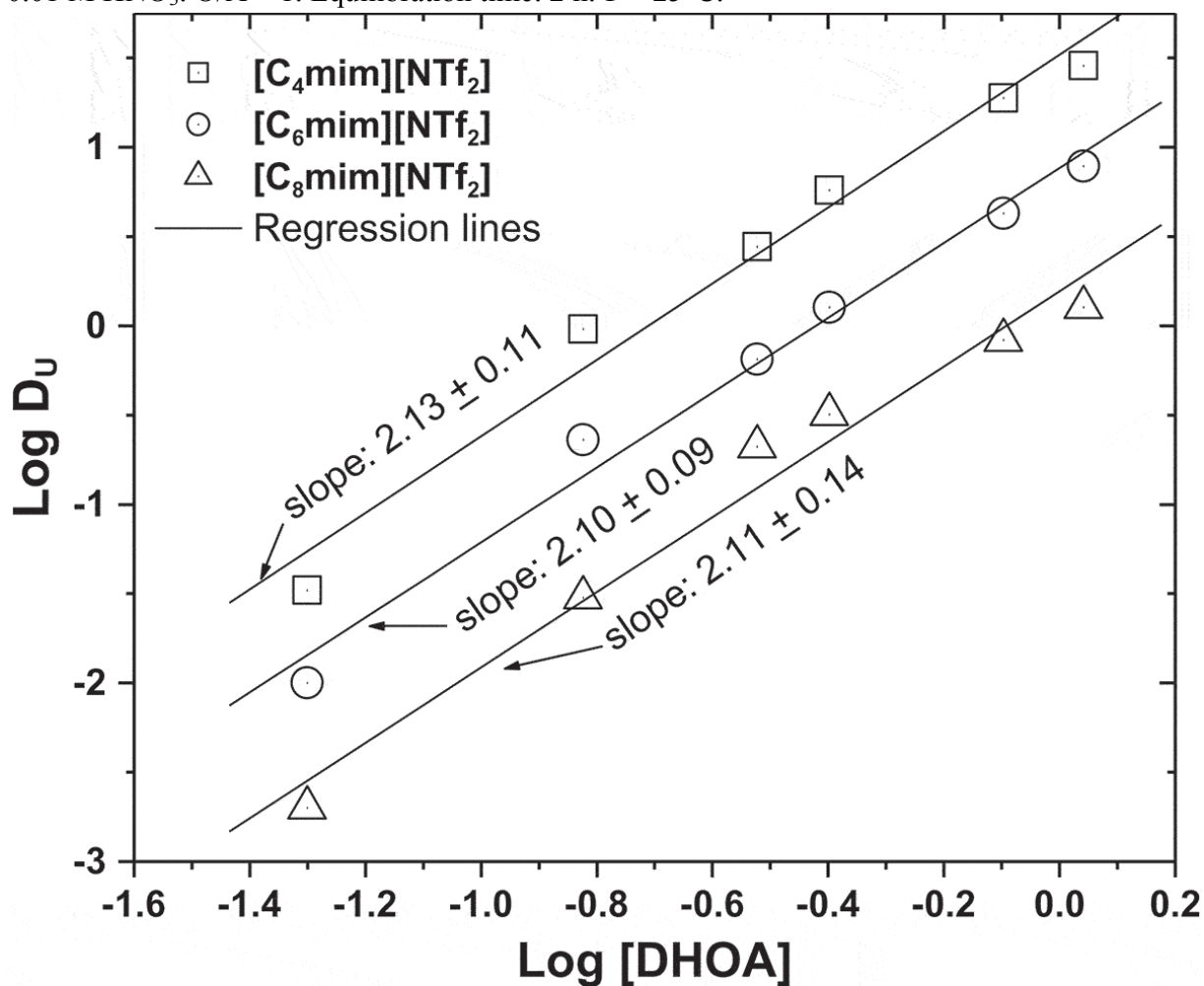


Figure 5: Variation of D_U with DHOA concentration in different diluents. Aqueous phase: $\sim 10^{-5}$ M ^{233}U in 4 M HNO_3 . O/A = 1. Equilibration time: 2 h. $T = 25^\circ\text{C}$.

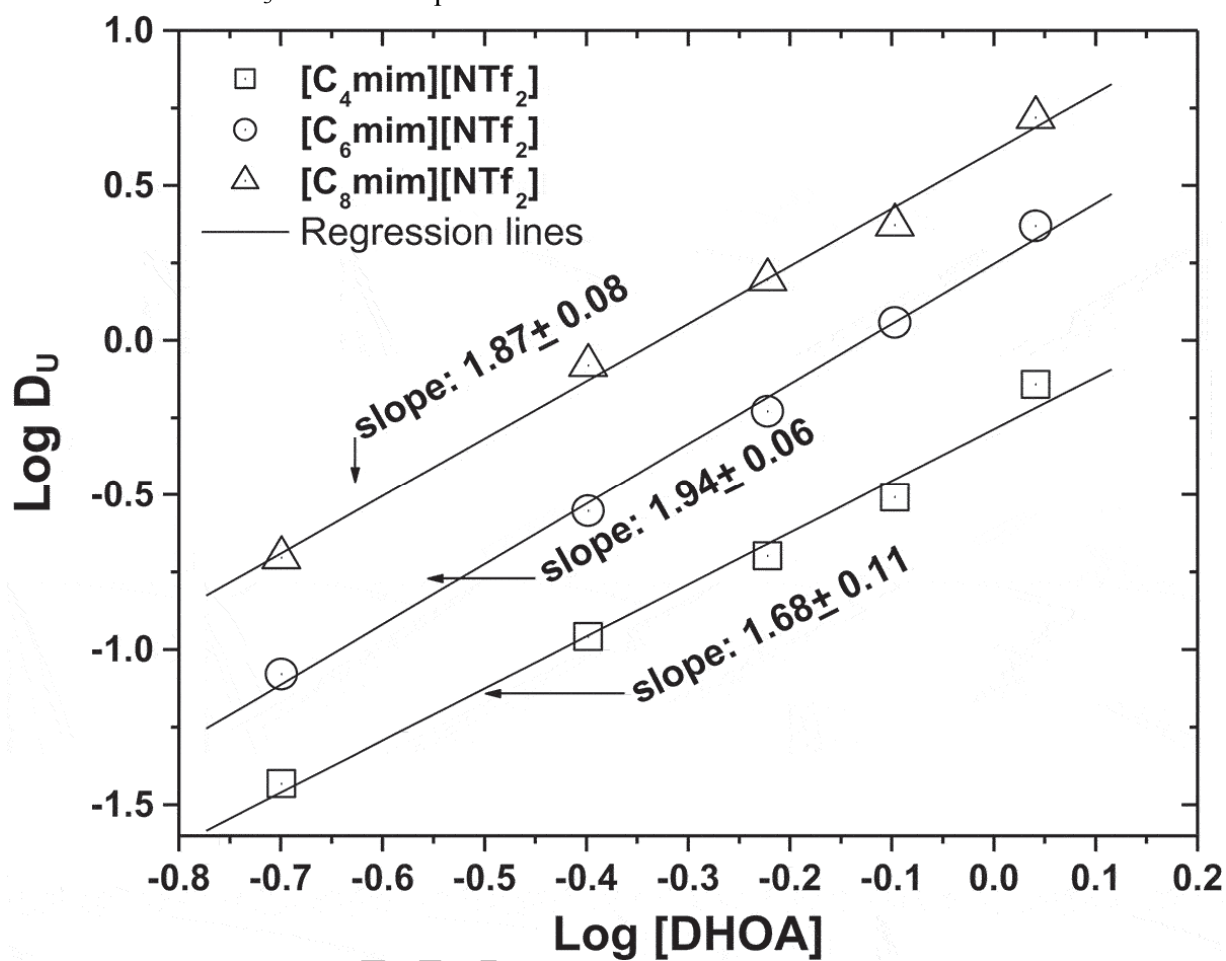
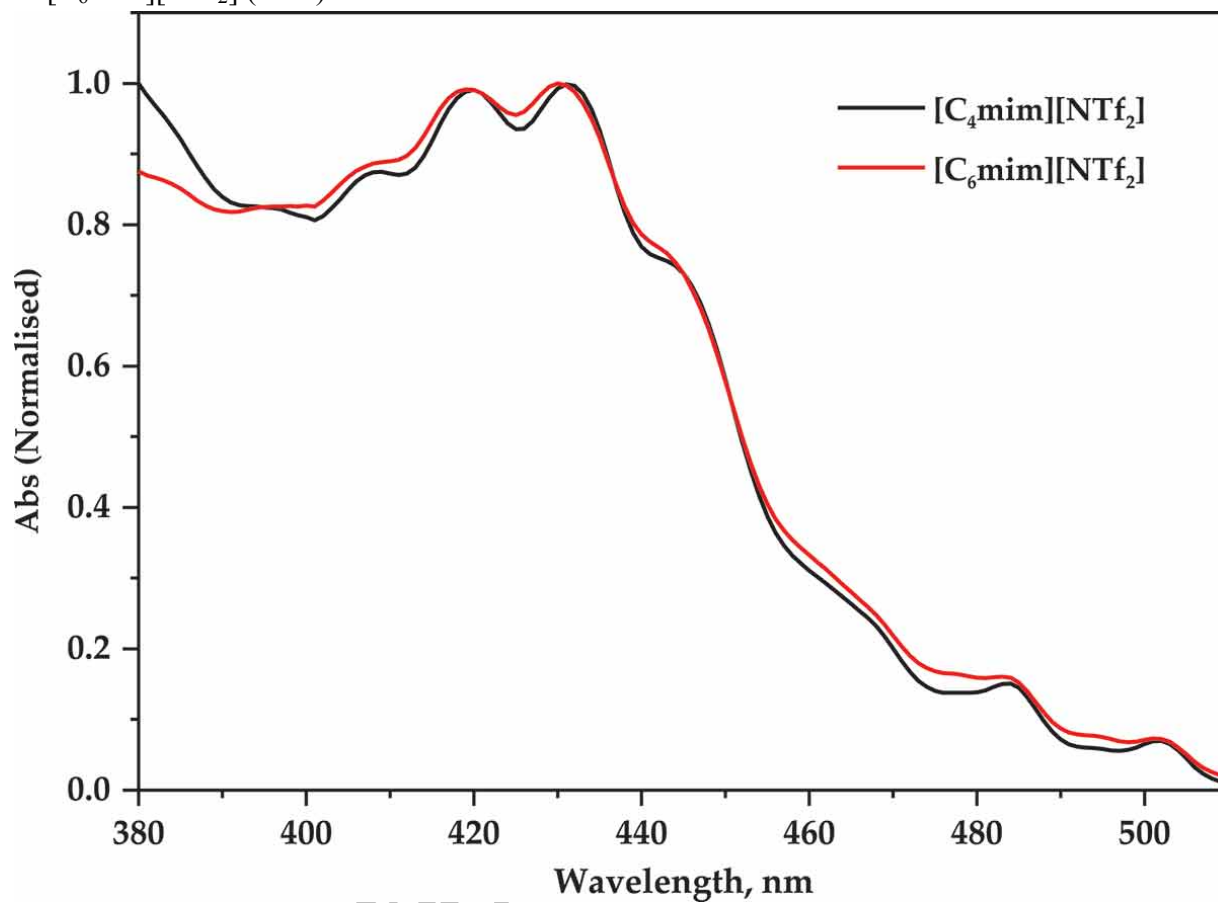
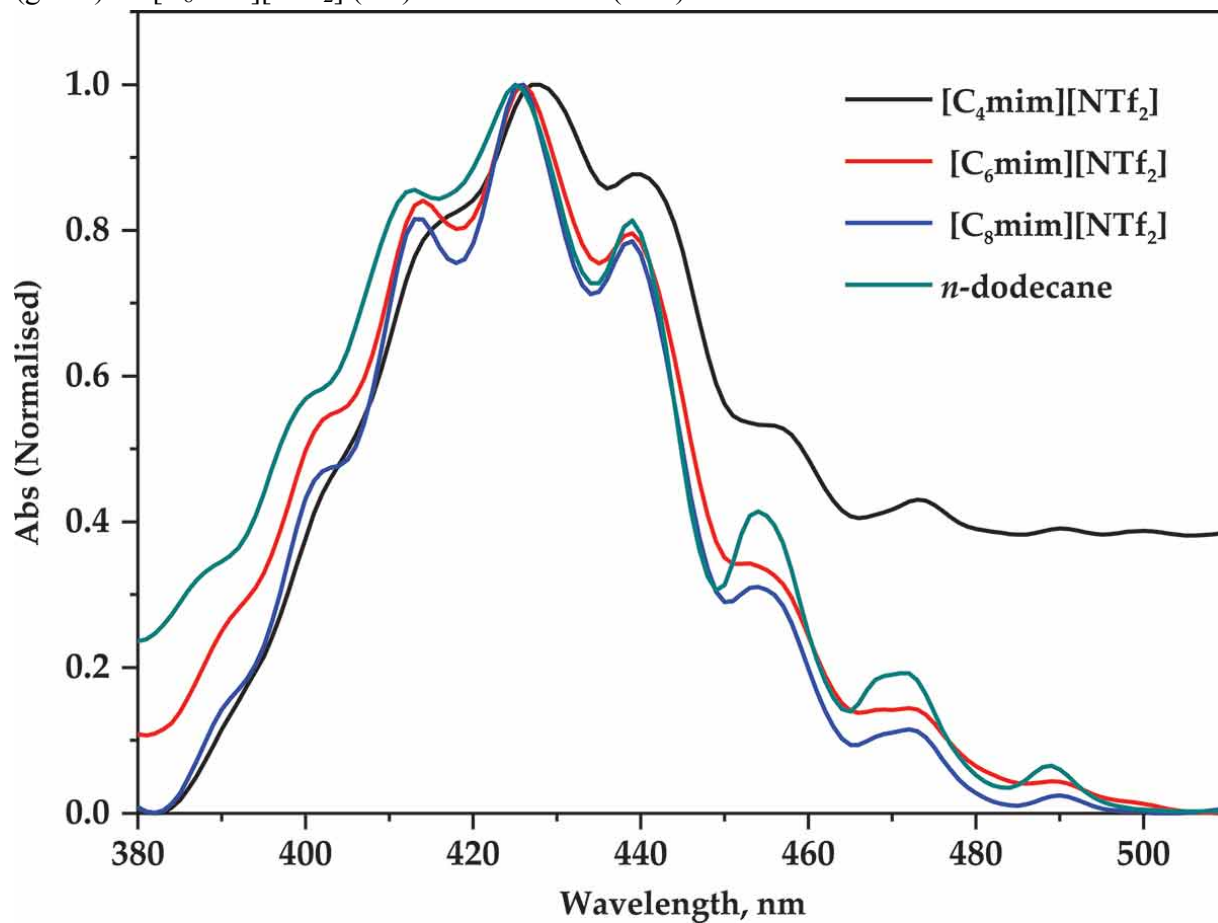


Figure 6: Absorption spectra of U(VI) extracted in 1.1 M DHOA solutions in different RTIL based diluents. Aqueous phase: 8.0×10^{-3} M U(VI) at 0.01 M HNO₃. 1: [C₄mim][NTf₂] (Green). 2: [C₆mim][NTf₂] (Blue).



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Figure 7: Absorption spectra of U(VI) extracted in 1.1 M DHOA solutions in different diluents. Aqueous phase: 8 mM U(VI) at 4 M HNO₃. 1: [C₄mim][NTf₂] (Grey-upper). 2: [C₆mim][NTf₂] (green). 3: [C₈mim][NTf₂] (red). 4: *n*-dodecane (blue).



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Figure 8: Proposed structure of the $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DHOA}$ complex.

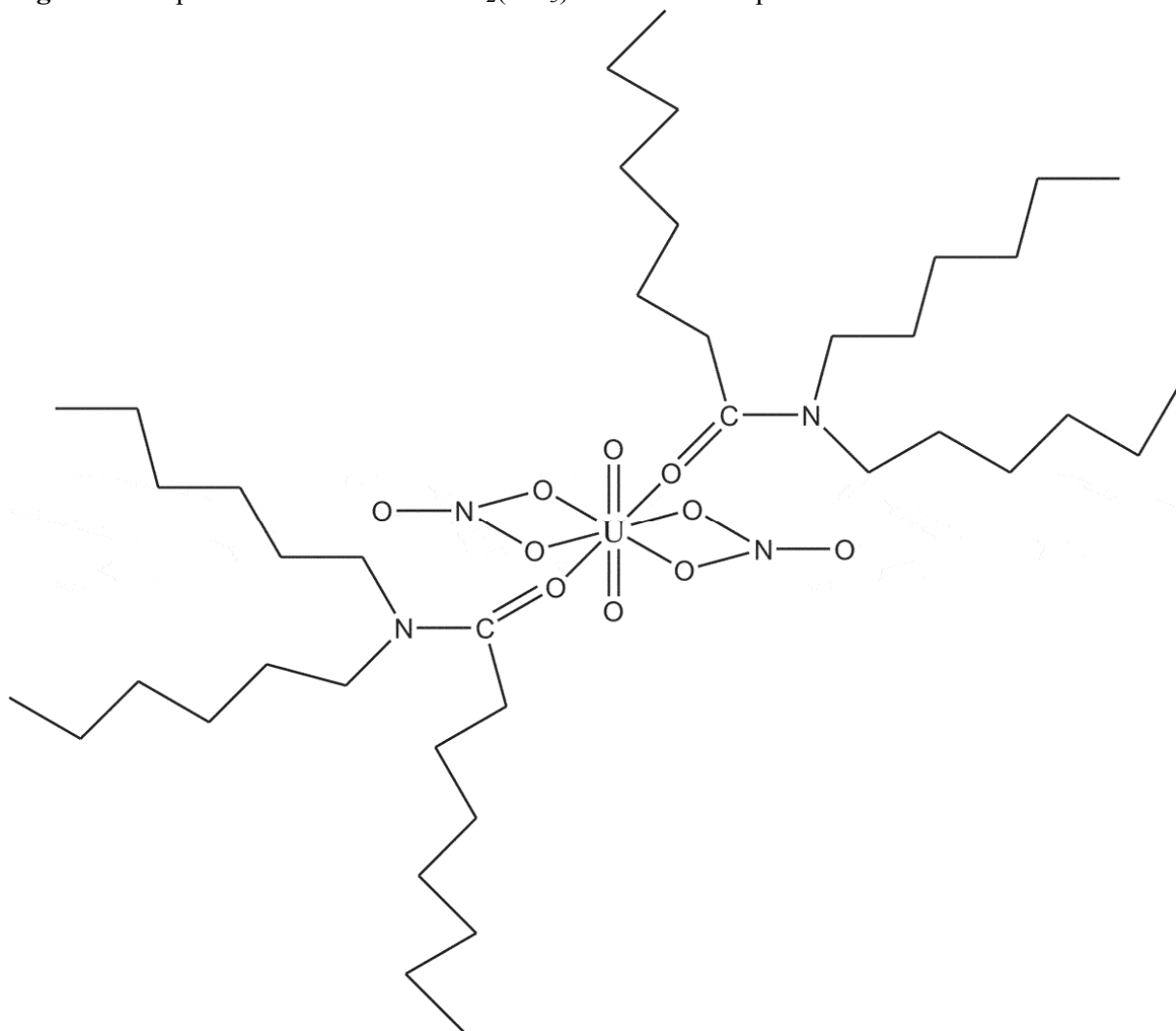


Figure 9: Solubility of the IL cations, $C_n\text{mim}^+$ in the aqueous phase as a function of the nitric acid concentration, in the presence of 1.1 M DHOA. Solid line for $n = 4$ corresponds to the empirical polynomial used to fit the data. ■: $n = 4$. ●: $n = 6$. △: $n = 8$.

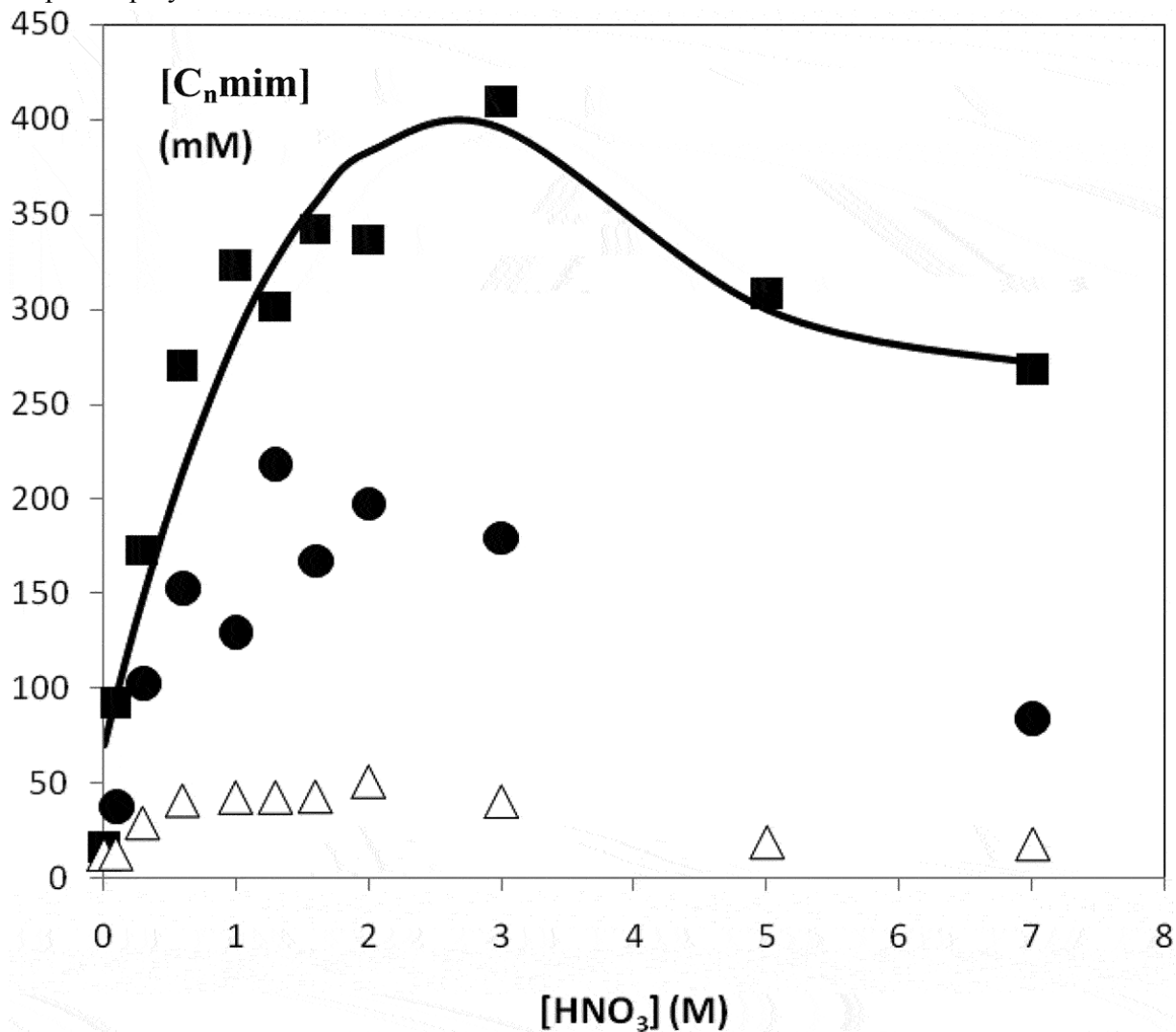


Figure 10: Experimental data for U extraction with $[C_4mim][NTf_2]$ (symbols) and fitted values (solid line).

