Electronic Supporting Information

Complexation of 2-thenoyltrifluoroacetone (HTTA) with trivalent $f$-cations in an ionic liquid: Solvent extraction and spectroscopy studies

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S1. Purification of $^{241}$Am

$^{241}$Am, which contained $^{237}$Np as its daughter product, was purified by first reducing Np to its $^{+4}$ state using hydroxylamine hydrochloride at 1 M HNO$_3$ and subsequently extracting the converted Np$^{4+}$ by a 0.5 M TTA (2-thenoyltrifluoroacetaone) solution in xylene (Merck). After two successive extractions of the same aqueous phase (containing $^{241}$Am and $^{237}$Np) with fresh TTA solutions taken each time, the aqueous phase was shaken with two lots of xylene (to extract the dissolved TTA in the aqueous phase) and subsequently evaporated to dryness; a few drops of a mixture of concentrated HNO$_3$ and HClO$_4$ (5:1 ratio) were added to destroy the organic impurities, if any. Alpha spectrometry of the purified $^{241}$Am stock was carried out to rule out the presence of impurities.

S2. Radiometric assay of $^{241}$Am and $^{152,154}$Eu

$^{241}$Am and $^{152,154}$Eu were assayed radiometrically using a well type NaI(Tl) scintillation counter (Para Electronics) which was interphased with a multi-channel analyzer (ECIL, India). For experiments where the extraction of Am or Eu were very large or very low, the aliquot size from the phase containing low counts was kept large enough to have more counts. Additionally, the counting time was increased (in some cases >10 h counting time was used as against only one minute for most samples). The counter was calibrated with known standards before the counting was done. Enough counts were collected (>10,000 counts) to neglect the counting statistics errors (<1%).

S3. Preparation of buffer

0.05 M Chloroacetate buffer solution was prepared by dissolving 236.2 mg of mono-chloroacetic acid crystals (Sigma Aldrich, CAS 79-11-8) in about 22 mL distilled water in a 25 mL standard volumetric flask. The pH of this solution was adjusted to the desired value (pH = 3 – 5) with dilute NaOH solution. After pH adjustment, the solution was diluted up to the mark in the 25 mL standard flask.

S4. Equilibrium kinetics measurements

The extraction kinetics of Am$^{3+}$ and Eu$^{3+}$ was investigated to establish the equilibration time needed for reaching the equilibrium condition during distribution measurements. As shown in Fig. S1, the extraction kinetics for both, Am$^{3+}$ and Eu$^{3+}$ was relatively slow and about 2 h of equilibration needed to reach the
equilibrium condition. The kinetics data in the present work established a time frame that was maintained during the extraction studies, and all the subsequent studies were carried out by keeping the equilibration time of at least 4 h.

![Extraction kinetics of Am(III) and Eu(III) by HTTA in C₄mim·Tf₂N](image)

**Figure S1.** Extraction kinetics of Am(III) and Eu(III) by HTTA in C₄mim·Tf₂N. C₄mim·Tf₂N phase: 0.01 M HTTA; Aqueous phase: 0.05 M chloroacetate buffer (pH 4.1).

### S5. Determination of acid and water content of RTIL

For determination of acid uptake by the ionic liquid, equal volumes of C₄mim·Tf₂N and aqueous solution of desired feed acidity (0.01 M – 6 M HNO₃) were equilibrated in a glass stoppered tube in a thermostated water bath maintained at 25±0.1°C for 1 h. After equilibration, the tubes were centrifuged; the two phases were separated followed by removal of suitable volumes of C₄mim·Tf₂N and aqueous phases for acid base titration with standard NaOH solution using phenolphthalein indicator. While RTIL phase was titrated in 50% ethanol/H₂O mixture previously neutralized to phenolphthalein, aqueous phase was directly titrated in water with standard NaOH solution. The reported acid concentration in the RTIL phase was the average value obtained by direct RTIL phase titration and the value obtained from the mass balance of aqueous phase titration.

For estimation of water content of the ionic liquid, Karl Fischer titration was carried out after its equilibration with the aqueous phase of desired acidity. Karl Fischer titrations were carried out on Metrohm 905-Titrando machine after its calibration.