Supplementary Information for: A multicomponent model for the prediction of nuclear waste / rare-earth extraction processes

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Study of harmonic approximation $(p - p_0)^2$

Influence of the spontaneous packing parameter p_0 on the position of the valley of zero-chain energy

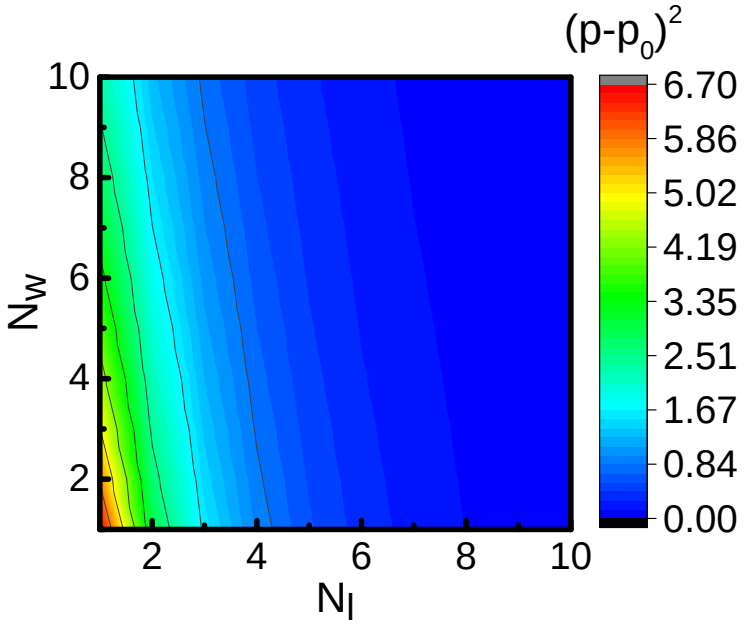

Figure S1: Map of squared differences between calculated packing parameter p for a given composition of the core of the aggregate and spontaneous packing parameter p_0. The core contains one salt molecule, namely $Eu(NO_3)_3$. N_l depicts number of extractant, whereas N_w depicts number of water molecules present in the core. The calculation has been made with $p_0 = 2.5$.

Figures S1 and S2 show a map of $(p - p_0)^2$ as a function of composition of aggregate core. In both examples the position of the 'valley' of low F_{chain} corresponds to the high aggregation numbers and high water content.

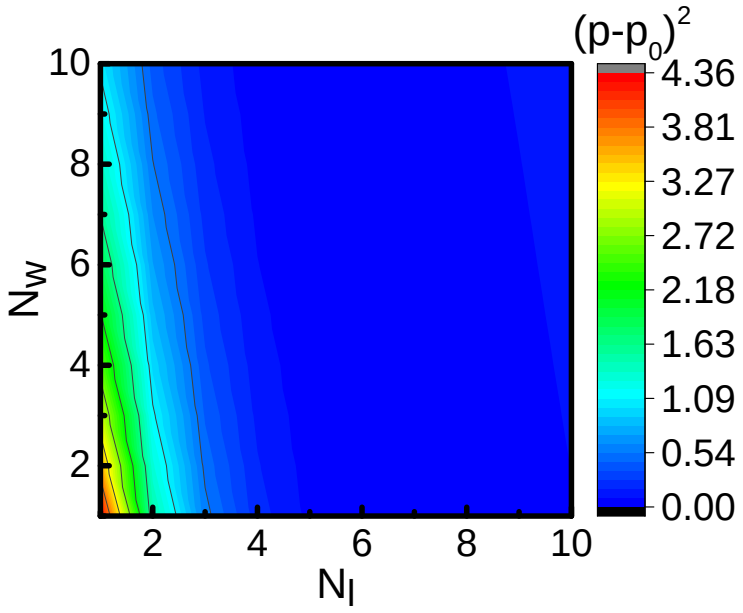

Figure S2: The map of squared differences between calculated packing parameter p and spontaneous packing parameter p_0 on a composition of the core of the aggregate. The core contains one salt molecule, namely $Eu(NO_3)_3$. N_l depicts number of extractant, whereas N_w depicts number of water molecules present in the core. The calculation has been made with $p_0 = 3$.

Influence of spontaneous packing parameter p_0 on aggregate probabilities

The value of p_0 effects the equilibrium aggregate compositions. Figure S3 and S4 show the calculated probabilities of aggregates using $p_0 = 2.5$ and 3, respectively. In both cases the method is not self-consistent, which means that the upper limit of N_l and N_w effects the results of the calculations. The most probable aggregates calculated using $p_0 = 2.5$ and 3 do not represent a realistic picture of the aggregates (when comparing these results with experiments).

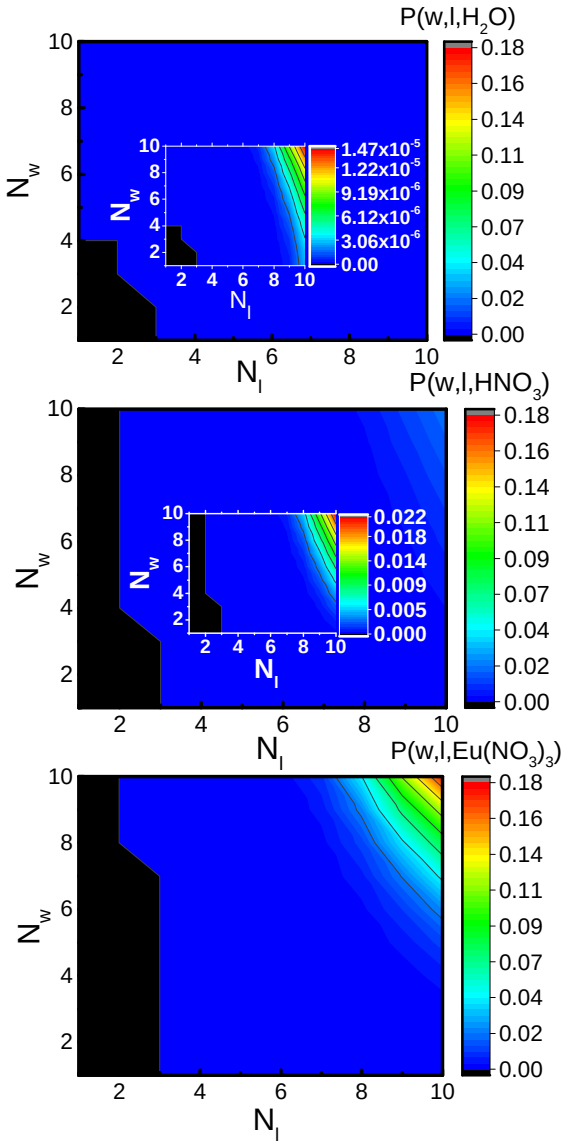

Figure S3: Calculated equilibrium aggregate probabilities as a function of the composition of the core of the aggregate. N_l depicts number of extractant, whereas N_w depicts number of water molecules present in the core. The model parameters are: $p_0 = 2.5$, $\kappa^\star = 16\ k_\mathrm{b}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 2.5$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{b}T$ per complexed ion. System in study: $c_{\mathrm{l,initial}} = 0.6$ mol dm^{-3}, $m_{\mathrm{H(NO_3),initial}} = 3$ mol kg^{-1},$m_{\mathrm{Eu(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. Figures show respectively the equilibrium aggregate probabilities for H_2O, HNO_3 and $Eu(NO_3)_3$ (solutes inside the core, from top to bottom). Insets in figures show scaled probabilities with purpose of easier understanding for the reader.

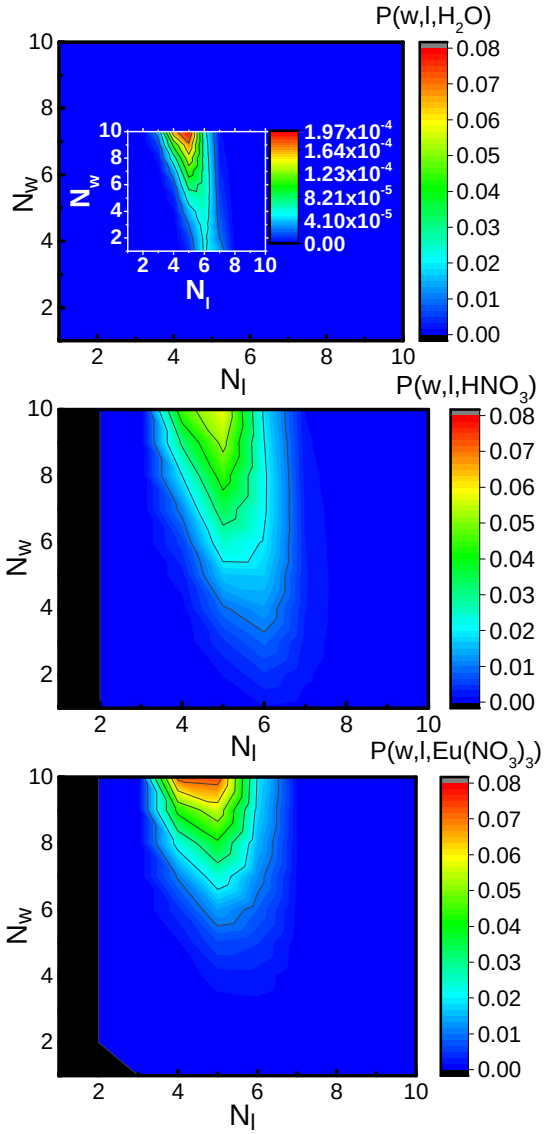

Figure S4: Dependence of the equilibrium aggregate probabilities on composition of the core of the aggregate. N_l depicts number of extractant, whereas N_w depicts number of water molecules present in the core. The model parameters are: $p_0 = 3$, $\kappa^\star = 16\ k_\mathrm{b}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 3$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{b}T$ per complexed ion. System in study: $c_{\mathrm{l,initial}} = 0.6$ mol dm^{-3}, $m_{\mathrm{H(NO_3),initial}} = 3$ mol kg^{-1},$m_{\mathrm{Eu(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. Figures show respectively the equilibrium aggregate probabilities for H_2O, HNO_3 and $Eu(NO_3)_3$ (solutes inside the core, from top to bottom). Insets in figures show scaled probabilities with purpose of easier understanding for the reader.

Influence of rigidity constant $\kappa^\star$ on the chain free energy, F_{chain} and aggregate probabilities

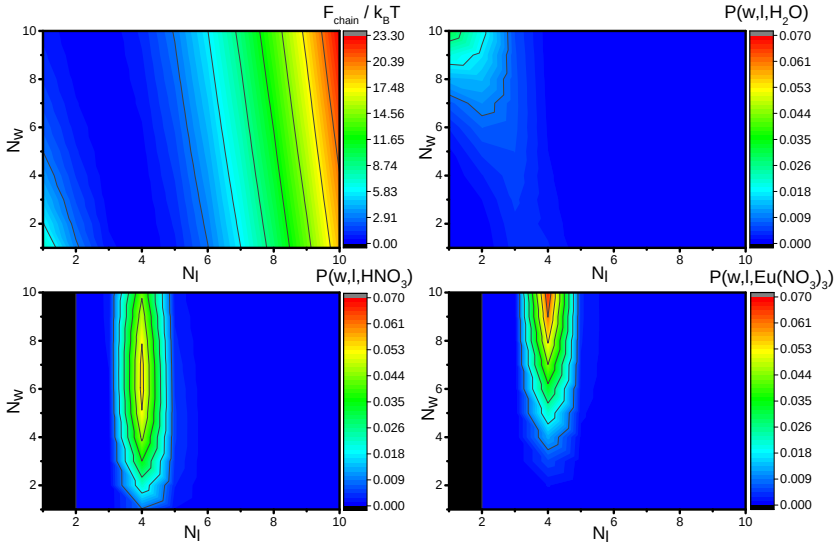

Figure S5: Dependence of the equilibrium aggregate probabilities and chain term energy on composition of the core of the aggregate. The model parameters are: $p_0 = 3.5$, , $\mu_{\text{l}}^\circ = 3$ kJ/mol, $E_{0,\text{HNO}_3} = 5$, $E_{0,\text{Eu(NO}_3)_3} = 15.6\ k_{\text{b}}T$ per complexed ion, $\kappa^\star = 6\ k_{\text{b}}T$ per extractant molecule. System in study: $c_{\text{l,initial}} = 0.6$ mol dm^{-3}, $m_{\text{H(NO}_3),\text{initial}} = 3$ mol kg^{-1},$m_{\text{Eu(NO}_3)_3,\text{initial}} = 0.05$ mol kg^{-1}. The upper right and the two bottom figures show respectively the equilibrium aggregate probabilities for H_2O, HNO_3 and $Eu(NO_3)_3$ (solutes inside the core). Insets in figures show scaled probabilities with purpose of easier understanding for the reader. Results: CAC=0.06M, $D_{\text{Eu}^{3+}} = 14.67$

$\kappa^\star$ influences the width of the chain energy valley in a way that increase of $\kappa^\star$ increases the gradient of F_{chain} plane. Consequently, higher values of $\kappa^\star$ (in our calculation 26 $k_{\text{B}}T$ per extractant molecule, Figure S7) allow assembly of aggregates with smaller number of water molecules. For $\kappa^\star = 6\ k_{\text{B}}T$ the valley of low F_{chain} is rather wide so the dilution of the core of the aggregate is highly favorable. As a consequence, the unrealistic aggregates are favored.

It can be concluded that higher rigidity reduces polydispersity in terms of water content.

Distribution coefficient of Eu^{3+}, $D_{Eu^{3+}}$ is around 15 and CAC around 0.06 M when $\kappa^\star = 6$ k_BT, whereas for $\kappa^\star = 26$ k_BT $D_{Eu^{3+}}$ is around 6 and CAC around 0.08 M. The best values are obtained when $\kappa^\star = 16$ k_BT. The extraction reads $D_{Eu^{3+}} = 9.15$ at $c_{l,initial} = 0.6$ mol dm^{-3}, $m_{H(NO_3),initial} = 3$ mol kg^{-1},$m_{Eu(NO_3)_3,initial} = 0.05$ mol kg^{-1}.

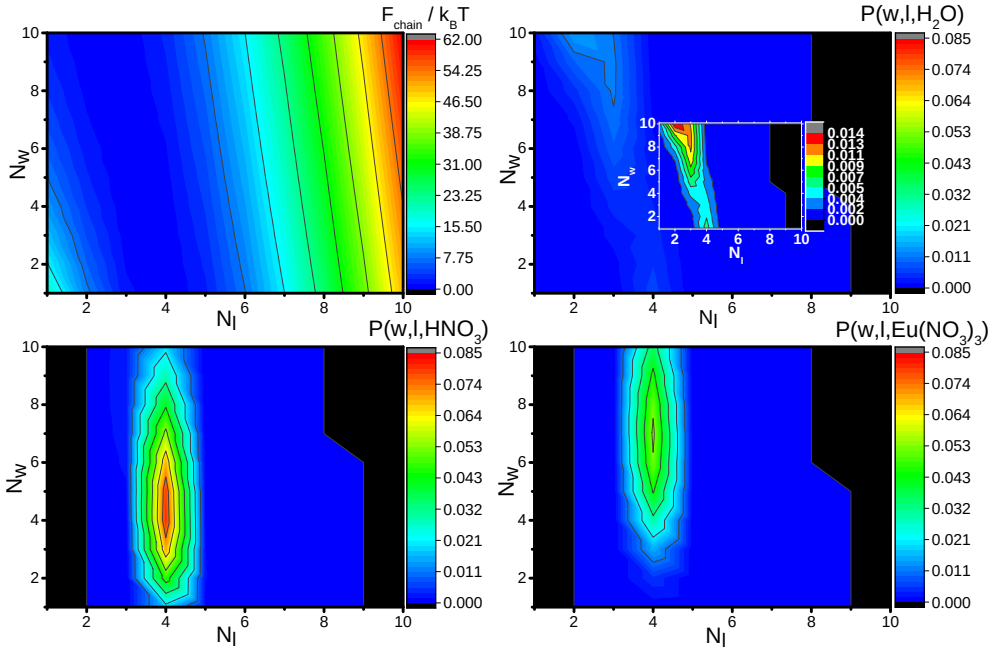

Figure S6: Dependence of the equilibrium aggregate probabilities and chain term energy on composition of the core of the aggregate. The model parameters are: $p_0 = 3.5$, , $\mu_l^\circ = 3$ kJ/mol, $E_{0,HNO_3} = 5$, $E_{0,Eu(NO_3)_3} = 15.6$ k_bT per complexed ion, $\kappa^\star = 16$ k_bT per extractant molecule. System in study: $c_{l,initial} = 0.6$ mol dm^{-3}, $m_{H(NO_3),initial} = 3$ mol kg^{-1},$m_{Eu(NO_3)_3,initial} = 0.05$ mol kg^{-1}. The upper right and the two bottom figures show respectively the equilibrium aggregate probabilities for H_2O, HNO_3 and $Eu(NO_3)_3$ (solutes inside the core). Insets in figures show scaled probabilities with purpose of easier understanding for the reader. Results: CAC=0.07M, $D_{Eu^{3+}} = 9.15$

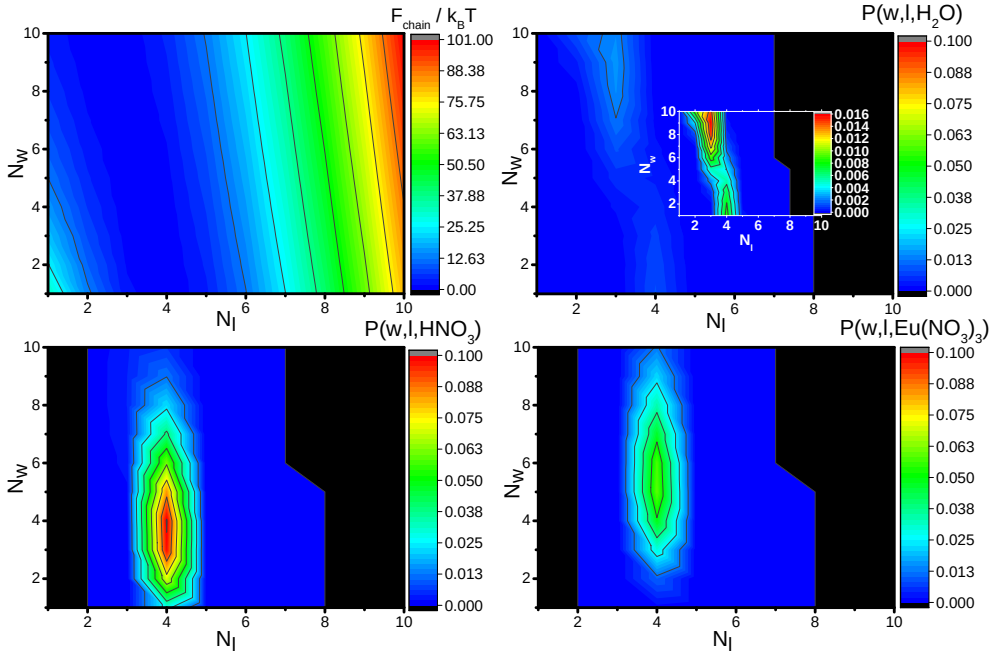

Figure S7: Dependence of the equilibrium aggregate probabilities and chain term energy on composition of the core of the aggregate. The model parameters are: $p_0 = 3.5$, , $\mu_{\mathrm{l}}^{\circ} = 3$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_{\mathrm{b}}T$ per complexed ion, $\kappa^{\star} = 26\ k_{\mathrm{b}}T$ per extractant molecule. System in study: $c_{\mathrm{l,initial}} = 0.6$ mol dm^{-3}, $m_{\mathrm{H(NO_3),initial}} = 3$ mol kg^{-1},$m_{\mathrm{Eu(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. The upper left figure shows F_{chain} as a function of the composition of aggregate core. The upper right and the two bottom figures show respectively the equilibrium aggregate probabilities for H_2O, HNO_3 and $Eu(NO_3)_3$ (solutes inside the core). Insets in figures show scaled probabilities with purpose of easier understanding for the reader. Results: CAC=0.08M, $D_{\mathrm{Eu^{3+}}} = 5.72$

Aggregate probabilities at different system compositions

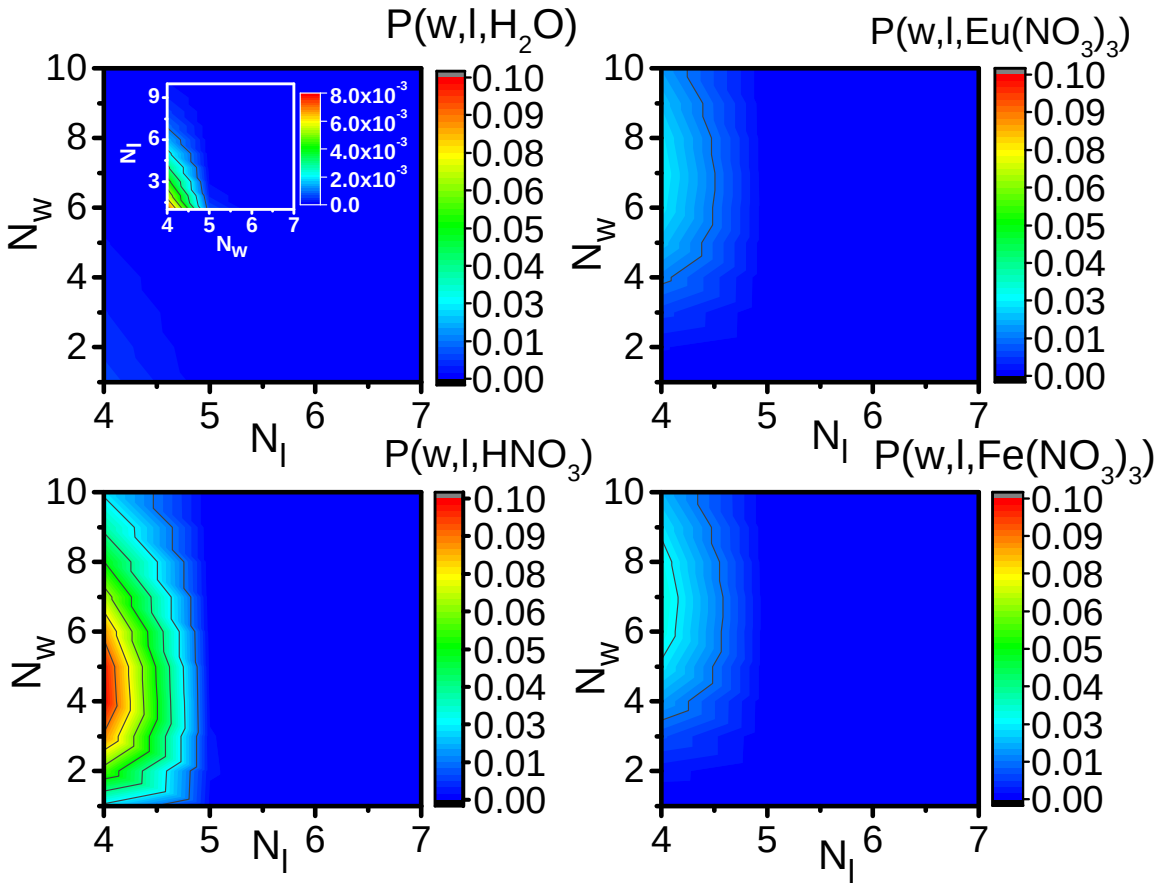

Figure S8: Dependence of the equilibrium aggregate probabilities on composition of the core of the aggregate. N_l depicts number of extractant, whereas N_w depicts number of water molecules present in the core. Scaled results of the upper left figure are shown in its inset. The model parameters are: $p_0 = 3.5$, $\kappa^\star = 16\ k_\mathrm{B}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 2.5$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5\ k_\mathrm{B}T$, $E_{0,\mathrm{Fe(NO_3)_3}} = 13\ k_\mathrm{B}T$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{B}T$ per complexed ion. The system in study is as follows: $c_{\mathrm{l,initial}} = 0.605$ mol dm^{-3}, $m_{\mathrm{HNO_3,initial}} = 3$ moi kg^{-1} and $m_{\mathrm{Eu(NO_3)_3,initial}} = 0.02$ mol kg^{-1}, $m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}.

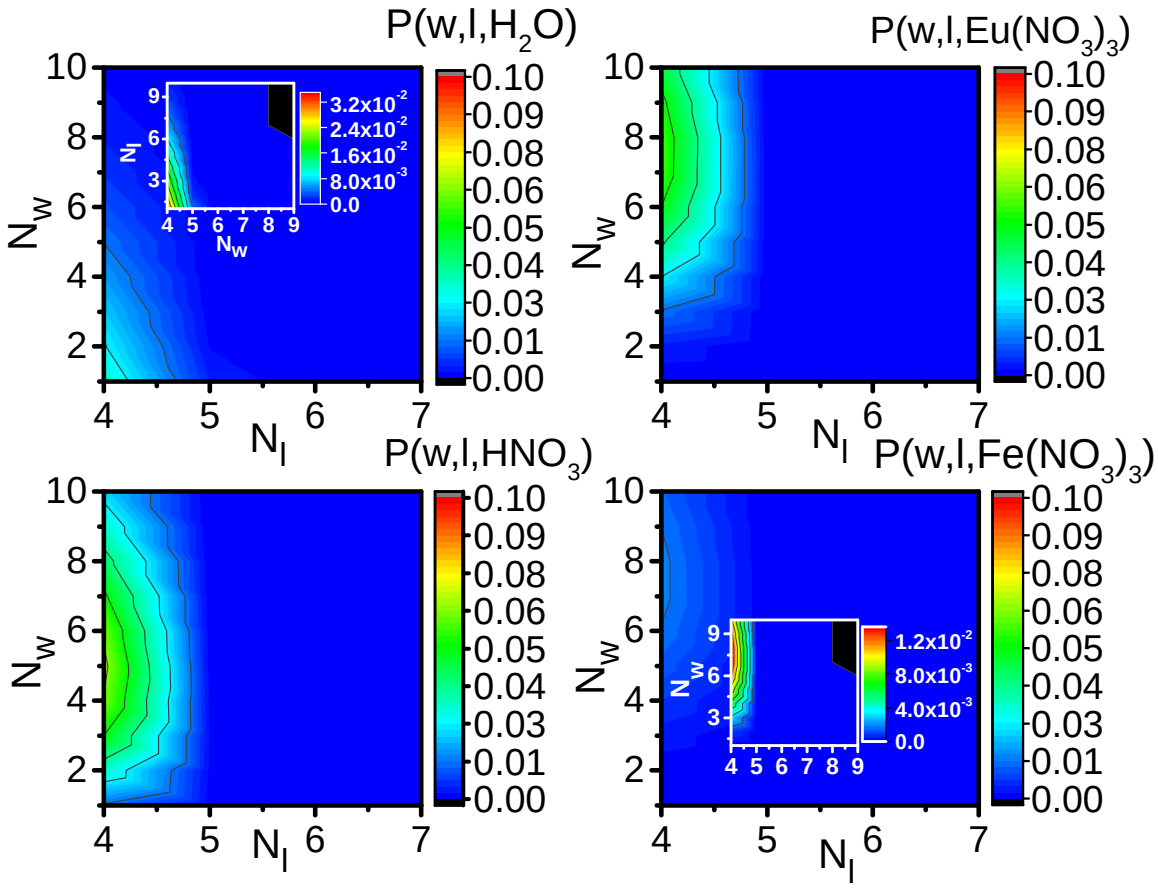

Figure S9: Dependence of the equilibrium aggregate probabilities on composition of the core of the aggregate. N_l depicts number of extractant, whereas N_w depicts number of water molecules present in the core. Scaled results of the upper left and lower right figure are shown in its insets. The model parameters are: $p_0 = 3.5$, $\kappa^\star = 16\ k_\mathrm{B}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 2.5$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5\ k_\mathrm{B}T$, $E_{0,\mathrm{Fe(NO_3)_3}} = 13\ k_\mathrm{B}T$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{B}T$ per complexed ion. The system in study is as follows: $c_{\mathrm{l,initial}} = 0.605$ mol dm^{-3}, $m_{\mathrm{HNO_3,initial}} = 1$ mol kg^{-1} and $m_{\mathrm{Eu(NO_3)_3,initial}} = 0.05$ mol kg^{-1}, $m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}.

The extraction of metal ions at various physical conditions

The extraction curve presented in Figure S12 shows the influence of $c_{\mathrm{l,initial}}$ on $D_{\mathrm{Eu^{3+}}}$. The results are shown for various HNO_3 concentration, ranging from 0.5 to 5 mol kg^{-1}.

The results show the nonlinear increase of distribution coefficients with increasing $c_{\mathrm{l,initial}}$. The increase in $m_{\mathrm{HNO_3,initial}}$ causes an increase in $D_{\mathrm{Cat,i}}$ which means that the extraction is enhanced upon addition of HNO_3 the system. This is a consequence of the decrease of gradient of NO_3^- concentrations between aqueous phase and the concentration in the core of aggregates.

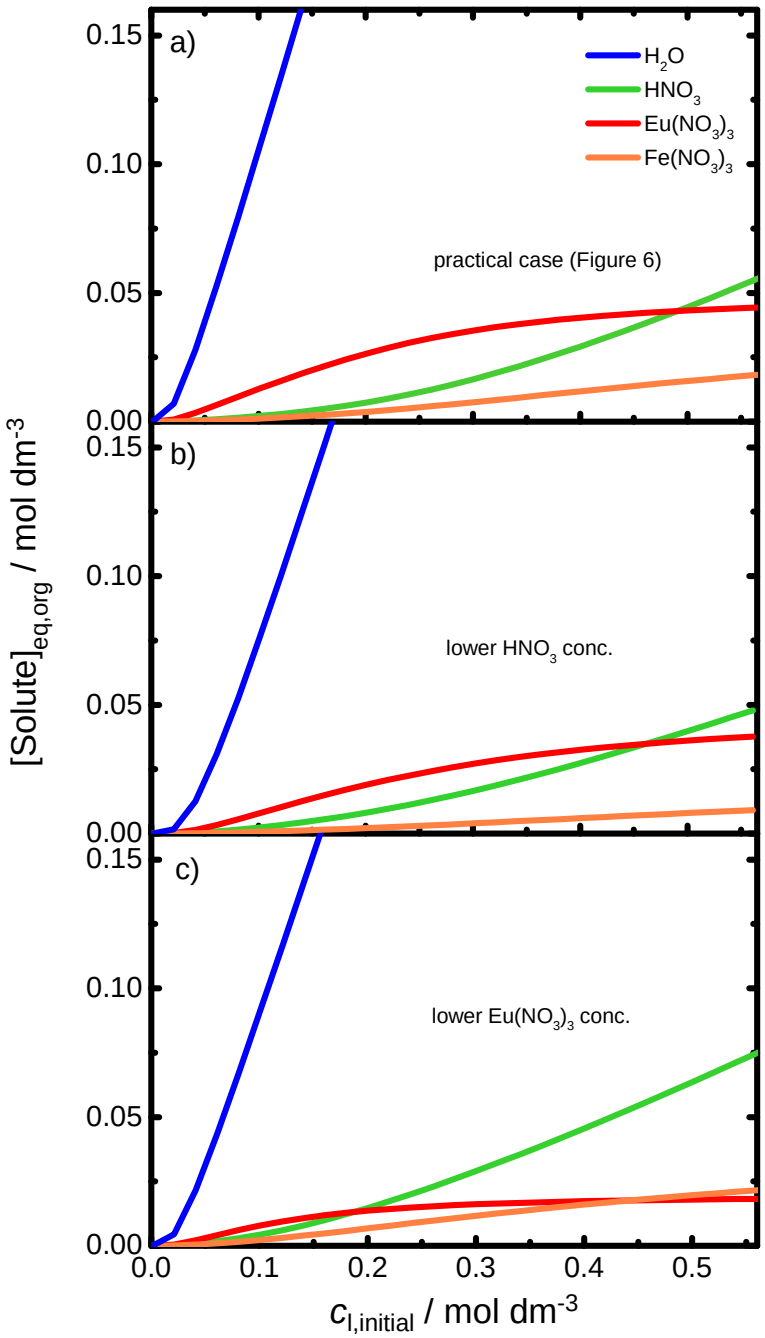

Figure S10: Calculated equilibrium concentrations of all extracted solutes as a function of the initial extractant concentration. The model parameters are: $p_0 = 3.5$, $\kappa^\star = 16\ k_\mathrm{B}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 2.5$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5\ k_\mathrm{B}T$, $E_{0,\mathrm{Fe(NO_3)_3}} = 13\ k_\mathrm{B}T$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{B}T$ per complexed ion. a) $m_{\mathrm{HNO_3,initial}} = 3$ mol kg^{-1}, $m_{\mathrm{Eu(NO_3)_3,initial}} = m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. b) $m_{\mathrm{HNO_3,initial}} = 1$ mol kg^{-1}, $m_{\mathrm{Eu(NO_3)_3,initial}} = m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. c) $m_{\mathrm{HNO_3,initial}} = 3$ mol kg^{-1}, $m_{\mathrm{Eu(NO_3)_3,initial}} = 0.02$ mol kg^{-1} , $m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}.

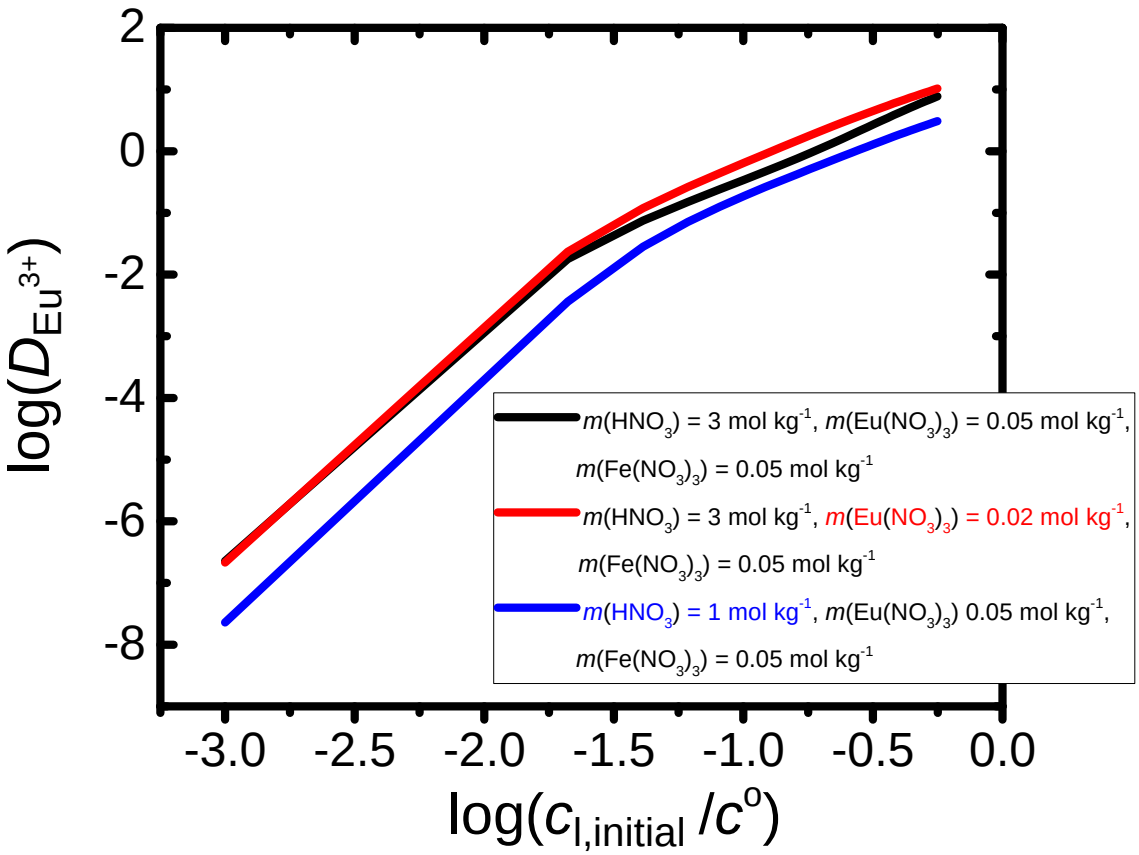

Figure S11: Decimal logarithm of Eu^{3+} distribution coefficient as a function of decimal logarithm of the initial extractant concentration. The model parameters are: $p_0 = 3.5$, $\kappa^\star = 16\ k_\mathrm{B}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 2.5$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5\ k_\mathrm{B}T$, $E_{0,\mathrm{Fe(NO_3)_3}} = 13\ k_\mathrm{B}T$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{B}T$ per complexed ion. The black curve depicts the system: $m_{\mathrm{HNO_3,initial}} = 3$ mol kg^{-1}, $m_{\mathrm{Eu(NO_3)_3,initial}} = m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. The red curve depicts the system: $m_{\mathrm{HNO_3,initial}} = 3$ mol kg^{-1}, $m_{\mathrm{Eu(NO_3)_3,initial}} = 0.02$ mol kg^{-1} , $m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. The blue curve depicts the system: $m_{\mathrm{HNO_3,initial}} = 1$ mol kg^{-1}, $m_{\mathrm{Eu(NO_3)_3,initial}} = m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}.

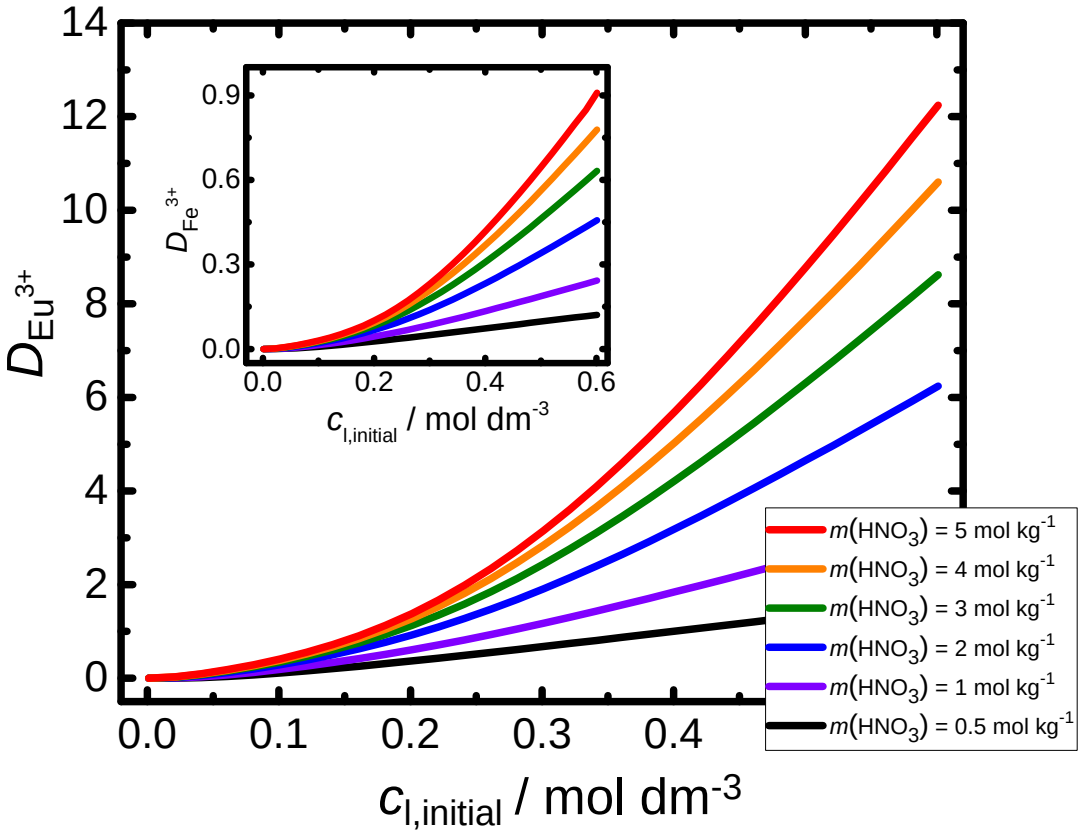

Figure S12: $D_{\mathrm{Eu}^{3+}}$ as a function of the initial extractant concentration. The model parameters are: $p_0 = 3.5$, $\kappa^\star = 16\ k_\mathrm{B}T$ per extractant molecule, $\mu_\mathrm{l}^\circ = 2.5$ kJ/mol, $E_{0,\mathrm{HNO_3}} = 5\ k_\mathrm{B}T$, $E_{0,\mathrm{Fe(NO_3)_3}} = 13\ k_\mathrm{B}T$, $E_{0,\mathrm{Eu(NO_3)_3}} = 15.6\ k_\mathrm{B}T$ per complexed ion. The system in study is: $m_{\mathrm{Eu(NO_3)_3,initial}} = m_{\mathrm{Fe(NO_3)_3,initial}} = 0.05$ mol kg^{-1}. The results are presented for various concentrations of nitric acid in aqueous phase. The equivalent curve for the extraction of Fe^{3+} is presented in the inset.