

## A novel CMPO-functionalized task specific ionic liquid: synthesis, extraction and spectroscopic investigations of actinide and lanthanide complexes†

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**A novel CMPO (carbamoylmethylphosphine oxide) based task specific ionic liquid (TSIL) with an NTF<sub>2</sub><sup>-</sup> counter anion was synthesized and evaluated for actinide/lanthanide extraction from acidic feed solutions using several room temperature ionic liquids (RTILs). The extraction data were compared with those obtained with CMPO in the same set of RTILs and also in the molecular diluent, *n*-dodecane. The extracted species were analyzed by the conventional slope analysis method and the extraction followed an ion-exchange mechanism. The nature of bonding in the extracted complexes was investigated by various spectroscopic techniques such as FT-IR and UV-visible spectroscopy.**

CMPO (carbamoylmethylphosphine oxide), one of the most widely studied phosphorous-based extractants, is capable of separating the trivalent actinides from acidic nuclear waste.<sup>1</sup> Room temperature ionic liquids (RTILs) have been drawing the attention of separation scientists as alternatives to the commonly used molecular diluents due to their near zero vapour pressure and high solubility of metal complexes.<sup>2</sup> Usually, the ionic liquids (ILs) consist of an organic cation such as quaternary ammonium, 1-alkyl-3-methylimidazolium (C<sub>*n*</sub>mim<sup>+</sup>), or *n*-alkylpyridinium derivatives and an anion such as PF<sub>6</sub><sup>-</sup> (hexafluorophosphate), NTF<sub>2</sub><sup>-</sup> (bis(trifluoromethane)sulfonimide), etc. Several reports have been published in the last few years involving ionic liquid-based separations for nuclear fuel cycle applications.<sup>3</sup> Out of those, quite a few are on actinide extraction, some of which involve CMPO as the extractant. CMPO solutions of ionic liquids have been used for the extraction of uranium,<sup>4</sup> lanthanides,<sup>5</sup> and trivalent actinides such as Am(III).<sup>6</sup> However, due to the ion-exchange mechanism involved with ionic liquids, they are mostly partly dissolved in the aqueous phase,<sup>7</sup> making their process scale application

unattractive. Recently, task specific functionalized ionic liquids (TSILs) have been employed for metal ion extraction which is supposed to alleviate this problem.<sup>8</sup> There are reports on actinide specific TSILs as well, which extract metal ions from a variety of feed conditions.<sup>9</sup> The only report on a CMPO-based TSIL is on the solid phase extraction of actinides such as Pu using a PAN fiber, acrylate resin Amberlit XAD-7R®, hyper-cross-linked polystyrene and multi-walled carbon nanotubes as the support material.<sup>10</sup> However, the use of CMPO-based TSILs for actinide solvent extraction is still unprecedented. The present paper deals with the synthesis and characterization of CMPO-based TSILs **L-I** and **L-II** with PF<sub>6</sub><sup>-</sup> and NTF<sub>2</sub><sup>-</sup> anions, respectively, and the use of their solutions in ionic liquids such as C<sub>*n*</sub>mimPF<sub>6</sub> and C<sub>*n*</sub>mimNTF<sub>2</sub>, respectively, for the extraction of actinide and fission product elements from nitric acidic medium.

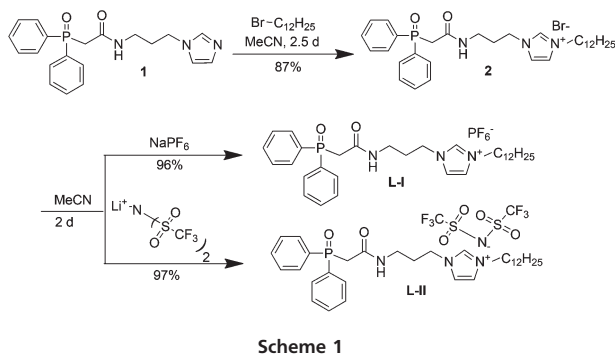
CMPO-imidazole propanamide **1**, synthesized in two steps by reaction of diphenyl phosphite with ethyl bromoacetate and subsequent reaction of the formed product with 3-(1*H*-imidazol-1-yl)propan-1-amine, was reacted with *n*-dodecyl bromide in refluxing acetonitrile to afford ionic liquid **2**.† In the <sup>1</sup>H NMR spectra, the NCHN proton shifted from 7.32 in **1** to 10.00 ppm in **2**. The formation of **2** also followed from the [M]<sup>+</sup> peak at *m/z* 536.3400 in the high resolution electrospray mass spectrum. The bromide counter-anion in **2** was exchanged with either hexafluorophosphate or bis(trifluoromethane)sulfonamide by treating with the corresponding sodium and lithium salts, to give TSILs **L-I** and **L-II**, respectively (Scheme 1). From the <sup>1</sup>H NMR spectra, their formation followed from the shift of the peak at 10.00 ppm in **2** to 8.83 ppm in **L-I** and 8.97 ppm in **L-II**. TSILs **L-I** and **L-II** also showed the corresponding [M + PF<sub>6</sub> + H]<sup>+</sup> and [M + NTF<sub>2</sub> + H]<sup>+</sup> peaks, respectively, in the high resolution electrospray mass spectrum.

Both the CMPO-based TSILs **L-I** and **L-II** were tested for the extraction of Am(III) from 3 M HNO<sub>3</sub>. The *D*<sub>Am</sub> value obtained with 0.1 M **L-II** in C<sub>8</sub>mimNTF<sub>2</sub> was 16 and that with 0.03 M **L-I** in C<sub>8</sub>mimPF<sub>6</sub> was only 0.16. It was not possible to prepare 0.1 M solutions of **L-I** in C<sub>8</sub>mimPF<sub>6</sub>. In view of the very low *D*<sub>Am</sub>

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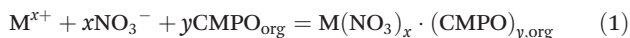
† Electronic supplementary information (ESI) available: Synthesis of **L-I** and **L-II**, Solvent extraction data, etc. See DOI: 10.1039/c3dt32967d



values at low concentrations, it was decided to carry out the rest of the studies with CMPO-TSIL **L-II**, having an  $\text{NTf}_2^-$  counter anion. For comparison,  $\text{Am(III)}$  extractions were also carried out with CMPO in  $C_n\text{mimNTf}_2$  and in *n*-dodecane (Table 1).

Due to the higher viscosity, the time taken for attaining equilibrium with ionic liquid-based diluents is much higher as compared to that required with a molecular diluent such as *n*-dodecane. The results with CMPO-TSIL **L-II** show a relatively slow extraction kinetics following the order  $C_4\text{mimNTf}_2 > C_8\text{mimNTf}_2 > C_6\text{mimNTf}_2$ .<sup>†</sup> The  $D_{\text{Am}}$  values follow the order  $C_4\text{mimNTf}_2 > C_6\text{mimNTf}_2 > C_8\text{mimNTf}_2$ , which is the order of their alkyl chain length. It is in line with literature reports<sup>11</sup> on metal ion extraction on the basis of the cation-exchange extraction mechanism, where the solubility of the cationic part of the ionic liquid decides the metal ion extraction and hence the least hydrophilic  $C_4\text{mimNTf}_2$  results in higher  $\text{Am(III)}$  extraction.

The effect of the aqueous phase acidity on the  $\text{Am(III)}$  and  $\text{U(VI)}$  extraction was investigated to evaluate the possibility of using CMPO-TSIL **L-II** for actinide extraction from acidic feeds similar to those encountered in high level liquid wastes (2–3 M  $\text{HNO}_3$ ). In general, with CMPO in *n*-dodecane as the solvent system (where TBP is used as the phase modifier), the extraction of metal ions involves the following equilibrium reaction:<sup>1</sup>



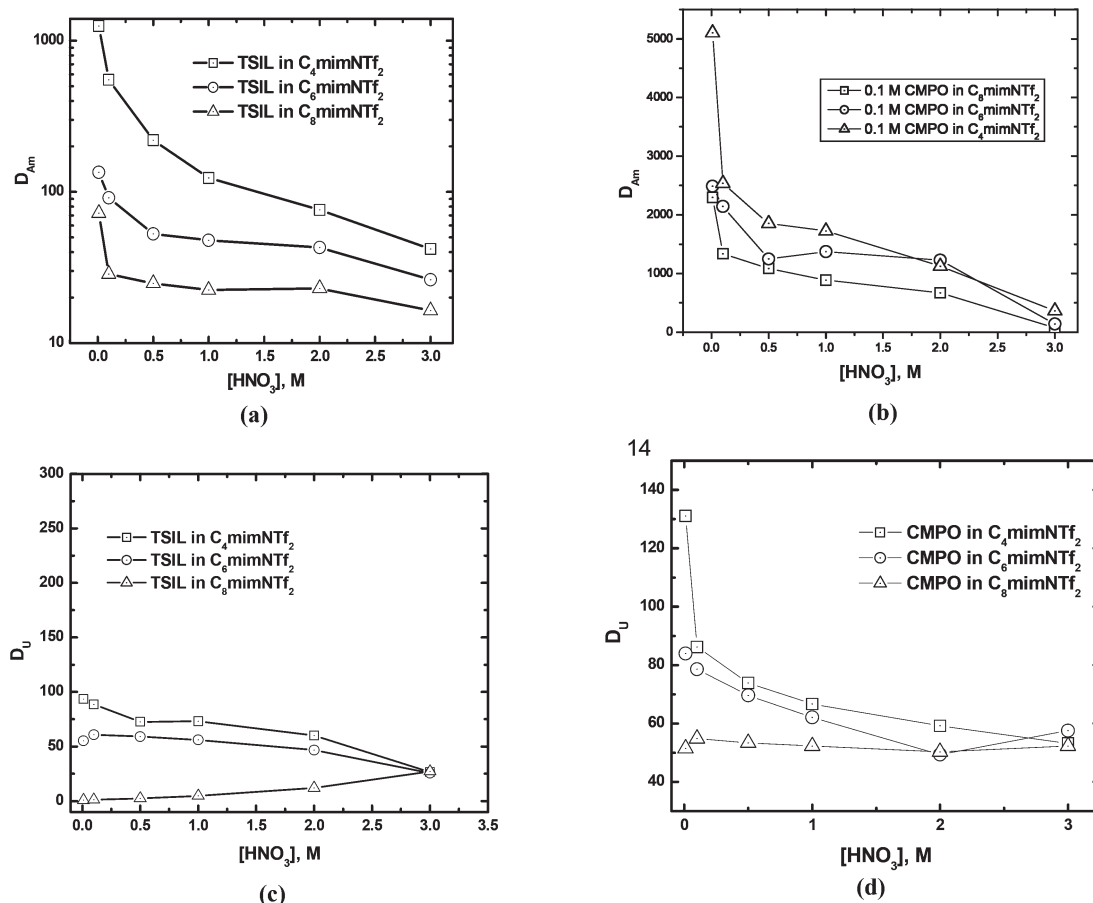
where the species with subscripts 'org' refer to species in the organic phase and those without subscripts refer to those present in the aqueous phase. Usually, the value of *y* is 2 for  $\text{UO}_2^{2+}$  and  $\text{Pu}^{4+}$  and 3 for  $\text{Am}^{3+}$ .<sup>1e</sup> It is clear from eqn (1) that the metal ion extraction should increase with increasing nitric acid concentration. The effect of varying aqueous phase acidity on the metal ion extraction was studied at 0.1 M CMPO-TSIL **L-II** in  $C_n\text{mim}^+\text{NTf}_2^-$  for  $\text{Am(III)}$  and  $\text{U(VI)}$  (Fig. 1). Fig. 1a shows that the distribution ratio of  $\text{Am(III)}$  decreases continuously with increasing acidity of the aqueous phase. With  $C_4\text{mimNTf}_2$  as the diluent, the  $D_{\text{Am(III)}}$  value falls much more rapidly than with  $C_6\text{mimNTf}_2$  and  $C_8\text{mimNTf}_2$ . This has also been reported in the case of  $\text{Eu(III)}$  extraction using CMPO in various ionic liquid systems.<sup>12</sup> This can be attributed not only to the hydrophobicity of the ionic liquids, but also to the decrease in the ability of ionic liquids to undergo ion exchange with increasing hydrophobicity (dependent on the alkyl chain length).

The distribution behaviour of  $\text{U(VI)}$  followed a slightly different order (Table 1 and Fig. 1). In  $C_4\text{mimNTf}_2$  as the diluent, the  $D_{\text{U(VI)}}$  value showed a continuous decrease with increasing acidity of the aqueous phase for both CMPO-TSIL **L-II** as well as for CMPO. On the other hand, while a continuous decrease in  $D_{\text{U}}$  over the entire acidity range was seen with CMPO-TSIL **L-II** in  $C_6\text{mimNTf}_2$  as the diluent, a decrease with increasing acidity at lower acidity followed by an increase at higher acidity was observed for CMPO in this IL. Furthermore, in the case of  $C_8\text{mimNTf}_2$ , the  $D_{\text{U(VI)}}$  value increased with increasing nitric acid concentration for CMPO-TSIL **L-II**, which may be due to the involvement of the nitrate ion in the extraction process. On the other hand, near constant  $D_{\text{U}}$  values were obtained with CMPO in  $C_8\text{mimNTf}_2$ . These observations suggest the involvement of an ion-exchange mechanism in the case of the butyl-substituted IL, whereas a solvation type extraction mechanism is possibly operative in the case of the octyl-substituted IL. Apparently, in the hexyl-substituted IL a combination of both mechanism types takes place. The higher  $D_{\text{M}}$  values at lower acidities, as compared to the extraction systems containing *n*-dodecane as the diluent, may be due to the independence of the extracted species from nitrate counter-anions and also the relatively high polarity of the ionic liquids as diluents.<sup>13</sup>

**Table 1** Distribution data of some important actinide and fission product element ions, present in the HLW solution, using various CMPO-based solvent systems from 3 M  $\text{HNO}_3$

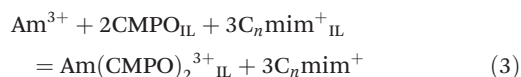
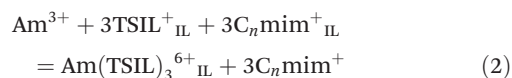
Solvent system <sup>a</sup>	Distribution coefficient					
	$\text{Am}^{3+}$	$\text{Pu}^{4+b}$	$\text{UO}_2^{2+}$	$\text{Eu}^{3+}$	$\text{Cs}^+$	$\text{Sr}^{2+}$
<b>L-II</b> in $C_4\text{mim}^+\text{NTf}_2^-$	41.9 ± 0.9	3550 ± 180	26.5 ± 1.2	30.4 ± 3.7	0.11 ± 0.02	<0.01
<b>L-II</b> in $C_6\text{mim}^+\text{NTf}_2^-$	26.0 ± 0.2	2217 ± 110	25.5 ± 0.9	16.1 ± 0.4	0.03 ± 0.01	<0.01
<b>L-II</b> in $C_8\text{mim}^+\text{NTf}_2^-$	16.6 ± 0.1	852 ± 25	27 ± 0.4	2.19 ± 0.04	0.02 ± 0.01	<0.01
CMPO in $C_4\text{mim}^+\text{NTf}_2^-$	364 ± 5	1381 ± 105	53.2 ± 0.6	172 ± 13	0.09 ± 0.01	<0.01
CMPO in $C_6\text{mim}^+\text{NTf}_2^-$	139 ± 1	2834 ± 350	57.6 ± 0.5	61.7 ± 5.3	0.03 ± 0.01	<0.01
CMPO in $C_8\text{mim}^+\text{NTf}_2^-$	75.9 ± 0.5	2827 ± 210	52.3 ± 1.2	33.7 ± 2.1	<0.01	<0.01
CMPO in <i>n</i> -dodecane	1.30 ± 0.02	7.55 ± 1.40	20.6 ± 2.1	1.05 ± 0.01	<0.01	<0.01

<sup>a</sup> Concentration of the extractant: 0.1 M. <sup>b</sup>  $\text{NaNO}_2$  was used as the holding oxidant.



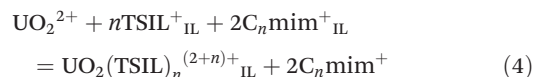
**Fig. 1** Dependence of metal ion extraction on acid concentration. (a) Am-TSIL system; (b) Am-CMPO-IL system; (c) U-TSIL system; (d) U-CMPO-IL system. Am concentration:  $\sim 1 \times 10^{-7}$  M; U concentration:  $\sim 1 \times 10^{-5}$  M.

Ligand concentration variation studies were carried out to determine the stoichiometry of the extracted species (metal-ligand complex) for Am<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> at a fixed aqueous phase acidity of 3 M HNO<sub>3</sub>. For Am<sup>3+</sup> extraction using L-II, a slope of  $\sim 3$  was obtained<sup>†</sup> for all three ionic liquids, suggesting the extraction of trisolvated complexed species. On the other hand, the log-log plots of the same experiments with CMPO gave a slope of  $\sim 2$ ,<sup>†</sup> which indicated the extraction of disolvated species in the organic phase. The two-phase extraction equilibrium for Am<sup>3+</sup> extraction can thus be generalized as

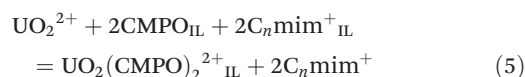


For UO<sub>2</sub><sup>2+</sup>, in all three diluent cases using L-II, there was a variable ligand dependency. While up to 0.025 M ligand concentrations, mixtures of 1 : 1 and 1 : 2 metal-ligand complexes are formed with the 1 : 1 species predominating, at ligand concentrations >0.025 M, predominantly 1 : 3 metal-ligand complexes are formed. The stoichiometry of the UO<sub>2</sub><sup>2+</sup>-CMPO complex was also studied in the different ionic liquids and

indicated di-solvated extracted species. Therefore, the extraction equilibrium can be presented for U extraction as



where  $1 < n < 3$  depending on the TSIL concentration. On the other hand, the two-phase extraction equilibrium for CMPO in the ionic liquids can be represented as



The nature of the extracted species was confirmed by ESI-MS studies.<sup>†</sup>

The distribution ratio of some of the important actinide and fission product ions was also determined. From Table 1 it is clear that for a particular ligand system, the distribution of metal ions follows the order Pu(IV) > U(VI) > Am(III) > Eu(III). However, at lower acidities, the D<sub>Am</sub> values are higher than those of D<sub>U</sub>, which is a unique observation. This can be explained on the basis of the differences in the nature of the extracted species. The higher charge on Pu may be the reason for its higher distribution coefficient over that of U(VI), which

has a charge of  $\sim 3.3$ . Mono- and divalent metal ions were extracted to a much lesser extent. Although Sr(II) was not extracted at all, Cs(I) was extracted to a small extent. As can be noticed from Table 1, with the TRUEX solvent (0.1 M CMPO + 1.2 M TBP in *n*-dodecane), the respective distribution ratio values are quite lower, suggesting the present system to be promising for actinide/lanthanide extraction from high level waste (HLW) feed conditions.

Stripping of the metal ions is an integral part of the evaluation of the novel solvent systems being developed for actinide extraction. EDTA was found to be quite effective for the stripping of  $\text{Am}^{3+}$  (>99% stripping achieved in 3 stages), while  $\text{Na}_2\text{CO}_3$  solution was effective for U.<sup>14†</sup> These results indicate that the CMPO based TSIL system can be used for effective extraction of actinide ions and recycling of the solvent system is possible based on the encouraging stripping data.

UV-visible spectral analysis of U(VI) extracts in CMPO and CMPO-TSIL L-II in  $\text{C}_8\text{mimNTf}_2$  (Fig. 2) shows that the spectra of the extracts are nearly identical suggesting equivalent complexation by both ligands, although a red shift was observed compared to the hydrated uranyl ion indicating strong complexation by CMPO and a nitrate anion. This is rather strange considering the slope analysis data (*vide supra*). Although 1:1:1 species containing U:CMPO: $\text{NO}_3^-$  were reported in different ionic liquid media by Visser *et al.*,<sup>4a</sup> their EXAFS studies were not conclusive about the mode of complexation. However, the absence of the anion component of the ionic liquid in the inner-sphere equatorial plane was suggested. Similar extracted species were found with CMPO in  $\text{C}_8\text{mimNTf}_2$  in the present study as well. However, although species containing 1–3 extractant molecules were observed in the tracer studies in the case of L-II, it appears that the stoichiometry is very similar to that observed with CMPO in the ionic liquid. This is possible due to the lower ligand to metal concentration ratio prevailing in the extracts prepared for the spectroscopic measurements. Inner-sphere coordination to the uranyl ion was also evident from the FT-IR spectra.<sup>†</sup> The C=O

and P=O stretching frequencies of CMPO are expected at 1600 and 1150  $\text{cm}^{-1}$ , respectively,<sup>15</sup> while that of the P=O of TBP at 1275  $\text{cm}^{-1}$  and the O=U=O stretching frequency in the range 925–950  $\text{cm}^{-1}$ .<sup>16</sup> The phosphoryl band for TBP is lowered to  $\sim 1192 \text{ cm}^{-1}$  due to interaction with nitric acid in the blank solvent and is not interacting with the uranyl ion in the ionic liquid extract. On the other hand, a significant change in the carbonyl band and almost no shift in the phosphoryl band of CMPO (around 1140  $\text{cm}^{-1}$ ) points to coordination through the carbonyl oxygen atom. The extraction of U was confirmed by the appearance of a new band at 930  $\text{cm}^{-1}$ . Similarly, U extraction by CMPO-TSIL L-II was also confirmed by the appearance of a new band at 934  $\text{cm}^{-1}$ . Apparently, the C=O band in L-II appearing at 1667  $\text{cm}^{-1}$  shifted to around 1630  $\text{cm}^{-1}$  in the U complex, confirming complexation through the carbonyl oxygen.

In the case of the spectroscopic analysis of Nd(III) extracts (Fig. 3), the peaks with the pure  $\text{Nd}(\text{NO}_3)_3$  solutions appeared at 521, 575 ( $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$  and  $^2\text{G}_{7/2}$  transitions), 741, 795 ( $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$  and  $^4\text{F}_{5/2}$  transitions), and 863 nm. Out of these, the hypersensitive 575 ( $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$  and  $^2\text{G}_{7/2}$  transitions) and 795 ( $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$  and  $^4\text{F}_{5/2}$  transitions) bands are sensitive probes for the metal ion coordination environment. They showed significant red shifts with CMPO and CMPO-TSIL L-II in  $\text{C}_8\text{mimNTf}_2$ .

In conclusion, the CMPO-functionalized TSILs L-I and L-II were synthesized and solvent extraction data with actinides are reported for the first time. The solvent extraction data with these TSILs were lower for  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  as compared to those reported with identical concentrations of CMPO in the same ionic liquids. This is rather surprising in view of the higher ligand dependency observed with CMPO-TSIL as compared to CMPO for  $\text{Am}^{3+}$ . On the other hand, CMPO-TSIL L-II extracted the  $\text{UO}_2^{2+}$  ion to a significantly larger extent than solvents containing CMPO in an IL. Although the trend for  $\text{UO}_2^{2+}$  extraction decreased in the order  $\text{C}_4\text{mimNTf}_2 > \text{C}_6\text{mimNTf}_2 >$

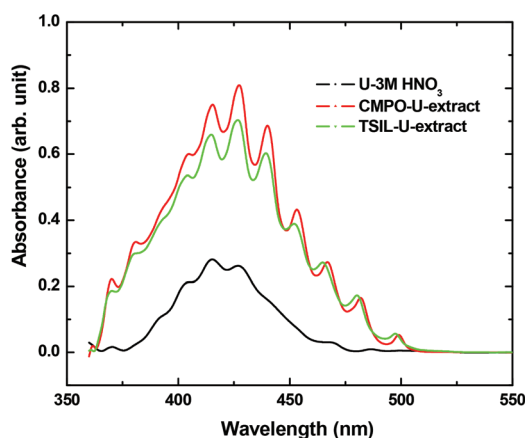


Fig. 2 UV-visible spectra of the U(VI) extracts in CMPO and CMPO-TSIL L-II in  $\text{C}_8\text{mimNTf}_2$  and comparison with the aqueous uranyl nitrate solution. U concentration:  $\sim 0.05 \text{ M}$ .

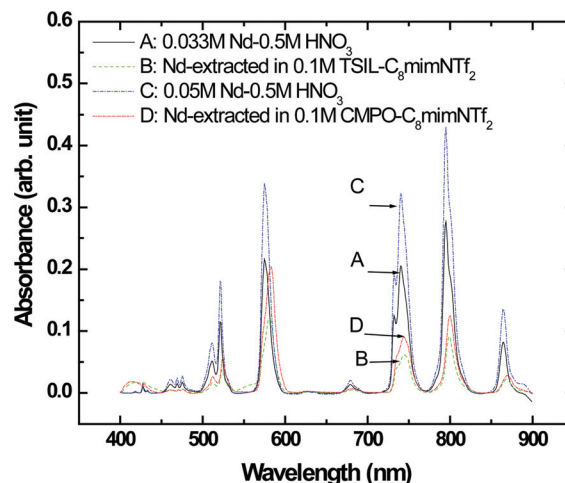


Fig. 3 UV-visible spectra of the Nd(III) extracts in CMPO and CMPO-TSIL L-II in  $\text{C}_8\text{mimNTf}_2$  and comparison with the aqueous uranyl nitrate solution. Nd concentration:  $\sim 0.033 \text{ M}$ .



C<sub>8</sub>mimNTf<sub>2</sub>, a near constant  $D_U$  value was obtained with the three ionic liquids when CMPO was used as the extractant. For Pu<sup>4+</sup> extraction, however, CMPO-TSIL L-II in C<sub>4</sub>mimNTf<sub>2</sub> yielded a higher extraction than CMPO in C<sub>4</sub>mimNTf<sub>2</sub>, while an entirely opposite trend was seen with the other two ILs. Spectroscopic investigations indicated coordination through the carbonyl oxygen atom and possibly formation of inner-sphere complexes for U and Nd.

The present CMPO-TSIL L-II is a pasty semi-solid compound at room temperature and hence required an RTIL as the diluent. It is planned to synthesize TSILs which exist in the liquid form at room temperature making use of a diluent redundant. This may lead to a significantly higher extraction of the metal ion as seen with a diglycolamide-functionalized ionic liquid.<sup>17</sup> Furthermore, this can alleviate the problem of IL solubility in the aqueous phase, making the solvent system robust for actual fuel cycle applications for actinide ion recovery.

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