

Understanding the recovery of rare-earth elements by ammonium salts

Supplementary Materials

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Figure S1: Slope Analysis

Slope analysis from associated log *D* plots. (Left) the recovery of La, Nd and Dy (0.01 M) from a NaNO₃ (7 M) aqueous solution varying **IL** concentration (0.01-1.0 M) in toluene. (Right) The recovery of La, Nd and Dy (0.01 M) using **IL** (0.10 M) in toluene varying NaNO₃ concentration (1-7 M).

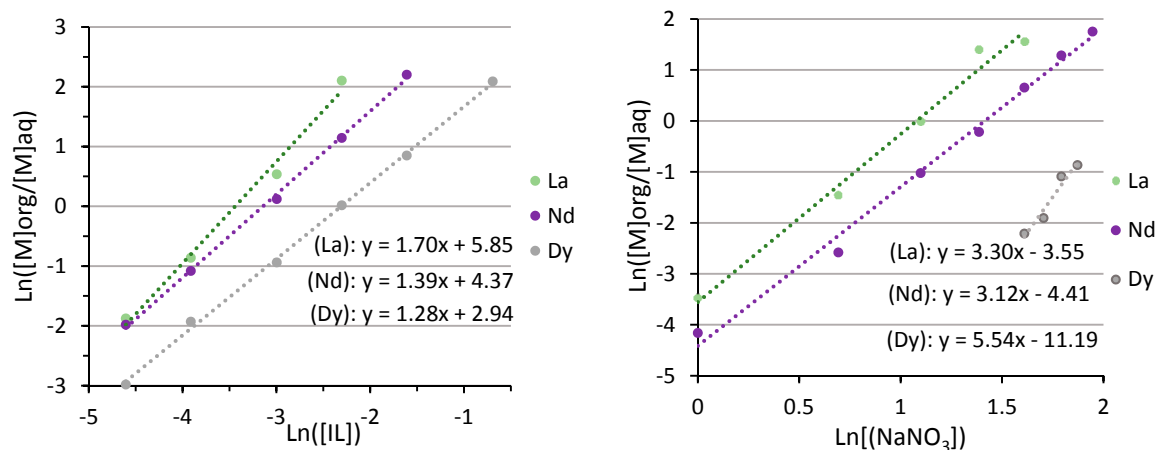


Figure S2: Back Extraction (Stripping) Studies of La, Nd and Dy

The back extraction (stripping) of La, Nd, Dy from a loaded organic phase containing **IL** (0.1 M) using water and NaNO₃ solution (0-7 M). Interpolation used to aid the eye only.

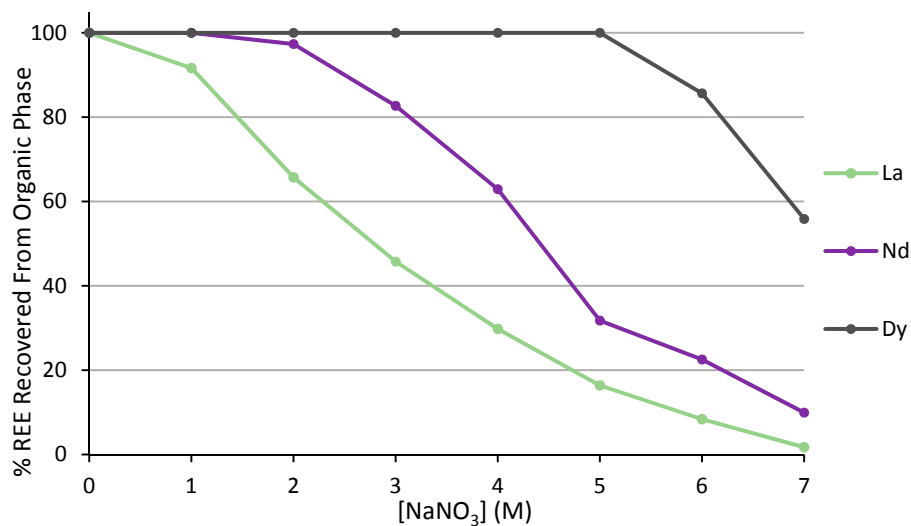
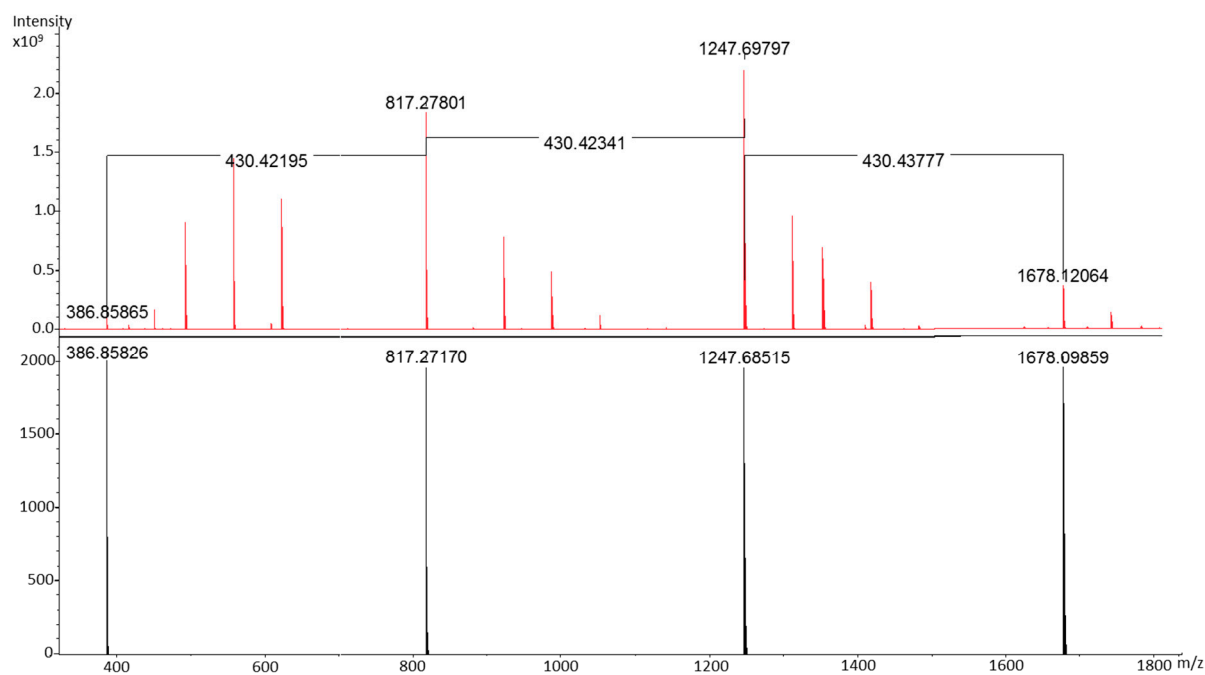


Figure S3: La and Dy Negative ion ESI-MS

Negative-ion mode ESI-MS of the **IL** organic phase (0.1 M **IL**) post-contact with a La or Dy aqueous phase diluted with methanol showing ions of $\text{REE}(\text{NO}_3)_4(\text{IL})_n^-$. La (Top) and Dy (Bottom) (0.05 M). Experimental negative-ion ESI-MS (red) compared with that calculated (black).



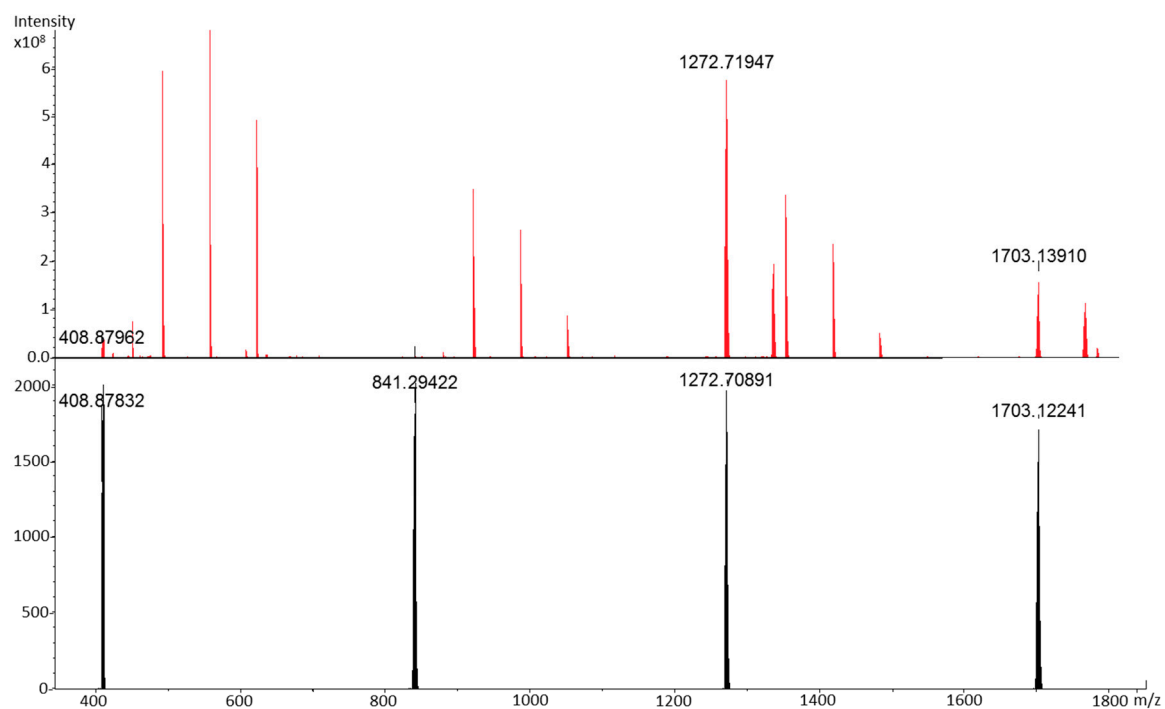


Figure S4: Variable Temperature ¹³⁹La NMR

¹³⁹La NMR spectra of the La standard, LaCl₃ (0.01 M, 0.0 ppm) in D₂O (purple) and the IL organic phase (0.05 M) after contact with a 0.05 M aqueous La solution obtained at -55 (dark blue), +5 (cyan), +25 (green), +45 (yellow), +65 °C (red).

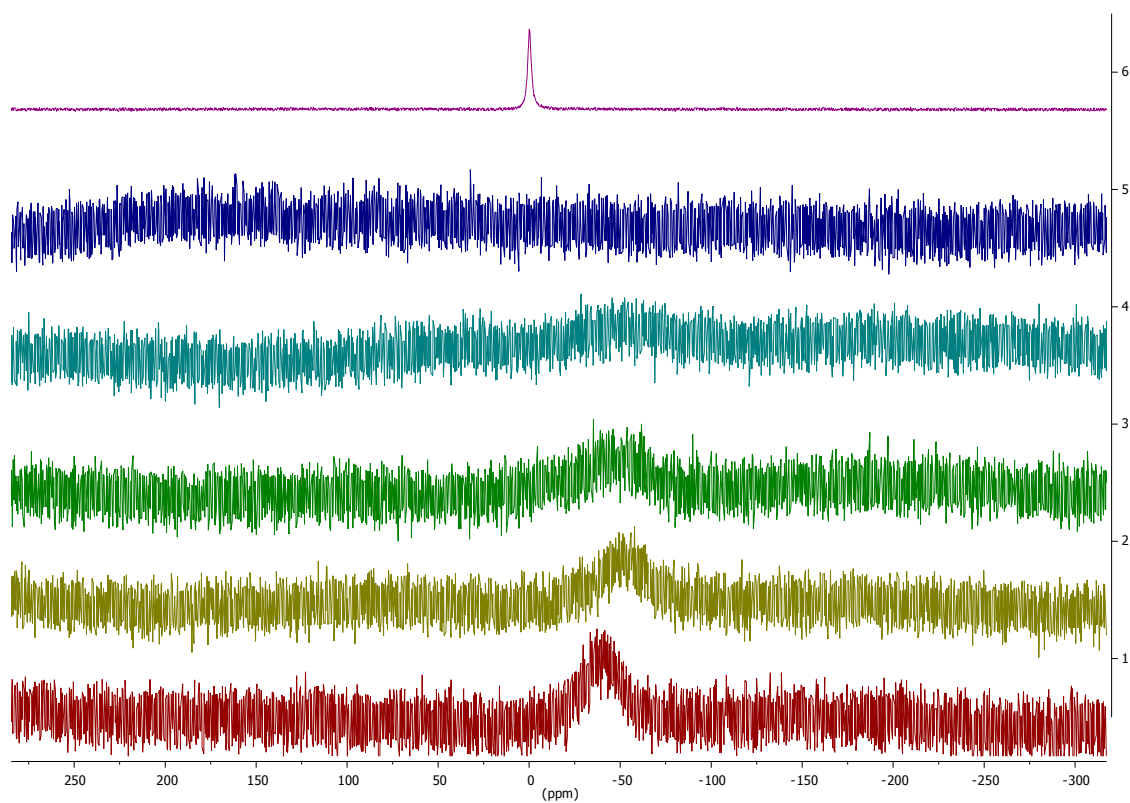


Figure S5: Computational Outputs

An output from classical MD simulations indicating how the average number of IL, water and nitrate associated with La increases as distance from La increases following formation of a La containing aggregate. On average, four NO_3^- anions are observed to be within 5.1 Å of the La centre, three H_2O molecules within 6.0 Å, and three nitrogen atoms from the encapsulating ammonium cations within 11 Å. All six NO_3^- are incorporated into the aggregate within 11 Å from the La^{3+} cation on average.

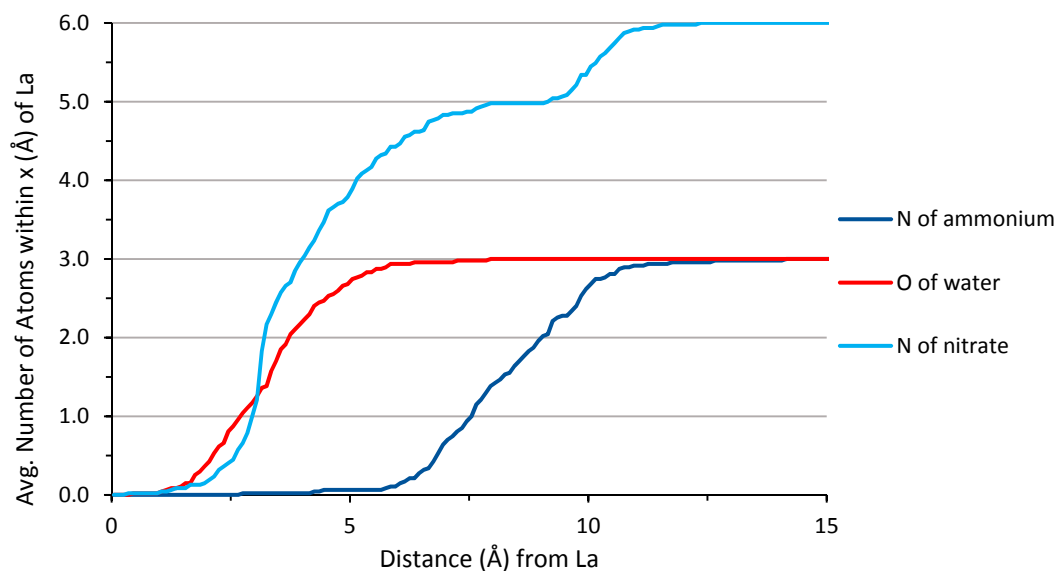
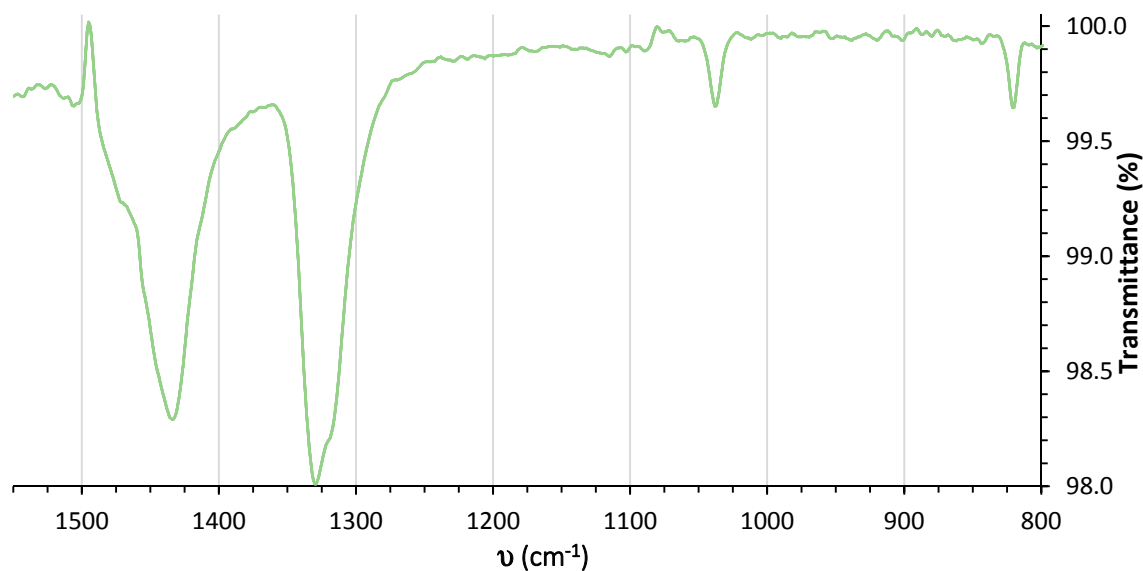


Figure S6: Infrared Spectroscopy

(Top) Infrared spectrum of the IL organic phase (0.05 M) after contact with a 0.05 M aqueous La solution. The IL organic phase pre-contact used as the background (Bottom). Peaks at 1328 and 1435 cm^{-1} in the IL organic phase loaded with La assigned as symmetric and asymmetric N-O nitrate stretches. Peaks at 1339 and 1467 cm^{-1} in the IL organic phase prior to La loading assigned as symmetric and asymmetric N-O nitrate stretches.



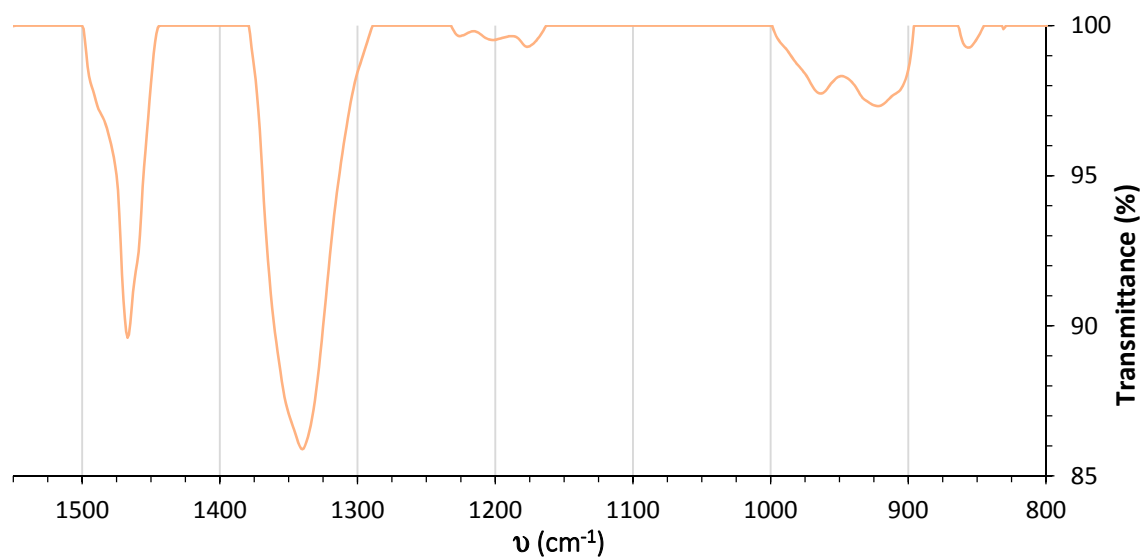


Table S1: Metal recovery data tabulated as distribution coefficients.

Distribution coefficients (REE recovered into org./REE remaining in aq.)							
Varying [IL]. Fixed [NaNO ₃] (7 M)				Varying [NaNO ₃]. Fixed [IL] (0.1 M)			
[IL] (M)	La	Nd	Dy	[NaNO ₃] (M)	La	Nd	Dy
0.01	0.15	0.14	0.05	1.0	0.03	0.02	----
0.02	0.42	0.34	0.15	2.0	0.23	0.08	----
0.05	1.73	1.13	0.40	3.0	0.98	0.36	0.05
0.10	66.17	4.03	1.06	4.0	4.06	0.81	0.10
0.20	86.93	9.11	2.41	5.0	4.78	1.93	0.26
0.50	28213	14.96	8.40	6.0	10.09	3.62	0.44
1.00	----	62.98	12.18	7.0	66.17	4.03	1.06
Varying [HNO ₃]. Fixed [NaNO ₃] (7 M), [IL] (0.1 M)							
[HNO ₃] (M)	La	Nd	Dy				
0.005	16.78	6.11	1.47				
0.010	12.16	3.02	1.42				
0.020	11.66	5.42	1.58				
0.050	6.96	2.27	1.09				
0.100	3.58	2.89	0.78				
0.200	6.05	1.05	0.68				
0.500	0.60	0.15	0.10				
1.000	0.09	0.00	0.00				