

# **Studies on neptunium complexation with CMPO and diglycolamide functionalized ionic liquids: Experimental and computational studies**

Arijit Sengupta<sup>a</sup>, Prasanta Kumar Mohapatra<sup>a,\*</sup>, Priyanath Pathak<sup>a</sup>, Tapan Kumar Ghanty<sup>b</sup> and Willem Verboom<sup>c</sup>

*[a] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*

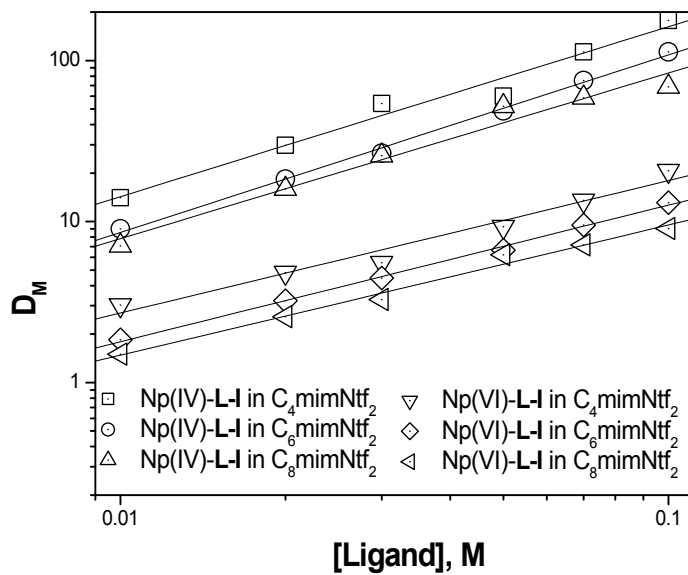
*[b] Theoretical Chemistry Section, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*

*[c] Laboratory of Molecular Nanofabrication, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

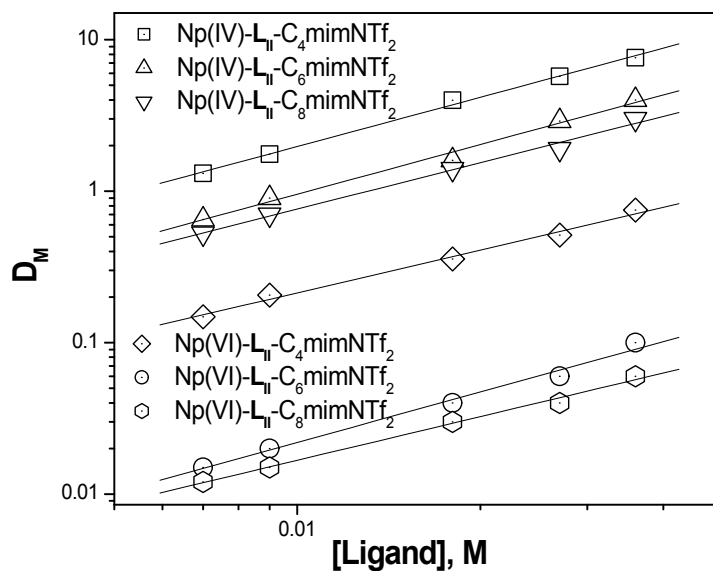
## **ELECTRONIC SUPPLEMENTARY INFORMATION**

## Solvent extraction studies

**Fig. S1** Extraction of Np(IV) and Np(VI) from 3 M HNO<sub>3</sub> with varying concentrations of L<sub>I</sub> (a) and L<sub>II</sub> (b) in ionic liquids, [C<sub>n</sub>mim][NTf<sub>2</sub>] (n = 4, 6, 8). Temp.: 25 °C.



(a)



(b)

## Calculation of extraction equilibrium constants

The two-phase extraction constant ( $K_{\text{ex}}$ ) (given in the main paper) can be expressed as follows:

$$K_{\text{ex}} = \frac{[\text{Np}(\text{TSIL})_n]^{(4+n)_{\text{IL}}} \cdot \{\text{C}_4\text{mim}^+\}_{\text{aq}}^{4+n}}{[\text{Np}^{4+}]_{\text{aq}} \cdot \{\text{TSIL}^+\}_{\text{IL}}^n \cdot \{\text{C}_4\text{mim}^+\}_{\text{IL}}^{4+n}} \quad (1)$$

where the braces indicate activity. As tracer concentrations of Np were used, the activity coefficient can be taken as 1 and concentration terms are used. Substituting  $D_{\text{Np}}$  as the ratio of  $[\text{Np}(\text{TSIL})_n]^{(4+n)_{\text{IL}}}$  to  $[\text{Np}^{4+}]_{\text{aq}}$ , one gets:

$$K_{\text{ex}} = \frac{D_{\text{Np}} \cdot \{\text{C}_4\text{mim}^+\}_{\text{aq}}^{4+n}}{\{\text{TSIL}^+\}_{\text{IL}}^n \cdot \{\text{C}_4\text{mim}^+\}_{\text{IL}}^{4+n}} \quad (2)$$

Rearranging eq. (2) gives:

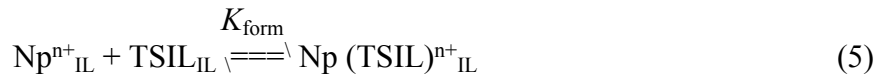
$$K_{\text{ex}} \cdot P_{\text{IL}}^{4+n} = D_{\text{Np}} \cdot \{\text{TSIL}^+\}_{\text{IL}}^n = K'_{\text{ex}} \quad (3)$$

where,  $P_{\text{IL}} = \{\text{C}_4\text{mim}^+\}_{\text{IL}} / \{\text{C}_4\text{mim}^+\}_{\text{aq}}$  and  $K'_{\text{ex}}$  is the conditional extraction constant.

$$\text{Log } D_{\text{Np}} = \text{Log } K'_{\text{ex}} + n \text{Log } [\text{TSIL}]_{\text{IL}} \quad (4)$$

Analogous equations can be obtained for the  $\text{NpO}_2^{2+}$  ion as well.

The complex formation equilibrium in an ionic liquid can be described by the following equations:



where  $\text{Np}^{n+}$  represents either  $\text{Np}^{4+}$  or  $\text{NpO}_2^{2+}$ . The complex formation constant ( $K_{\text{form}}$ ) can be expressed as:

$$K_{\text{form}} = [\text{Np}(\text{TSIL})^{n+}]_{\text{IL}} / ([\text{Np}^{n+}]_{\text{IL}} \cdot [\text{TSIL}]_{\text{IL}}) \quad (6)$$

$$K_{\text{form}} = (K'_{\text{ex}} \cdot [\text{Np}^{n+}]_{\text{aq}}) / [\text{Np}^{n+}]_{\text{IL}} \quad (7)$$

$$K_{\text{form}} = K'_{\text{ex}} / P_{\text{Np}} \quad (8)$$

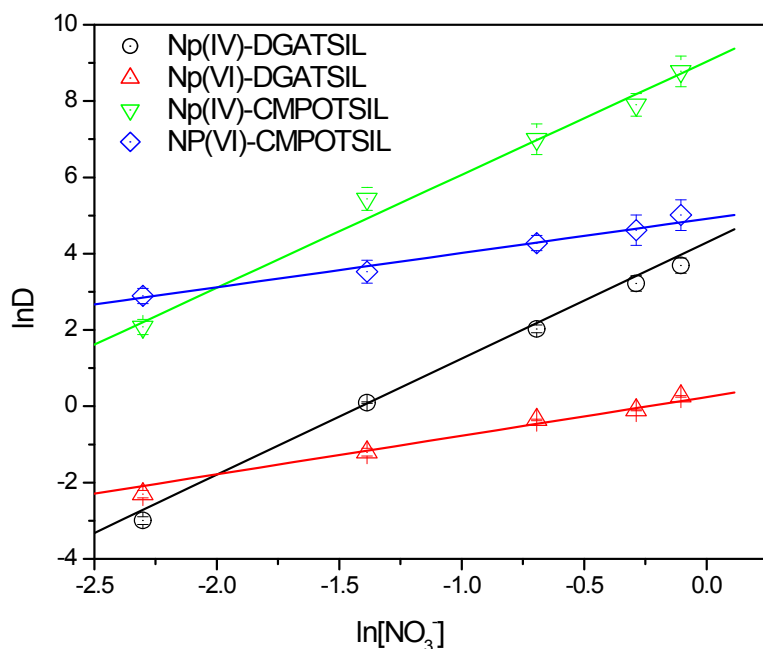
where  $P_{\text{Np}}$  is the partition coefficient of Np in the given oxidation state defined as the ratio of the metal ion concentration in the ionic liquid phase to that in the aqueous phase. They were experimentally determined to be 0.015, 0.015, and 0.014 for  $\text{Np}^{4+}$  and 0.013, 0.012, and 0.011 for  $\text{NpO}_2^{2+}$  in  $[\text{C}_4\text{mim}][\text{NTf}_2]$ ,  $[\text{C}_6\text{mim}][\text{NTf}_2]$ , and  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , respectively, from 3 M  $\text{HNO}_3$ .

**Table S1** Slope and intercept values from the above plots (Figs. S1)

Extraction system	Slope	Intercept
$\text{Np}^{4+}\text{-L}_I - [\text{C}_4\text{mim}][\text{NTf}_2]$	$1.06 \pm 0.09^c$	$3.27 \pm 0.13$
$\text{Np}^{4+}\text{-L}_I - [\text{C}_6\text{mim}][\text{NTf}_2]$	$1.10 \pm 0.03^d$	$3.14 \pm 0.04$
$\text{Np}^{4+}\text{-L}_I - [\text{C}_8\text{mim}][\text{NTf}_2]$	$1.03 \pm 0.08^e$	$2.95 \pm 0.13$
$\text{NpO}_2^{2+}\text{-L}_I - [\text{C}_4\text{mim}][\text{NTf}_2]$	$0.82 \pm 0.07^c$	$2.08 \pm 0.11$
$\text{NpO}_2^{2+}\text{-L}_I - [\text{C}_6\text{mim}][\text{NTf}_2]$	$0.85 \pm 0.02^d$	$1.95 \pm 0.03$
$\text{NpO}_2^{2+}\text{-L}_I - [\text{C}_8\text{mim}][\text{NTf}_2]$	$0.80 \pm 0.05^e$	$1.78 \pm 0.07$
$\text{Np}^{4+}\text{-L}_{II} - [\text{C}_4\text{mim}][\text{NTf}_2]$	$1.08 \pm 0.03$	$2.45 \pm 0.06$
$\text{Np}^{4+}\text{-L}_{II} - [\text{C}_6\text{mim}][\text{NTf}_2]$	$1.09 \pm 0.06$	$2.16 \pm 0.11$
$\text{Np}^{4+}\text{-L}_{II} - [\text{C}_8\text{mim}][\text{NTf}_2]$	$1.02 \pm 0.05$	$1.92 \pm 0.09$
$\text{NpO}_2^{2+}\text{-L}_{II} - [\text{C}_4\text{mim}][\text{NTf}_2]$	$1.00 \pm 0.03^c$	$1.21 \pm 0.08$
$\text{NpO}_2^{2+}\text{-L}_{II} - [\text{C}_6\text{mim}][\text{NTf}_2]$	$1.10 \pm 0.06^d$	$0.554 \pm 0.110$
$\text{NpO}_2^{2+}\text{-L}_{II} - [\text{C}_8\text{mim}][\text{NTf}_2]$	$0.96 \pm 0.04^e$	$0.137 \pm 0.073$

### Nitrate concentration variation

**Fig. S2** Effect of varying concentration of nitrate ion ( $\text{NaNO}_3$ ) on the distribution ratio values of Np(IV) and Np(VI).



**Table S2** Slopes of the nitrate concentration variation studies

metal ion	ligand	slope	error
Np(IV)	DGA-TSIL	3.02	0.07
Np(VI)	DGA-TSIL	1.03	0.02
Np(IV)	CMPO-TSIL	2.96	0.14
Np(VI)	CMPO-TSIL	0.96	0.05

### Determination of thermodynamic parameters

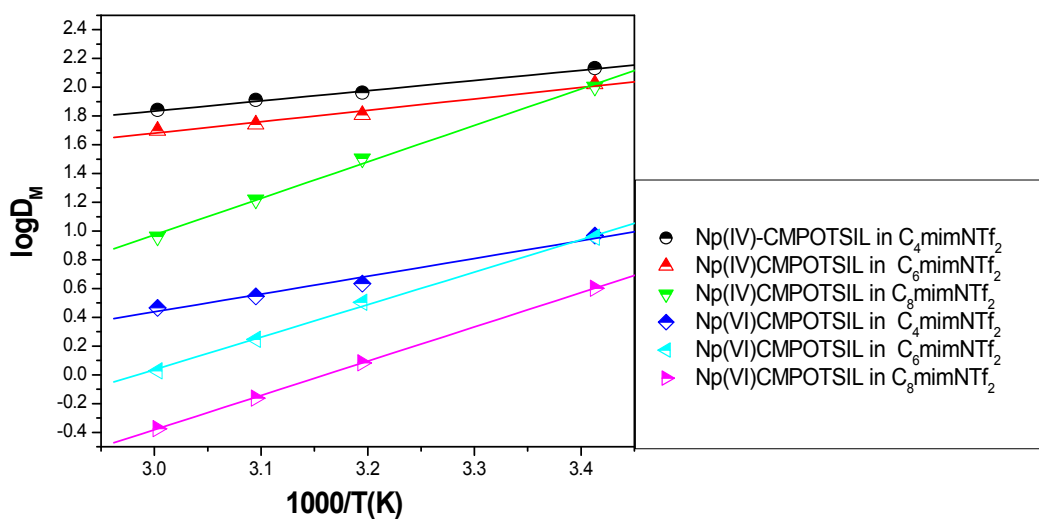
The Van't Hoff plots for the distribution ratio data as a function of the temperature ( $1/T$ ) resulted in straight lines with positive slopes. The changes in the enthalpy ( $\Delta H$ ) during the complexation can be calculated by using the well known van't Hoff equation from plots of  $\log D$  vs  $1/T$ . The changes in the free energy ( $\Delta G$ ) and the entropy ( $\Delta S$ ) at a particular temperature were calculated from the following equations:

$$\Delta G = -2.303RT \log K'_{\text{ex}} \quad (9)$$

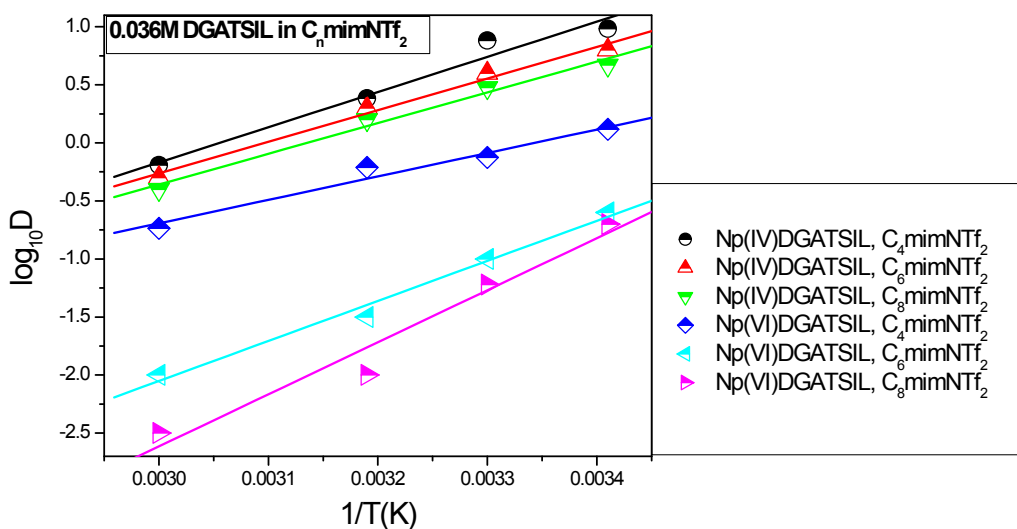
$$\Delta G = \Delta H - T\Delta S \quad (10)$$

The calculated thermodynamic parameters are listed in Table S3. Thermodynamic parameters have previously been calculated for other ionic liquid-based extraction systems in an analogous manner.

**Fig. S3** Extraction of Np(IV) and Np(VI) from (a) 3 M HNO<sub>3</sub> with 0.1 M CMPO-TSIL (L<sub>I</sub>) and (b) 0.5 M HNO<sub>3</sub> using 0.036 M DGA-TSIL (L<sub>II</sub>) at varying temperature. Equilibration time: 3 h.



(a)



(b)

## Stripping studies

**Table S3** Stripping data for three stages using the Np extracts in the CMPO-TSIL (**L<sub>I</sub>**) and DGA-TSIL (**L<sub>II</sub>**) in ionic liquids. Data for Np(VI) are given inside brackets. Strippants: 1 M oxalic acid for Np<sup>4+</sup> and 1 M Na<sub>2</sub>CO<sub>3</sub> for NpO<sub>2</sub><sup>2+</sup>

Solvent system	$D_{\text{Np}}$	% Stripping (cumulative)		
		Stage I	Stage II	Stage III
<b>L<sub>I</sub></b> in [C <sub>4</sub> mim][NTf <sub>2</sub> ]	0.129 (0.676)	88.56 (59.66)	98.69 (83.73)	99.85 (93.44)
<b>L<sub>I</sub></b> in [C <sub>6</sub> mim][NTf <sub>2</sub> ]	0.195 (1.055)	83.64 (48.64)	97.32 (73.62)	99.56 (86.45)
<b>L<sub>I</sub></b> in [C <sub>8</sub> mim][NTf <sub>2</sub> ]	0.426 (1.544)	70.11 (39.3)	91.07 (63.16)	97.33 (77.64)
<b>L<sub>II</sub></b> in [C <sub>4</sub> mim][NTf <sub>2</sub> ]	0.168 (0.016)	85.6 (98.37)	97.93 (99.97)	99.7 (99.99)
<b>L<sub>II</sub></b> in [C <sub>6</sub> mim][NTf <sub>2</sub> ]	0.250 (0.086)	80 (92)	96 (99.36)	99.2 (99.94)
<b>L<sub>II</sub></b> in [C <sub>8</sub> mim][NTf <sub>2</sub> ]	0.333 (0.098)	75 (91)	93.75 (99.19)	98.44 (99.93)

## DFT calculations

**Table S4** The natural charge values on the Np centre for both complexes

Complexes	NPA charge on Np centre ( $q_{\text{Np}}$ )
Np <sup>IV</sup> (NO <sub>3</sub> ) <sub>3</sub> - <b>L<sub>I</sub></b>	1.589
Np <sup>VI</sup> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> - <b>L<sub>I</sub></b>	1.347
Np <sup>IV</sup> (NO <sub>3</sub> ) <sub>3</sub> - <b>L<sub>II</sub></b>	1.543
Np <sup>VI</sup> (NO <sub>3</sub> )(H <sub>2</sub> O)- <b>L<sub>II</sub></b>	1.365