



Uncharted waters – Determining the influence of polar solutes on lanthanide solvent extraction by hydrophobic eutectic solvents

Rodrigo Colhe^a, Amélie Tropres^b, Maísa Saldanha Pinheiro^a, Thaís S. Soares^c, Takafumi Hanada^d, Duarte Ananias^a, Felipe Olea^a, Inês C.M. Vaz^a, João A.P. Coutinho^a, Nicolas Schaeffer^{a,*}

^a CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^b Université Claude Bernard, 69622 Villeurbanne, Lyon, France

^c Group of Analysis and Education for Sustainability (GAES), Chemistry Department, Federal University of Viçosa (UFV), Viçosa, MG 36570-900, Brazil

^d Department of Applied Chemistry, Graduate School of Technology, Industrial and Social Sciences, Tokushima University, 2-1 Minamijosanjima, Tokushima 770-8506, Japan

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ABSTRACT

Hydrophobic eutectic solvents (HES) were shown to be effective alternatives to conventional organic phases in solvent extraction (SX) for the separation of metal ions. However, their extraction performance is largely attributed to the extractant component of the HES mixture, with the second component considered as a “spectator”. In this work, the contribution of the non-complexing component of the HES mixture is investigated towards the extraction of lanthanide cations from nitric acid media. Three HES constituted by a common chelating hydrogen bond acceptor (HBA) trioctylphosphine oxide (TOPO) combined with carboxylic acids of different chain lengths (acetic, hexanoic, and decanoic acid) as hydrogen bond donors (HBDs) were studied. The influence of SX parameters was ascertained and complemented by the characterization of the HES phase before and after extraction. A marked effect of the HBD alkyl-chain length was observed, with distribution coefficients increasing by an order of magnitude replacing decanoic acid by acetic acid, while largely preserving the selectivity trend across the lanthanide series. Furthermore, unlike in the more hydrophobic systems no suppression of lanthanide distribution was observed with the decrease of the TOPO molar fraction in the acetic acid-based HES. Experimental and molecular dynamic simulations assign these differences to polar solute extraction (water and HNO₃) and the resulting restructuring of the HES hydrogen-bond network. The findings highlight the role of the non-chelating component in HES during SX and provide a straightforward route for tuning extraction performance.

1. Introduction

Lanthanides (Ln), a family of 15 elements spanning from lanthanum to lutetium, possess distinctive physical and chemical properties that make them difficult to substitute in many essential technologies [1]. Production of Ln oxide in 2024 reached 394 thousand tons and is forecasted to increase, driven by the growth of key sectors including permanent magnets, automotive and industrial catalysis, and electronic applications [2]. Despite the importance of these elements, identified as critical raw materials due to their high economic importance and supply risk by multiple entities, approximately only 1% of the Ln in e-waste is recycled [3]. This is largely due to the widespread use of Ln as dopants in numerous e-waste components, the complexity of these materials, and

the additional challenge posed by the chemical similarities among different Ln [4].

The hydrometallurgical processing of Ln³⁺ cations represents a technological challenge due to the dominance of the +3 oxidation state along the series and their similar aqueous phase speciation, with separation processes relying instead on the small monotonic decrease in the ionic radius with atomic number [5]. Solvent extraction (SX) is the major industrial process used for inter-lanthanide separation and purification [6] and involves the selective partition of a target ion between two immiscible phases. To overcome the penalty to dehydration of Ln³⁺, SX relies on amphiphilic molecules (extractants) with a chelating polar group to ensure metal coordination and a hydrophobic part providing solubility in the nonpolar phase (diluent) [7]. However, the SX

* Corresponding author.

E-mail address: nicolas.schaeffer@ua.pt (N. Schaeffer).

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efficiency and selectivity do not solely depend on extractant-ion coordination chemistry, but also on “soft” interactions between the extractant, diluent, potential phase modifiers, and their relation to the mesoscopic organization of the apolar phase to accommodate the incoming polar solutes (ions, acid, water) [8,9]. For example, a simple change in the supposedly “inert”, i.e. non-coordinating, diluent or phase modifier was shown to affect the extraction of Ln^{3+} cations from nitrate media [10–12]. Structure and reorganization during Ln SX is not a trivial question, but manipulation of these soft interactions provides an interesting and relatively “low-cost” avenue to modulate SX performance relative to the synthesis and validation of new extractants. This is particularly relevant given recent efforts to minimize the environmental impact of metal extraction via the application of new solvents and process intensification.

Hydrophobic eutectic solvents (HES) composed entirely of non-ionic compounds (Type V HES) are garnering interest as alternatives to traditional organic phases in SX for the separation of Ln^{3+} through the incorporation of various extractants as part of the eutectic mixture. Reported examples include trioctylphosphine oxide (TOPO), tetraoctyldiglycolamide (TODGA), or bis(2-ethylhexyl)amine among others [13–15]. HES typically results from the binary interaction between a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), with the relative magnitude of the latter influencing the non-ideality of the mixture [16]. More practically, suitable HES for SX must present a useable liquidus window at room temperature and not be fully miscible with aqueous solutions. As for any mixtures, properties can be fine-tuned by varying the HES components or their molar ratios, influencing physical properties such as density and viscosity as well as SX yields and selectivity [17,18].

Despite being mixtures presenting a complex set of intermolecular interactions, HES performance to date in SX is primarily attributed to the extractant component due to the absence of direct metal complexation from the second component as suggested by various spectroscopic analysis [13,14,19]. This simplistic view is contradicted by recent works which show the extraction of Ln^{3+} in TOPO-based systems vary significantly with the nature of the HBD. For example, Guidugli and Reza observed a significant increase in Ce^{3+} extraction efficiencies from aqueous nitrate media upon substitution of octanoic acid by menthol in the TOPO + HBD mixture for a fixed TOPO molar fraction [20]. Similarly, Dumet et al. studied mixtures of TOPO with various carboxylic acids for the extraction of various Ln^{3+} from NaNO_3 solution and reported a three-fold increase in the extraction efficiency when octanoic acid was replaced by the more hydrophilic lactic acid [21]. Unfortunately, no fundamental explanation was provided, but the reported data suggests the non-trivial influence of the “second” component nature on the extraction, being the HBD in this case.

In this work, the contribution of the non-metal ion complexing component of a HES mixture is explicitly considered on the extraction from HNO_3 media of various Ln^{3+} cations covering the series from light to heavy. To this end, HES mixtures based on TOPO with three HBDs (acetic, hexanoic, and decanoic acid) presenting a similar general structure and dissociation constants (pKa) from 4.76 to 4.90 [22] but greatly differing in their hydrophilicity were studied. This work seeks to address how the nature of the binary interactions in the pure HES is affected under SX conditions due to the co-extraction of polar solutes (namely water, acids, and metal ions), the subsequent rearrangement of the hydrogen bond network, and its relation to ion partition in SX. Through the understanding of the role of polar-apolar segregation in non-ionic HES and the influence of water and acid on the latter, new avenues for HES designs relevant to various strategic metal separations are proposed.

2. Material and methods

2.1. Reagents

Nitric Acid (HNO_3 , 65 wt%), sodium hydroxide (NaOH , 99 wt%), potassium hydrogen phthalate (KHP, 99 wt%), trioctylamine (TOA, 99 wt%), trioctylphosphine oxide (TOPO, 99 wt%), hexanoic acid (HexA, 99 wt%) and decanoic acid (DecA, 98 wt%), lanthanum (III) oxide (La_2O_3 , 99.9 wt%), neodymium (III) oxide (Nd_2O_3 , 99 wt%), europium (III) oxide (Eu_2O_3 , 99.99 wt%), terbium (III) oxide (Tb_2O_3 , 99.9 wt%), and lutetium (III) oxide (Lu_2O_3 , 99.9 wt%), were obtained from Sigma Aldrich (USA). Acetic acid (AceA, > 98 wt%) was obtained from chemical manufacturer JMGS. Oxalic acid dihydrate (> 99.5 wt%) and calcium chloride dihydrate (> 99 wt%) were obtained from Fujifilm-Wako Pure Chemical (Japan). Phosphoric acid (>85 wt%) was obtained from Kanto Chemical (Japan). All chemicals were used without further purification. Ultrapure water obtained from Milli-Q plus 185 water purification apparatus (18.2 $\text{M}\Omega\cdot\text{cm}$ at 298 K), was used for all experiments.

2.2. System preparation and characterization

All HES systems, both binary and ternary mixtures, were prepared gravimetrically under ambient atmosphere using a digital balance T2 (VWR, USA) with associated error of ± 0.1 mg and agitated at 323 K until a homogenous transparent liquid is formed. The resulting mixtures were kept sealed for a maximum of one week until use. Binary HES systems are composed of TOPO with one of three carboxylic acids: AceA, HexA, or DecA. Each system was respectively studied for two molar fractions of TOPO of 0.3 and 0.5. Ternary HES mixtures were prepared with a fixed TOPO mole fraction ($x_{\text{TOPO}} = 0.5$), while the remaining acid fraction ($x_{\text{HBD}} = 0.5$) was composed of varying molar proportions of AceA to DecA from 0.0 to 1.0 in increments of 0.25.

Solid-liquid equilibrium (SLE) phase diagrams of the TOPO + AceA and TOPO + HexA systems were measured over the full composition range at x_{TOPO} intervals of 0.1 using differential scanning calorimetry (DSC). Measurements were performed at atmospheric pressure using a DSC 7000 $\times$ ® (Hitachi) coupled to an electric cooling unit. Following preparation, the sample (between 2 and 10 mg) was transferred to an aluminum crucible, sealed and weighted in a PerkinElmer AD6 micro-analytical balance with an accuracy of ± 0.00005 g. The DSC thermal program consisted of two consecutive cooling and heating cycles. During the first cycle, the sample was cooled from room temperature to 193 K at a cooling rate of $5 \text{ K}\cdot\text{min}^{-1}$, held isothermally at 193 K for 5 min and then heated to 353 K at a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$. At the end of the first heating step, the sample was held at 353 K for 2 min. Subsequently, the second cycle was initiated following the same procedure as the first cycle but with no isothermal hold at the maximum temperature. The melting temperature was determined from the maximum of the endothermic melting peak observed during heating.

SLE diagrams were constructed to evaluate the phase behavior and thermodynamic ideality deviation of the pure HES system. Neglecting heat capacity effects, the SLE of the eutectic mixtures with complete immiscibility in the SLE can be described by eq. (1) [23]:

$$\ln(x_i\gamma_i) = \frac{\Delta H_{m,i}}{R} \left(\frac{1}{T_{m,i}} - \frac{1}{T} \right) \quad (1)$$

where x_i is the mole fraction of component i and γ_i it's the activity coefficient in the liquid phase, T is the absolute temperature, R is the ideal gas constant, $T_{m,i}$ and $\Delta H_{m,i}$ are the melting temperature and molar enthalpy of fusion of the pure component, respectively.

^1H and ^{31}P nuclear magnetic resonance (NMR) spectroscopy of the HES phases before and after H_2O and HNO_3 equilibration was recorded on a Bruker Avance III 300 NMR spectrometer. To avoid any modifications of the HES structure, NMR analysis was performed on undiluted

HES mixtures using a co-insert sealed capillary containing D₂O with tetramethylsilane propionate (TSP) as internal standard.

Viscosity measurements of the HES phases after preparation were done at 298.15 K using a cone-plate viscometer RM 100 CP-2000 PLUS from Lamy Rheology, with a shear rate range of 10–700 s^{−1}. Surface tension of the pure HES (with air) and the interfacial tension between the HES phase (previously equilibrated) with H₂O or 1.0 mol·L^{−1} HNO₃ solutions were measured in a tensiometer OCA 15 Dataphysics. Each system was measured 3 times (3 droplets of around 15.0 μL), each droplet was measured continuously for 1 min. Surface/interfacial tension values were determined by applying the fitted droplet profiles to the Young–Laplace equation, considering the density and contact angle of the droplet (HES) phase and respective surrounding media, namely air, H₂O or 1.0 mol·L^{−1} HNO₃.

2.3. Solvent extraction

All SX aqueous phases were prepared using stock solutions of Ln (NO₃)₃, namely Lanthanum (La), Neodymium (Nd), Europium (Eu), Terbium (Tb) and Lutetium (Lu), prepared by dissolution of the respective oxides in a solution of known HNO₃ molarity. These were subsequently diluted to yield a multielement solution with, unless otherwise stated, a final individual Ln³⁺ concentration of 7.5 mmol·L^{−1} in either 1.0 mol·L^{−1} or 6.0 mol·L^{−1} HNO₃, considering the initial stock solutions HNO₃ concentration. The same procedure was applied to the preparation of mono-elemental Eu³⁺ solution of varying concentrations in 1.0 mol·L^{−1} HNO₃. The SX systems were prepared by addition of pre-equilibrated HES phase with the respective aqueous phases at a fixed organic to aqueous mass ratio (O/A) of 0.5. All extraction results reported were obtained from at least three independent measurements (*n* = 3), with uncertainty reported as the standard deviation (SD). The extractions were conducted by vigorous agitation using a vortex mixer at 2400 rpm for 1 min at room temperature, followed by phase separation using centrifugation for 10 min at 10⁴ rotations per minute (rpm) at room temperature. Each Ln³⁺ partition is given by the respective distribution coefficient (*D*_{Ln}) as:

$$D_{Ln} = \frac{[Ln]_{HES,f}}{[Ln]_{aq,f}} = \frac{2 \times ([Ln]_{aq,ini} - [Ln]_{aq,f})}{[Ln]_{aq,f}} \quad (2)$$

In which [Ln] is the Ln³⁺ concentration in mol·L^{−1} at equilibrium, the suffixes “HES” and “aq” indicate the respective phase, whilst “ini” and “f” indicate the timeframe (initial and final). The Ln³⁺ concentration in the HES phase was obtained by mass balance from measurement of the aqueous phase before and after SX, considering the applied mass O/A ratio. From eq. (3), the separation factor between two metals (*α*_{M1/M2}) is defined as:

$$\alpha_{M1/M2} = \frac{D_{M1}}{D_{M2}} \quad (3)$$

The loading capacities of each HES at the two tested molar fraction were measured following an identical extraction procedure but using an initial mono-elemental Eu³⁺ aqueous concentration of 0.2 mol·L^{−1} in 1.0 mol·L^{−1} NO₃[−].

The stripping of the HES phase, also known as back extraction, was evaluated following the extraction of 7.5 mmol·L^{−1} Eu(NO₃)₃ from 1 mol·L^{−1} HNO₃ solution with an O/A of 0.5. The individual isolated HES phases were thereafter contacted with various stripping solutions following the same conditions as for the extraction described above, namely HCl concentrations between 0.5 mol·L^{−1} to 8.0 mol·L^{−1}, 2.0 mol·L^{−1} HNO₃, 2.0 mol·L^{−1} AceA, 2.0 mol·L^{−1} CaCl₂, 1.0 mol·L^{−1} H₃PO₄ or 1.0 mol·L^{−1} oxalic acid (OxaA). The stripping efficiency (*S*%) was evaluated according to eq. (4). As before, the lanthanide content in the HES phase was not measured directly but inferred by mass balance from the aqueous phase concentration after stripping.

$$S\% = 100 \bullet \frac{2 \bullet [Ln]_{aq,f}}{[Ln]_{HES,ini}} \quad (4)$$

2.4. Measurements of solute partition

The quantification of Ln³⁺ in the aqueous phase before and after extraction was performed by total X-ray fluorescence (TXRF) spectroscopy using a Bruker S2 Picofox spectrometer equipped with a molybdenum X-ray source. Prior to analysis, sample carriers were treated with 10 μL of Serva™ (silicon solution in isopropanol from SERVA Electrophoresis GmbH) and dried at 353 K for 15 min to provide a hydrophobic surface. TXRF samples were prepared by diluting 50 to 250 μL of the aqueous solution after SX (depending on the sample concentration) in 900 μL of a 0.2 wt% polyvinyl alcohol solution (PVA, 87–90 wt%) and spiked with a known volume of certified gallium chloride (GaCl₃) internal standard (1000 ± 4 mg/L) both from Sigma-Aldrich. Ten microliters of each solution containing the metals and the GaCl₃ standard were added onto a clean quartz sampler carrier and dried on a hot plate at 353 K for 30 min. The X-ray tube was operated at 50 kV and 1000 μA; spectra acquisition time was set at 300 s. Complementarily, selected measurements for experiments presenting high *D*_{Ln} were performed on an inductively coupled plasma optical emission spectroscopy (ICP-OES, Avio 550 Max, Perkin Elmer). Nitrate anion and water partition to the HES phase, as well as loss of the HBD component to the aqueous phase after contact were determined in the absence of metal ions, under agitation using a rotary agitator Trayster (IKA) inside of a temperature-controlled incubator, fixed at 298.15 K. Each analysis was carried out in triplicate, and the average result is reported. Nitrate quantification in the aqueous phase was performed by UV–vis using a UV-1800 spectrometer (Shimadzu) at a wavelength of 205 nm in quartz cuvette (10 mm). The calibration curve was established using as matrix an aqueous phase previously equilibrated with the HES (O/A = 0.5), in the absence of metals, to which HNO₃ was spiked to yield a HNO₃ standard range with concentrations between 0.05 mol·L^{−1} and 0.2 mol·L^{−1}. The water content in the HES phase after equilibration with H₂O or 1.0 mol·L^{−1} HNO₃ was determined using an EcoKF Titrator (Metrohm, Switzerland). Volumetric Karl Fischer titration was performed at room temperature using Hydranal Titrant 5 using approximately 15 mg of HES per measurement. Due to the incompatibility of HNO₃ with the titrant solution, samples were analyzed after neutralization with trioctylamine (TOA), calculated based on nitrate partition, resulting in the [TOAH][NO₃] salt. The water content of the TOA solution was measured prior and considered in the calculation of the final HES phase water content. Loss of the HES acid component to the aqueous phase was measured by acid-base titration using an automatic titrator Thermo Scientific OrionStar T940. Sample resulting from the equilibration of HES in water were measured directly. Samples were diluted in ultrapure water, and the titration was performed using a standardized 0.01 mol·L^{−1} NaOH solution. The NaOH solution was standardized using a previously dried potassium hydrogen phthalate (KPH).

2.5. Luminescence measurements

The emission and excitation spectra of Eu³⁺ were recorded at ambient-temperature using a Fluorolog®-3Horiba Scientific (Model FL3-2 T) spectroscope with a modular double grating excitation spectrometer (fitted with a 1200 grooves/mm grating blazed at 330 nm) and a TRIAX 320 single emission monochromator (fitted with a 1200 grooves/mm grating blazed at 500 nm; reciprocal linear density of 2.6 nm·mm^{−1}) coupled to a R928 Hamamatsu photomultiplier using the right angle acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. The emission decay curves were

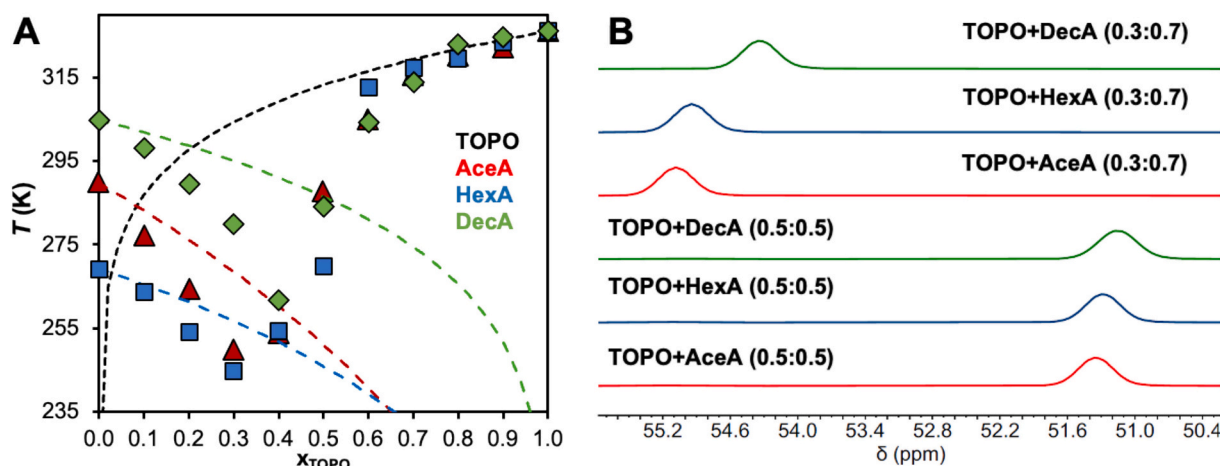


Fig. 1. A) SLE phase diagrams of TOPO + HBD for AceA (red), HexA (blue), and DecA (green). Symbols correspond to experimental T_m values measured by DSC, whilst dashed lines indicate the ideal liquidus curve. The SLE diagram of TOPO + DecA was obtained from reference [37]. B) ^{31}P NMR spectra of the P=O shift from TOPO in the various HES at two different molar fractions of $x_{\text{TOPO}} = 0.3$ and $x_{\text{TOPO}} = 0.5$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

acquired with the spectrofluorometer coupled to a FL1073 single photon counting module (Horiba Scientific) working at 950 V, and using a pulsed SpectraLED-355 (Horiba Scientific) as the excitation source.

2.6. Computational methods and simulations

The Conductor-like Screening Model for Real Solvents (COSMO-RS) [24] implemented in COSMOthermX (version 25.0.0) was applied to predict the liquid-liquid partitioning of water, HNO_3 , TOPO and different HBDs. Individual molecules were optimized in TURBOMOLE [25] using density functional theory (DFT) at the BP86/def-TZVP level of theory [26,27], which provides a reasonable compromise between computational cost and accuracy for describing non-covalent interactions and hydrogen-bonding environments. The partitioning behavior was modeled by iteratively solving the distribution of each component between the aqueous and organic-like phases until phase equilibrium conditions were reached, considering pure water as one phase and different mass ratios of TOPO + HBD as the second phase. In this framework, the HES was represented using a constituent-based COSMO-RS approach, in which the HBD and HBA were treated as independent species at their corresponding molar ratios.

Non-polarizable molecular dynamics (MD) simulations were carried out using Gromacs 2024 package [28] within the NpT ensemble by adopting the leapfrog algorithm to integrate the equations of motion at a fixed temperature (298 K) and pressure (1 bar). The OPLS all-atom force field was used for organic molecules, with the topologies generated using LigParGen [29,30], whilst water molecules were represented by the SPC/E model [31]. Hydrogen bonds were constrained by the LINCS algorithm [32] whilst LJ and Coulombic interactions were computed up to a cut-off radius of 1.2 nm. The force-switch van der Waals potential modifier was employed for LJ, where the energy decays smoothly to zero between 0.9 and 1.2 nm. All simulations contained a fixed number of 1000 HES molecules with varying water content and were started from a randomly distributed configuration. Production runs were carried for 40 ns with a time step of 2 fs following an energy minimization step using the steepest descent algorithm and two 0.5 ns equilibrium runs in the NVT and NpT ensembles, respectively. The temperature and pressure were controlled through the Nose–Hoover thermostat and the Parrinello–Rahman barostat [33,34], respectively. All analysis was carried out on the last 20 ns of the simulation run. MD simulation outputs were visualized using the VMD software package [35]. Radial distribution functions (RDFs) and coordination numbers (CNs) were calculated using Gromacs in-built tools [28], whilst domain analysis was performed using

Table 1

Experimental eutectic composition, eutectic temperature (T_e), ideal eutectic temperature (T_e^{id}), their difference ΔT_e , and the experimental activity coefficient ($\gamma_{e,i}$) of component i at the eutectic composition. Values for the TOPO + DecA system are taken from reference [38].

HBD	Eutectic Composition (x_{TOPO})	T_e (K)	T_e^{id} (K)	ΔT_e (K)	$\gamma_{e,\text{TOPO}}$	$\gamma_{e,\text{HBD}}$
AceA	~0.3	249.65	268.50	18.85	0.02	0.65
HexA	~0.3	244.77	256.70	11.93	0.01	0.69
DecA	~0.4	261.78	298.58	36.80	0.07	0.28

TRAVIS [36].

3. Results and discussion

3.1. HES characterization

Prior to discussing the SX performance of each system and their different tendencies, it is important to ascertain if significant differences exist between the HES composed of TOPO with AceA, HexA, or DecA prior to SX that could impact their performance. To this end, a description of the solid-liquid equilibria (SLE) of the three HES along with the relative magnitude of the binary TOPO – HBD interaction as probed by NMR is presented in Fig. 1. The complete experimental SLE data is available in Table S1, with the melting properties of the pure compounds available in Table S2. Although pure AceA and HexA are liquid at 293 K and could therefore be directly used as solvents, it is important to note that these are used as (i) model systems to better appreciate how HBD selection influences HES performance and (ii) do not present by themselves the required hydrophobicity for SX.

As shown in Fig. 1A, all mixtures exhibit a phase behavior consistent with a single eutectic point with a wide operational liquidus range at 293 K, and present notable deviations to ideality. To provide a more objective comparison of the different systems, the activity coefficients of each component at the eutectic composition are summarized in Table 1. The “deepness” of HES can be interpreted as their deviation from ideal thermodynamic behavior, reflected by the extent of the depression in melting temperature relative to the predicted ideal value. Activity coefficients (γ) allow to quantify this deviation from ideal behavior. As shown in Table 1, the AceA and HexA systems, both at $x_{\text{TOPO}} = 0.3$, present similar activity coefficients for the TOPO ($\gamma_{e,\text{TOPO}}$) and HBD ($\gamma_{e,\text{HBD}}$) respectively, with $\gamma_{e,\text{TOPO}}$ presenting the greater non-ideality. In

Table 2

Experimental viscosity, density, and surface tension of the as-prepared TOPO-based HES at 298 K as a function of the HBD selection and x_{TOPO} .

HBD	x_{TOPO}	$[\text{TOPO}]_{\text{HES}}$ ($\text{mol}\cdot\text{kg}^{-1}$)	Viscosity ^a ($\text{mPa}\cdot\text{s}$)	Density ^a ($\text{g}\cdot\text{cm}^{-3}$)	Surface tension ^b ($\text{mN}\cdot\text{m}^{-1}$)
Acetic acid	0.3	1.90	19.0 ± 0.1	0.909 ± 0.001	29.5 ± 0.5
	0.5	2.24	32.5 ± 0.1	0.891 ± 0.002	29.7 ± 0.9
Hexanoic acid	0.3	1.52	26.3 ± 1.3	0.895 ± 0.001	28.8 ± 0.3
	0.5	1.99	44.4 ± 0.1	0.885 ± 0.001	29.9 ± 0.4
Decanoic acid	0.3	1.27	36.9 ± 0.1	0.886 ± 0.001	29.7 ± 0.2
	0.5	1.79	50.3 ± 2.1	0.881 ± 0.001	30.9 ± 0.5

^a Reported uncertainties represent the standard deviation calculated independent measurements ($n = 3$).

^b Reported uncertainties represent the propagated error for average of each droplet (independent measurements ($n = 3$)).

contrast, the TOPO + DecA system ($x_{\text{TOPO}} = 0.4$) displays a larger melting point depression ($\Delta T_e = 36.80$ K), and is accompanied by a

decrease in γ_{eHBD} (0.28). This increased non-ideality of the HBD is primarily assigned to the disruption of the decanoic acid crystal packing by TOPO, as reflected by the jump of in ΔH_m from HexA to DecA (Table S2), and not to a substantially different liquid-phase association strength.

The observed deviations to ideality are expectable considering the lone HBA nature of TOPO and the electronegativity of the phosphine oxide moiety, capable of partially disrupting the carboxylic dimer. The favorable nature of the TOPO – carboxylic acid hydrogen bond was previously reported by isothermal titration calorimetry for the AceA system, with a 1:1 binding constant in the range of 11 to 57 with an associated enthalpy between -16 $\text{kJ}\cdot\text{mol}^{-1}$ to -28 $\text{kJ}\cdot\text{mol}^{-1}$ depending on the polarity of the diluent [39]. Considering the identical functional groups and the similar pKa values (from $\text{pKa} = 4.76$ to $\text{pKa} = 4.90$), interactions of similar magnitude are anticipated for the other systems. To verify this assumption, the strength of the TOPO – HBD interaction in the various HES as a function of the carboxylic acid alkyl chain length and the HES molar fraction ($x_{\text{TOPO}} = 0.3$ and $x_{\text{TOPO}} = 0.5$) was indirectly assessed through the dislocation of the ^{31}P NMR shift of TOPO, with the spectra presented in Fig. 1B. Trialkylphosphine oxides are known to be highly sensitive probe molecules to the local hydrogen bonding environment through monitoring of the ^{31}P NMR shift [40]. The addition of carboxylic acid induces a downfield shift in the TOPO ^{31}P signal, coherent with the formation of intermolecular hydrogen bonding

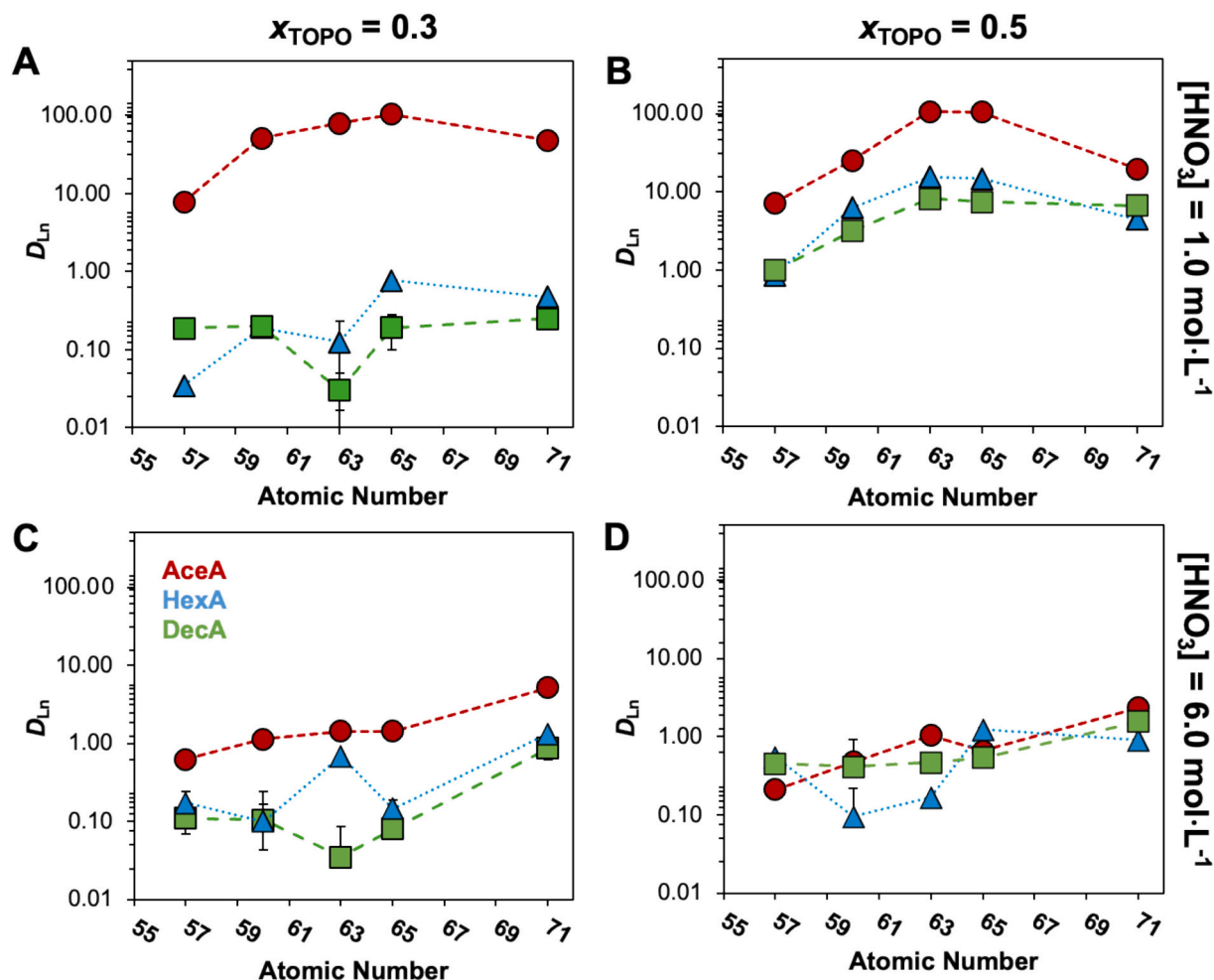


Fig. 2. Distribution coefficient (D_{Ln}) of five lanthanide cations, identified by their atomic number, in the HES systems as a function of initial aqueous phase HNO_3 concentration (rows) and the x_{TOPO} molar fraction (columns) for $T = 298$ K, $[\text{Ln}^{3+}] = 7.5$ $\text{mmol}\cdot\text{L}^{-1}$, and $\text{O/A} = 0.5$. A) $[\text{HNO}_3] = 1.0$ $\text{mol}\cdot\text{L}^{-1}$ and $x_{\text{TOPO}} = 0.3$, B) $[\text{HNO}_3] = 1.0$ $\text{mol}\cdot\text{L}^{-1}$ and $x_{\text{TOPO}} = 0.5$, C) $[\text{HNO}_3] = 6.0$ $\text{mol}\cdot\text{L}^{-1}$ and $x_{\text{TOPO}} = 0.3$, and D) $[\text{HNO}_3] = 6.0$ $\text{mol}\cdot\text{L}^{-1}$ and $x_{\text{TOPO}} = 0.5$. Colour code corresponds to: red – TOPO + AceA; blue – TOPO + HexA; green – TOPO + DecA. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

interactions and the potential formation of higher order aggregates at lower x_{TOPO} , thereby decreasing the relative amount of unbound TOPO. Importantly, no significant difference between HES mixtures for a given TOPO molar fraction is observed in Fig. 1B, suggesting a similar magnitude of the pairwise TOPO – HBD hydrogen bond interaction across all systems.

To complement these findings, additional macroscopic characterization of parameters relevant to SX, namely viscosity and surface tension, are provided in Table 2. Viscosity of the phases increases with the presence of the bigger molecular size constituents, either through increasing TOPO molar fraction for a given HES or increasing the carboxylic acid alkyl chain length for a given x_{TOPO} . For example, at $x_{\text{TOPO}} = 0.3$ the viscosity increases from 19.0 mPa·s to 36.9 mPa·s as the HBD alkyl chain augments from ethyl to decyl, whilst for the AceA-based system the viscosity increases from 19.0 mPa·s to 32.5 mPa·s as molar fraction of TOPO raises to $x_{\text{TOPO}} = 0.5$. No difference was observed for the surface tension across the various HBD and molar fractions tested, with an approximate value of $\sim 30 \text{ mN}\cdot\text{m}^{-1}$ obtained. This value is in the range of previously reported decanoic acid-based HES ($29.7 \text{ mN}\cdot\text{m}^{-1}$ for thymol + DecA) as well as that reported for $1 \text{ mmol}\cdot\text{L}^{-1}$ of decanoic acid at the air/water interface ($33.1 \pm 0.3 \text{ mN}\cdot\text{m}^{-1}$), suggesting that the surface tension in the studied HES is strongly influenced by the most tensioactive component [41,42]. Results in Table 2 further underline the lack of discernable macroscopic properties in the as-prepared HES liable to justify the observed differences in their SX behavior presented in the following section.

3.2. Solvent extraction

The distribution factors of La^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} , and Lu^{3+} in the three TOPO-based HES were evaluated as a function of the carboxylic acid chain length, the TOPO molar fraction, and the aqueous phase solution containing HNO_3 concentration of $1.0 \text{ mol}\cdot\text{L}^{-1}$ and $6.0 \text{ mol}\cdot\text{L}^{-1}$. The results are shown in Fig. 2, with all reported D_{Ln} values available in Table S3 and S4 of the ESI. Importantly, at the investigated HNO_3 concentrations, deprotonation of the HBDs is suppressed such that Ln^{3+} – carboxylate interactions are non-existent, facilitating phase separation and visually reducing emulsification of the system. Furthermore, despite the differing solubilities of the HBDs, no third-phase formation was observed. Because La^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} and Lu^{3+} were extracted simultaneously, the reported distribution coefficients describe the behavior of each ion under mixed-lanthanide conditions. Consequently,

possible competitive effects between co-extracted Ln^{3+} species cannot be quantitatively separated from the measured D_{Ln} values. Nevertheless, the large excess of TOPO and HNO_3 concentration relative to the cumulative lanthanide ion concentration suggests that the overall Ln^{3+} partitioning is not dependent on potential competitive and/or salting effects.

Starting from an HES with $x_{\text{TOPO}} = 0.5$ in equilibrium with an aqueous phase containing $1.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 (Fig. 2B), a clear dependence of the HES carboxylic acid alkyl chain length is observed on the magnitude of the D_{Ln} . Although the $\alpha_{\text{Eu/Ln}}$ separation factors show some quantitative variations between HBDs (Tables S5 and S6), the overall selectivity trend across the Ln^{3+} series remains consistent between the three systems. All systems present a maximum in the distribution coefficient for the middle lanthanides Eu^{3+} and Tb^{3+} (atomic number 63 and 65), similarly to that observed when using TOPO or commercial phosphine oxide formulations like Cyanex 923 diluted in conventional organic solvents [43,44]. This maximum is assigned to competitive forces between the increasing apparent equilibrium constant ($\log(K_{\text{ex}})$) between phosphine oxide ligands and Ln^{3+} along the series and steric hindrances to coordination brought about by the lanthanide contraction and the resulting decrease in Ln^{3+} coordination number from 9 to 8 from light to heavy lanthanides respectively [43,45]. Taking the distribution of Eu^{3+} as a reference for the comparison of HBDs in the studied HES systems, D_{Eu} increases from DecA, to HexA and AceA, reaching 8.16 ± 0.19 , 15.6 ± 0.73 , and 107 ± 2.47 , respectively. Surprisingly, an improvement of D_{Eu} by one order of magnitude is achievable by the simple substitution of DecA by AceA, keeping all functional groups and aqueous phase conditions equal. These results are even more interesting if we consider the absence of relatable differences in the NMR spectra, viscosities or surface tension of the as-prepared HES, as demonstrated previously. Dumet et al. [21] also reported an improvement in the extraction efficiency of Dy^{3+} using TOPO-based HES from approximately 20% for octanoic acid as HBD, to $\sim 80\%$ for lactic acid and $> 95\%$ for formic acid, suggesting that the trend in Fig. 2 is extrapolable to other short chained carboxylic acids.

The influence of the HBD alkyl chain length is even more pronounced when the TOPO molar fraction is reduced from $x_{\text{TOPO}} = 0.5$ to $x_{\text{TOPO}} = 0.3$, keeping the HNO_3 concentration constant at $1.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 (Fig. 2A). An excess of HBD to TOPO drastically suppresses D_{Ln} in the case of HexA and DecA, possibly due to the decrease in the population of less hydrogen bonded TOPO available for metal complexation. Such an observation is consistent with the ^{31}P NMR spectra in Fig. 1B that shows

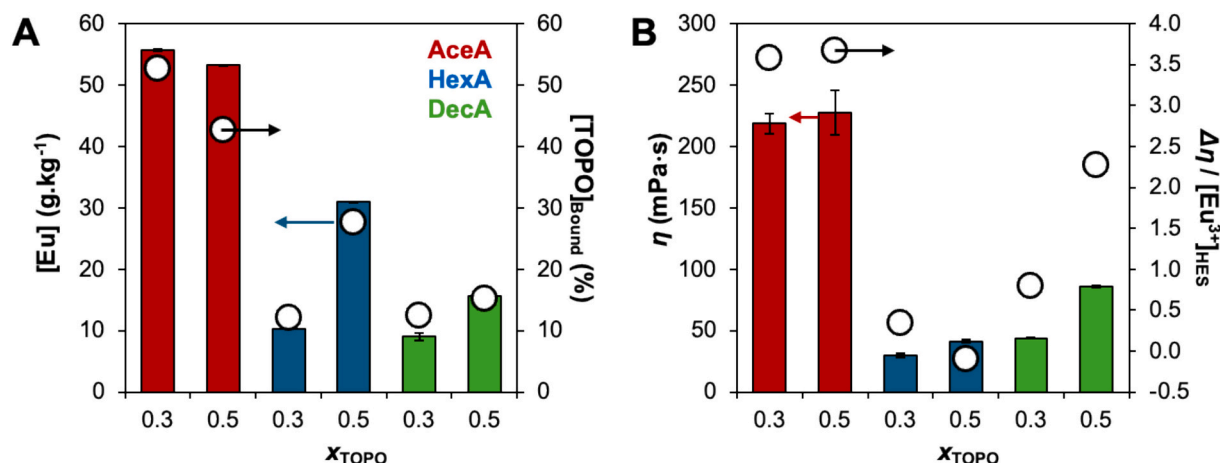


Fig. 3. A) $\text{Eu}(\text{NO}_3)_3$ loading of the HES systems and B) corresponding viscosity (η) of the HES phase as a function of the HBD and x_{TOPO} , after equilibration with a $0.2 \text{ mol}\cdot\text{L}^{-1}$ $\text{Eu}(\text{NO}_3)_3$ solution at a total nitrate concentration of $1.0 \text{ mol}\cdot\text{L}^{-1}$ NO_3^- , O/A = 0.5, and $T = 298 \text{ K}$ (TOPO + AceA – red; TOPO + HexA – blue; TOPO + DecA – green). The concentration of bound TOPO to Eu^{3+} was calculated from the total TOPO concentration in the HES, the final extracted Eu^{3+} concentration and assuming a 3:1 TOPO:Eu stoichiometry of the complex. $\Delta\eta$ represents the viscosity difference between the Eu^{3+} -saturated HES and the as-prepared HES listed in Table 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

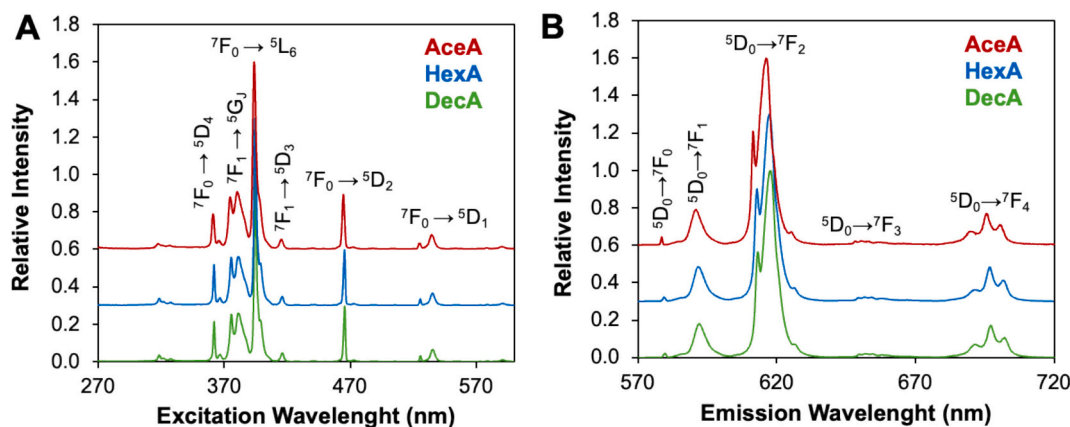


Fig. 4. Normalized Eu^{3+} A) excitation spectra (emission at 617.4 nm) and B) emission spectra (excitation at 394.3 nm), as a function of the HBD selection in the TOPO + carboxylic acid systems for $x_{\text{TOPO}} = 0.5$ (initial aqueous phase composition of $[\text{Eu}^{3+}] = 7.5 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{HNO}_3] = 1.0 \text{ mol}\cdot\text{L}^{-1}$ and $\text{O/A} = 0.5$).

a greater acidity of the P=O bond for $x_{\text{TOPO}} = 0.3$ arising from the increased incorporation of TOPO in the HES hydrogen bond network. In an apparent contradiction to the proposed explanation, no influence of TOPO molar fraction is observed in the TOPO + AceA system, with similar D_{Ln} values obtained for $x_{\text{TOPO}} = 0.3$ or $x_{\text{TOPO}} = 0.5$, despite presenting an analogous ^{31}P NMR spectra to the other HES after prior to SX. To directly assess the effect of water on the TOPO–HBD interactions and understand the special case of the AceA system, ^{31}P NMR spectra were acquired for the HES phases after equilibration with pure water in the absence of metal (**Fig. S1**). The magnitude and direction of the shift depend on the HBD, indicating that the response to hydration is related to the HES selection and x_{TOPO} . Whilst small to negligible changes are observed in the HexA and DecA systems irrespective of x_{TOPO} , hydration moves the ^{31}P δ resonance in the AceA-based HES substantially towards lower δ , demonstrating that water alone perturbs the local environment of the P=O group. The effect is particularly pronounced for $x_{\text{TOPO}} = 0.3$ where the ^{31}P δ decreases from ~ 55 ppm to 51.7 ppm. Coincidentally, the latter value is close to the value of the HES for $x_{\text{TOPO}} = 0.5$, providing a plausible explanation for the otherwise unexpected insensitivity of the AceA system to the TOPO molar fraction on SX performance.

Irrespective of the molar fraction and HBD selection, raising the HNO_3 concentration to $6.0 \text{ mol}\cdot\text{L}^{-1}$ (**Fig. 2C and D**) inhibits all D_{Ln} and forces a change in the extraction tendency across, with a gradual increase in D_{Ln} along the Ln^{3+} series reaching a maximum for the heavier Lu^{3+} . Under these conditions, the influence of the HBD and molar fraction are relatively diminished due to the competing co-extraction of HNO_3 over Ln^{3+} cations as observed in previous phosphine oxide based SX systems, including HES [43,44,46]. This is supported by ^{31}P NMR spectra of the HES phase after equilibrium with 1.0 and $6.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 presented in **Fig. S2 and S3** respectively. Taking a molar fraction of $x_{\text{TOPO}} = 0.5$ as example, a moderate increase in the ^{31}P δ is observed going from ~ 51.5 ppm in the three prepared HES (**Fig. 1B**) to ~ 56.0 ppm after equilibration with $1.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 (**Fig. S2**). In turn, equilibration with $6.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 results in not only a significant downshift to ~ 65.0 ppm but also the loss of system specific differences, with all systems presenting approximately the same signature independent of the HBD and x_{TOPO} (**Fig. S3**).

3.3. Loading capacity and stripping

To better understand if the observed ten-fold increase in D_{Ln} going from DecA to AceA (for moderate HNO_3 concentrations) is reflected across other relevant SX properties, the loading capacity of the various system was evaluated after contact with a $0.2 \text{ mol}\cdot\text{L}^{-1}$ mono-elemental $\text{Eu}(\text{NO}_3)_3$ solution. The Eu^{3+} was selected to ensure that metal loading saturation was achieved in all HES systems. The total nitrate concentration was kept constant at $1.0 \text{ mol}\cdot\text{L}^{-1} \text{NO}_3^-$. The results, presented in

Fig. 3A with the associated values available in Table S7, mirror the trends in D_{Ln} and highlights the salient influence of the HBD selection and molar fraction for a given extractant.

For $x_{\text{TOPO}} = 0.5$, the selection of AceA as HBD raises the loading capacity to $53 \text{ g}\cdot\text{kg}^{-1}$ of HES, representing a $\sim 1.7\times$ and $\sim 3.4\times$ increase relative to the HexA ($31 \text{ g}\cdot\text{kg}^{-1}$ of HES) and DecA systems ($16 \text{ g}\cdot\text{kg}^{-1}$ of HES), respectively. The differences are plainer when looking at $x_{\text{TOPO}} = 0.3$; the loading increases from $10.3 \text{ g}\cdot\text{kg}^{-1}$ and $9.1 \text{ g}\cdot\text{kg}^{-1}$ in HexA- and DecA-based systems to $56 \text{ g}\cdot\text{kg}^{-1}$ of HES increasing the loading capacity between ~ 5.4 to 6.1 times. Considering the loading capacity not in weight but in molar ratio of TOPO to Eu^{3+} , for $x_{\text{TOPO}} = 0.3$ this represents a final ratio of 5.7, 25 and 24 mol TOPO / mol Eu in the AceA-, HexA-, and DecA-based HES. For $x_{\text{TOPO}} = 0.5$ the atomic efficiency of the extraction improves to 11 and 19 in the HexA and DecA-based HES whilst remains practically constant in the AceA system (~ 7). Assuming an expected 3 to 1 stoichiometry of the $\text{Eu}(\text{NO}_3)_3(\text{TOPO})_3$ complex, consistent with that reported in traditional SX for the equivalent separation [43,44,46], the final fraction of bound TOPO to Eu^{3+} for each HES composition can be estimated and is presented in **Fig. 3A**. All systems at saturation present a lower atomic efficiency than the theoretical limit, but the extent of which varying greatly. Interestingly, the best and worst case occurs for $x_{\text{TOPO}} = 0.3$. The suppression of “free” TOPO molecules at $x_{\text{TOPO}} = 0.3$ in the HexA and DecA-based HES results in only $\sim 10\%$ of available TOPO ligand engaging in Ln^{3+} extraction. In these systems, varying x_{TOPO} not only influences the total TOPO concentration but most importantly it shifts the TOPO concentration engaged in intermolecular HES interaction rather than available for coordination. In contrast, the same system with AceA as HBD is insensitive to x_{TOPO} variation, with over 50% TOPO chelating Ln^{3+} cations at saturation.

To accompany the loading essays, the viscosity of the HES phase at saturation was measured and presented in **Fig. 3B**. A major hurdle towards the application of HES to SX is the significant increase in viscosity at saturation, limiting the gains afforded in process intensification from the high extractant concentration. As would be expected based on the Eu^{3+} loadings, the TOPO + AceA HES exhibits the greatest viscosity after Eu^{3+} saturation, over 200 cP. To better reflect the change in the system compositions and loading, normalization of the viscosity increase ($\Delta\eta$) by the Eu^{3+} loading is presented in **Fig. 3B**. Interestingly, a pronounced minima is observed for the HexA system. Despite representing an intermediate loading, negligible viscosity increase is observed at saturation and serves to further exemplify how the simple variation in the HBD nature can serve to tune SX properties.

Results in **Figs. 2 and 3** highlight the differing nature of the TOPO + AceA relative to the longer alkyl chain HBD. These results provide a possible pathway for the manipulation of HES properties for improved SX (higher D_{Ln}) without sacrificing selectivity. Compared to the HES

Table 3

Asymmetry ratio (AR_{L}), luminescence lifetime (τ) after SX in H_2O and D_2O media and number of inner-sphere water molecules ($n_{\text{H}_2\text{O}}$) of the extracted Eu^{3+} complex in the TOPO-based HES as a function of the carboxylic acid selection and TOPO molar fraction.

HBD	x_{TOPO}	AR	$\tau_{\text{H}_2\text{O}}$ (ms)	$\tau_{\text{D}_2\text{O}}$ (ms)	$n_{\text{H}_2\text{O}}$
Acetic acid	0.5	5.4	1.613	1.792	0.1
	0.3	5.4	1.617	1.811	0.1
Hexanoic acid	0.5	5.4	1.624	1.822	0.1
	0.3	5.4	1.270	1.555	0.2
Decanoic acid ^a	0.5	5.2	1.607	1.799	0.1
	0.3	5.3	1.336	1.745	0.2

^a Values taken from reference [14].

composed of longer chain carboxylic acids, the use of AceA allows to overlap the *liquidus* compositional range (derived from SLE) with the “operational” one (HES molar fractions which present elevated D_{Ln}). However, a trade-off is apparent between the favorable nature of the extraction and the ease of metal stripping. Stripping tests from the different HES loaded phases ($x_{\text{TOPO}} = 0.5$) after contact with $7.5 \text{ mmol}\cdot\text{L}^{-1} \text{Eu}^{3+}$ at $1.0 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$ indicate that reasonable recovery is possible under dilute acid conditions for HexA and DecA systems (Fig. S4). In contrast, stripping of the AceA based HES was only achieved for concentrated HCl solutions greater than $6.0 \text{ mol}\cdot\text{L}^{-1}$ or through the addition of oxalic acid as a precipitating agent. A more hydrophilic HBD

can promote the accommodation and extraction of polar Ln-containing species, but the resulting increase in extraction strength may also hinder subsequent metal release. Consequently, optimisation of HES composition for solvent extraction should consider not only the magnitude and selectivity of metal extraction, but also stripping efficiency and solvent regeneration.

In the following sections, two potential hypotheses are investigated to identify the observed SX differences between AceA and HexA or DecA as HBD, namely the (i) potential speciation differences in the extracted Ln species between HES, and (ii) the influence of co-extracted polar solutes (H_2O and HNO_3) during SX on the HES phase structuration.

3.4. Influence of speciation

The lanthanide cation speciation in the HES after extraction from $1.0 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$ aqueous solution was followed by Eu^{3+} photoluminescence and emission lifetime measurements as a probe element. The normalized excitation spectra and emission spectra of Eu^{3+} in the three HES phases for $x_{\text{TOPO}} = 0.5$ are presented in Fig. 4, along with the identified transitions.

The normalized emission and excitation spectra of Eu^{3+} in the three TOPO–carboxylic acid eutectic systems display the characteristic intra-4f transitions of Eu^{3+} [47,48]. The excitation spectra, monitored at the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission (617.4 nm), show well-resolved $^7\text{F}_0 \rightarrow ^5\text{L}_6$ (394 nm) and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ (465 nm) primary transitions, alongside weaker

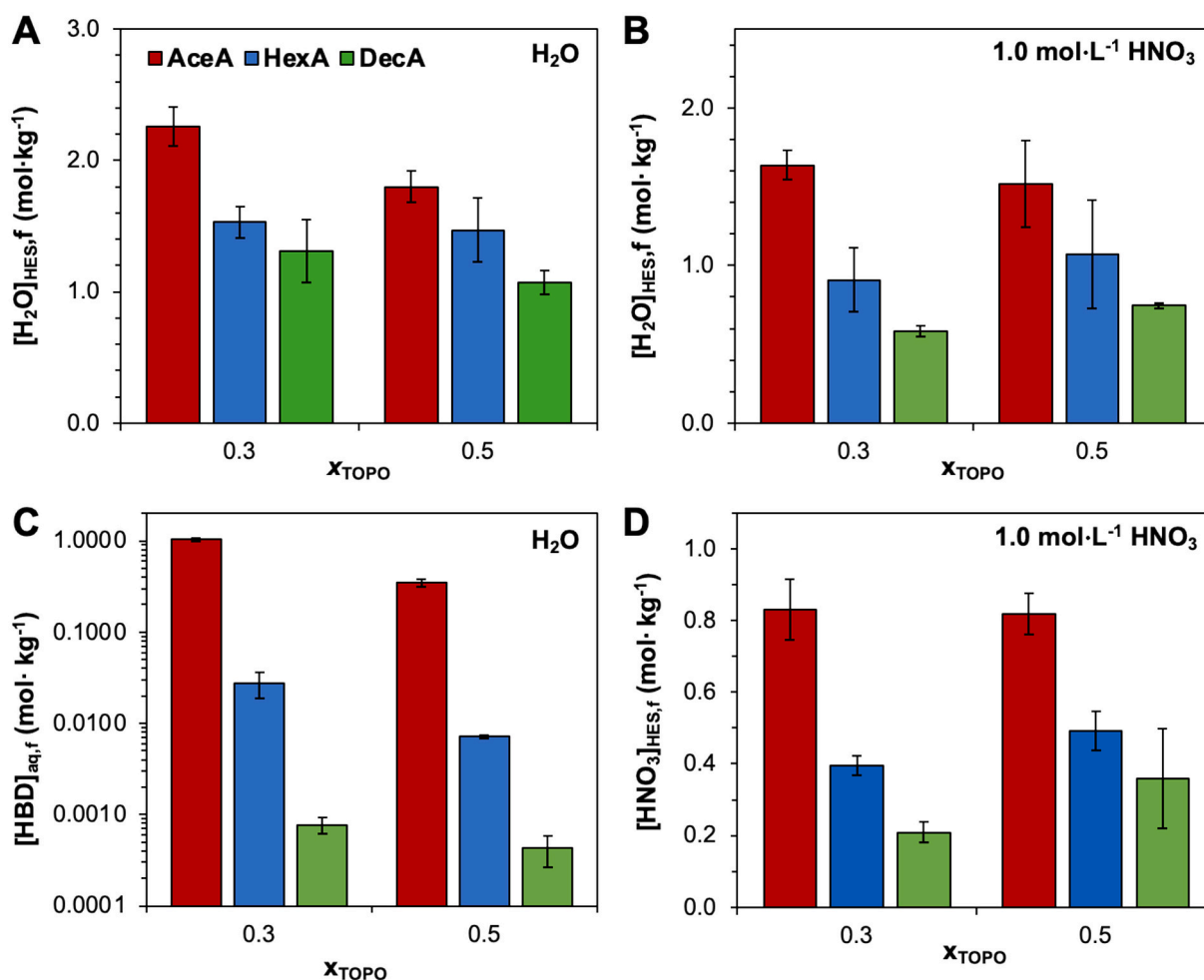


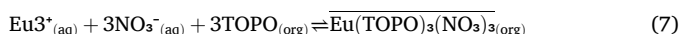
Fig. 5. H_2O (A & B) and HNO_3 (D) concentration in the HES phase and HBD loss to the H_2O phase (C) as a function of the HBD after contact with either H_2O or $1.0 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$ as indicated in the inset. All partition were measure in the absence of Ln^{3+} ions at $O/A = 0.5$ and $T = 298 \text{ K}$. Colour code corresponds to TOPO + AceA – red; TOPO + HexA – blue; TOPO + DecA – green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

features. The emission spectra of all three systems are very similar, showing the typical $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) Eu^{3+} transitions and a strong dominance of the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition with maximum at 617.4 nm. In the $^7F_0 \rightarrow ^5D_0$ region it is identified a single emission line suggesting the presence of a single Eu^{3+} site for all eutectic system. The predominance of the electric dipole $^5D_0 \rightarrow ^7F_2$ transition over the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition in each HES indicates a coordination environment around Eu^{3+} without inversion center. The absence of an inversion center it is also corroborated by the presence of the $^5D_0 \rightarrow ^7F_0$ transition only allowed in low-symmetry environments. The emission spectra were further analyzed using the asymmetric ratio (AR, eq. 5), as well by Eu^{3+} emission lifetime measurements in H_2O and D_2O solutions from which the number of inner-sphere water molecules ($n_{\text{H}_2\text{O}}$) was extracted using the relation of Supkowski and Horrocks [47] (eq. 6). The results are summarized in Table 3.

$$\text{AR} = \frac{I^5D_0 \rightarrow 7F_2}{I^5D_0 \rightarrow 7F_1} \quad (5)$$

$$n_{\text{H}_2\text{O}} = 1.05 \cdot \left(\frac{1}{\tau_{\text{H}_2\text{O}}} - \frac{1}{\tau_{\text{D}_2\text{O}}} \right) \quad (6)$$

where $\tau_{\text{H}_2\text{O}}$ and $\tau_{\text{D}_2\text{O}}$ is the Eu^{3+} luminescence lifetime in H_2O and D_2O , respectively. All systems show a similar AR value of approximately 5.4, confirming an asymmetric, non-centrosymmetric coordination environment with substantial ligand-field effects as would be expected in the mixed ligand complexes. The $\text{Eu}^{3+} ^5D_0$ emission decay curves detecting the emission at 617.4 nm after excitation at 355 nm in the same HES phases after SX from 1.0 mol·L⁻¹ HNO_3 in H_2O and D_2O are available in Fig. S5 and Fig. S6, respectively. All profiles were fitted with single exponential decay functions, and the obtained lifetimes are available in Table 3. A τ greater than 1.5 ms combined with $n_{\text{H}_2\text{O}}$ below 0.2 reinforces the existence of an inner-sphere complex of $\text{Eu}(\text{III})$ with NO_3^- and TOPO ligand devoid of water molecules. Interestingly, previous studies by Rout and Ramanathan [46] found that the initial aqueous phase HNO_3 concentration did not influence the resulting Eu^{3+} in the TOPO + DecA HES, with similar τ reported to those in Table 3. Taken together, the spectroscopic data indicate that Eu^{3+} forms a single predominant, low-symmetry complex in all three TOPO-based HES. Recent X-ray spectroscopy data of Eu^{3+} in the TOPO + DecA suggests the existence of the capped square antiprism $\text{Eu}(\text{NO}_3)_3(\text{TOPO})_3$ complex [19], such that the extraction mechanism in all three systems, irrespective of x_{TOPO} , can be written as per eq. (7):



3.5. Influence of polar solute co-extraction

Having excluded speciation for the varied SX tendencies of TOPO + AceA in Figs. 2 and 3 relative to the HexA and DecA systems, attention is now paid to the change in the HES phase structure caused by the co-extraction of polar solute under SX conditions. To this end, the partition of H_2O and HNO_3 from the aqueous to the HES phase is measured, upon equilibration of each HES (for $x_{\text{TOPO}} = 0.3$ and $x_{\text{TOPO}} = 0.5$) with either H_2O or 1.0 mol·L⁻¹ HNO_3 solution. In turn, the loss of the HBD component to the aqueous phase was also recorded. The associated error with the determination of HBD loss in 1.0 mol·L⁻¹ HNO_3 meant these were only determined after contact with H_2O . Due to the salting-in nature of HNO_3 , equivalent or greater HBD losses to the aqueous phase are anticipated following contact by 1.0 mol·L⁻¹ HNO_3 relative to the reported values in pure H_2O , although the trends are not expected to differ. The results are presented in Fig. 5A-D, with the values available in Table S8. No TOPO concentration could be detected in the aqueous phase after equilibration by ^{31}P NMR, consistent with its very low solubility in water of 0.15 mg·L⁻¹ (3.9×10^{-7} mol·L⁻¹) [49]. In addition, the ability of the thermodynamic model COSMO-RS, a computationally

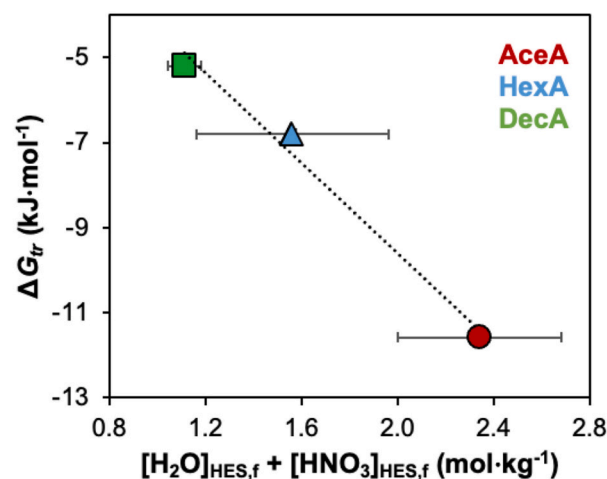


Fig. 6. Gibbs energy of transfer of Eu^{3+} as a function of the HES phase concentration of H_2O and HNO_3 in the three TOPO + Carboxylic acid HES for $x_{\text{TOPO}} = 0.5$, $[\text{HNO}_3] = 1.0 \text{ mol·L}^{-1}$, $T = 298 \text{ K}$ and $\text{O/A} = 0.5$. Colour code corresponds to TOPO + AceA – red; TOPO + HexA – blue; TOPO + DecA – green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

efficient predictive model for the liquid-liquid equilibria of complex aqueous-organic mixtures [50,51], to determine the ternary TOPO/HBD/ H_2O system component partition was evaluated and compared against experimentally obtained tie-lines in Fig. S7.

The nature of the HBD and its concentration in the HES has a pronounced influence on the water partition to the organic phase, with approximately a 1.5- to 2-fold increase in co-extracted water when progressing from the hydrophilic AceA to hydrophobic DecA depending on x_{TOPO} (Fig. 5A-B). This reduction is independent of the presence of HNO_3 , even if the latter reduces H_2O partition due to its more favorable interaction with TOPO [52,53]. The partition of HNO_3 to the various HES phases (Fig. 5D) follows a similar trend to water, with partition increasing with the reduction of the alkyl chain length of the HBD as well as with increasing x_{TOPO} . The formation of TOPO- HNO_3 adduct is observable by ^{31}P NMR, previously shown in Figs. S2 and S3, with the extent of the downshift in signal relative to the as-prepared HES in accordance with the measured extracted HNO_3 extraction. Importantly, considering the suppressed D_{Ln} obtained for all systems at 6.0 mol·L⁻¹ HNO_3 , it can be reasonably assumed that HNO_3 co-extraction alone is not responsible for the differences in D_{Ln} between AceA and HexA or DecA, with water appearing as the predominant driver. Importantly, the concentration of water and acid, although small in weight percent, are substantial when considered in mol fraction. Depending on the HBD nature, aqueous phase composition and x_{TOPO} , the final polar solute molar fraction in the HES phase is between approximately 20 to 35 mol % and represent a major component of a phase defined by its hydrogen-bonded interactions.

The significant variations in water partition to the HES phase with the alkyl chain of the HBD are mirrored by the partition of the HBD to the aqueous phase (Fig. 5C). Pure AceA is fully miscible across all compositions with water, and its protonated form presents a logarithm of the octanol/water partition ($\log_{10}\text{POW}$) of -0.31 [54]. In turn, HexA and DecA possess orders of magnitude lower solubilities of approximately $\sim 9.3 \times 10^{-2} \text{ mol·L}^{-1}$ and $\sim 8.7 \times 10^{-4} \text{ mol·L}^{-1}$ respectively, reflected in their increase of $\log_{10}\text{POW}$ to 1.91 and 4.09. Aqueous solubilities trends of the pure HBDs are preserved upon their incorporation as HES components. The loss of the HBD is correlated to its $\log_{10}\text{POW}$ as shown in Fig. S8, albeit with a synergistic decrease in their solubility when used in a HES. Of relevance for HES reuse during continuous SX,

Table 4

Experimental interfacial tension of HES equilibrated with water or 1.0 mol·L⁻¹ HNO₃ at 298 K in the absence of lanthanide salts.

HBD	x_{TOPO}	HES-H ₂ O (mN·m ⁻¹)	HES-HNO ₃ (mN·m ⁻¹)
AceA	0.3	9.0 ± 0.6	8.9 ± 0.3
	0.5	17.5 ± 0.3	5.2 ± 0.1
HexA	0.3	18.4 ± 0.7	12.3 ± 0.7
	0.5	16.3 ± 0.3	14.2 ± 0.5
DecA	0.3	19.9 ± 1.2	14.5 ± 0.4
	0.5	16.9 ± 1.0	16.3 ± 1.2

the relative magnitude of the synergistic decrease in solubility varies with the x_{TOPO} molar fraction and the solubility of the pure compound. For illustration, the aqueous solubility of AceA diminishes from entirely miscible in the pure state to 1.03 and 0.35 mol·L⁻¹ for $x_{\text{TOPO}} = 0.3$ and 0.5 after contact with 1.0 mol·L⁻¹ HNO₃ (O/A = 0.5). A similar observation was reported for the TOPO + Malonic acid system, with the loss of the acid component increasing with the HBD molar fraction and aqueous phase HCl concentration [49]. Interestingly, COSMO-RS was able to provide an excellent description of the HES phase compositions in all ternary TOPO/HBD/H₂O system as shown in Fig. S7 but an approximate prediction of the aqueous phase composition for AceA. Nevertheless, COSMO-RS can provide a rapid computational method for the estimation of water partition in HES to guide the discovery of other relevant SX systems in which water solubility and HBD partition play a defining role.

Relating the solute partition results to Ln³⁺ SX trends in Fig. 2 for $x_{\text{TOPO}} = 0.5$ and 1.0 mol·L⁻¹ HNO₃, the SX condition presenting the

highest D_{Ln} values for all systems, the Gibbs energy of transfer (ΔG_{tr}) of Eu³⁺ in the three HES systems is plotted against the polar solute partition as shown in Fig. 6. The ΔG_{tr} is given by eq. (8) [55]:

$$\Delta G_{\text{tr}}(\text{Eu}^{3+}) = -RT \ln(D_{\text{Eu}}) \quad (8)$$

In this scenario, the standard state of ΔG_{ex} is for a solvent containing all the species but Eu(NO₃)₃; it represents the free energy per mole of the transferred species. The ΔG_{tr} of Eu³⁺ from nitrate media shows a clear and systematic dependence on the nature of the carboxylic acid component as evidenced in Fig. 6.

The strong correlation between ΔG_{tr} and various metrics related to the hydrophilicity of the carboxylic acid demonstrates that water and HNO₃ incorporation into the eutectic phase plays a decisive role in Ln³⁺ transfer. ΔG_{tr} can be expressed as the result of several contributions, namely the favorable complexation energy of Ln³⁺ and TOPO ($\Delta G_{\text{Complexation}}$) dampened by the unfavorable effect of electrolyte confinement from an aqueous phase to the highly concentrated polar domains of the organic phase ($\Delta G_{\text{Confinement}}$) and molecular-level solvent-phase reorganization around the extracted and co-extracted species ($\Delta G_{\text{Structuration}}$) [55]. It is worth highlighting again that no inner-sphere water molecules were found in the inner coordination sphere of Eu³⁺ (Table 3) such that the differing water concentration does not alter the direct speciation across the three systems (not considering the outer-shell). It is here proposed that rather than acting as a competitive ligand, water appears to participate in restructuring the hydrogen-bond network of the HES ($\Delta G_{\text{Structuration}}$), increasing its polarity ($\Delta G_{\text{Confinement}}$) and improving its compatibility with the lanthanide–nitrate complex. The electrostatic penalties associated with transferring an electrolyte across the aqueous–HES interface as well as its solvation in

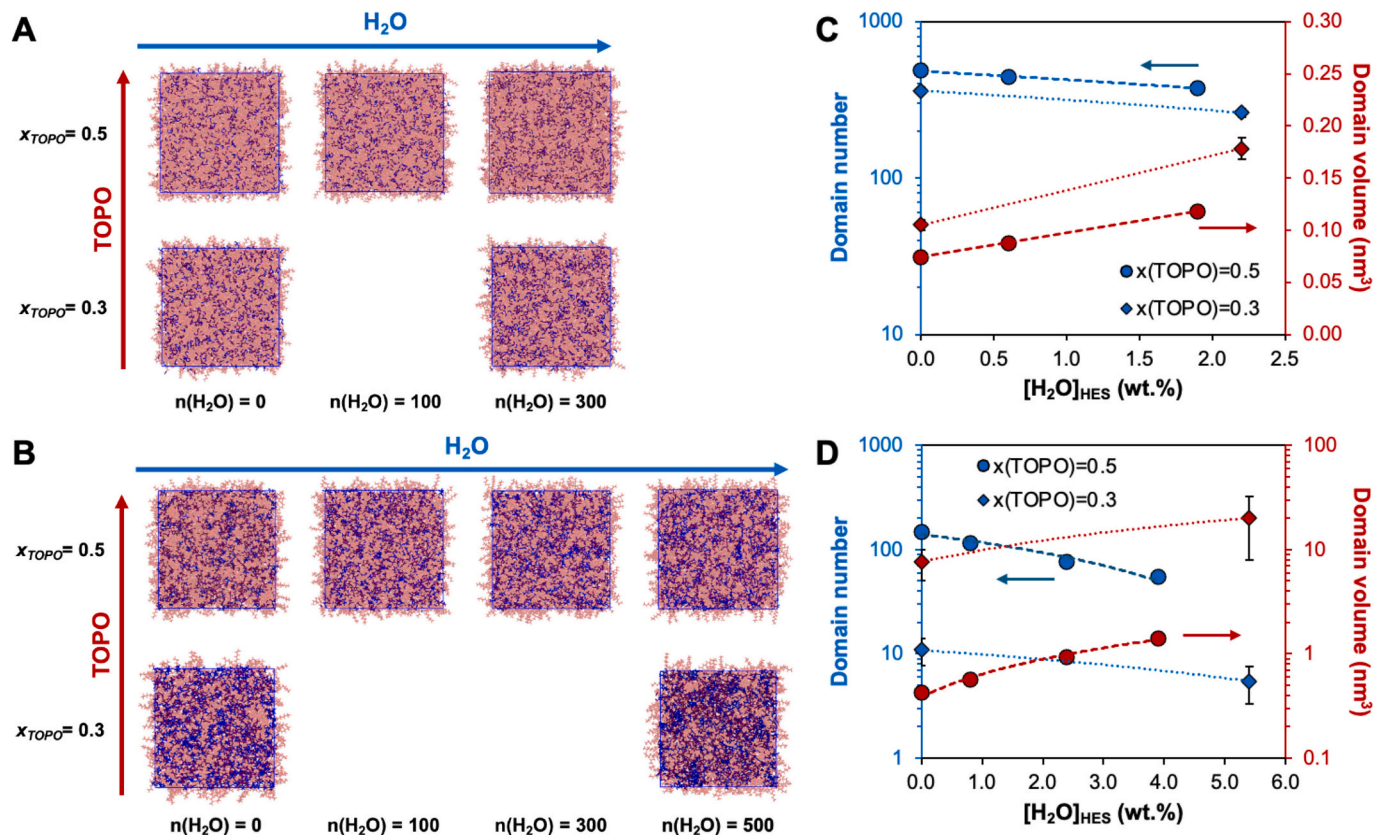


Fig. 7. Classical MD simulations of the TOPO + DecA (A and C) and TOPO + AceA (B and D) HES phases at x_{TOPO} of 0.3 and 0.5 with increasing water content. The x_{TOPO} corresponds to the HES composition before water addition. A & B) Final simulation snapshot box (blue – polar domain including COOH of the HBD, P=O of TOPO, and water; red – apolar domain including alkyl chains). C & D) Time averaged polar domain analysis and polar domain volume (C and D). Lines are drawn as guides to the eye. Simulation box details are provided in Table S9. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the HES phase ($\Delta G_{\text{Confinement}}$) is related to the difference in dielectric environment (ϵ_r) between the phases. This penalty can be approximated by the Born energy of the electrolyte and scales with $(1/\epsilon_{\text{HES}} - 1/\epsilon_{\text{H}_2\text{O}})$, with the ϵ_{HES} expected to vary with the volume fraction of HES phase water molecules due to its large ϵ relative to that of the HES components.

Beyond bulk effect, the $\Delta G_{\text{Confinement}}$ also influences the free energy penalty of crossing the interface due to a lower energetic cost to distort or “open” the interface, compounded by a more gradual polarity transition between phases, translating in a reduced penalty for moving species across. Macroscopically, the equilibrated HES interfacial tensions with H_2O and $1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ (presented in Table 4) reflect the preferential Ln^{3+} distribution in the systems with decreasing alkyl chain lengths of the HBD. The HexA and DecA-based HES present interfacial tension values consistent with that of TOPO in organic diluents, in the range of 10 to $35 \text{ mN}\cdot\text{m}^{-1}$ depending on the HNO_3 concentration and presence of secondary extractants [56]. In turn, a particularly low interfacial tension is obtained in the AceA systems with $1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ akin to that obtained in SX in the presence of phase modifiers such as hydrotropes and further hinting at a break in trends from the more surface active HexA and DecA to the hydrophilic AceA [57,58]. This is likely due to a combination of the increased formation of TOPO-nitrate adducts, greater HES phase water content, and significant AceA aqueous phase partition.

3.6. HES structure upon polar solute co-extraction

To evaluate the change in the hydrogen-bond network of the HES upon water extraction liable to influence $\Delta G_{\text{Structure}}$, classical non-polarizable MD simulations of the TOPO + AceA and TOPO + DecA systems were carried-out with increasing water content up to approximate HES saturation as determined in Fig. 5. In these simulations AceA loss to the aqueous phase was not considered, with the initial HES proportions (x_{TOPO} of 0.3 and 0.5) maintained upon water addition. In fact, when accounting for AceA loss to the aqueous phase taken from Fig. 5, the final experimental x_{TOPO} changes from a starting composition of 0.3 and 0.5 to 0.45 and 0.59 respectively. As such, although the loss of AceA is not explicitly simulated, the simulations for $x_{\text{TOPO}} = 0.5$ approximates the experimental post-equilibrium composition of the initial $x_{\text{TOPO}} = 0.3$ system and serves to confirm that the key trends remain valid.

The final snapshot of each production run for DecA and AceA systems are presented in Fig. 7A and B respectively, with the polar domain composed of water molecules, phosphine oxide bond of TOPO and the carboxylic group of the HBD shown in blue and the apolar alkyl domain highlighted in red. Differences between the systems are apparent, with the polar network of the DecA-based HES confined to discrete clusters at the center of apolar reverse micelle-like aggregates composed of mixed TOPO and DecA, irrespective of the molar fraction and hydration. This morphology may limit additional water uptake, as swelling of the confined polar core appears constrained. In contrast, AceA-based systems show the emergence of extended hydrogen-bonded percolating channels, together increased segregation of the polar/apolar network with increasing water content and/or decrease in x_{TOPO} . This is due to the minimal apolar volume of AceA, facilitating its intercalation in the polar network and its growth.

The change in the binary interactions within the HES components with water, namely HBA – HBD, HBD – HBD, and HES – H_2O , were computed through the respective radial distribution functions (RDFs) and associated coordination number (CNs) in Fig. S9 and S10. Despite the different alkyl chain lengths, no significant transformations are observed in local pair interactions. Water addition increases the number of free TOPO molecules by disrupting the TOPO – carboxylic acid hydrogen bond and subsequent solvation of the resulting polar group as evidenced by the decrease in the TOPO – HBD CN from 0.82 to 0.46 and from 0.77 to 0.57 in the AceA and DecA systems respectively at

maximum water loading (for $r = 0.3 \text{ nm}$). These observations are consistent with the experimental NMR results (Fig. S1). Together, these support the interpretation that water uptake disrupts and reorganises the TOPO–HBD hydrogen-bonding network, increasing the population of less HBD-bound TOPO and, more broadly, restructuring the polar domains of the HES. In contrast, the influence of water on the carboxylic dimer is minimal, suggesting a preferential solvation of the phosphine oxide bond. RDF analysis suggests that differences between systems do not originate from local hydrogen-bonding interactions, but rather from differences in mesoscale organization arising from the extent of water uptake.

To support the visual observations in Fig. 7, the number of polar domains and the volume of the largest domain were calculated based on the Voronoi tessellation method [36] as function of the HES x_{TOPO} and water content. A domain number of 1 indicates the continuous nature of the polar domain subset whilst larger values reflect its dispersed nature. The results are presented in Fig. 7C and D and the simulation box details and domain analysis are summarized in Table S9. Irrespective of the HBD selection and x_{TOPO} , increasing the number of water molecules results in the reduction in the number of discrete polar domains and the growth of the polar volume. However, the extent of the HES phase reorganization is highly dependent on the HBD selection, with DecA-based systems presenting an elevated domain number and limited growth of the polar domain volume upon water addition up to a non-negligible water mol fraction of $x_{\text{H}_2\text{O}} = 0.23$ ($n(\text{H}_2\text{O}) = 300$). In contrast, AceA system exhibits a more pronounced decrease in the domain number with the number of added water molecules, approaching an almost continuous domain upon water saturation for $x_{\text{TOPO}} = 0.3$. This also results in maximum aggregate volumes being one to two orders of magnitudes (depending on x_{TOPO}) compared to the DecA based HES. The larger polar domain volume, composed of the $\text{P}=\text{O}$ bond of TOPO, AceA, and H_2O , not only raises the local dielectric constant favoring Ln^{3+} partition as previously discussed, but also increases the configuration entropy of the extracted species due to the greater number of hydrogen bonded configurations thereby reducing the penalty to $\Delta G_{\text{Structure}}$.

This behavior is reminiscent with that reported for conventional SX in the presence of hydrotropes such as 1-propoxy-2-propanol, either as phase modifiers or directly as diluent [59,60], drawing parallels to discussed HES systems. Hydrotropy refers to the ability of a molecule to enhance the solubility of otherwise poorly soluble species by modifying solvent structure and disrupting long-range organization without itself presenting a defined self-aggregation [61]. Taken together, these experimental and computational observations suggest a transition from a more surfactant-like mode of organization for the longer-chain HBDs to a more hydrotrope-like behavior for AceA. Here, ‘hydrotrope-like’ and ‘surfactant-like’ are used as descriptors of the observed solvent organization rather than as strict molecular classifications. The low interfacial tension, enhanced water uptake and significant aqueous partitioning of AceA are consistent with a more hydrophilic, structure-disrupting role, while the MD domain analysis indicates that DecA-based systems retain more discrete, aggregate-like polar domains. Thus, by simply varying the hydrophilicity of the HES components for a given HBD-HBA functional group pairing, the ability of the eutectic phase to accommodate polar species in a structured yet adaptable environment is obtained, playing on the nuance between hydrotrope vs surfactant-like behavior on the HES microheterogeneity and the balance between polar and apolar domains.

3.7. Tuning the extraction performance – Towards ternary mixtures

A practical impediment to the implementation of “hydrotrope” based HES for SX is the important loss of the component to the aqueous phase as shown in Fig. 5. Although changes in the HES molar ratio did not negatively affect the D_{Ln} as shown in Fig. 2, loss of AceA remains problematic and could impact on its recycle and reuse. As previously

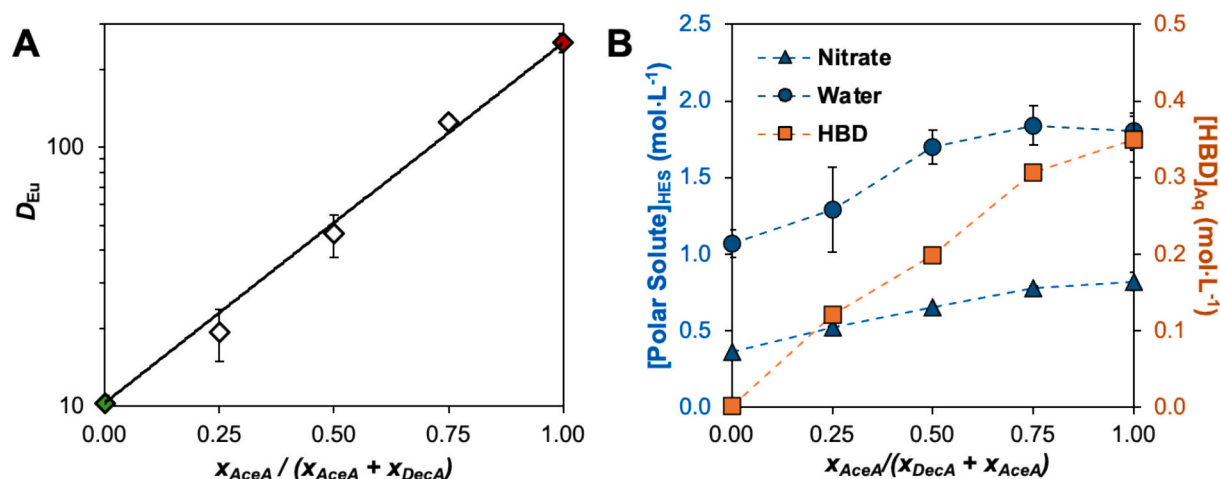


Fig. 8. A) Eu^{3+} distribution coefficient and B) H_2O , HNO_3 , and HBD concentrations as a function of the AceA to DecA molar ratio in the ternary system of TOPO/AceA/DecA at $x_{TOPO} = 0.5$. Solid line in panel (A) corresponds to the predicted values assuming ideal mixing between the binary TOPO + AceA and TOPO + DecA. All systems were equilibrated with a $1.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 aqueous phase in the absence of Ln^{3+} ions ($O/A = 0.5$).

discussed, the final x_{TOPO} increases to 0.45 and 0.59 for a starting composition of 0.3 and 0.5 respectively. One potential solution to overcome this drawback is to matrix match the HBD component to the acid used during leaching, thereby keeping the overall concentration of the organic acid in the process constant. Given the reported use of many short chained organic acids such as acetic, lactic, or malonic acid for leaching application and their reported inclusion as HBD in HES, this appears as a promising avenue [21,49]. It is not however a universal solution, and its applicability is system and extractant specific. In the case of the studied TOPO + AceA system, substitution of the aqueous acid from $1.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 to AceA suppressed lanthanide partition, with D_{Eu} decreasing to 0.25 ± 0.01 . In contrast, in a previously reported TODGA + carboxylic acid-based HES system, $D_{Ln} > 10$ were obtained from AceA leachates [13]. A second approach investigated here is the possibility of ternary mixtures in which the short chain acid is added to a hydrophobic system, in this case TOPO + DecA, as a sacrificial agent to improve D_{Ln} whilst minimizing its overall loss. Under the same optimal SX conditions previously reported and for a fixed $x_{TOPO} = 0.5$, the D_{Eu} , H_2O , and HNO_3 concentration in the HES phase and the loss of AceA to the aqueous phase were measured as a function of the AceA to DecA molar ratio for the ternary mixture composed of TOPO/AceA/DecA. The results are shown in Fig. 8 and show Table S10.

The inclusion of AceA in TOPO-based HES favors Ln^{3+} extraction compared to DecA derived from the increasing of polar and hydrophilic nature of AceA HES. Interestingly, the variation in D_{Eu} is predictable and obeys ideal mixing laws, such that the mixture composition can be predictably tuned to obtain a desired metal distribution threshold. The polar solute partition, namely H_2O and HNO_3 to the HES phase and the HBD to the aqueous phase, follow a similar trend as Eu^{3+} distribution albeit with an approximately linear evolution compared to the exponential trend in D_{Eu} with composition. The loss of the HBD to the aqueous phase in ternary systems is entirely assigned to AceA, justifying its sharp increase upon inclusion of AceA to the previously binary DecA-based systems and thereafter increases linearly with subsequent increases in x_{AceA} . The results in Fig. 8 clearly illustrates how the HES performance can be balanced with its SX properties and reuse, presenting a compromise between increased distribution upon inclusion of a hydrophilic structure breaking component and loss of the latter during aqueous phase contact.

4. Conclusion

Although the non-extractant component is not directly involved in metal-ion chelation, as it is absent from the inner coordination sphere,

this work demonstrates that the nature of the hydrogen-bond donor exerts a strong and measurable influence on the SX of Ln^{3+} ions. This effect arises from the HBD's impact on the molecular structure of the HES and the resulting polarity of the solvent network. By varying the carboxylic acid used as the HBD, the TOPO molar fraction, and the acidity of the aqueous phase, relationships were established between solvent organization, solute co-extraction, and metal partitioning. These results demonstrate that maximizing hydrophobicity is not necessarily advantageous for Ln^{3+} extraction in eutectic systems. Instead, optimal extraction thermodynamics are achieved by reducing the energetic penalties associated with both $\Delta G_{\text{Structure}}$ and $\Delta G_{\text{Confinement}}$ through a transition from surfactant-like to hydrotrope-like HBD behavior, as exemplified by DecA and AceA.

Water uptake was identified as a key factor governing D_{Ln} , determined by the hydrophilicity of the HBD modulated in this work by the change in the alkyl chain length. Increased incorporation of polar species, especially water, disrupts the HBA-HBD hydrogen-bonding network, leading to a higher concentration of free TOPO in the organic phase. However, a trade-off exists: benefits in improved metal partition, atomic efficiency of the extractant and viscosity of the loaded HES phase must be balanced against and loss of the HBD component to the aqueous phase and ease of stripping. These findings provide a framework for the design of new hydrophobic eutectic solvents for lanthanide separations. Specifically, tuning the hydrophilicity of the hydrogen-bond donor offers a thermodynamic handle for modulating metal transfer without altering the extractant chemistry itself. More broadly, the results establish a mechanistic basis for HES constituent selection and provide guidelines for improving the efficiency of sustainable solvent-extraction processes. Although demonstrated here for Ln^{3+} extraction from nitrate media, the underlying principles may also be relevant to other HES-based metal-extraction systems employing neutral extractants, and to conventional solvent-extraction systems in which hydrotropic or phase-modifying components influence the accommodation of polar extracted species. The applicability of this framework to other metal ions, extractant chemistries and aqueous media, however, remains to be established experimentally.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contribution

Rodrigo Colhe – Investigation, Data Curation, Formal Analysis, Visualization, Writing - Original Draft. Amélie Tropres – Investigation, Formal Analysis, Writing - Review & Editing. Maísa Saldanha Pinheiro – Investigation, Data Curation, Writing - Review & Editing. Thaís S. Soares – Investigation, Data Curation, Writing - Review & Editing. Takafumi Hanada – Investigation, Writing - Review & Editing. Duarte Ananias – Investigation, Formal Analysis, Writing - Review & Editing. Felipe Olea – Investigation, Writing - Review & Editing. Inês Vaz – Investigation, Writing - Review & Editing. João A.P. Coutinho – Supervision, Writing - Review & Editing. Nicolas Schaeffer – Investigation, Formal Analysis, Supervision, Project Administration, Funding Acquisition, Writing - Review & Editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2026.140316>.

Data availability

Research Link Provided

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