Supplementary Information

A Kinetic Interpretation of the Effect of Extractant and Acid on Lanthanide Extraction by a Diglycolamide

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Synthesis of TODGA

Synthesis of *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA) was adapted from a published diglycolamide synthesis procedure.[1] Di(*n*-octyl)amine (0.33 mol) and triethylamine (0.35 mol) were dissolved in ~400 mL of methylene chloride (DCM) and stirred vigorously in a round bottom flask in an ice bath. Diglycolyl chloride (0.18 mol) was added dropwise while the reaction was flushed with argon gas. The reaction was allowed to progress at room temperature for 1-2 hours. The organic phase was washed with equal volumes of DI H_2O twice, 1 M HCl twice, and brine solution two or three times until it was clear. The DCM, containing TODGA and impurities, was dried over $MgSO_4$, filtered using a Büchner funnel and filter paper, and then removed under reduced pressure using a rotary evaporator. The crude product, with ~90% crude yield, was purified using column chromatography. Columns were packed with silica gel wet with 10% ethyl acetate (EtOAc) in hexanes. Crude product was loaded, and 10% EtOAc was used to elute the initial impurity band, then a gradient of 10-50% EtOAc in hexanes was used to elute purified TODGA from the column. The final product, at ~70% yield and 99+% purity, was concentrated under reduced pressure and characterized using ^{1}H NMR. (500 MHz, $CDCl_3$ δ 7.260, 20.4 °C, 64 scans), δ 0.874 (12H, m), δ 1.268 (40H, s), δ 1.513 (8H, m), δ 3.172 (4H, t), δ 3.285 (4H, t), δ 4.306 (4H, s).

Equilibrium Extraction Model

The equilibria involved in the extraction of Nd from nitric acid by TODGA/*n*-dodecane (Equation S1) were examined using a modified version of the extraction model of Picayo et al.[2] with the following changes necessary for modeling the TODGA system: the formation of nitric acid adducts with the extracted Nd complexes was considered; the average TODGA stoichiometry of the extracted Nd complex determined from slope analysis of the equilibrium extraction data, $\ell = 3.25$, was used for all the extracted complexes; for the purposes of the extraction, the hydronium ions formed by the aqueous dissociation of nitric acid were considered to exist as the Eigen cation, $H(H_2O)_4^+$ or $H_9O_4^+$ in the aqueous phase;[3] and all equilibria involving HEH[EHP] (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) in the original work were omitted. The resulting equilibrium model includes equilibria for dissociation of nitric acid in the aqueous phase, formation of aqueous $Nd(NO_3)^{2+}$ and $Nd(NO_3)_2^+$, and extraction of

HNO_3 to give 1:1 and 1:2 TODGA: HNO_3 complexes in the organic phase in addition to the general Nd extraction equilibrium,

$$\mathrm{Nd^{3+}} + 3.25\,\overline{\mathrm{TODGA}} + (n+m)\,\mathrm{NO_3^-} + m\,\mathrm{H^+} \rightleftharpoons \overline{\mathrm{Nd(TODGA)_{3.25}(NO_3)_{\mathit{n}} \cdot \mathit{m}\,HNO_3}} \tag{S1}$$

with the equilibrium constant $K_{ex,m}$,

$$K_{ex,m} = \frac{\left[\overline{\mathrm{Nd(TODGA)_{3.25}(NO_3)_{\mathit{n}} \cdot \mathit{m}\,HNO_3}}\right]\{\mathrm{H_2O}\}^{(9\,+\,3(n\,+\,m)\,+\,4m)}}{\{\mathrm{Nd^{3+}}\}\{\mathrm{NO_3^-}\}^{(n+2m)}[\overline{\mathrm{TODGA}}]_{\mathrm{f}}^{3.25}} \tag{S2}$$

where $n = 3$ as required for charge balance in the organic phase, $m = 0$, 1, or 2, and $\{H^+\} \approx \{NO_3^-\}$ in our system. The activity coefficients of the organic phase species were considered to be constant over the composition range studied so molar concentrations were used for all organic phase species. However, activities were used for all aqueous species because of the wide range of aqueous phase ionic strengths spanned in these experiments. Neodymium(III) activities were determined according to Lalleman et al.,[4] water activities were determined following Clegg and Brimblecombe,[5] and the dissociation constant of nitric acid and activity of nitric acid and the average activity coefficients of nitrate and hydronium ions were determined according to Levanov et al.[6]

The auxiliary equilibria considered in the model and their equilibrium constants were

$$\mathrm{Nd^{3+}} + \mathrm{NO_3^-} \rightleftharpoons \mathrm{Nd(NO_3)^{2+}}; \qquad \beta_1 \tag{S3}$$

$$\mathrm{Nd(NO_3)^{2+}} + \mathrm{NO_3^-} \rightleftharpoons \mathrm{Nd(NO_3)_2^+}; \quad \beta_2/\beta_1 \tag{S4}$$

$$\mathrm{HNO_3} \rightleftharpoons \mathrm{H^+} + \mathrm{NO_3^-}; \qquad K_a \tag{S5}$$

$$\mathrm{HNO_3} + \overline{\mathrm{TODGA}} \rightleftharpoons \overline{\mathrm{TODGA \cdot HNO_3}}; \qquad K_1^{DGA} \tag{S6}$$

$$2\,\mathrm{HNO_3} + \overline{\mathrm{TODGA}} \rightleftharpoons \overline{\mathrm{TODGA \cdot 2HNO_3}}; \qquad K_2^{DGA} \tag{S7}$$

Values for β_1, β_2/β_1, and K_a were taken from the literature,[6–8] while those for K_1^{DGA} and K_2^{DGA} were derived by fitting literature data for the nitric acid extraction by TODGA[9] to the mass balance equation,

$$\overline{[\mathrm{HNO_3}]} = \overline{[\mathrm{TODGA \cdot HNO_3}]} + 2\overline{[\mathrm{TODGA \cdot 2HNO_3}]} = \frac{K_1^{DGA}\{\mathrm{HNO_3}\} + K_2^{DGA}\{\mathrm{HNO_3}\}^2}{\overline{[\mathrm{TODGA}]}_\mathrm{f}} \quad \text{(S8)}$$

as illustrated in Figure S1. The values of the equilibrium constants for these auxiliary equilibria are summarized in Table S1.

The Nd distribution ratio can thus be defined as

$$D = \frac{\overline{[\mathrm{Nd(TODGA)_{3.25}(NO_3)_3}]} + \overline{[\mathrm{Nd(TODGA)_{3.25}(NO_3)_3 \cdot\ HNO_3}]} + \overline{[\mathrm{Nd(TODGA)_{3.25}(NO_3)_3 \cdot 2\ HNO_3}]}}{[\mathrm{Nd^{3+}}] + [\mathrm{Nd(NO_3)^{2+}}] + [\mathrm{Nd(NO_3)_2^{+}}]} \quad \text{(S9)}$$

where

$$\overline{[\mathrm{Nd(TODGA)_{3.25}(NO_3)_3 \cdot} m\ \mathrm{HNO_3}]} = K_{ex,m}\{\mathrm{NO_3^-}\}^{(3+2m)}\left(\frac{\gamma_{Nd}[\mathrm{Nd^{3+}}]\overline{[\mathrm{TODGA}]}_f^{3.25}}{\{\mathrm{H_2O}\}^{(18\,+\,7m)}}\right) \quad \text{(S10)}$$

from Equation S2, and

$$[\mathrm{Nd^{3+}}] + [\mathrm{Nd(NO_3)^{2+}}] + [\mathrm{Nd(NO_3)_2^{+}}] = [\mathrm{Nd^{3+}}](1 + \frac{\gamma_{Nd}}{\gamma_{Nd(NO_3)}}\beta_1\{\mathrm{NO_3^-}\} + \frac{\gamma_{Nd}}{\gamma_{Nd(NO_3)_2}}\beta_2\{\mathrm{NO_3^-}\}^2) \quad \text{(S11)}$$

from the neodymium nitrate equilibria in Equations S3 and S4.

Together Equations S9 – S11 enable calculation of the values for $K_{ex,m}$ and the speciation of the extracted Nd complexes from the variation in the experimental distribution coefficients with nitric acid concentration using the data in Figure 2B. The error-weighted experimental distribution ratios were fit to Equation S9 using the Excel Solver (Figure S2). The uncertainties in the resulting best fitting $K_{ex,m}$ values were calculated by the jackknife method (Table S1).[10] The resulting speciation in the organic phase (Figure S3) agrees well with the speciation of Eu(III)-TEHDGA complexes in dodecane determined by Campbell et al. using the solvent extraction modeling program SXLSQI.[11]

Table S1. Equilibrium constants for modeling the Nd extraction dependence on aqueous nitric acid concentration.

Equilibrium Constant	**Log *K***	**Reference**
K_a	1.55	6
K_1^{DGA}	1.17 ± 0.12	Fig. S1
K_2^{DGA}	1.68 ± 0.19	Fig. S1
β_1	1.33	7
β_2/β_1	-0.13	8
$K_{ex,0}$	5.19 ± 0.06	Fig. S2
$K_{ex,1}$	5.79 ± 0.11	Fig. S2
$K_{ex,2}$	5.90 ± 0.05	Fig. S2

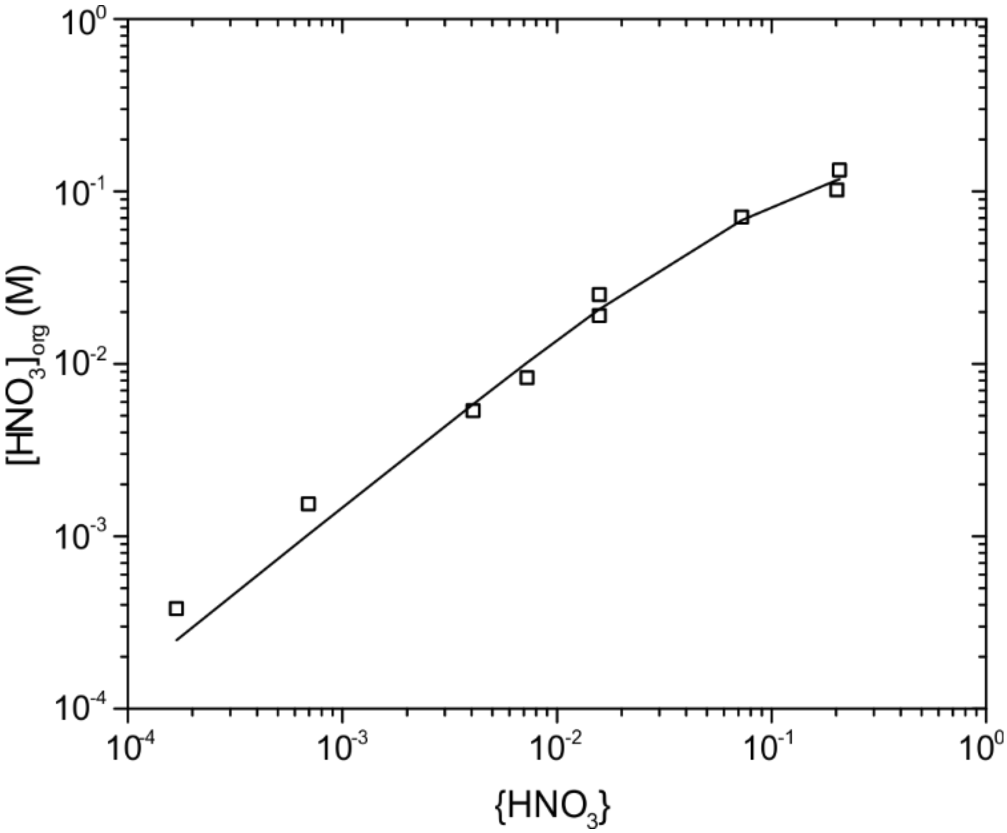

Figure S1. Nitric acid extraction by 0.10 M TODGA/*n*-dodecane from 0.098 – 3.0 M HNO_3 as a function of the molar scale activity of undissociated nitric acid in the aqueous phase. (□) Nitric acid extraction data from reference 39, (—) best fit to Equation S8.

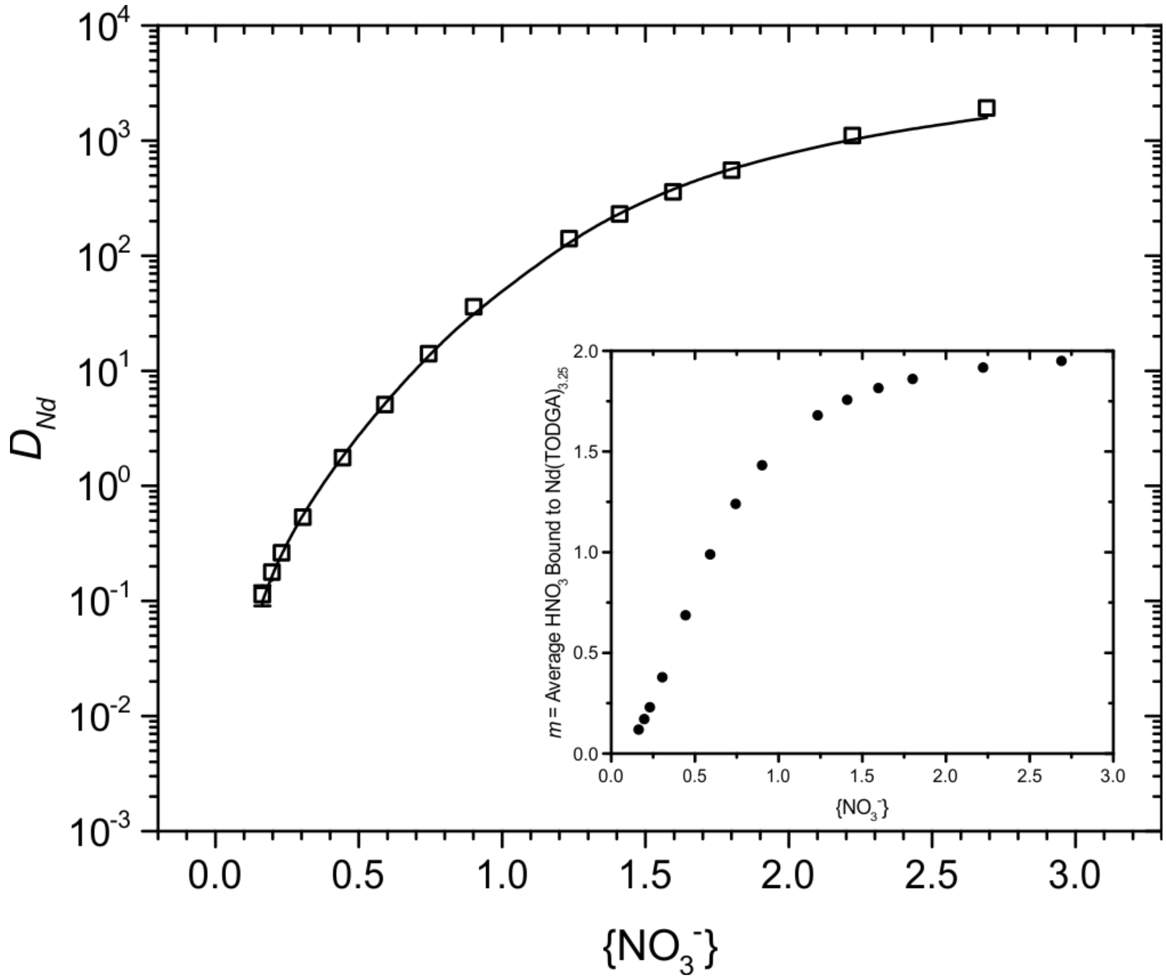

Figure S2. Determination of $K_{ex,m}$ by fitting (□) the Nd extraction data from Figure 2B to obtain (—) the best fit to Equation S9. The uncertainty in D_{Nd} is shown when the ±2σ error bars are larger than the data symbol. Inset: Variation in the calculated average number of nitric acid molecules associated with $Nd(TODGA)_{3.25}(NO_3)_3$ in the organic phase as represented by the stoichiometric coefficient, *m*.

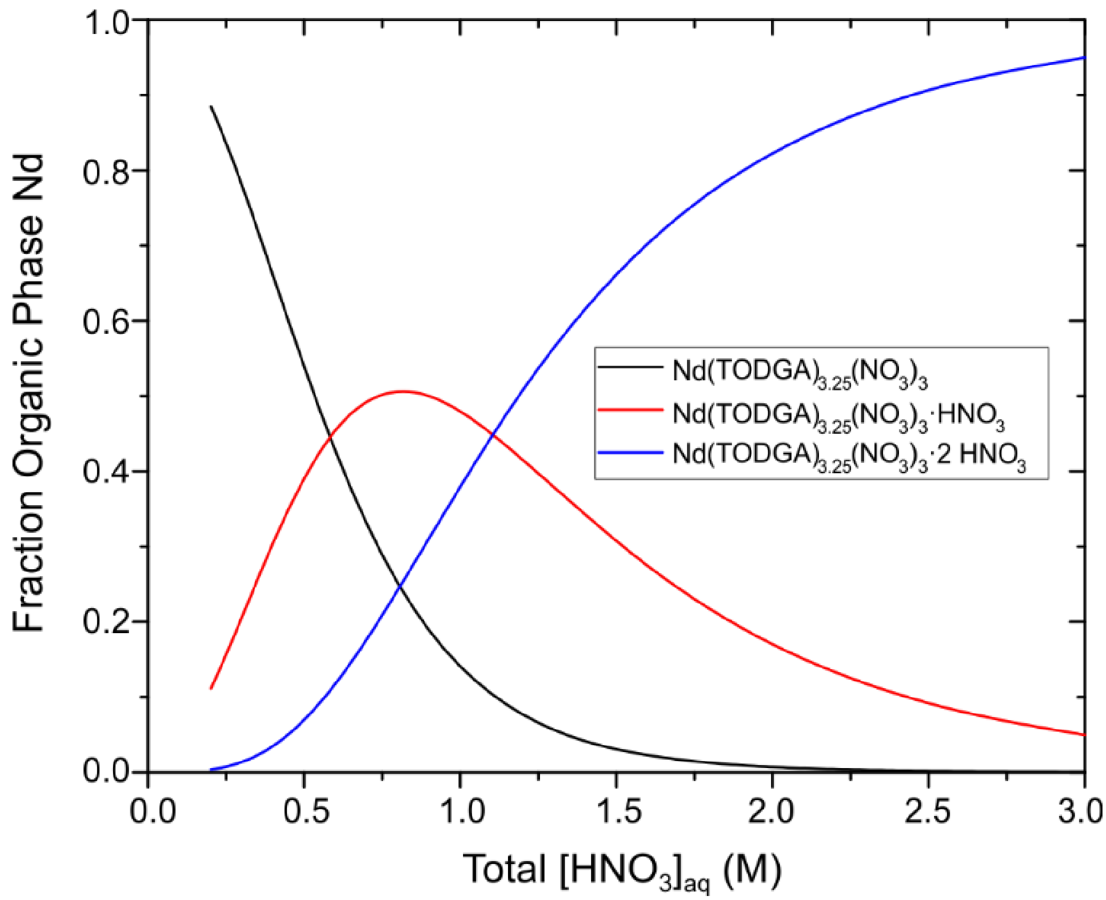

Figure S3. Speciation of Nd complexes in the equilibrium organic phase calculated from the values of $K_{ex,0}$, $K_{ex,1}$, and $K_{ex,2}$ in Table S1.

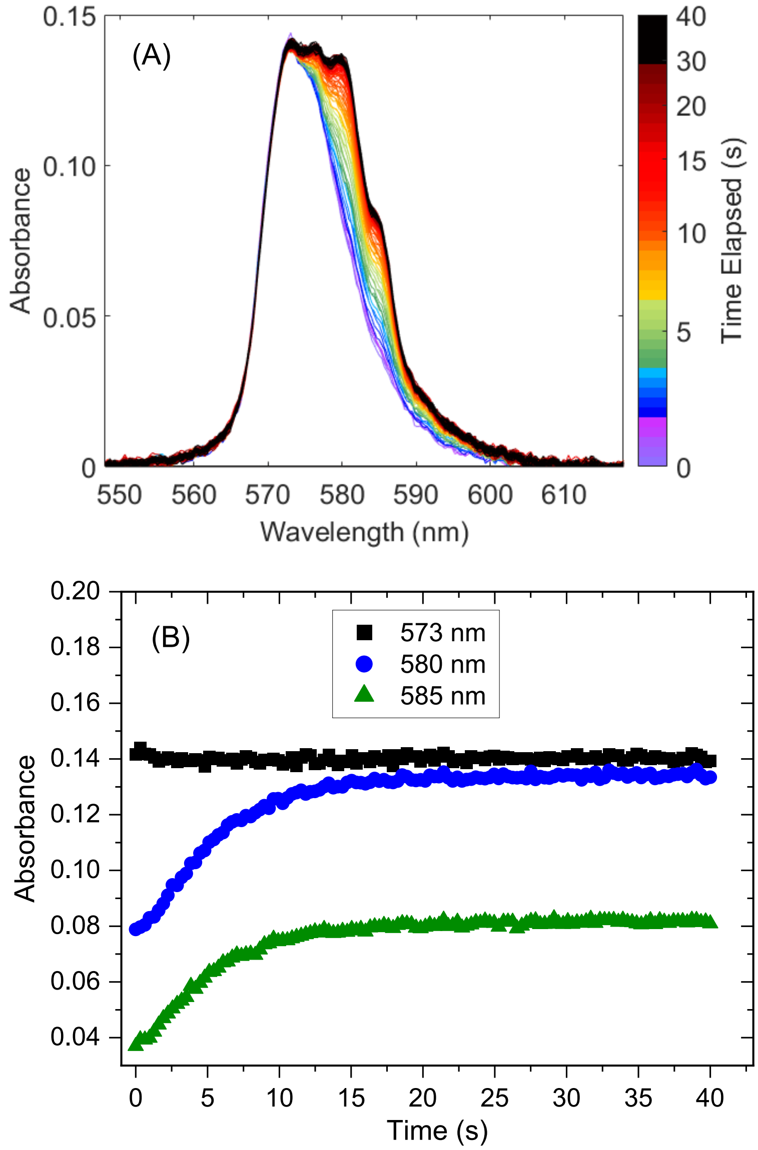

Figure S4. (A) UV/Visible spectra collected during the solvent extraction of Nd(III) from 0.40 M HNO_3 and (B) absorbance changes over time for three of the most prominent wavelengths.

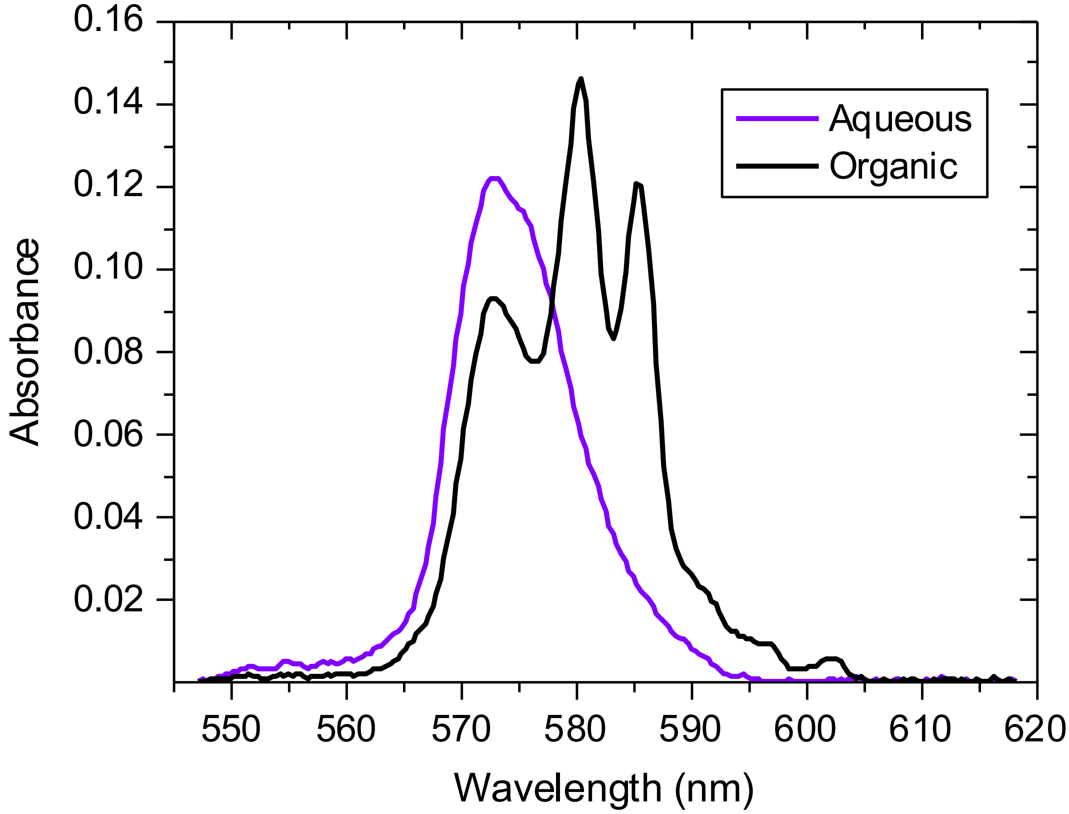

Figure S5. Isolated UV/Visible spectra of 5 mM Nd(III) in the (purple) aqueous phase before any extraction has occurred and (black) organic phase after complete extraction of Nd.

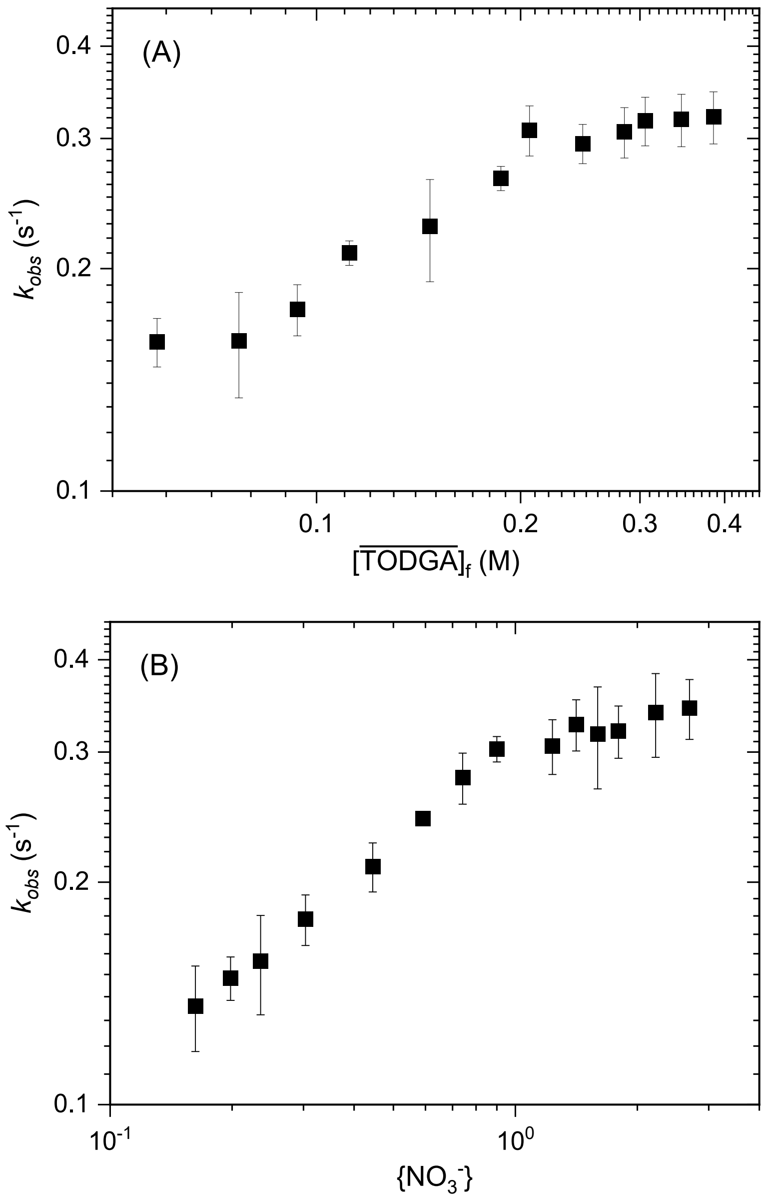

Figure S6. Changes in the observed rate constant k_{obs} with respect to increasing (A) extractant concentration in the organic phase and (B) aqueous nitrate activity.

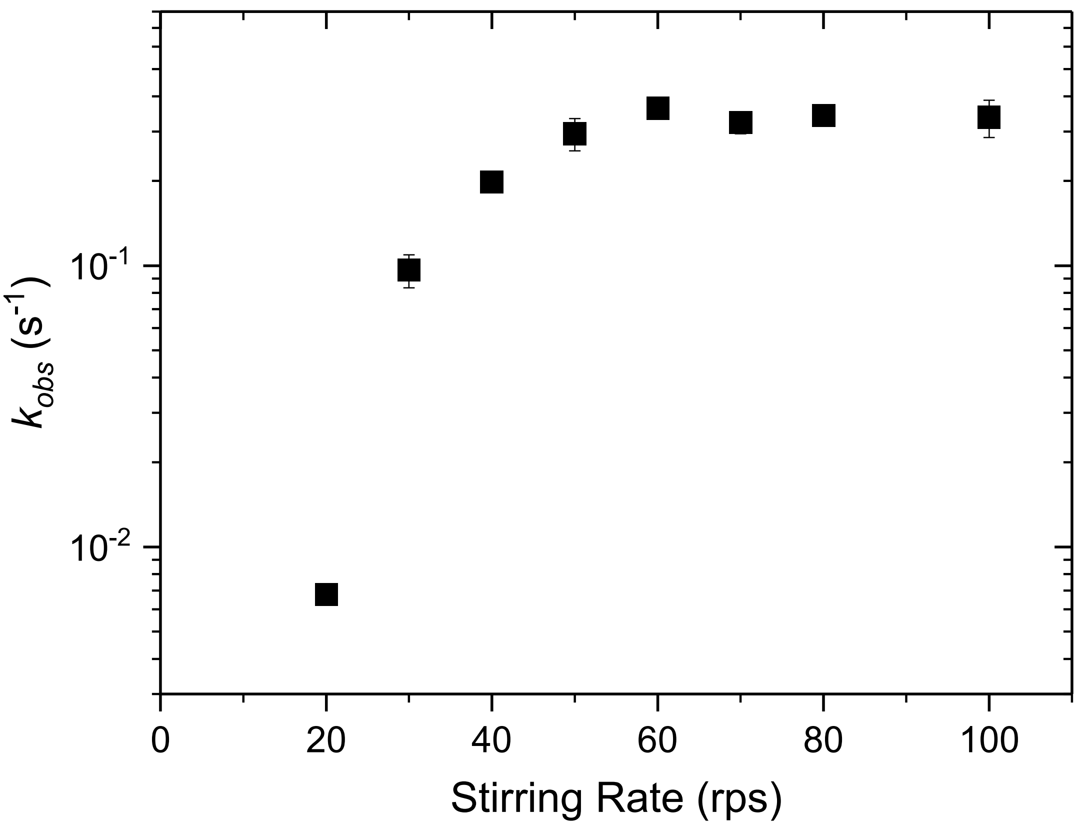

Figure S7. Dependence of the observed rate constant as a function of increasing stirring speed of the overhead stirrer.

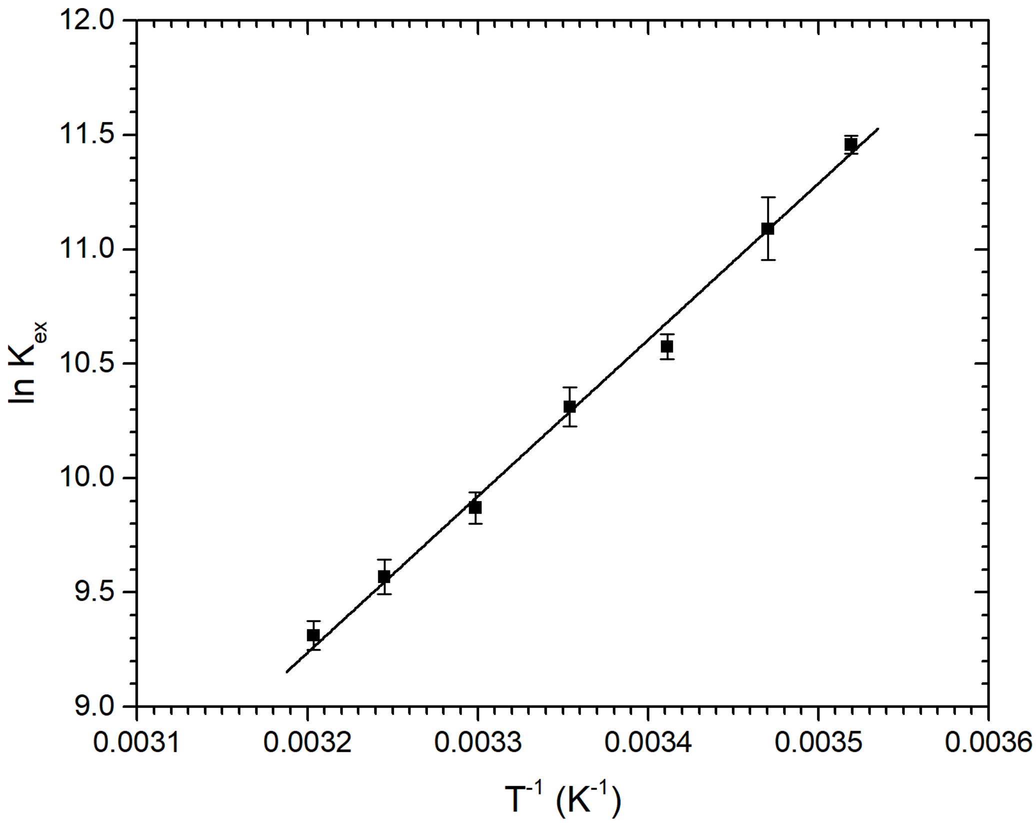

Figure S8. Determination of the enthalpy of extraction of Nd(III) from 0.5 M HNO_3 into 0.1 M TODGA/n-dodecane for Equilibrium 2 with $\boldsymbol{\ell} = 3.25$, $n = 3$, and $m = 0$. Error-weighted best fit line: $\ln K_{ex} = (6.84 \pm 0.43) \times 10^3\, T^{-1} - (12.64 \pm 1.46)$. $\Delta H^0 = -56.7 \pm 3.6$ kJ/mol.

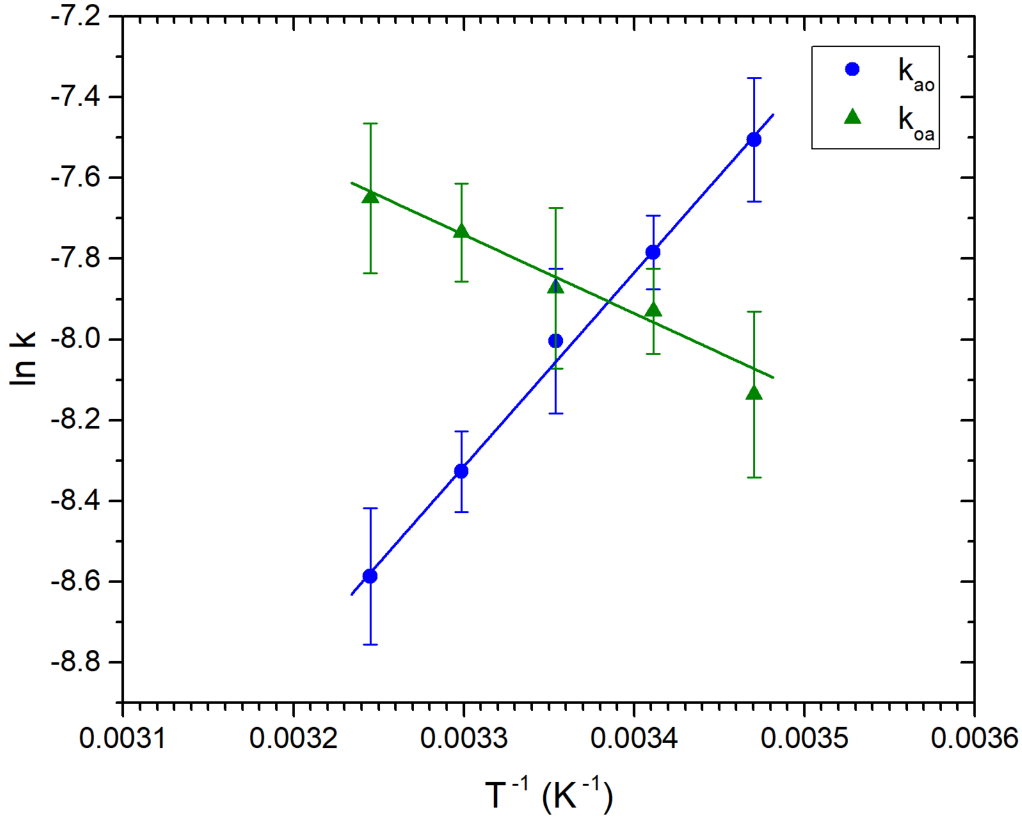

Figure S9. Temperature dependence of the forward (k_{ao}) and reverse (k_{oa}) rate constants for extraction of Nd(III) from 0.5 M HNO_3 into 0.1 M TODGA/*n*-dodecane. Error-weighted best fit lines:
$\ln k_{ao} = (4.80 \pm 0.27) \times 10^3\, T^{-1} - (24.15 \pm 0.91)$. E_a = -39.9 ± 2.2 kJ/mol.
$\ln k_{oa} = (-1.95 \pm 0.46) \times 10^3\, T^{-1} - (1.31 \pm 1.56)$. E_a = 16.1 ± 3.8 kJ/mol.

Table S2. Interfacial tension values reported in Figure 3.

$[\overline{\mathbf{TODGA}}]$ **(M)**	$[\mathbf{HNO_3}]$ **(M)**	**IFT (mN m^{-1})**	**2σ**
1.00 x 10^{-10}	1.0 x 10^{-3}	50.9	0.1
1.00 x 10^{-7}	1.0 x 10^{-3}	49.8	0.3
3.19 x 10^{-7}	1.0 x 10^{-3}	50.7	0.4
1.02 x 10^{-6}	1.0 x 10^{-3}	49.7	0.2
3.16 x 10^{-6}	1.0 x 10^{-3}	48.2	0.2
1.01 x 10^{-5}	1.0 x 10^{-3}	45.0	0.1
3.20 x 10^{-5}	1.0 x 10^{-3}	43.0	0.1
9.96 x 10^{-5}	1.0 x 10^{-3}	40.7	0.2
3.18 x 10^{-4}	1.0 x 10^{-3}	38.3	0.2
1.01 x 10^{-3}	1.0 x 10^{-3}	34.6	0.1
3.15 x 10^{-3}	1.0 x 10^{-3}	31.9	0.06
1.01 x 10^{-2}	1.0 x 10^{-3}	28.8	0.05
3.40 x 10^{-2}	1.0 x 10^{-3}	25.8	0.03
1.00 x 10^{-1}	1.0 x 10^{-3}	23.7	0.02
1.00 x 10^{-10}	1.0 x 10^{-1}	48.9	0.1
1.00 x 10^{-7}	1.0 x 10^{-1}	50.5	0.2
3.19 x 10^{-7}	1.0 x 10^{-1}	50.8	0.1
1.02 x 10^{-6}	1.0 x 10^{-1}	48.7	0.07
3.16 x 10^{-6}	1.0 x 10^{-1}	47.4	0.1
1.01 x 10^{-5}	1.0 x 10^{-1}	45.4	0.1
3.20 x 10^{-5}	1.0 x 10^{-1}	43.0	0.1
9.96 x 10^{-5}	1.0 x 10^{-1}	40.5	0.08
3.18 x 10^{-4}	1.0 x 10^{-1}	38.0	0.07
1.01 x 10^{-3}	1.0 x 10^{-1}	34.4	0.05
3.15 x 10^{-3}	1.0 x 10^{-1}	31.7	0.04
1.01 x 10^{-2}	1.0 x 10^{-1}	28.7	0.03
3.40 x 10^{-2}	1.0 x 10^{-1}	25.6	0.03
1.00 x 10^{-1}	1.0 x 10^{-1}	23.5	0.03
1.00 x 10^{-10}	4.6 x 10^{-1}	48.6	0.09
1.00 x 10^{-7}	4.6 x 10^{-1}	49.7	0.1
3.19 x 10^{-7}	4.6 x 10^{-1}	50.1	0.1
1.02 x 10^{-6}	4.6 x 10^{-1}	48.7	0.3
3.16 x 10^{-6}	4.6 x 10^{-1}	46.7	0.1
1.01 x 10^{-5}	4.6 x 10^{-1}	43.8	0.06
3.20 x 10^{-5}	4.6 x 10^{-1}	41.2	0.06
9.96 x 10^{-5}	4.6 x 10^{-1}	38.6	0.06
3.18 x 10^{-4}	4.6 x 10^{-1}	36.0	0.06

1.01×10^{-3}	4.6×10^{-1}	32.7	0.04
3.15×10^{-3}	4.6×10^{-1}	30.0	0.03
1.01×10^{-2}	4.6×10^{-1}	26.8	0.06
3.40×10^{-2}	4.6×10^{-1}	23.9	0.04
1.00×10^{-1}	4.6×10^{-1}	22.0	0.02
1.00×10^{-10}	9.8×10^{-1}	49.7	0.2
1.00×10^{-7}	9.8×10^{-1}	49.7	0.08
3.19×10^{-7}	9.8×10^{-1}	48.8	0.09
1.02×10^{-6}	9.8×10^{-1}	48.0	0.09
3.16×10^{-6}	9.8×10^{-1}	45.5	0.1
1.01×10^{-5}	9.8×10^{-1}	42.6	0.08
3.20×10^{-5}	9.8×10^{-1}	39.7	0.09
9.96×10^{-5}	9.8×10^{-1}	37.1	0.06
3.18×10^{-4}	9.8×10^{-1}	34.3	0.06
1.01×10^{-3}	9.8×10^{-1}	31.2	0.03
3.15×10^{-3}	9.8×10^{-1}	28.3	0.04
1.01×10^{-2}	9.8×10^{-1}	25.3	0.03
3.40×10^{-2}	9.8×10^{-1}	22.4	0.02
1.00×10^{-1}	9.8×10^{-1}	20.7	0.02
1.00×10^{-10}	3.14	42.7	0.05
1.00×10^{-7}	3.14	43.5	0.04
3.19×10^{-7}	3.14	42.2	0.05
1.02×10^{-6}	3.14	42.5	0.05
3.16×10^{-6}	3.14	39.3	0.07
1.01×10^{-5}	3.14	36.4	0.04
3.20×10^{-5}	3.14	33.8	0.03
9.96×10^{-5}	3.14	31.7	0.03
3.18×10^{-4}	3.14	28.7	0.02
1.01×10^{-3}	3.14	25.7	0.01
3.15×10^{-3}	3.14	22.9	0.01
1.01×10^{-2}	3.14	20.5	0.01
3.40×10^{-2}	3.14	18.8	0.01
1.00×10^{-1}	3.14	18.1	0.01

Table S3. Rate constant values reported in Figure 5.

$[\mathbf{TODGA}]_f$ (M)	k_{ao} (cm s^{-1})	2σ k_{ao}	k_{oa} (cm s^{-1})	2σ k_{oa}
0.055	7.44 x 10^{-5}	1.55 x 10^{-5}	3.88 x 10^{-4}	9.7 x 10^{-5}
0.063	1.20 x 10^{-4}	2.0 x 10^{-5}	4.59 x 10^{-4}	9.1 x 10^{-5}
0.072	1.89 x 10^{-4}	2.3 x 10^{-5}	4.02 x 10^{-4}	5.6 x 10^{-5}
0.079	2.45 x 10^{-4}	2.2 x 10^{-5}	4.27 x 10^{-4}	4.6 x 10^{-5}
0.088	3.12 x 10^{-4}	2.3 x 10^{-5}	4.23 x 10^{-4}	3.8 x 10^{-5}
0.105	4.13 x 10^{-4}	3.2 x 10^{-5}	3.10 x 10^{-4}	2.6 x 10^{-5}
0.139	6.21 x 10^{-4}	8.8 x 10^{-5}	1.90 x 10^{-4}	2.8 x 10^{-5}
0.176	7.76 x 10^{-4}	1.07 x 10^{-4}	9.88 x 10^{-5}	1.4 x 10^{-5}
0.194	7.41 x 10^{-4}	5.6 x 10^{-5}	8.11 x 10^{-5}	6.7 x 10^{-6}
0.133	8.54 x 10^{-4}	1.03 x 10^{-4}	4.52 x 10^{-5}	5.6 x 10^{-6}
0.269	8.40 x 10^{-4}	6.5 x 10^{-5}	3.10 x 10^{-5}	2.5 x 10^{-6}
0.289	7.65 x 10^{-4}	5.9 x 10^{-5}	2.19 x 10^{-5}	1.8 x 10^{-6}
0.327	9.21 x 10^{-4}	6.6 x 10^{-5}	1.66 x 10^{-5}	1.2 x 10^{-6}
0.364	8.01 x 10^{-4}	1.07 x 10^{-4}	1.09 x 10^{-5}	1.5 x 10^{-6}

Table S4. Rate constant values reported in Figure 6A.

$\{\mathbf{NO_3}^-\}$	k_{ao} (cm s^{-1})	2σ k_{ao}	k_{oa} (cm s^{-1})	2σ k_{oa}
0.164	4.73 x 10^{-5}	1.2 x 10^{-5}	3.92 x 10^{-4}	1.34 x 10^{-4}
0.198	8.11 x 10^{-5}	1.6 x 10^{-5}	4.09 x 10^{-4}	1.05 x 10^{-4}
0.231	1.12 x 10^{-4}	1.8 x 10^{-5}	4.11 x 10^{-4}	8.8 x 10^{-5}
0.305	2.21 x 10^{-4}	3.1 x 10^{-5}	4.11 x 10^{-4}	6.9 x 10^{-5}
0.444	4.59 x 10^{-4}	4.2 x 10^{-5}	2.58 x 10^{-4}	2.9 x 10^{-5}
0.591	6.63 x 10^{-4}	7.7 x 10^{-5}	1.36 x 10^{-4}	1.8 x 10^{-5}
0.744	7.78 x 10^{-4}	7.9 x 10^{-5}	5.52 x 10^{-5}	6.2 x 10^{-6}
0.901	8.77 x 10^{-4}	1.14 x 10^{-4}	2.42 x 10^{-5}	3.3 x 10^{-6}
1.23	9.44 x 10^{-4}	1.07 x 10^{-4}	7.41 x 10^{-6}	9.2 x 10^{-7}
1.41	9.63 x 10^{-4}	1.08 x 10^{-4}	4.80 x 10^{-6}	6.2 x 10^{-7}
1.60	9.60 x 10^{-4}	1.75 x 10^{-4}	2.91 x 10^{-6}	5.5 x 10^{-7}
1.80	1.03 x 10^{-3}	1.72 x 10^{-4}	2.12 x 10^{-6}	3.9 x 10^{-7}
2.22	1.08 x 10^{-3}	1.39 x 10^{-4}	1.05 x 10^{-6}	1.5 x 10^{-7}
2.69	1.13 x 10^{-3}	1.54 x 10^{-4}	5.82 x 10^{-7}	8.8 x 10^{-8}

Table S5. Rate constant values reported in Figure S6A.

$\overline{[\mathbf{TODGA}]}_f$ **(M)**	k_{obs} **(s^{-1})**	**2σ**
0.055	0.131	1.9×10^{-2}
0.063	0.164	2.0×10^{-2}
0.072	0.168	1.6×10^{-2}
0.079	0.191	1.2×10^{-2}
0.088	0.209	1.2×10^{-2}
0.105	0.205	1.4×10^{-2}
0.139	0.230	3.2×10^{-2}
0.176	0.248	3.4×10^{-2}
0.194	0.233	1.6×10^{-2}
0.133	0.255	3.0×10^{-2}
0.269	0.247	1.8×10^{-2}
0.289	0.223	1.6×10^{-2}
0.327	0.266	1.8×10^{-2}
0.364	0.230	3.0×10^{-2}

Table S6. Rate constant values reported in Figure S6B.

$\{\mathbf{NO_3}^-\}$	k_{obs} **(s^{-1})**	**2σ**
0.164	0.124	2×10^{-3}
0.198	0.139	1.0×10^{-2}
0.231	0.148	1.6×10^{-2}
0.305	0.179	1.2×10^{-2}
0.444	0.203	1.4×10^{-2}
0.591	0.227	1.6×10^{-2}
0.744	0.236	2.8×10^{-2}
0.901	0.255	3.2×10^{-2}
1.23	0.270	2.8×10^{-2}
1.41	0.274	2.4×10^{-2}
1.60	0.273	5.0×10^{-2}
1.80	0.293	6.0×10^{-2}
2.22	0.307	4.6×10^{-2}
2.69	0.321	3.4×10^{-2}

Table S7. Rate constant values reported in Figure S7.

Stirring speed (rps)	k_{obs} (s^{-1})	2σ
20	0.007	1 x 10^{-3}
30	0.096	1.3 x 10^{-2}
40	0.198	1.3 x 10^{-2}
50	0.295	3.8 x 10^{-2}
60	0.363	2.4 x 10^{-2}
70	0.323	2.8 x 10^{-2}
80	0.343	2.4 x 10^{-2}
100	0.336	5.1 x 10^{-2}

Table S8. Temperature dependence of the extraction equilibrium constants reported in Figure S8.

Temperature (°C)	D_{Nd}	2σ	ln K_{ex}	2σ
11.0	2.89	0.12	11.46	0.04
15.0	1.98	0.27	11.09	0.14
20.0	1.16	0.06	10.57	0.05
25.0	0.875	0.075	10.31	0.09
30.0	0.552	0.038	9.87	0.07
35.0	0.401	0.030	9.57	0.08
39.0	0.306	0.019	9.31	0.06

Table S9. Temperature dependence of the rate constants reported in Figure S9.

Temperature (°C)	ln k_{ao}	2σ	ln k_{oa}	2σ
15.0	-7.51	0.15	-8.14	0.21
20.0	-7.78	0.09	-7.93	0.11
25.0	-8.00	0.18	-7.87	0.20
30.0	-8.33	0.10	-7.73	0.12
35.0	-8.59	0.17	-7.65	0.19

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