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Introduction

The prices of rare-earth (RE) elements (Sc, Y, and the lanthanides) have been volatile in the past decade after the “Rare-Earth Crisis” between 2009 and 2011, leading to supply shortages of these critical metals.¹ Recycling RE elements from their mixtures can help mitigate this balance problem by adding recycled REs to the global supply chain.² Historically and commercially, RE elements are separated using technologies such as solvent extraction, ion exchange chromatography, and selective precipitation, all of which use the difference in sizes of the RE elements.^{3–5} However, these processes require large amounts of solvents and energy, which contributes to the price of the elements and generates waste causing negative environmental footprints, especially near RE processing facilities.^{6,7}

Previous works in our group demonstrated various low-energy and environmentally friendly RE separation methods that used minimal solvents, targeted intrinsic properties of RE ions other than size, and were controlled by molecular speciation.⁸ A recent study aimed at targeting magnetic properties of RE³⁺ cations, due to their unfilled 4f orbitals, to achieve a magnetic separation step based on variable migration of paramagnetic cations in the presence of an applied magnetic field.⁹ This strategy was used in separating molecular RE-complexes of the [TriNOx]³⁻ ligand using Fe₁₄Nd₂B permanent magnets (Chart 1).¹⁰ This low energy input separation

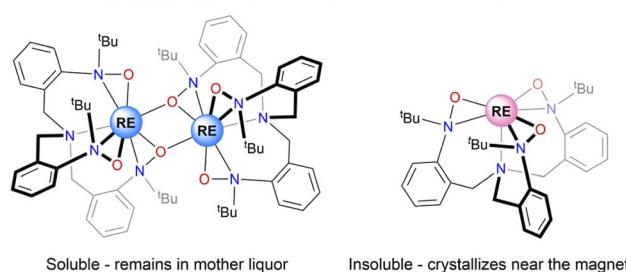
Harnessing magnetic fields for rare-earth complex crystallization–separations in aqueous solutions†

Amit Kumar, Han Geng and Eric J. Schelter *

Magnetic field-directed crystallization separation of rare-earth (RE) metals is emerging as a new direction in the field of separation science, due to its simplicity, low energy input, and low cost of operation, as compared to traditional separation methods such as solvent extraction. Here, we report the use of Fe₁₄Nd₂B magnets for selective crystallization of paramagnetic Nd, Dy, Er, and Tm rare earth compounds from a mixture with diamagnetic La ones using the RE–DOTA complex system. All the separations were performed at milder temperatures of 3 °C to provide a thermal gradient, and the crystallizations were set up in aqueous solutions using the benign solvents water and acetone. A four-fold increase in the separation factor (41.4 ± 0.6) was observed for the Dy/La pair in the presence of a magnetic field as compared to the separation factor (10.5 ± 0.9) obtained without the application of the field. These results indicate that the use of the magnetic crystallization method for RE separations is effective in aqueous systems and can be a useful strategy for energy-efficient molecular separations of RE metals.

method allowed for the enhancement of experimental separation factors¹¹ by approximately 100% for the La/Dy pair. It was also suggested that the achieved separation depended on the free-ion angular momentum ($J = 7.5$ for Dy³⁺) of the trivalent RE cations in its electronic ground state as well as on the monomer–dimer equilibrium that was studied for this system. In this case, solubility differences between the more soluble dimeric

Previous Work - Separations performed in 1:3 CHCl₃/hexane



This Work - Separations performed in 1:3 H₂O/acetone

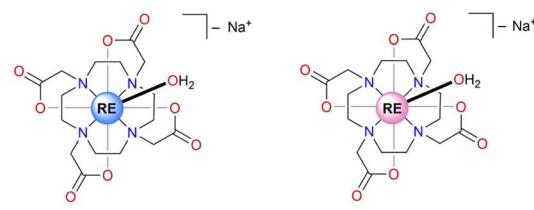


Chart 1

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 S. 34th St., Philadelphia, PA, 19104, USA. E-mail: schelter@sas.upenn.edu

† Electronic supplementary information (ESI) available. See <https://doi.org/10.1039/d2ra04729b>



[RE(TriNOx)]₂ complex, formed by LRE (light rare earth), and the less soluble monomeric [RE(TriNOx)], formed by HRE (heavy rare earth), were primarily responsible for the enhancement in the separation factors (SF) (Chart 1). Due to the air-sensitive nature of [RE(TriNOx)] complexes, the separations were performed under an inert atmosphere and required the use of organic solvents including a chlorinated solvent, CHCl₃.

For the current work, we were interested in investigating the effect of magnetic crystallization separation in environmentally friendly solvents, such as water, and using an established ligand framework that does not have monomer–dimer equilibrium. We hypothesized that the absence of this equilibrium would ensure that the effect of the magnetic field on the separations was only dependent on the identity of the RE ion.

For our work, we chose a common chelating ligand DOTA⁴⁻ (1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetate), whose chemistry with RE cations is well-established, to prepare a series of complexes. We chose this system since, in addition to its well-established coordination chemistry and inertness towards exchange of the cations, magnetic studies have been performed on the RE–DOTA complexes, especially to understand properties such as their magnetic anisotropy and magnetic relaxation.^{12–14} Ideal magnetic crystallization separation ligand systems would include ligands that promote large magnetic anisotropy differences at the metal cations under aerobic conditions.

Herein, we report the separation of selected paramagnetic RE ions (Nd, Dy, Er, and Tm) from a diamagnetic RE ion (La) using a magnetic crystallization process. For these studies, we subjected the RE–DOTA complexes to magnetic and thermal-gradient crystallization using an external field provided by a Fe₁₄Nd₂B magnet. After performing ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) to analyze metal content of the crystals and the mother liquor, we observed an enrichment of paramagnetic RE ions in the crystals and enrichment of diamagnetic La in the mother liquor, giving an upper bound of a four-fold increase in the separation factor for the Dy/La pair.

Results & discussion

For the current study, RE–DOTA (formulated as Na[RE(DOTA)(H₂O)]·4H₂O, RE = La, Nd, Dy, Er, Tm) complexes were synthesized using published procedures.^{12,15} Refluxing the RE-oxides RE₂O₃ with 0.5 equiv. H₄DOTA (1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid) in the presence of 1 equivalent of NaOH in Milli-Q water for 3–4 days afforded the corresponding RE–DOTA complexes in 50–60% yields. The crude complexes were crystallized for the separations experiments by vapor diffusion of acetone into a concentrated solution of RE–DOTA complexes in water at room temperature. We performed unit cell checks on the single crystals of RE–DOTA complexes using X-ray diffraction (XRD) and confirmed the expected formulation of these complexes as Na[RE(DOTA)(H₂O)]·4H₂O, as previously reported.¹⁴ The presence of the RE-bound H₂O molecule was of interest in our experiments, as the position of the hydrogen atoms on the bound water molecule

dictates the easy axis orientation, and magnetic anisotropy therein, of the molecule in question.¹⁴ We envisioned that these magnetic properties of RE–DOTA complexes will result in enhanced separation of a paramagnetic RE ion from a diamagnetic RE ion in the presence of a magnetic field.

With the RE–DOTA complexes in hand, we moved on to performing separations experiment using Fe₁₄Nd₂B permanent magnets (12.7 × 12.7 × 3.2 mm³) as was previously used in work by Evans,¹⁶ and also by our group in the recent work on separations using magnetic crystallization.¹⁰ Following similar experimental protocols from our previous work, we carried out our separations experiment on selected binary mixtures of RE–DOTA complexes where the concentration of individual RE–DOTA complexes in solution was kept constant at 0.025 M at 3 °C (Fig. 1). The binary mixtures were dissolved in 1 mL of water and layered with 3 mL of acetone to induce crystallization. The Fe₁₄Nd₂B permanent magnet in our group's previous work was attached to the vial by using an insulating tape or a rubber band. To avoid any changes to the experimental setup, we designed a sample holder using a 3D printer that contained a slot for holding a 4 mL vial and a slot for the magnet at a 2 mm distance from the vial (Fig. 2). The distance of 2 mm was chosen based on the reported magnetic flux density as a function of distance, measured by Berlinguette & coworkers using a Hall probe.¹⁷

After 72 h, crystals were observed near the magnet and the solid and filtrate portions were separated by decantation and analyzed by ICP-OES. As a control, we also performed the separations without the presence of a magnetic field. The results from the ICP-OES were used to calculate the enrichment factors (EF) and separation factors (SF) in both fractions (see ESI† for example calculation) (Table 1).

The observed separation factors with RE–DOTA complexes are relatively smaller as compared to that observed for the RE–TriNOx complexes (41.4 *versus* 494 for La/Dy pair). This difference is presumably due to the monomer–dimer equilibrium in

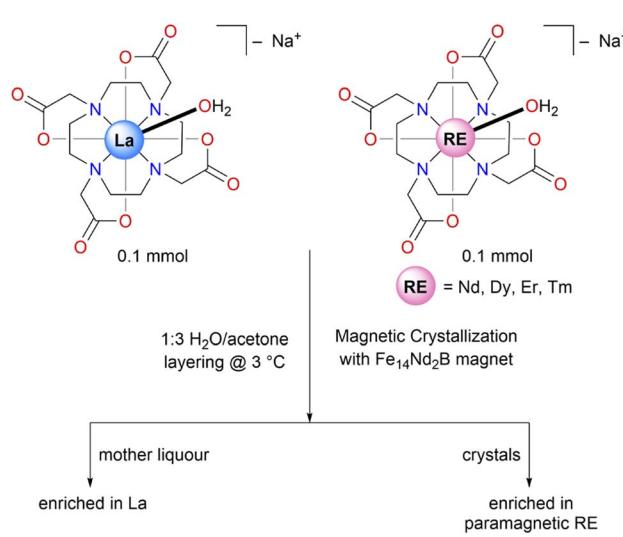


Fig. 1 Schematic diagram of the La/RE (RE = Nd, Dy, Er, Tm) separation process.





Fig. 2 Left: 3D printed holder containing the binary mixture of RE elements at 2 mm distance to a $\text{Fe}_{14}\text{Nd}_2\text{B}$ magnet. Right: Crystals formed near the magnet after holding the binary mixture solution at the magnet for 72 h at 3 °C.

Table 1 Separation factors¹¹ for RE binary mixtures at 3 °C in the absence of a magnetic field (entries 1–4) and the presence of a magnetic field (entries 5–8). All measurements were performed in triplicate

| Entry | Rare-earth pair | EF (crystals) | EF (mother liquor) | SF |
|-------|-----------------|---------------|--------------------|-------------|
| 1 | La/Nd | 2.14 ± 0.18 | 1.48 ± 0.07 | 3.56 ± 0.36 |
| 2 | La/Dy | 2.95 ± 0.19 | 3.57 ± 0.54 | 10.5 ± 0.9 |
| 3 | La/Er | 2.61 ± 0.75 | 1.70 ± 0.36 | 4.60 ± 0.15 |
| 4 | La/Tm | 3.82 ± 0.76 | 1.20 ± 0.15 | 4.63 ± 1.49 |
| 5 | La/Nd | 2.48 ± 0.28 | 1.78 ± 0.04 | 3.86 ± 0.38 |
| 6 | La/Dy | 3.41 ± 0.06 | 12.1 ± 0.1 | 41.4 ± 0.6 |
| 7 | La/Er | 3.48 ± 0.39 | 1.78 ± 0.38 | 6.01 ± 0.26 |
| 8 | La/Tm | 4.08 ± 0.42 | 1.76 ± 0.17 | 7.15 ± 0.05 |

the case of RE-TriNO_x complexes, an equilibrium that is tied to the solubility differences for the two metal complex forms. Such a speciation equilibrium is not present in the case of the RE-DOTA complexes, however. Nonetheless, we see an increase in the SFs for all four pairs of binary mixtures with the application of the field as compared to SFs obtained without an applied field. Moreover, for La/Dy binary mixture, a four-fold increase in the SF in the presence of a magnet was observed as compared to separations performed without a magnet. This result could be attributable to the high *J* value of Dy³⁺ ion and also the presence of “missed” easy plane anisotropy in Dy-DOTA species.¹⁴ Notably, the four-fold increase in the SF observed for La/Dy pair for RE-DOTA complexes (from 10.5 to 41.4) is more than the two-fold increase in the SF observed for the RE-TriNO_x case (from 258 to 494). On the other hand, the magnetic-field assisted enhancement in the separation factor (from 3.56 to 3.86) for the LRE (Nd) is significantly smaller than that observed (from 4.63 to 7.15 for Tm) for the HREs (Dy, Er, Tm). These could be attributed to both the differences in the ionic radii of the RE³⁺ ions and their total angular momentum values (*J*). For instance, the Nd³⁺ ion has the smallest *J* value (4.5) in our series

and is closest in size to the La³⁺ ion (1.16 and 1.22 for C.N. of 10, respectively).¹⁸ We hypothesize that these collective properties could be responsible for the smaller enhancement in the separation factor observed for La/Nd pair as compared to La/HRE pairs. Notably, similar ionic radii of Er³⁺ and Tm³⁺ (1.06 and 1.05 for C.N. of 10, respectively) and the closeness in their *J* values (7.5 and 6.5, respectively) are reflected in their similar separation factors (6.01 and 7.15, respectively).

Unlike our group's previously published work in magnetic field-directed RE separations, for the current system we did not observe any meaningful trends in the enrichment and separation factors with the total angular momentum (*J*) for the free ion of the RE³⁺ cations (see ESI, Fig. S7 and S8†). Future work on magnetic crystallization separations will target systems that contain strong axial field ligands and weaker equatorial ligands to further increase the magnetic anisotropy at the metal cations and systems that include a solution equilibrium process. This strategy could possibly offer greater separation, especially in the case of a binary mixture containing a diamagnetic RE ion and a paramagnetic, oblate RE ion that are also similar in size.

Conclusions

We demonstrated that the magnetic crystallization method along with a concentration gradient controlled by temperature reduction can be used as a strategy for RE separations using a simple ligand system under aqueous and aerobic conditions. A four-fold increase in the separation factor was observed for the La/Dy pair indicating the importance of the total angular momentum (*J*) for the free ion of the paramagnetic RE³⁺ cation and magnetic anisotropy of the RE-DOTA complexes in the separation process. Notably, unlike our previous work, no clear trend was observed between the enrichment and separation factors and the *J* values for the free ion of the RE³⁺ cations. Moreover, the results described here indicate the presence of the monomer–dimer equilibrium for the previously reported RE(TriNO_x) system is evidently an important design feature for achieving significant amplification of magnetic crystallization–separations performance. Future work will involve extending this method to other molecular systems that exhibit high magnetic anisotropy, and incorporation of metal complex equilibria.

Author contributions

Amit Kumar synthesized the RE-DOTA complexes (RE = La, Nd, Dy, Er, and Tm), developed the separation procedure, and wrote/edited the manuscript and ESI. Han Geng assisted in the ICP-OES technique for determining the metal content after separation and contributed to the writing of the ESI. Eric J. Schelter provided guidance, support and funding for the experimental studies described within, contributed to the writing/editing of the manuscript and ESI, and managed all aspects of the project.

Conflicts of interest

There are no conflicts to declare.



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