# Sequestration of tetravalent neptunium from acidic feeds using diglycolamide-functionalized dendrimers in a room temperature ionic liquid: extraction, spectroscopic and electrochemical studies

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ELECTRONIC SUPPORTING INFORMATION

S1. Np(IV) valency adjustment by ferrous sulphamate

A solution of ferrous sulfamate (FS) solution was freshly prepared by dissolving a known amount of iron powder (BDH) in sulfamic acid (Aldrich). For the conversion of Np to the Np(IV) state, a few drops of hydroxylamine nitrate (HAN) (1 M) as the reductant were added followed by the freshly prepared ferrous sulfamate. In case of ^{239}NP tracers, the oxidation state of the resultant solution was confirmed by a TTA variation experiment at 1 M HNO_3, which resulted in a slope value of ca. 4 in the fitted log D vs log [TTA] concentration plot. A direct spectroscopic investigation was preferred for ^{237}Np oxidation state confirmation after the addition of the reducing (FS+HAN) agents. The presence of peaks at 964 nm and 723 nm confirms the presence of Np(IV) with subsequent disappearance of the peak at 980 nm for Np(V) (Fig. S1).
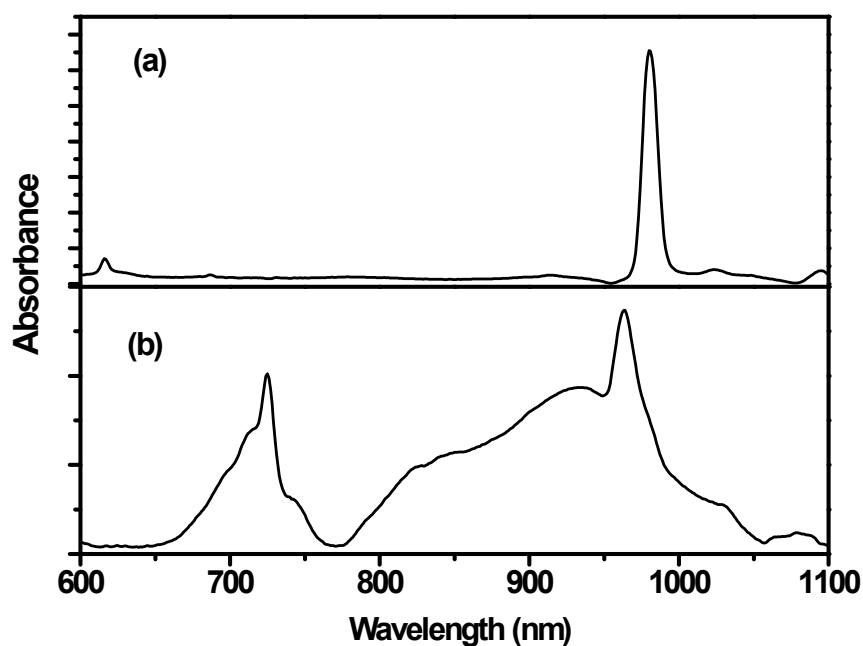
Fig. S1. UV-Vis spectrum of Np **a)** before and **b)** after the addition of ferrous sulphamate and hydroxylamine; T: 298 K.
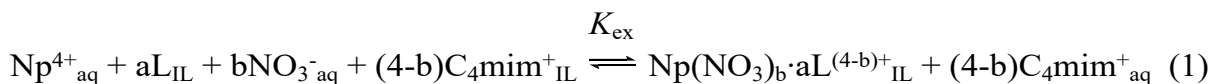
S2. Kinetics of the extraction
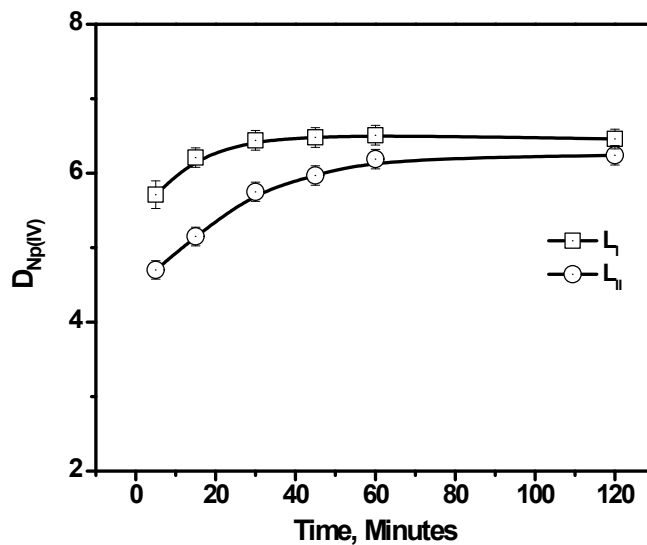
Fig. S2. Plot of the D_{Np} *vs* time for the extraction of Np(IV) with L_I or L_{II} dissolved in C_4mim.NTf$_2$ for 3 M HNO$_3$ at 298 K. (steady state reached in 45-46 minutes)

Extraction equilibrium and distribution ratio correction

The extraction equilibrium constant (K_{ex}) for the cation-exchange mechanism (equation 1) can be given by equation 2

$$Np^{4+}_{aq} + aL_{IL} + bNO_3^-_{aq} + (4-b)C_4mim^+_{IL} \overset{K_{ex}}{\rightleftharpoons} Np(NO_3)_b \cdot aL^{(4-b)+}_{IL} + (4-b)C_4mim^+_{aq} \quad (1)$$

where the subscripts, 'aq' and 'IL' refer to the species present in the aqueous and the ionic liquid phases, respectively.

$$K_{ex} = \frac{[Np(NO_3)_b \cdot aL^{(4-b)+}]_{IL}}{[Np^{4+}]_{aq}[NO_3^-]^b_{aq}[L]^a_{IL} \cdot \gamma(Np^{4+})_{aq} \cdot \gamma(NO_3^-)^b_{aq} \cdot \gamma(L)^a_{IL}} \quad (2)$$

where, K_{ex} is the two phase extraction constant, square bracket represent concentration of each species, γ is the activity coefficient for the given species, as indicated. The activity coefficient for L_{IL} and $Np_{(aq)}^{4+}$ can be assumed to unity because of their very low concentration (i.e., $[L_{IL}] \leq 10^{-4}$ M and $Np_{(aq)}^{4+} < 10^{-12}$ M) and the equation 2 can be reduced to equation 3 under the above assumptions

$$K'_{ex} = \frac{[Np(NO_3)_b \cdot aL^{(4-b)+}]_{IL}}{[Np^{4+}]_{aq}[NO_3^-]^b_{aq}[L]^a_{IL} \cdot \gamma(NO_3^-)^b_{aq}} \quad (3)$$

where, K'_{ex} is conditional two-phase extraction constant. Since, the Np^{4+} extraction is taking place from the NO_3^- media, one has to take care for the NO_3^- complexation with Np^{4+} in the aqueous feed.[1,2] The various species of the Np^{4+} such as $Np(NO_3)^{3+}$, $Np(NO_3)_2^{2+}$, $Np(NO_3)_3^+$, $Np(NO_3)_4$ etc, can be present in the aqueous phase and the total concentration of Np_{aq}^{4+} can be given by equation 4.

$$[Np^{4+}]_{aq} = [Np^{4+}]\left[1 + \sum_i^n \beta_b [NO_3^-]^b\right] \tag{4}$$

Where, β_b for the complex $Np(NO_3)_b^{(4-b)+}$ by equation 5

$$Np^{4+}_{aq} + b\ NO_3^-_{aq} \rightleftharpoons Np(NO_3)_b^{(4-b)+}_{aq} \tag{5}$$

Equation (6) can be easily derived by combining equation (3) and (4),

$$K'_{ex} = \frac{[Np(NO_3)_b.aL_{IL}]^{(4-b)+}}{[Np^{4+}]\left(1 + \sum_i^n \beta_b[NO_3^-]^b\right)[NO_3^-_{(aq)}]^b[L_{IL}]^a \cdot \gamma_{NO_3^-_{(aq)}}^b} \dots 6$$

The $D_{Np}^{4+}(exp)$ is the experimental distribution ratio of the Np^{4+} in the biphasic system (equation (7)). Hence, nitrate complexation corrected distribution ratio $D_{Np}^{4+}(corr)$ is given of equation 8 as also suggested by others[1,2]

$$D_{Np^{4+}}(exp) = \frac{[Np(NO_3)_b.aL_{IL}]^{(4-b)+}}{[Np^{4+}]\left(1 + \sum_i^n \beta_b[NO_3^-]^b\right)} \dots 7$$

$$D_{Np^{4+}}(corr) = D_{Np^{4+}}(exp).\left(1 + \sum_i^n \beta_b[NO_3^-]^b\right) \dots 8$$

On combining equation 6,7, 8 and taking log on both sides gives equation 9

$$logD_{Np^{4+}}(corr) = logK'_{ex} + a.log[L_{(org)}] + b.loga_{[NO_3^-_{(aq)}]} \quad \dots 9$$

The equation 9 gives the linear dependence of log $(D_{Np}^{4+}(corr))$ with the activity of nitrate ($a_{[NO_3^-{(aq)}]}$) and ligand concentration at a given temperature. The stoichiometry of the extracted complex in the organic phase can be found out if the value of 'a' and 'b' are known from the equation (9). The value of 'a' and 'b' can be easily determined by evaluating the D_{Np}^{4+} with varying ligand and nitrate concentration, respectively, and keeping other variables constant. The log β value (log $β_1$: 0.34 ; log $β_2$: 0.08 ; and log $β_3$: -0.26)[3] for the Np^{4+} nitrate complexation were used for the estimation of $D_{Np}^{4+}(corr)$ using experimental D_{Np} and the activity coefficient for nitrate ions were taken from ref.[4] The resulting log $D_{Np}(corr)$ vs log $a(NO_3^-)$ plot shows nitrate dependence of ~3 for the extraction of Np^{4+} by both L_I and L_{II} dissolved in the $C_4mim.NTf_2$.

S3. Cyclic Voltammetric studies
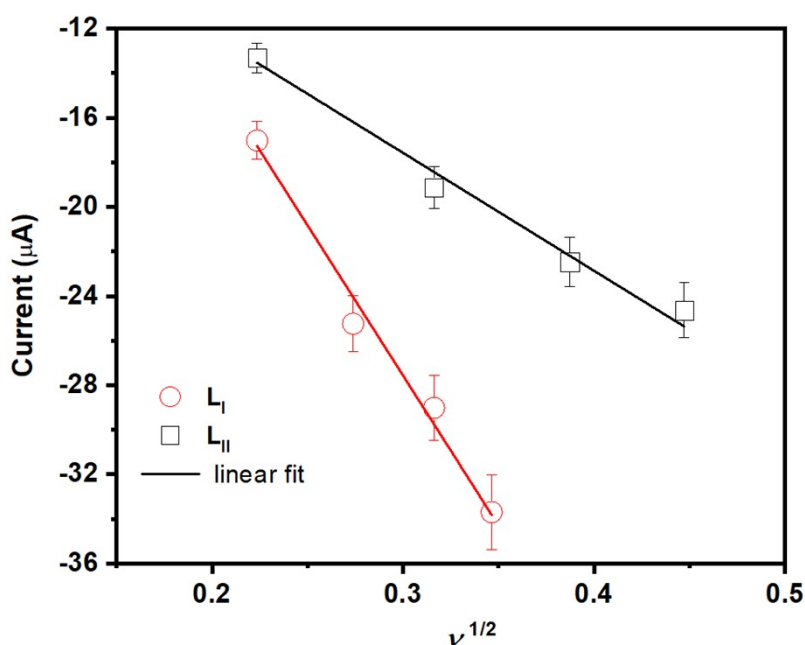
Fig. S3. Linear relationship of the current *vs* $v^{1/2}$ for the CV studies of the extracted Np(IV) complex with a) **L_I** and b) **L_{II}** dissolved in $C_4mim.NTf_2$ at different scan rates at 298 K.

References

1 J. N. Mathur and K. L. Nash, *Solvent Extr. Ion Exch.*, 1998, **16**, 1341–1356.

2 G. Suresh, M. S. Murali and J. N. Mathur, *Solvent Extr. Ion Exch.*, 2001, **19**, 947–964.

3 G. Burney and R. Harbour, *Radiochemistry of Neptunium*, Technical Information Center, Office of Information Services UNITED STATES ATOMIC ENERGY COMMISSION, NAS-NS-3060, 1974.

4 M. D. M. Marcos-Arroyo, M. K. Khoshkbarchi and J. H. Vera, *J. Solution Chem.*,

1996, **25**, 983–1000.