Interactions Between Trivalent Rare Earth Oxides and Mixed [Hbet][Tf$_2$N]:H$_2$O Systems in the Development of a One-step Process for the Separation of Light from Heavy Rare Earth Elements

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Keywords

Abstract

The factors, including ionic liquid:water ratios, temperature, solvent:solute contact times, and the effect of dissolved rare earth metal ions on the [Hbet][Tf$_2$N]:H$_2$O thermometric phase change are determined to develop a process for separating the light from the heavy rare earth metal oxides in [Hbet][Tf$_2$N]:H$_2$O mixtures. The relative solubility data for three light (La$_2$O$_3$, Nd$_2$O$_3$, and Eu$_2$O$_3$), two heavy (Y$_2$O$_3$ and Yb$_2$O$_3$) rare earth metal oxides (REOs), and Gd$_2$O$_3$ at different temperatures and different solute:solvent contact times are reported for 1:1 [Hbet][Tf$_2$N]:H$_2$O. The light REOs dissolve easily at 57 ^{o}C with the La and Eu reaching maximum solubility within minutes while the heavy REOs have very low solubilities at this temperature with negligible amounts being dissolved for contact times less than 80 min. Gd$_2$O$_3$ dissolves more slowly than the La, Eu, and Nd oxides at 57 ^{o}C reaching maximum solubility only after 160 min. Changing the [Hbet][Tf$_2$N]:H$_2$O ratio from 1:1 to 16:1 increases the time required to dissolve the REOs. The times taken to reach maximum solubility decrease for all of the REOs up to 95 ^{o}C, resulting in the separations between the light and heavy rare earth elements, and Gd becoming less distinct. The presence of rare earth metal ions in [Hbet][Tf$_2$N]:H$_2$O results in a reduction in the upper critical solution temperature (UCST) of the solvent from 55.6 ^{o}C to as low as 31.8 ^{o}C with Gd^{3+}. The best separation of light from heavy REOs is achieved at 57 ^{o}C but better separation of Gd from the light REOs is achieved at 40

°C, below the solvent UCST. The best conditions for a one-step separation of light from heavy REOs in [Hbet][Tf$_2$N]-H$_2$O mixtures is achieved with 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 °C using short contact oxide:solvent times (maximum 5 min). Separations of light from heavy REOs, in waste phosphor samples, containing La$_2$O$_3$, CeO$_2$, Eu$_2$O$_3$, Gd$_2$O$_3$, Tb$_3$O$_4$ and Y$_2$O$_3$, are also achieved even in the presence of high concentrations of heavy REOs using short contact times. The use of [Hbet][Tf$_2$N]:H$_2$O as a means of separating light and heavy REOs is aided by the ease of recycling the solvent which can be recycled and reused at least five times with little loss of solvent quality or efficiency.

1. Introduction

The rare earth (RE) elements (the lanthanide elements, yttrium and scandium), classified as light or heavy (based on their electronic configuration), have distinctive metallurgical, chemical, catalytic, electrical, magnetic and optical properties that are exploited in electrical and electronic applications such as permanent magnets, rechargeable NiMH batteries, fibre optics, LEDs, catalysts and phosphors. With alternatives to RE elements limited, and demand for them increasing dramatically in recent years [1], the European Union has classified them as critical materials [2]. Although Waste Electrical and Electronic Equipment (WEEE) represents a potential source of RE metals, currently only 1% of these metals present in WEEE is recovered and recycled [3].

Conventional industrial processing to separate RE elements from RE oxide ores involves a combination of hydrometallurgy and solvent extraction [4]. Although the conventional method is favoured on the basis of being a simple process, with relatively low capital costs, recovery of the pure metals or metal oxides requires extraction and separation techniques, that: (i) use aggressive acid or alkali digestion, (ii) involve multi-stage separation procedures, (iii) produce large aqueous waste streams which require further treatment, and (iv) in the solvent extraction process, make use of solvents which are potentially flammable, volatile and toxic solvents.

Ionic liquids are a class of solvent usually consisting of organic cations and inorganic anions with melting points below 100 °C [5], that have properties (low melting point, low vapour pressure, density, viscosity, hydrophobicity, chemical and thermal stability etc.) that can be adjusted by varying either the anion or the cation to achieve applications that are credible

alternatives to conventional solvents for the extraction, separation and purification of metals and metal oxides [5-10]. A series of publications from Binneman's and Nockemann's research groups [6,11-16] and other authors [17] have described the use of the task-specific ionic liquid, betaine bis(trifluoromethylsulfonyl)imide, ([Hbet][Tf$_2$N]), in solubilising and separating trivalent RE oxides. Addition of water to [Hbet][Tf$_2$N] results in mixed [Hbet][Tf$_2$N]:H$_2$O systems that have lower viscosity than the pure IL and exhibit thermomorphic behaviour - forming two immiscible phases, below an upper critical solvent temperature (UCST), and a single homogeneous phase, above this temperature [6]. The lower viscosities of the mixed [Hbet][Tf$_2$N]:H$_2$O systems result in easier mass transfer of RE species into the single phase and a consequent higher extraction efficiency. This phase transition extraction has been used in the liquid-liquid extraction of neodymium(III) from an aqueous solution into [Hbet][Tf$_2$N] using betaine as an extractant [12, 13], and in the recovery of europium (Eu) and yttrium (Y) from lamp phosphor waste powders [14]. The solubility of the rare earth oxides in [Hbet][Tf$_2$N]:water mixtures is high due to the formation of complexes between the RE and oxygen atoms of the betaine carboxylate groups [11, 18].

We now report on a study of the interactions between RE oxides and mixed [Hbet][Tf$_2$N]:H$_2$O systems as a basis for development of a one step process to separate light RE elements from heavy RE elements in oxide mixtures and waste phosphors.

2. Experimental Section

2.1. Chemicals and Instrumentation

All chemicals were purchased from Sigma-Aldrich and used without any further purification. La$_2$O$_3$ and Nd$_2$O$_3$ were chosen to represent the light RE elements and Y$_2$O$_3$ and Yb$_2$O$_3$, the heavy RE elements. Eu$_2$O$_3$ and Gd$_2$O$_3$ were used as elements that are at the boundary between what is normally regarded as the light and heavy RE elements. The solubility of metal oxides in [Hbet][Tf$_2$N]:H$_2$O is known to vary with their oxidation state but the studies in this work only apply to the stable RE (III) oxides. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 spectrometer. All samples, liquid and solid, were examined directly using a Quest Single Reflection Attenuated Total Reflectance (ATR) accessory (Specac, UK). Metal analyses were obtained by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 7000 DV spectrometer.

2.2. Synthesis of [Hbet][Tf₂N]

[Hbet][Tf$_2$N], (Figure 1), was synthesised according to the metathesis reaction described by Nockemann and co-workers [6]. Lithium bis(trifluoromethylsulfonyl)imide (50.0g, 0.174 mol) and betaine hydrochloride (26.7g, 0.174 mol) were dissolved in 50 mL of water and stirred for one hour at room temperature. The resulting IL was phase-separated from the aqueous phase and washed with small amounts of cold distilled water until no chloride impurities could be detected by a silver nitrate test in the wash effluent. The product was dried in a rotary evaporator at 150 mbar and 80 °C for 6 h to give [Hbet][Tf$_2$N] as a white solid in 78% yield. The solvents used in this study were [Hbet][Tf$_2$N]:H$_2$O mass ratio mixtures prepared by adding weighed amounts of [Hbet][Tf$_2$N] to the appropriate mass of deionized water.
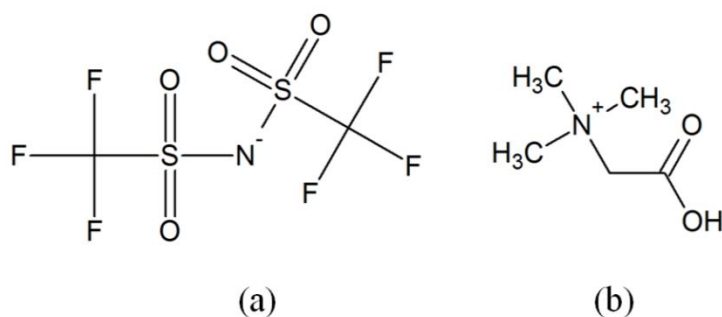

Figure 1. Structure of [Hbet][Tf$_2$N] with the (a) bis(trifluoromethylsulfonyl)imide anion and (b) protonated (carboxymethyl)trimethylammonium cation

2.3. Relative Solubilities of Rare Earth Oxides in Mixed [Hbet][Tf₂N]:H₂O Systems

To study the solubilities of the light and heavy RE oxides (La$_2$O$_3$, Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Y$_2$O$_3$, and Yb$_2$O$_3$), known to be insoluble in pure [Hbet][Tf$_2$N], single phase [Hbet][Tf$_2$N]:water mass ratio mixtures (1:1 and 2:1) for all of the RE oxides studied, and at (4:1, 8:1 and 16:1) for La$_2$O$_3$, as an example of a light RE oxide, were prepared by dissolving known weights of solid [Hbet][Tf$_2$N] in the appropriate amount of deionised water at four temperatures (57, 65, 80 and 95 °C) above the reported UCST [6]. Each study involved the addition of a 10 wt. % excess of the RE oxide to [Hbet][Tf$_2$N]:H$_2$O mixtures containing 1g of [Hbet][Tf$_2$N] over different periods of time (up to 180 min.), heated to the respective temperatures under reflux in a temperature-controlled silicone oil bath with mixing at 500 rpm. The RE oxide:[Hbet][Tf$_2$N]:H$_2$O mixtures were hot-filtered through 0.22 µm cellulose nitrate filter papers and the filtrand washed with deionised water at 60 °C to remove any residual IL prior to determination of RE metal content by ICP-OES. To minimise IL losses during filtration, the RE oxide:[Hbet][Tf$_2$N]:H$_2$O mixtures were filtered under vacuum at temperatures above the

UCST to recover both the IL and aqueous phases in the filtrate. Because of the lower viscosities of [Hbet][Tf$_2$N]:H$_2$O mixtures and the temperatures of the solutions used, vacuum filtration took only a few minutes. The [Hbet][Tf$_2$N]:H$_2$O mixture was recovered and contacted with 1 M hydrochloric acid containing 0.1 M betaine hydrochloride for 6 h with mixing at 50 rpm to obtain solutions for analysis of rare earth elements by ICP-OES. Betaine hydrochloride was added to the stripping solution in order to minimise the loss of the water-soluble betaine cation from the IL to the aqueous phase. In order to ensure consistent measurements, the residual undissolved RE oxides were dried, weighed and the recorded mass subtracted from the known initial amount of RE metal fraction added to the mixed IL:water system. All tests were performed in triplicate and the standard deviations of the relative solubilities found to be in the range 0-0.016 gRE/ g[Hbet][Tf$_2$N]. Unless otherwise stated, all reported concentrations represent the total amount of RE oxide dissolved in the [Hbet][Tf$_2$N]:H$_2$O mixture, which includes both the IL and aqueous phase concentrations

The results of the relative solubility measurements at different temperatures and times for the RE oxides dissolved in a 1:1[Hbet][Tf$_2$N]:H$_2$O mixture are shown in Figure 2, the effect of increasing the [Hbet][Tf$_2$N]:H$_2$O ratio to 2:1 on the relative solubilities of the RE oxides at 57 ^{o}C is shown in Figure 3, and the effect of increasing the [Hbet][Tf$_2$N]:H$_2$O ratio from 1:1 to 16:1 for La$_2$O$_3$ as an example of a light RE oxide, at 57 ^{o}C, are shown in Figure 4.

The distributions of RE species between the aqueous and [Hbet][Tf$_2$N] phases after extraction of the RE oxides at half saturation were measured by contacting half of the saturation amounts of each RE oxide (80 mg La$_2$O$_3$, 50 mg Y$_2$O$_3$ etc) with a 1:1 [Hbet][Tf$_2$N]:H$_2$O mixture containing 1g of [Hbet][Tf$_2$N] at above 57°C until the oxide dissolved completely and then standing the mixture for 12 h at 5°C to allow the two phases to separate completely. The RE content of the aqueous phase was determined by ICP-OES and that of the IL phase obtained from the difference between the half-saturation amount of RE added and the aqueous phase concentration. The results are in Table 1.
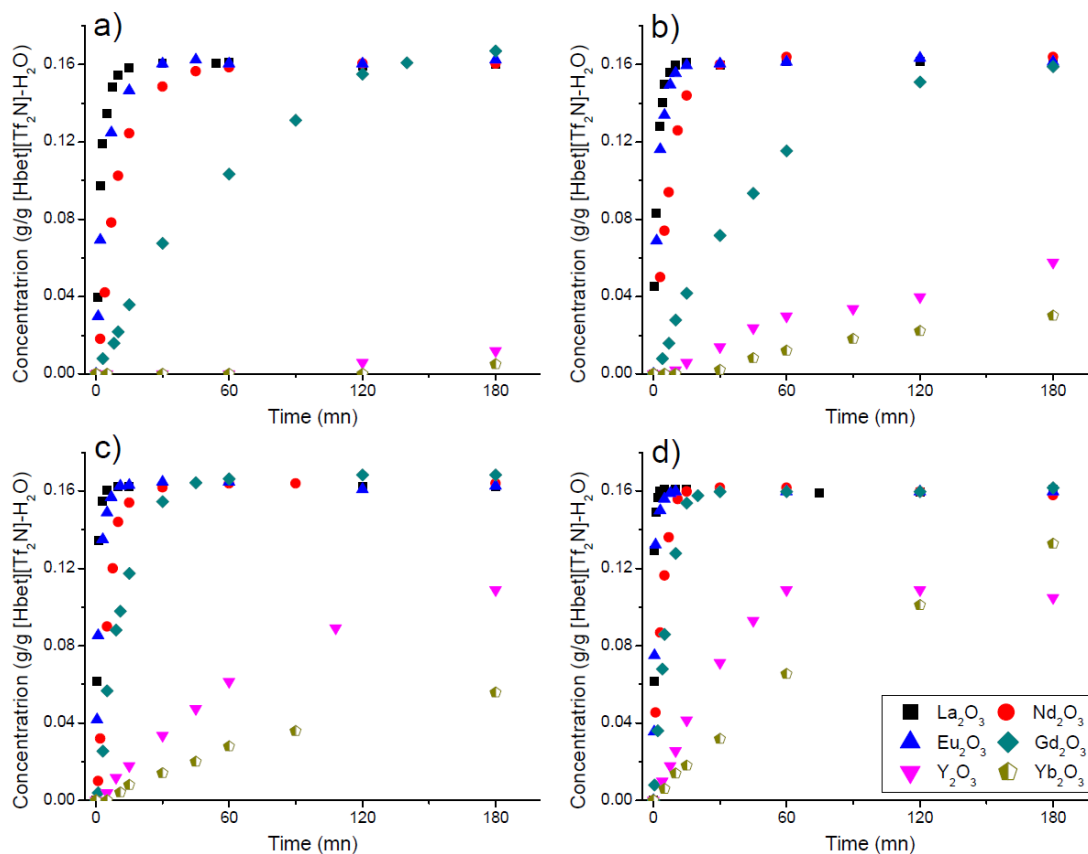
Figure 2 Solubilities of La_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Y_2O_3 and Yb_2O_3 in 1:1 [Hbet][Tf$_2$N]:H$_2$O as a function of time at the following temperatures: (a) T=57 ^{o}C, (b) T= 65 ^{o}C, (c) T=80 ^{o}C,(d) T=95 ^{o}C.
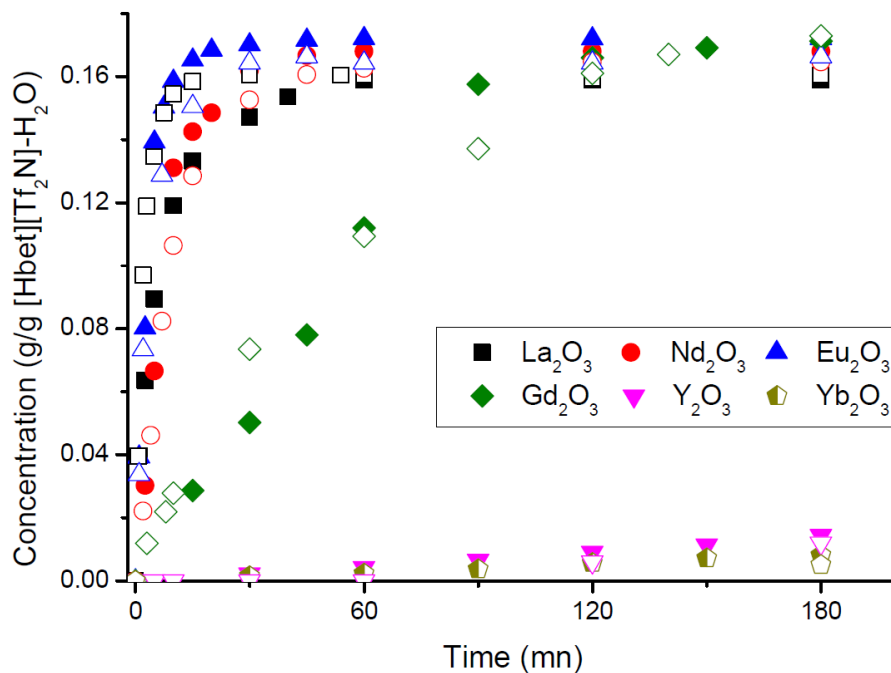
Figure 3 Solubilities of La_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Y_2O_3 and Yb_2O_3 in 2:1 [Hbet][Tf$_2$N]:H$_2$O (filled symbols) and 1:1 [Hbet][Tf$_2$N]:H$_2$O (empty symbols) at T=57 ^{o}C

2.4. Effect of the Presence of Rare Earth Oxides on the UCST of the [Hbet][Tf₂N]:H₂O system

The effect on the UCST of dissolving RE oxides in the 1:1 [Hbet][Tf$_2$N]:H$_2$O mixture was determined using the cloud point method [17]. Single phase solutions, containing known quantities of RE metal oxide dissolved in 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 °C in a flask, in a temperature-controlled silicone oil bath, were cooled gradually from 57 °C, with stirring at 500 rpm, until the first point of cloudiness appeared, indicating the temperature at which the IL:water phases separated. The results for the measurement of the UCST in 1:1 [Hbet][Tf$_2$N]:H$_2$O systems as a function of RE oxide loading are in Table 2.
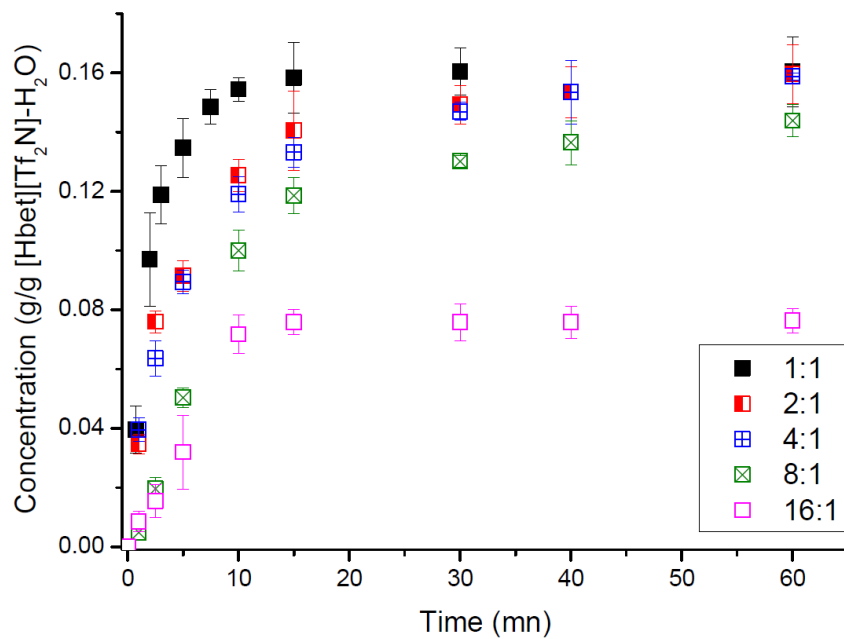

Figure 4 Dissolution of La$_2$O$_3$ against time in X:1 [Hbet][Tf$_2$N]:H$_2$O (where X=1, 2, 4, 8, 16) at T=57 °C

Table 1 Distribution of rare earth elements between the aqueous and [Hbet][Tf$_2$N] phases for La$_2$O$_3$, Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Y$_2$O$_3$ and Yb$_2$O$_3$ at half saturation concentrations in 1:1[Hbet][Tf$_2$N]: H$_2$O

% RE in phase	La$_2$O$_3$	Nd$_2$O$_3$	Eu$_2$O$_3$	Gd$_2$O$_3$	Y$_2$O$_3$	Yb$_2$O$_3$
[Hbet][Tf$_2$N]	70.5	71.6	82.1	80.4	84.0	84.0
Aqueous	29.5	28.4	17.9	19.6	16.0	16.0

2.5. Relative Solubilities of Rare Earth Oxides in [Hbet][Tf₂N]:H₂O:RE oxide mixtures at temperatures below the UCST

To determine the solubility of rare earth oxides in $[Hbet][Tf_2N]:H_2O:RE$ oxide mixtures at temperatures below the UCST, the relative solubilities of La_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Y_2O_3, and Yb_2O_3 in 1:1 $[Hbet][Tf_2N]:H_2O$, pre-saturated with the RE oxide, separately, as a function of time were determined in the single liquid phase mixtures at 40 °C, and the results compared in Figure 5 with those obtained at 57 °C. All reported concentrations represent the total amount of RE oxide dissolved in the $[Hbet][Tf_2N]:H_2O$ mixture.

Table 2 UCST as a function of La_2O_3, Gd_2O_3 and Y_2O_3 loading.

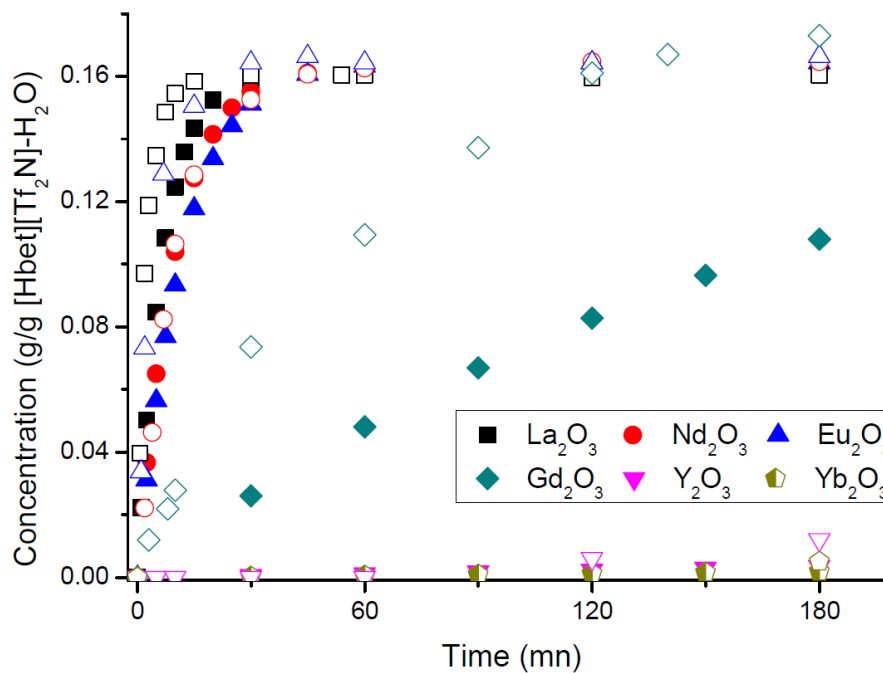| Average molar ratio (mol REO/mol [HBet][Tf₂N])	UCST (°C)		
	La_2O_3	Gd_2O_3	Y_2O_3
0.0 (±0.000)	55.6 (±1.0)	55.6 (±1.0)	55.6 (±1.0)
0.032 (±0.0030)	48.8 (±1.7)	48.8 (±1.9)	48.8 (±2.0)
0.059 (±0.0063)	41.6 (±1.3)	43.6 (±2.6)	43.7 (±2.3)
0.082 (±0.0034)	36.6 (±1.2)	34.6 (±2.2)	39.6 (±1.0)
0.125 (±0.0024)	32.5 (±1.2)	31.8 (±2.6)	28.5 (±2.3)

Figure 5 Solubilities of La_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Y_2O_3 and Yb_2O_3 in 1:1 $[Hbet][Tf_2N]:H_2O$ as a function of time at the following temperatures: (a) T=40 °C (filled symbols) and (b) T= 57 °C (empty symbols)

2.6. Separation studies

The potential of the [Hbet][Tf$_2$N]:H$_2$O solvents as a medium for separating light from heavy RE(III) oxides from mixtures of the oxides and from waste electronic materials such as waste phosphor powders was studied. The IL stripping procedure is described in section 2.3 and the reported concentrations represent the total amount of RE oxide dissolved in the [Hbet][Tf$_2$N]:H$_2$O mixture, which includes both the IL and aqueous phase concentrations.

2.6.1. Separation of RE oxides from Binary Rare Earth Oxide Mixtures

Equimolar binary mixtures of Eu$_2$O$_3$/La$_2$O$_3$, Nd$_2$O$_3$/La$_2$O$_3$, Gd$_2$O$_3$/La$_2$O$_3$, Y$_2$O$_3$/La$_2$O$_3$, and Yb$_2$O$_3$/La$_2$O$_3$ were stirred into 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 $^{\circ}$C for 30 s with stirring at 500 rpm. Each mixture was hot-filtered through a 0.22 µm cellulose nitrate filter paper to remove any undissolved RE oxides prior to stripping and analysis by ICP-OES. The same procedure was repeated with equimolar binary mixtures of the same RE oxides with Eu$_2$O$_3$ as La(III) and Eu(III) are the most easily dissolved RE oxides. The results, shown in Table 3 are expressed as separation ratios defined as the percentage of La$_2$O$_3$ (or Eu$_2$O$_3$) dissolved in the IL phase to the percentage of the other RE metal oxides dissolved in the IL phase.

Table 3 Separation Ratios of La and Eu from equimolar binary mixtures containing RE (where RE= Nd, Eu, Gd, Y or Yb). Separation ratios defined as the percentage of La$_2$O$_3$ (or Eu$_2$O$_3$) dissolved in the IL phase to the percentage of the other RE metal oxides dissolved in the IL phase

RE oxides separated	Separation Ratio in 1:1 [Hbet][Tf$_2$N]:H$_2$O	RE oxides separated	Separation Ratio in 1:1 [Hbet][Tf$_2$N]:H$_2$O
La : Eu	66.3 : 33.7	-	
La : Nd	73.7 : 26.3	Eu : Nd	52.0 : 48.0
La : Gd	92.8 : 7.2	Eu : Gd	76.4 : 23.6
La : Y	97.8 : 2.2	Eu : Y	91.5 : 8.5
La : Yb	99.0 : 1.0	Eu : Yb	95.4 : 4.6

2.6.2. Separation of REs Oxides from Phosphor Wastes

Waste fluorescent tube powders contain a number of RE elements and the separation of the light RE fraction from the heavy RE fraction would be a convenient first separation step in recovering value from these wastes. Waste phosphor powder was obtained from a fluorescent tube recycler (Balcan Engineering Limited, Horncastle, UK). The as-received phosphor powder was sieved through a fine mesh to separate off the larger glass fractions prior to

washing with 0.5M HCl at room temperature to remove soluble Ca, Ba and other metal compounds – very little of the RE elements (<4%) are removed at this stage. The pre-treated powder was then leached with 5M HNO_3 at 160 °C and the RE elements were selectively separated from the cooled solution by solvent extraction into N,N-dioctyldiglycolamic acid. The REs were stripped from the organic phase with 5 M HNO_3 and precipitated out by addition of oxalic acid to give an oxalate that was calcined at 750 °C to yield the following RE oxide mixture containing La_2O_3 (11.9 wt.%), CeO_2 (8.5 wt.%), Eu_2O_3 (4.5 wt.%), Gd_2O_3 (2.1 wt.%), Tb_3O_4 (3.4 wt.%) and Y_2O_3 (69.6 wt.%) that was used in the RE recovery studies. Using a similar procedure to that described in section 2.6.1, the separation of LRE oxides from HRE oxides, as a function of time, from the RE oxide mixtures obtained from the waste phosphors was investigated by treating 60 mg of the powders with 2 g of a 1:1 [Hbet][Tf$_2$N]-H_2O at 57°C with mixing at 500 rpm for pre-determined times between 0.25 – 15 min. The results on the separation of RE oxides from the waste phosphor are time-dependent as shown in Table 4.

Table 4 Separation of La and Eu from Y, Gd and Tb from RE oxide mixtures obtained from waste phosphors using 1:1 Hbet][Tf$_2$N]:H_2O at 57°C for various phosphor:solvent contact times

Phosphor:solvent contact time (mn)	Percentage (%) RE dissolved					
	La_2O_3	CeO_2	Eu_2O_3	Gd_2O_3	Tb_3O_4	Y_2O_3
0.25	89	0.0	62	10	0.6	2
0.5	100	0.0	86	21	0.9	5
1	100	0.0	100	35	1.3	7
2.5	100	0.0	100	63	1.7	13
5	100	0.0	100	74	3.5	17
10	100	0.0	100	89	5.8	21
15	100	0.0	100	98	9.2	26

2.7. Recovery of [Hbet][Tf$_2$N] for Reuse and Recycle

The ability to recover the ionic liquid, [Hbet][Tf$_2$N], for reuse in rare earth recovery and separation was investigated by comparing the half-saturation concentration of Eu_2O_3 in [Hbet][Tf$_2$N]:H_2O after the ionic liquid had been recovered and regenerated a number of times. The [Hbet][Tf$_2$N] layer in each regeneration cycle, following removal of rare earth components in 0.5 M hydrochloric acid and 0.1 M betaine chloride solution was washed with deionized

water to remove residual chloride impurities and dried in a rotary evaporator at 150 mbar and 80 °C for 6 h to recover the IL for reuse. The FTIR spectra in Figure 6 show that [Hbet][Tf$_2$N] is recovered unchanged even after being regenerated for reuse five times from a 1:1 solvent mixture with water for dissolving Eu$_2$O$_3$, while the data in Figure 7 show that the efficiency of [Hbet][Tf$_2$N] as a solvent decreases by less than 5% over the cycle of five regenerations. Average recovery of the dried [Hbet][Tf$_2$N] was determined gravimetrically after each regeneration step at 97.9 wt.%.
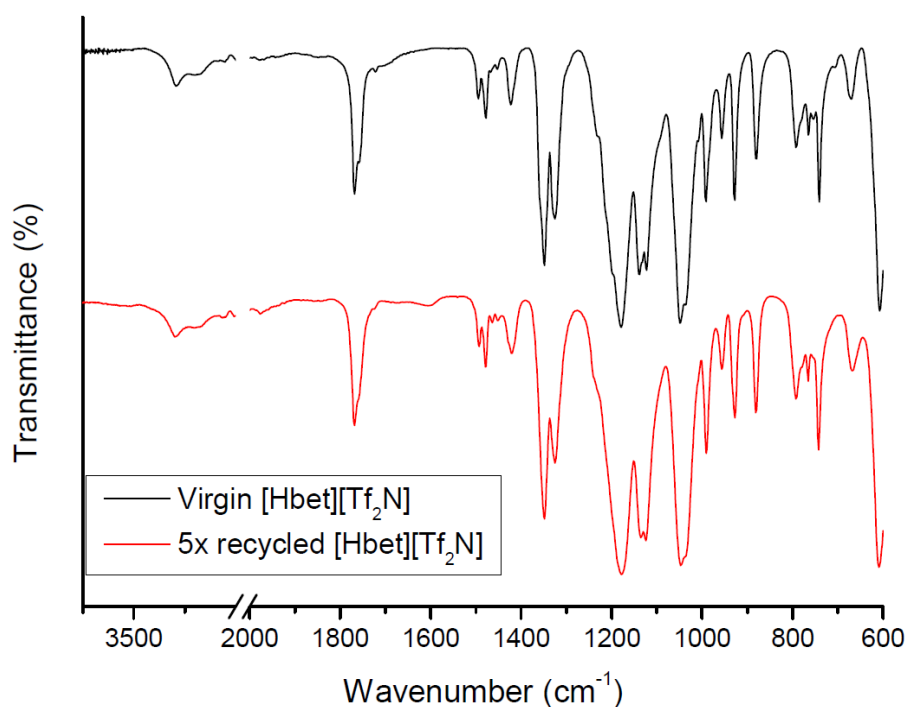

Figure 6 FTIR spectra of pure [Hbet][Tf$_2$N] (upper trace) and five times regenerated [Hbet][Tf$_2$N] (lower trace) [Note: Spectra are offset for clarity].

3. Results and Discussion

The factors affecting the solubilities of rare-earth metal oxide in [Hbet][Tf$_2$N]:H$_2$O solvent mixtures have been determined in order to develop a process methodology for separating light rare earth metal oxides from heavy rare earth metal oxides. The data from measurement of the relative solubilities of three light rare earth oxides (La$_2$O$_3$, Nd$_2$O$_3$, and Eu$_2$O$_3$), two heavy rare metal oxides (Y$_2$O$_3$ and Yb$_2$O$_3$) and of Gd$_2$O$_3$ which has intermediate properties at different temperatures and different solute:solvent contact times are in Figure 2. The light rare earth oxides dissolve easily in 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 °C with the La and Eu reaching maximum solubility within 20 min. and Nd within 40 min., while the heavy rare earth oxides have very

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low solubilities at this temperature with negligible amounts being dissolved for solute:solvent contact times less than 80 min. Gd_2O_3 dissolves more slowly than the oxides of La, Eu, and Nd at 57 °C reaching maximum solubility only after 160 min. The solubilities of Y_2O_3, Yb_2O_3 and Gd_2O_3 increase with temperature and the time taken to reach maximum solubility decreases for all of the rare metal oxides over the range of temperatures studied up to 95 °C and, as a result the separations between the light rare earth elements and both Gd and the heavy rare earth elements become less distinct.
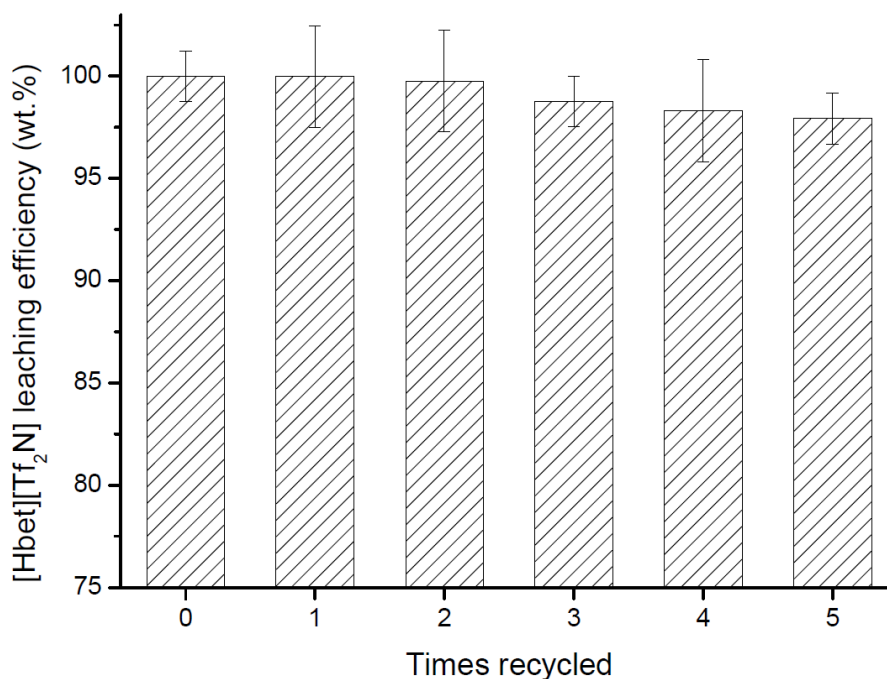

Figure 7 Efficiency of [Hbet][Tf_2N] as a solvent for lanthanide oxide recovery as a function of number of times regenerated and reused.

The data in Figure 3 suggest that increasing the [Hbet][Tf_2N]:H_2O ratio in this case from 1:1 to 2:1 increases the time taken to reach maximum solubility for all of the rare earth metal oxides. This is confirmed by the results in Figure 4 for the relative solubilities of La_2O_3 in solvents with [Hbet][Tf_2N]:H_2O ratios ranging from 1:1 to 16:1 that show that the dissolution rate and total solubility of La_2O_3 in [Hbet][Tf_2N]-H_2O mixtures decrease with increasing IL content. These data show that the presence of water is crucial for the optimal application of [Hbet][Tf_2N]. Breaking of hydrogen bonding within the IL by water above the UCST drastically lowers the viscosity of the mixture and increases the mobility of the carboxylic acid-bearing betaine cation. This leads to a greater diffusion coefficient, more efficient mixing and a general increase in the dissolution kinetics. Furthermore, single-crystal X-ray diffraction studies of Nd:[Hbet][Tf_2N] complexes obtained from solutions containing a lower

stoichiometric ratio of [Hbet][Tf$_2$N] to Nd reveal that some betaine ligands were replaced by coordinated H$_2$O molecules [17].

RE oxides are insoluble in water but dissolve in [Hbet][Tf$_2$N]:H$_2$O mixtures because of the presence of the coordinating ligand in the IL. The data in Table 1 show that at half-saturation the RE complexes are distributed between both the IL and aqueous phases when they are separated at temperatures below the UCST. At near saturation, however, a greater solubility of the light REs in the IL and the fact that they dissolve much more quickly than the heavy REs results in the preference shown by the light REs for the IL phase that leaves the heavy REs as a solid phase in the aqueous phase after short oxide-solvent contact times. It is these differences in the solubilities and rates of dissolution between LREs and HREs, along with the use of temperatures just above the UCST, that are exploited in the separation process developed in this work.

Dissolving the light rare earth metal oxides in [Hbet][Tf$_2$N]-H$_2$O solvents results (Table 2) in a reduction in the UCST leading to the possibility of achieving separations of light from heavy rare earth oxides at temperatures lower than 57°C. The measurements of the relative solubilities of La$_2$O$_3$, Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Y$_2$O$_3$ and Yb$_2$O$_3$ in 1:1 [Hbet][Tf$_2$N]:H$_2$O as a function of time at 40°C are compared in Figure 5 with those obtained at 57°C and show that the potential separation of La, Nd and Eu is better at 57°C than it is at 40°C but that the potential separation of the light rare earth elements from Gd would be better at 40°C. In the case of Gd the lowest value for UCST recorded is 31.8°C.

The results in Figures 2-5 suggest that the best conditions for achieving a separation of the light rare earth elements from the heavy rare earth elements that remain undissolved in [Hbet][Tf$_2$N]:H$_2$O solvents should be achieved with 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 $^{\circ}$C with short contact times (0.5 min) between the oxides and the solvent. The separations achieved in studies of equimolar binary mixtures of Eu$_2$O$_3$/La$_2$O$_3$, Nd$_2$O$_3$/La$_2$O$_3$, Gd$_2$O$_3$/La$_2$O$_3$, Y$_2$O$_3$/La$_2$O$_3$, and Yb$_2$O$_3$/La$_2$O$_3$ and of Nd$_2$O$_3$/Eu$_2$O$_3$, Gd$_2$O$_3$/Eu$_2$O$_3$, Y$_2$O$_3$/Eu$_2$O$_3$, and Yb$_2$O$_3$/EuO$_3$ contacted with 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 $^{\circ}$C for 30 s with stirring at 500rpm are in Table 3 and show that excellent separations of light from heavy rare earth elements can be achieved by this method.

As an example of the use of [Hbet][Tf$_2$N]:H$_2$O solvents in separating light from heavy rare earth oxides, separations carried out using mixed oxides powder containing La$_2$O$_3$, CeO$_2$, Eu$_2$O$_3$, Gd$_2$O$_3$, Tb$_3$O$_4$ and Y$_2$O$_3$ recovered from waste phosphor showed (Table 4) that the light and heavy rare earth elements can be separated using short dissolution times from these complex oxide systems even in the presence of high HRE oxide concentrations. The data in Table 4 show that with contact times of 0.25 min 100% of the La and Eu oxides are completely dissolved in 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 ^{o}C leaving greater than 97% of Y and Tb oxides in the undissolved solid fraction. Increasing the contact times, however, because of the large amounts of Y present in the phosphors does result in larger quantities of Y being dissolved in the solvent reducing the effectiveness of the separation of the light from heavy rare earth oxides.

The use of [Hbet][Tf$_2$N]:H$_2$O as a means of separating light and heavy RE oxides is favoured by the ability to recycle the solvent. The data in Figures 6 and 7 show that the [Hbet][Tf$_2$N] can be reused at least five times with little change in either the FTIR spectrum of the solvent or in the effectiveness of the separations achieved.

4. Conclusions

The results of studies on the factors affecting the interactions between rare earth metal oxides and [Hbet][Tf$_2$N]:H$_2$O solvents including ionic liquid:water ratios, temperature, solvent:solute contact times, and the effect of dissolved rare earth metal ions on the thermometric phase change in [Hbet][Tf$_2$N]:H$_2$O mixtures have been used to develop a process for separating light from the heavy rare earth metal oxides. The light rare earth metal oxides dissolve easily at 57 ^{o}C with the La and Eu reaching maximum solubility within minutes while the heavy rare earth metal oxides have very low solubilities at this temperature with negligible amounts being dissolved for contact times less than 80 min. The presence of rare earth metal ions in [Hbet][Tf$_2$N]:H$_2$O results in a reduction in the phase separation temperature (UCST) of the solvent from 55.6 ^{o}C to as low as 31.8 ^{o}C with Gd^{3+} permitting the use of lower temperatures in the development of separation processes. The best separation of light from heavy rare earth oxides in 1:1[Hbet][Tf$_2$N]:H$_2$O is achieved at 57 ^{o}C but better separation of Gd from the light REOs can be achieved at 40 ^{o}C i.e below the solvent UCST. The conditions for a one-step separation of light from heavy rare earth metals in [Hbet][Tf$_2$N]-H$_2$O mixtures is achieved with 1:1 [Hbet][Tf$_2$N]:H$_2$O at 57 ^{o}C using short contact oxide:solvent times (maximum 5 min). This

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process has been used to separate light from heavy rare earth metals in waste phosphor samples, even in the presence of high concentrations of the heavy rare earth metal, Y. The use of [Hbet][Tf$_2$N]:H$_2$O as a means of separating light and heavy rare earth elements is aided by the ease of recycling the solvent which can be recycled and reused at least five times with little loss of solvent quality or efficiency.

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