Liquid–liquid extraction of europium(III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid

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A new non-fluorinated malonamide-based ionic liquid extractant was synthesized and investigated for the extraction behavior of europium(III) and other trivalent rare-earth ions from nitric acid medium. The extractant was the functionalized ionic liquid trihexyl(tetradecyl)phosphonium \( \text{N}_4\text{N}_4\text{N}_4\text{N}_4 \)-tetra(2-ethylhexyl)malonate, \([\text{P}66614] \text{[MA]}\), and it was used in combination with the non-fluorinated ionic liquid trihexyl(tetradecyl)phosphonium nitrate, \([\text{P}66614] \text{[NO}_3\text{]}\), as diluents. The extraction behavior of europium in this ionic liquid solution was studied as a function of various parameters such as the pH, concentration of the extractant, the type of acidic medium, temperature, concentration of the salting-out agent and the metal concentration of the aqueous feed. The extraction behavior of \([\text{P}66614] \text{[MA]}\) in \([\text{P}66614] \text{[NO}_3\text{]}\) was compared with that of \([\text{P}66614] \text{[MA]}\) in the chloride-containing ionic liquid diluent trihexyl(tetradecyl)phosphonium chloride, \([\text{P}66614] \text{[Cl]}\) (Cyphos IL 101). The nitrate system was found to be superior. Marked differences in extraction behavior were observed between \([\text{P}66614] \text{[MA]}\) and the molecular malonamide extractant \( \text{N}_4\text{N}_4\text{N}_4\text{N}_4 \)-tetra(2-ethylhexyl)malonamide (TEHMA), i.e. the compound from which the anion of the ionic liquid extractant was prepared. The extraction behavior of other rare earths (La, Ce, Nd, Sm, Ho, Yb) and some transition metals (Ni, Co, Zn) was investigated using this functionalized ionic liquid. A good separation of the rare earths from the transition metals could be achieved. For the rare earths, the extraction efficiency increases over the lanthanide series. The effects of thermodynamic parameters, the stripping of europium(III) from the ionic liquid and the reusability of the functionalized ionic liquid were studied in detail.

Introduction

The discovery of water-stable hydrophobic ionic liquids has opened the door for many new research opportunities in hydrometallurgy, because the ionic liquid can be used as a replacement for the conventional molecular diluents in solvent extraction processes. Since ionic liquids (ILs) are solvents that consist entirely of ions, they have a negligible vapor pressure and they are non-volatile.\(^1,2\) Replacement of volatile organic solvents in solvent extractions could lead to inherently safer processes.\(^3\) Earlier studies on the extraction of metal ions with ionic liquids made use of fluorinated hydrophobic ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate, \([\text{C}_4\text{mim}] \text{[PF}_6\text{]}\), or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, \([\text{C}_4\text{mim}] \text{[Tf}_2\text{N]}\), and the ionic liquid was used as a solvent for a molecular extractant.\(^4\)–\(^13\) The ionic liquid acted as a mere diluent or solvent for the extractant. However, it has been realized already for a long time that the extraction mechanisms in ionic liquid can differ from those observed in molecular solvents.\(^14\)–\(^16\) This can be an advantage, but it could also be a disadvantage if ionic liquid components are lost to the aqueous phase by an ion exchange mechanism. Later developments led to the introduction of task-specific ionic liquids (TSILs) or functionalized ionic liquids (FILs), in which a metal-coordinating group was attached to the ionic liquid cation.\(^17\),\(^18\) Ionic liquids with a coordinating anion can also be considered as functionalized ionic liquids. These functionalized ionic liquids diluted in a fluorinated ionic liquid (or undiluted in some cases) became popular extraction phases for lanthanes, actinides and fission products.\(^19\)–\(^31\) A recent development is the use of these ionic liquids for homogeneous liquid–liquid extraction processes.\(^32\) Ionic liquids with fluorinated anions are not ideal for use in solvent extraction processes, both from an economical and an environmental point of view. Replacement of the imidazolium cation by quaternary ammonium or phosphonium cations with long alkyl chains allowed obtaining hydrophobic ionic liquids with non-fluorinated anions. Well-known...
examples are ionic liquids based on Aliquat® 336 or on the trihexyl(tetradecyl)phosphonium cation.33–45 These ionic liquids are similar to the anion exchange extractants (basic extractants).46–50 It was thought for some time that these ionic liquids are too viscous to be used in an undiluted form.51 However, many of the potential advantages of ionic liquids are lost by adding molecular solvents as diluents. Recent research has shown that such quaternary ammonium and phosphonium ionic liquids can be used without molecular diluents, provided that the ionic liquid phase is presaturated with water and/or the extraction process is carried out at elevated temperatures.52–55 These non-fluorinated ionic liquids can also be used as diluents for functionalized ionic liquids or for molecular extractants.

In this paper, the extraction of europium(III) by a solvent extraction system using a novel non-fluorinated ionic liquid system, consisting of the ionic liquid extractant trihexyl(tetradecyl)phosphonium chloride with different diluents. The stripping of europium from the pregnant ionic liquid phase before and after the extraction was determined with a Mettler-Toledo DL 39 coulometric Karl Fischer titrator.

**Experimental section**

**Materials/reagents**

All the chemicals and reagents used in this study were of analytical grade. The chemicals, nitric acid (Sigma-Aldrich), chloroform (Sigma-Aldrich), toluene (Sigma-Aldrich), trihexyl(tetradecyl)phosphonium chloride (98%, Cyphos® IL 101, Cytec Industries), sodium nitrate and sodium chloride (99%, Sigma-Aldrich), malonyl chloride (99%, Sigma Aldrich), bis(2-ethylhexyl)amine (99%, Sigma-Aldrich) and sodium hydrogen carbonate (Alfa Aesar) were used as received. Europium(III) nitrate hexahydrate (>99%) and other metal nitrates (purity 99% or better) were purchased from ACROS Organics (Geel, Belgium) or Sigma-Aldrich (Diegem, Belgium). A 1000 ppm gallium standard was purchased from Merck (Overijse, Belgium).

**Instrumentation and analysis**

The concentrations of rare earths in the aqueous phase were determined with a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). The extraction experiments were performed with small vials in a temperature-controllable compact benchtop turbo thermo-shaker (model: TMS – 200, Hangzhou Allsheng Instrument Co. Ltd, China). After 1 hour of equilibration, part of the aqueous phase was removed and a gallium internal standard was added until a total volume of 1 mL was obtained. The quartz glass sample carriers were first treated with 20 μL of silicone solution in isopropanol (silicone solution SERVA for siliconizing glass and metal, SERVA Electrophoresis GmbH, Heidelberg, Germany) in order to bind the sample droplet by its polar sites. Then, the sample carriers were dried for 5 minutes in a hot air oven at 60 °C, followed by the addition of 5 μL of the sample and a drying process of 20 minutes at the same temperature. The samples were measured for 200 seconds in the TXRF spectrometer. All samples were diluted with MilliQ water, if necessary. A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of the samples after extraction. FTIR spectra of the functionalized ionic liquid were measured using a Bruker Vertex 70 spectrometer with a single reflection diamond ATR accessory (Platinum ATR). 1H NMR and 13C NMR spectra of ionic liquids were recorded on a Bruker Avance 300 spectrometer, operating at 300 MHz for 1H. 31P NMR spectra were recorded using a Bruker Avance 400 spectrometer, operating at 121.49 MHz for 31P, and using H2PO4 (85%) (external standard) as a reference. CDCl3 was used as the solvent for recording all the NMR spectra and the data were analyzed with the SPINWORKS software package. The mass of the ionic liquid was determined by LCQ Advantage ESI Mass spectrometer. The viscosity of the ionic liquid was measured using an automatic Brookfield plate cone viscometer, Model LVDV-II-P CP (Brookfield Engineering Laboratories, USA) and pH measurements were performed with an S220 SevenCompact™ pH/Ion meter (Mettler-Toledo) and a Sliptide (Hamilton) electrode. The water content of the ionic liquid phase before and after the extraction was determined with a Mettler-Toledo DL 39 coulometric Karl Fischer titrator.

**Synthesis of trihexyl(tetradecyl)phosphonium nitrate**

Trihexyl(tetradecyl)phosphonium nitrate was synthesized by equilibrating trihexyl(tetradecyl)phosphonium chloride with an equal volume of an aqueous potassium nitrate solution.
(2 to 3 M) for 1 hour. The organic phase was separated and the process was repeated three to four times in order to remove the chloride impurities as well as possible. Then, the organic phase trihexyl(tetradecyl)phosphonium nitrate was washed with distilled water, followed by drying in vacuo. Yield: 98% (43.8 g). $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si, δ/ppm): 2.33–2.22 (m, 8H), 1.25–1.55 (m, 48H), 0.82–0.918 (m, 12H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ/ppm): 31.89, 31.02, 29.62, 29.52, 29.33, 22.65, 22.32, 19.02, 14.09, 13.93. $^{31}$P NMR (161.92 MHz, CDCl$_3$): 33.1 ppm (85% H$_2$PO$_4$ as external standard). The chloride content was found to be below 100 ppm (i.e. below the detection limit of chlorine by TXRF).

The precursor $N,N,N',N'$-tetra(2-ethylhexyl)malonamide (abbreviated here onwards as “TEHMA”) was prepared by the reaction between malon chloride and bis(2-ethylhexyl)amine in a 1:3 molar ratio, as described elsewhere. A solution of malon chloride (5.64 g) and bis(2-ethylhexyl)amine (28.9 g) in chloroform was refluxed for 24 hours, in the presence of triethylamine (TEA). Then the product was washed several times with 1 M HCl solution, followed by washing thoroughly with water (6 to 7 times). The solvent was removed in vacuo. The compound was obtained as an orange oil (yield: 65%, 14.4 g).

The first step in the synthetic procedure for the functionalized ionic liquid involved refluxing a solution of TEHMA in toluene with sodium hydroxide suspended in toluene. The reaction was carried out for 2 to 3 hours to ensure that there was no further evolution of hydrogen gas. The second step involved the addition of the ionic liquid trihexyl(tetradecyl)phosphonium chloride, $[\text{P}_{66614}\text{Cl}]$, dissolved in toluene to the sodium salt of the malonamide and the reaction was again refluxed for 6 to 7 hours. The final product was washed with water several times, followed by removal of toluene in vacuo. The yield of the final product was 95% (19.5 g). $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si, δ/ppm): 3.49 (s, 1H, CH$_2$ groups), 14.14, 13.95, 10.97, 10.48 (various CH$_3$ groups), 2.64 (m, 4H), 2.42–2.49 (m, 8H, −CH$_2$−), 1.25–1.55 (m, 80H, various −CH$_2$−), 0.82–0.92 (m, 36H, various −CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, δ/ppm): 167.7 (2 × −CO−), 164.0 (C=O stretch), 145.8, 1378 (C−H bending), 1311, 1140 (C−N stretch), 723 (CH rock, long aliphatic chain). Viscosity: 1002 cP (at 30 °C). Density: 0.87 g cm$^{-3}$ (at 30 °C). Water content of dry ionic liquid: 0.04 wt%. The chloride content was below 100 ppm (measured by TXRF).

### Extraction procedures

All the extraction studies were carried out at 303 K, with the exception of the experiments at variable temperatures for determination of the thermodynamic parameters, where the temperature was varied between 303 to 333 K. Various solutions of $[\text{P}_{66614}\text{Cl}]$ in $[\text{P}_{66614}\text{NO}_3]$ were prepared. Since the ionic liquid phase contains compounds with several long alky chains, the equilibration with only nitric acid resulted in the formation of an emulsion that became segregated at the interface after centrifuging the mixture, and it took quite a long time to complete phase separation. In order to avoid such problems and to have a good and fast phase separation, a 0.1 M NaNO$_3$ solution was added to the aqueous phase for all experiments. The ionic liquid phase was pre-equilibrated with the desired concentration of nitric acid to fix the equilibrium acidity. The extraction of europium(III) as a function of nitric acid concentration was studied by equilibrating the ionic liquid phase (1 mL) with the aqueous phase (1 mL) containing the europium(III) solution ([Eu(III)] = 6 × 10$^{-4}$ M) at the desired pH value. The pH of the aqueous solution was varied between 1 and 6, by the addition of 1 M HNO$_3$ or 1 M NaOH solutions. Similar pH values were found before and after the extraction process. This shows that no protons are transferred to the ionic liquid phase or transferred from the ionic liquid phase to the aqueous phase. Extractions were performed by intensive shaking (2000 rpm) of the extraction mixture for 1 hour. After the extraction, separation of the phases was assisted by centrifugation for 5 minutes at 3000 rpm. The concentrations of Eu(III) and other metal ions distributed between the ionic liquid and the aqueous phases were measured by TXRF. The loading test was performed by varying the initial europium concentration in the aqueous phase between 0.6 mM and 35 mM. The nitrate concentration was varied from 0.1 to 1.0 M in the aqueous solution (pH 4) in order to investigate the salting-out effect. The variation of the concentration of the salting agent, loading tests, variation of the temperature, extraction from chloride media, and separation of lanthanides from their mixture with transition metal ions were all carried out at pH 4. For stripping experiments, the pregnant ionic liquid phase was scrubbed with 0.5 M HNO$_3$ a few times, followed by scrubbing with MilliQ water. Subsequently, the ionic liquid phase was equilibrated with a 0.5 M NaOH solution several times, followed by washing with an aqueous solution of a pH at which the new extraction experiments had to be performed.

The distribution ratio ($D$) is the ratio of the concentration of the metal ion M in the organic phase (ionic liquid phase) to
the concentration of the metal ion in the aqueous phase, at equilibrium:

\[ D = \frac{[M]_{\text{IL}}}{[M]_{\text{aq}}} \]  

(1)

In practice, the distribution ratio is measured most conveniently by measuring the concentration of the metal ion in the aqueous phase after extraction and by comparing it to the initial concentration:

\[ D = \frac{C_i - C_f}{C_f} \times \frac{V_{\text{aq}}}{V_{\text{IL}}} \]  

(2)

\( C_i \) and \( C_f \) are the concentrations of the metal ions in the aqueous phase before \( (i = \text{initial}) \) and after extraction \( (f = \text{final}), \) respectively. \( V_{\text{aq}} \) and \( V_{\text{IL}} \) are the volumes of the aqueous and ionic liquid phase, respectively. In most of the experiments, a phase volume ratio of 1 was used \( (V_{\text{aq}} = V_{\text{IL}}). \) The extraction efficiency \( (\%E) \) was determined by using the following equation:

\[ \%E = \frac{D}{D + \frac{V_{\text{aq}}}{V_{\text{IL}}}} \times 100 \]  

(3)

The separation factor \( \alpha(M_1, M_2) \) was calculated as follows:

\[ \alpha(M_1, M_2) = \frac{D_{M_1}}{D_{M_2}} \]  

(4)

\( D_{M_i} \) and \( D_{M_2} \) are the distribution ratios of the metal ions \( M_1 \) and \( M_2, \) respectively. The effect of the concentration of \([P_{66614}][\text{MA}]\) in the organic phase was studied by varying the concentration from 0.005 M to 0.08 M.

**Results and discussion**

**Extraction of europium by \([P_{66614}][\text{MA}]\) in \([P_{66614}][\text{NO}_3]\)**

A study of the extraction behavior of \( \text{Eu(III)} \) by \([P_{66614}][\text{MA}]\) diluted in \([P_{66614}][\text{NO}_3]\) showed that the distribution ratio increased with an increase in \( pH \) at low \( pH \) values, but that the increase in \( D_{\text{Eu}} \) became marginal become marginal for \( pH > 3 \) (Fig. 2). This shows that above \( pH 3, \) the complex formation of \( \text{Eu(III)} \) with the functionalized ionic liquid \([P_{66614}][\text{MA}]\) is more or less independent of the feed acidity in this \( pH \) region and that the extraction is efficient under these conditions. The decrease in \( D \) values at low \( pH \) \((< \text{pH } 2)\) can be attributed to protonation of the malonate ion in the ionic liquid to form molecular malonamide TEHMA. In strongly acidic solutions, the ionic liquid \([P_{66614}][\text{MA}]\) is transformed in a mixture of \([P_{66614}][\text{NO}_3]\) and the malonamide molecule TEHMA. For this reason, we have not further investigated the extraction behavior of \([P_{66614}][\text{MA}]\) in contact with aqueous solutions with a \( pH < 1.\)

In order to know the extraction behavior of the malonamide molecule TEHMA, the extraction of \( \text{Eu(III)} \) in 0.05 M \( \text{MA/}[P_{66614}][\text{NO}_3]\) was investigated (Fig. 2). It is quite surprising to observe that the extraction of \( \text{Eu(III)} \) is insignificant at all \( pH \) values and that the \( D_{\text{Eu}} \) values are close to those observed for pure \([P_{66614}][\text{NO}_3]\). There are several literature reports on the extraction of trivalent actinides and lanthanides using malonamide-based extractants dissolved in molecular diluents.58–65 These reports mention that the extraction of metal ions by malonamide extractants is influenced by several factors: (1) basicity of the carbonyl center; (2) alkyl (alkoxy) substitution at the methylene center, (3) length of the alkyl chains attached to the nitrogen center and (4) steric effect of all the substituents together. The distribution ratios of metal ions become insignificantly small with an increase in the alkyl chain length and an increase in the basicity of the ligating site, without any substitution at the methylene carbon center and any increase in bulkiness (sterically crowded) around two nitrogen atoms. All the above points are satisfied in the case of the present malonamide molecule TEHMA and this is probably the explanation for the negligible distribution ratio. However, the most important point among all these factors is that the torsion angle is larger in the malonamide molecule TEHMA since there is no substitution at the methylene carbon center. As a consequence of this larger torsion angle, more conformational changes are required to form the metal–solvate complex.58,61 In contrast, the same extracting moiety extracts efficiently \( \text{Eu(III)} \) from the feed acidity when combined in the form of an anion \([\text{MA}]^-\) with the trihexyl(tetradecyl)phosphonium cation \([P_{66614}]^+.\) The difference in extraction behavior between \([P_{66614}][\text{MA}]\) and TEHMA is a nice example of differences in extraction properties of ionic liquid and molecular extractants. Thus, despite using the same malonamide skeleton, the extraction behavior of \([P_{66614}][\text{MA}]\) indicates that an inner synergistic effect operates between two ions \([P_{66614}]^+\) and \([\text{MA}]^-\) during extraction.46–68 In the presence of the diluent \([P_{66614}][\text{NO}_3]\), the functionalized ionic liquid \([P_{66614}][\text{MA}]\) feels a more ionic environment and the inner-synergism becomes more prominent. Moreover, from Fig. 2, it can be noticed that the \( D_{\text{Eu}} \) values slowly decrease with increasing \( pH \) values in \([P_{66614}][\text{MA}]/[P_{66614}][\text{NO}_3]\).
[NO$_3$] at high pH (>pH 5). This could be attributed to the hydrolysis of Eu(III) ions at these high pH values, resulting in the formation of monomeric and oligomeric hydrolysis products.$^6$ It must be mentioned that a more effective extraction with malonamide-functionalized ionic liquids compared to molecular malonamides was also observed by other authors for the extraction of uranyl.$^7$

**Extraction kinetics**

In a study of a solvent extraction system, it is always important to consider the issue of extraction kinetics, i.e. how fast the extraction equilibrium is established. The kinetics depends on physical parameters such as the viscosity, density and hydrophobicity of the extracting phase. Since the diluent [P$_{66614}$][NO$_3$] contains long alkyl chains, the viscosity under the conditions is high (1440 cP at 22 °C). However, the viscosity of the pure ionic liquid decreased to 201 cP at 30 °C after pre-equilibration with acidified water (pH 4) and the viscosity of a 0.05 M [P$_{66614}$][MA]/[P$_{66614}$][NO$_3$] solution after pre-equilibration was measured to be 192 cP at 30 °C. This further decrease compared to pure [P$_{66614}$][NO$_3$] is attributed to a larger co-extraction of water (6 wt%). Although a viscosity of 192 cP is high compared to the viscosity of commonly used molecular diluents, it was possible to successfully carry out extraction experiments and reproducible results could be obtained. The viscosity of the ionic liquid phase did not vary remarkably as a function of the pH of the aqueous phase used for pre-equilibration: the viscosity of the ionic liquid phase after equilibration at pH 3 was 187 cP at 30 °C, which is very close to the value of 192 cP found for pH 4 at the same temperature. Fig. 3 shows the extraction kinetics of Eu(III) in 0.05 M [P$_{66614}$][MA]/[P$_{66614}$][NO$_3$]. It is observed that the distribution ratio of Eu(III) increases slowly as a function of equilibration time and remains almost constant after 1 hour, irrespective of further increase in shaking time. Thus, the kinetics of the present extraction system suggest that the equilibrium conditions can be reached in about 1 hour. The time required to reach equilibrium was found to depend on the nitrate concentration in the aqueous phase. At high NaNO$_3$ concentrations in the aqueous phase (>0.5 M) with a given shaking speed, equilibrium was achieved slightly faster than in the studies with 0.1 M NaNO$_3$, due to the more efficient salting-out effect as well as the occurrence of a dual mechanism (ion-pair extraction and anion exchange). The phase disengagement time was short, thanks to the addition of 0.1 M NaNO$_3$ (or more in studies on the influence of the nitrate concentration) as the salting agent to the aqueous phase in the extraction studies to facilitate a fast phase separation. The addition of the salt prevented the formation of an emulsion during equilibration between the organic phase and aqueous phase and this emulsion formation has a strong negative effect on the extraction efficiency and on the phase disengagement times. Emulsions are easily formed with ionic liquids of the type used in this study due to the long alkyl chains and their corresponding surfactant properties. It is well known that surfactants lead to emulsion formation in solvent extraction systems. The salting-out agent destabilizes the emulsion and fastens the phase separation process. It is difficult to measure the exact amount of metal concentration in the ionic liquid phase as well as viscosity of the ionic liquid phase without salting-out agents in the aqueous phase. NaNO$_3$ was selected as a salting-out agent to avoid contamination of the solvent extraction system with other anions and due to the fact that no interference of the extraction of Eu(III) by sodium ions is expected.

**Extraction stoichiometry**

A variation of the distribution ratio of Eu(III) as a function of the ionic liquid concentration in the organic phase at pH 4 shows that the distribution ratio increases with increasing the concentration of the ionic liquid (Fig. 4). A linear regression analysis of the extraction data resulted in a straight line with a
slop of 3.58, suggesting the involvement of 3 to 4 molecules of \([\text{P66614}]\text{[MA]}\) during the extraction process:

\[
\text{Eu}^{3+} + 3\text{NO}_3^- + x[\text{P66614}]\text{[MA]} \rightleftharpoons \text{Eu(NO}_3)_3 \cdot (x[\text{P66614}]\text{[MA]})_x \tag{5}
\]

here, \(x = 3\)–4, and the bar indicated molecules in the organic phase (ionic liquid phase). Such a type of observation has been observed by Tian and Hughes while studying the extraction of Nd(III) by molecular malonamide in molecular diluents at low acid concentration.\(^{57}\) In the case of a malonamide/IL extraction system reported in literature, a stoichiometry of 1:3 observed for extraction of Am(III).\(^{26,71}\) Eqn (5) indicates that three nitrate ions are co-extracted with the Eu\(^{3+}\) ion. The available experimental data do not allow determination of the coordination number of the europium(III) complex during extraction. Up to four [MA]\(^-\) anions could bind to Eu(III), but this high number is unlikely due to steric hindrance by the malonamide anions. It can be assumed that the coordination number of the Eu(III) center is eight, so that four bidentate anionic ligands bind to the metal center. These ligands can be either NO\(_3^-\) or [MA]\(^-\) anions. The non-coordinating [MA]\(^-\) anions can reside in the second coordination sphere. Further speciation studies are required to solve this problem of coordination sphere in the future.

\([\text{P66614}]\text{[MA]}\) is a so-called binary extractant or mixed ionic solvent.\(^{72–74}\) Binary extractants are quaternary ammonium or phosphonium salts of acidic extractants. Such a type of extractant extracts metal salts rather than metal ions. The advantage of binary extractants is that no ionic liquid components are lost to the aqueous phase during extraction, in contrast to many ionic liquid extraction systems with dissolved molecular extractants.

In the present ionic liquid system, the trihexyl(tetradecyl)phosphonium cation is very hydrophobic due to the long alkyl chains and hence it has a very low solubility in the aqueous phase (the precursor Cyphos IL 101 is highly insoluble in the water phase and a well-known hydrophobic ionic liquid). In a recent paper, we reported that the concentration of the trihexyl(tetradecyl)phosphonium cation in the aqueous is between 40 and 80 ppm after extraction.\(^{75}\) This is a very low value. It can be expected that the concentration in the aqueous phase for our extraction experiments is comparable. The actual concentration of the phosphonium cation depends also on the salt concentration in the aqueous phase, but one can conclude that the loss of the ionic liquid cation to the aqueous phase is negligible, unlike in the case of fluorinated imidazolium-based ionic liquids. As far as the diluent, \([\text{P66614}]\text{[NO}_3\text{]}\) is concerned, there will be no loss of nitrate ions to the aqueous phase since the aqueous phase contains nitrate ions and due to the common-ion effect, the nitrate ion prefers to be in the organic phase and hence the ionic liquid \([\text{P66614}]\text{[NO}_3\text{]}\) remains intact after equilibration. The malonamide anion is a very hydrophobic anion due to the long alkyl chains, so that losses to the aqueous phase can be expected to be of the same order as that of the phosphonium cation.

**Effect of concentration of the salting-out agent**

As mentioned in the section on “extraction procedures” in the experimental part, salting-out agents play a vital role in the \([\text{P66614}]\text{[MA]}]/[\text{P66614}]\text{[NO}_3\text{]}\) extraction system. In order to obtain a detailed insight into the effect of the salting-out agent on the distribution ratio of Eu(III), the concentration of NaNO\(_3\) in the aqueous feed solution (pH 4) was varied. The distribution ratio \(D_{\text{Eu}}\) increases with an increase in the nitrate concentration in the aqueous phase, but this increase is not reflected in the extraction efficiency %\(E\) due to the insensitivity of %\(E\) to changes in \(D\) at high \(D\) values (Fig. 5). The extraction efficiency %\(E\) is close to 100% over the entire nitrate ion concentration range. This result indicates that the extractant \([\text{P66614}]\text{[MA]}\) has same coordinating affinity towards Eu(III) irrespective of the nitrate ion concentration in the aqueous phase, and the increase in \(D_{\text{Eu}}\) can be attributed to the occurrence of an anion exchange mechanism at high nitrate ion concentrations wherein the complex \([\text{Eu(NO}_3)_3\text{[MA]}]\)– get exchanged with NO\(_3^-\) ions in the organic phase. In order to confirm this hypothesis, the extraction of Eu(III) was carried out at the same range (0.1–1.0 M) of nitrate ion concentration in the aqueous phase with \([\text{P66614}]\text{[NO}_3\text{]}\) alone (Fig. 5). As expected, %\(E\) increased from 6% to 76% with an increase in the nitrate ion concentration from 0.1 to 1.0 M in the aqueous phase. At very high nitrate concentrations, the extraction of Eu(III) is mainly driven by anion exchange rather than complex formation by the functionalized ionic liquid \([\text{P66614}]\text{[MA]}\). However, the complex formation mechanism also operates simultaneously. In the absence of the \([\text{P66614}]\text{[MA]}\) extractant, the extraction efficiency of \([\text{P66614}]\text{[NO}_3\text{]}\) increases at high nitrate concentrations, but the maximum efficiency of \([\text{P66614}]\text{[NO}_3\text{]}\) is less than 80% extraction at maximum, whereas >99.8% extraction is observed for \([\text{P66614}]\text{[NO}_3\text{]}\) in the presence of the extractant \([\text{P66614}]\text{[MA]}\). Therefore, it is justified to state that Eu(III) gets extracted through the complex formation mechanism at low salt

![Fig. 5 Variation in the extraction efficiency of Eu(III) as a function of the nitrate ion concentration in the aqueous phase. Organic phase: 0.05 M \([\text{P66614}]\text{[MA]}]/[\text{P66614}]\text{[NO}_3\text{]}\) or \([\text{P66614}]\text{[NO}_3\text{]}\) alone; aqueous phase: pH 4 and NaNO\(_3\) (0.1–1.0 M) and 6 × 10\(^{-4}\) M Eu(III).]
concentrations, but that the anion exchange mechanism cooperates at high nitrate concentrations. At low nitrate concentrations, the extraction is solely due to the complex formation mechanism, because the amount of nitrate ions present in the aqueous phase are not sufficient to extract Eu(III) in the form of $[\text{Eu(NO}_3\text{)}_3]^{3-}$ complexes.

**Loading test**

Based on the above observation that extraction efficiency increases with an increase in the aqueous nitrate concentration, the loading of the ionic liquid phase by europium was carried out at different initial Eu(III) concentrations in the aqueous phase, with two different salting agent concentrations (0.2 M and 1.0 M). The extraction isotherm is shown in Fig. 6. An extraction study with 0.1 M nitrate ion concentration in the aqueous phase resulted in the formation of a turbid layer at the interface. This problem could be solved by increasing the concentration of the $\text{NO}_3^-$ ion in the aqueous phase to 0.2 M. It is observed that the Eu(III) loading in the ionic liquid phase increased with an increase in the initial aqueous feed concentration. However, only 9 mM (about 1.37 g L$^{-1}$) of Eu(III) could be loaded when the initial feed concentration was 35 mM (about 5 g L$^{-1}$) at a 0.2 M $\text{NO}_3^-$ ion concentration in the aqueous phase. In contrast, loading of 22 mM (about 3.35 g L$^{-1}$) of Eu(III) was possible from 35 mM (about 5 g L$^{-1}$) of the initial feed phase when the $\text{NO}_3^-$ ion concentration in the aqueous phase was increased to 1.0 M. Further loading of Eu(III) should be possible from high feed concentration by increasing the aqueous nitrate ion concentration and also by increasing the ionic liquid concentration in the organic phase.

**Extraction in chloride medium**

The distribution ratios of Eu(III) for extraction to a solution of $[\text{P}_{66614}]\text{[MA]}$ in the ionic liquid trihexyl(tetradecyl)phosphonium chloride, $[\text{P}_{66614}]\text{[Cl]}$, were measured at different pH values, in order to determine the differences in the extraction behavior, compared to that from nitrate medium. For the extraction in chloride medium, the 0.1 M NaNO$_3$ salting-out agent was replaced by a 0.1 M NaCl solution, in order to avoid contamination by nitrate ions. Eu(III) is not extracted efficiently from chloride medium, unlike what is observed for the extraction from nitrate medium (Fig. 7). The distribution ratios are insignificant for the extraction of Eu(III) by the ionic liquid system $[\text{P}_{66614}]\text{[MA]}/[\text{P}_{66614}]\text{[Cl]}$ ($D_{\text{Eu}} \sim 0.2$) at all pH values. Assuming that the same extraction mechanism holds for the extraction of Eu(III) from chloride medium as for the extraction from nitrate medium, the poorer extractability of Eu(III) from chloride medium can be attributed to the fact that chloride ions are more hydrated than nitrate ions, as a result of which they lead to less uptake of Eu$^{3+}$/Cl$^-$ compared to Eu$^{3+}$/NO$_3^-$. The poor extractability of Eu(III) by $[\text{P}_{66614}]\text{[Cl]}$ is in agreement with what was observed for the separation of Nd(III) and Fe(III) by extraction of Fe(III) with trihexyl(tetradecyl)phosphonium chloride. However, the distribution ratio increased slowly with an increase in chloride concentration up to 1.0 M in the aqueous phase (in form of NaCl) (Fig. 8). A maximum of about 50% of Eu(III) could be extracted at a chloride concentration of 1.0 M in the aqueous phase in the presence of the functionalized ionic liquid. Without the ionic liquid $[\text{P}_{66614}]\text{[MA]}$, an increase in the chloride content did not result in any significant change in the extraction efficiencies (Fig. 8). It might be possible that with the system $[\text{P}_{66614}]\text{[MA]}/[\text{P}_{66614}]\text{[Cl]}$, more Eu(III) can be loaded with further increasing the chloride concentration in the aqueous phase, but the increasing trend suggests that very high distribution ratios cannot be achieved, whatever the chloride concentration.

**Extraction of other rare earths and transition metals**

The extraction performance of the malonate-based functionalized ionic liquid $[\text{P}_{66614}]\text{[MA]}$ was explored for trivalent rare-
earth ions other than Eu(III) as well as for the transition metal ions Co(II), Ni(II) and Zn(II) (Fig. 9). There is no significant extraction for the transition metal ions, even though Zn(II) extracts to some extent. For the rare-earth ions, \( D_{\text{Ln}} \) increases with an increase in the atomic number of the lanthanide and it reaches a maximum at holmium and then slightly decreases towards ytterbium. This behavior, with a maximum in the curve of the distribution ratios as a functional of the atomic number, is similar to what is observed for the extraction of rare earths with dimethylheptyl methyl phosphate (P350).76

The most important observation from Fig. 9 is that rare earths could be extracted with appreciable \( D_{\text{Ln}} \) values from their mixture with transition metal ions. For example, the separation factors \( \alpha(\text{Ce},\text{Ni}) = 16 \), \( \alpha(\text{Nd}, \text{Ni}) = 38 \), \( \alpha(\text{Sm}, \text{Co}) = 120 \) and \( \alpha(\text{Eu}, \text{Zn}) = 33 \) were obtained for rare earths over transition metal ions. This shows that the extraction system \([\text{P66614][MA]}/[\text{P66614][NO3]}\) could be useful for the recovery of rare earths from end-of-life consumer goods, such as NiMH batteries or permanent magnets (SmCo magnets).77 Separation of europium(III) from zinc(II) is relevant, because reduction of europium(III) to europium(II) by zinc metal is used for selective separation of europium from the other rare earths and impurities of zinc ions have to be removed. The fact that the distribution ratios are smaller in the case of mixtures of rare earths compared to single rare-earth elements (Fig. 9) is attributed to the competition between the different metals for coordination to the extractant. The differences are most pronounced for the light rare earths, due to a preference of the ionic liquid extractant for extraction of the heavy rare earths.

**Effect of temperature**

The extraction of Eu(III) by \([\text{P66614][MA]}\) in \([\text{P66614][NO3]}\) was performed at temperatures from 303 K to 333 K, to determine the influence of the temperature on the extraction process (Fig. 10). It was noticed that \( D_{\text{Eu}} \) decreased with an increase in temperature. The enthalpy change of the extraction was derived from the slope obtained in the plot of \( \log D \) versus \( 1000/T(K) \) using the van ‘t Hoff equation:

\[
\Delta H_{\text{tot}} = -2.303 R \Delta \log D \Delta (1/T)
\]

The enthalpy change during the extraction was found to be \(-24.26 \text{ kJ mol}^{-1}\). This shows that the extraction process is exothermic. The overall enthalpy change \( \Delta H_{\text{tot}} \) during mass transfer in the solvent extraction process is a combination of several factors, including (1) dehydration of the metal ion; (2) complex formation of the metal ion with the extractant; (3) dissolution of the metal solvate in the organic phase; (4)
rearrangement of the organic phase to attain a stable configuration. In the solvent extraction process, during the formation of the metal–extractant complex, the metal–solvate needs room in the organic phase to be dissolved and stabilized. Therefore, the previous molecular arrangement of organic phase gets distorted in the presence of the metal complex and it rearranges in order to have a stable configuration at the phase gets distorted in the presence of the metal complex and it rearranges in order to have a stable configuration at the expense of some enthalpy change. The magnitude of enthalpy change is governed by one of the four factors mentioned above. The change in Gibb’s free energy ($\Delta G$) can be calculated from eqn (7):

$$\Delta G = -2.303RT \log K_{ex}$$

The value of $\log K_{ex}$ was obtained from Fig. 3. The value of $\Delta G$ was found to be $-41.2$ kJ mol$^{-1}$. This indicates that the process is highly energetically favored and spontaneous. The change in entropy ($\Delta S$) at a fixed temperature can be evaluated using eqn (8):

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The value of $\Delta S$ was determined to be 55.9 J K$^{-1}$ mol$^{-1}$. The positive $\Delta S$ value could be attributed to the fact that there exist more degrees of freedom (more randomness) during the complex formation process which arises due to the dehydration from the inner core of the central metal ion and the process is known as an “entropy driven” process. Therefore, the positive entropy value suggests the existence of an inner-sphere (primary coordination sphere) complex formed between Eu(III) and $[P66614][MA]$.

**Stripping and reusability studies**

It is important to study the back-extraction (stripping) of the metal ions under investigation from the loaded (pregnant) ionic liquid phase. A stripping study was carried out from the pregnant ionic liquid phase. It was observed that complete stripping of Eu(III) was possible with a 0.5 M nitric acid solution, without the need of adding any complex-forming agent to the aqueous phase. This is also an extra advantage of the present ionic liquid extraction system, since the presence of an aqueous complex-former requires an additional clean-up step after stripping, in order to decompose the complex and to recover the nitrate ions. After the back extraction step, the nitrate ions in the aqueous phase to reform the ion pair $[P66614][NO_3]$ and this remains in the organic phase.

**Conclusions**

A novel non-fluorinated functionalized ionic liquid extraction system based on a malonamide was designed for the recovery of europium(III) and other rare earths from an acidic medium. The extraction system consists of the functionalized ionic liquid $[P66614][MA]$ diluted in the ionic liquid $[P66614][NO_3]$. The present ionic liquid system is easily recyclable unlike other fluorinated functionalized ionic liquids. A $[P66614][MA]$ concentration of 0.05 M was sufficient to get ~100% recovery of europium(III), despite the relatively high viscosity of the ionic liquid diluent $[P66614][NO_3]$. The extraction stoichiometry indicates the formation of a 1:3 (or possibly 1:4) complex between $[P66614][MA]$ and europium(III). Extraction from nitrate medium is far superior to extraction from chloride medium. The presence of a salting-out agent has a dramatic effect on the distribution ratios, as well as loading in the ionic liquid phase. Using the present ionic liquid system, it was possible to separate efficiently the rare-earth ions from transition metal ions which are normally present along with rare-earth ions in lamp phosphors as well as magnets. The negative value of enthalpy change ($\Delta H$) and free energy change ($\Delta G$) suggest the exothermicity and spontaneity of the extraction process. The positive values of $\Delta S$ confirm the randomness in the system and the formation of an inner-sphere complex. Complete stripping of Eu(III) from the pregnant ionic liquid solution was possible under relatively mild conditions (3 to 4 washing steps with a 0.5 M HNO$_3$ solution) without the need of using a complex-forming agent in the aqueous phase. The ionic liquid extraction system could be regenerated and re-used for the next extraction system without loss of extraction efficiency.

Ongoing research in our laboratory is directed towards the development of new greener and non-fluorinated ionic liquid based solvent extraction systems for the recovery of rare earths. Extraction studies with $[P66614][MA]/[P66614][NO_3]$ and similar ionic liquid systems are being extended to extraction from aqueous phases with high metal concentrations and to speciation studies.

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