



Solvent extraction of intra-lanthanides using a mixture of TBP and TODGA in ionic liquid

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ABSTRACT

The recovery and separation of trivalent lanthanides into individual elements is difficult owing to their similar chemical behaviours. In this study, the solvent extraction of trivalent lanthanide ions from nitric acid solutions in an organic phase comprising a mixture of two electrically neutral extractants, viz. tri(*n*-butyl)phosphate (TBP) and *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA), is investigated. The hydrophobic room-temperature ionic liquid (IL), 1-methyl-3-butyl-imidazolium bis(trifluoromethanesulfonyl)imide, is employed as a more environmentally benign diluent compared to the conventional molecular solvents. The results reveal that the addition of TBP as a co-extractant with TODGA not only significantly enhances the metal ion extraction but also affords high intra-lanthanide ion selectivity. This is attributed to the formation of complex lanthanide species with both TBP and TODGA. In addition, when IL is used as a diluent, the cationic exchange between metal-organic ligand species and IL cations, as well as neutral complex extraction result in a more efficient extraction. Moreover, the hydrophobic anionic IL entities can also be involved in the extraction mechanism, affording lipophilic metal-organic ligand complexes. The synergistic solvent combination of TODGA, TBP, and IL can afford an excellent separation of the lanthanide(III) ions.

1. Introduction

The recovery and separation of trivalent lanthanides (Ln) into individual elements is challenging owing to close similarity in their chemical behaviours (Aspinall, 2001; Choppin, 1983; Nash et al., 2006). The separation is typically performed using a solvent extraction technique, which is based on the transfer of metallic species with lipophilic ligands (extractants) from an aqueous medium into an immiscible organic phase (Hudson et al., 2012; Jensen et al., 2015; Mincher et al., 2012). Many different extractants including cationic (e.g., organophosphorus and carboxylic acids), anionic (amines), and solvating (phosphate esters, phosphine oxides, etc.) species have been extensively studied for Ln(III) extraction from various media (Jha et al., 2016; Li, 2019; Xie et al., 2014). Among these compounds, diglycolamide-based extractants, particularly the extensively studied *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA, Fig. 1), have been identified as promising molecules for the separation of trivalent Ln ions from nitric acid solutions because of their strong extraction affinities to the *f*-elements (Ansari et al., 2012; Ansari et al., 2005; Hudson et al., 2012;

Whittaker et al., 2018). Moreover, diglycolamides comprise only C, H, O, and N atoms (the CHON principle), allowing these to be used as green extractants. However, the volatile organic compounds used as diluents with large volumes in solvent extraction can lead to health, safety, and environmental problems because of their toxicities and flammabilities. A drawback of TODGA is that it is prone to forming the third phase in diluents, and therefore, a phase modifier, e.g., tri(*n*-butyl)phosphate (TBP), is needed (Woodhead et al., 2019). TBP is a well-known extractant and can also be employed as a co-solvent and synergistic agent (Stepinski et al., 2005).

Ionic liquids (ILs) have attracted significant attention as one of the alternatives to the conventional molecular diluents for solvent extraction (Billard et al., 2011; Stojanovic and Keppler, 2011). ILs are a class of compounds with melting points of below 100 °C, which comprise dissociated ions (Wasserscheid and Welton, 2008). Many ILs are stable in air and water, non-volatile, and nonflammable. Moreover, ILs have also been reported to considerably enhance the metal extraction efficiency (Billard, 2012; Stojanovic and Keppler, 2011).

Recently, researchers studied the solvent extraction. For instance,

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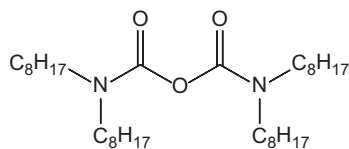


Fig. 1. Chemical structure of *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA).

TBP is shown to synergically enhance the strontium(II) extraction from HNO_3 solutions by dicyclohexano-18-crown-6 in ILs (Stepinski et al., 2005) of Ln(III) from nitric acid (HNO_3) solutions using diglycolamide ligand, tetrabutylglycolamide, in IL (Mincher et al., 2012). At high acidic concentrations, the extraction efficiency was lower when IL was used as a diluent instead of 1-octanol. Moreover, lower separation factors were observed in the IL-based system. To afford selectivity and improve the efficiency of solvent extraction, a combination of different extractants can be employed to combine their coordination and solvating capabilities toward target metal ions (Lumetta et al., 2010; Quinn, 2017; Ritcey, 2006). This co-operative effect of two (or more) extractants that results in a greater distribution ratio than the largest individual distribution ratios is defined as synergism (Rice et al., 1993).

The synergic effect of mixed systems involving various extractants and ILs has been previously reported in literature (Atanassova, 2016; Atanassova and Kurteva, 2017; Atanassova et al., 2014; Atanassova et al., 2015; Okamura et al., 2014; Petrova, 2016; Stepinski et al., 2005; Turanov et al., 2016; Turanov et al., 2017; Zhu et al., 2015). To date, a few studies have investigated the extraction of metal ions using mixtures of neutral extractants and these will be briefly discussed here. The researches have also studied the combination of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and TBP extractants diluted in a hydrophobic IL for the solvent extraction of metal ions. Rout et al. reported that the distribution ratio values for the extraction of trivalent americium (Rout et al., 2009) and europium (Rout et al., 2011) from HNO_3 using CMPO into 1-alkyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ($[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$) decreased with an increase in the concentration of TBP, and proposed that TBP was not involved in the extraction. Similarly, Gujar et al. concluded that TBP played an important role in the complexation of CMPO with metal ions, but it was not expected to be directly involved in the complex formation (Gujar et al., 2019). Moreover, Visser et al. spectroscopically identified the uranyl complexes extracted with CMPO and TBP in both dodecane and IL as $\text{UO}_2(\text{NO}_3)_2(\text{CMPO})_2$ and $\text{UO}_2(\text{NO}_3)(\text{CMPO})^+$, respectively (Visser et al., 2003).

Atanassova et al. (Atanassova, 2016) observed no synergism between TODGA and CMPO during Ln(III) extraction from acidic solutions into $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ ($n = 8$ or 10).

Synergism was reported for strontium(II) extraction from HNO_3 solution using dicyclohexano-18-crown-6 and TBP in ILs (Stepinski et al., 2005). Rama et al. (Rama et al., 2016) described that Eu(III) extraction from HNO_3 solution with TODGA in $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ was enhanced by TBP. The authors explained this extraction behaviour through the synergic participation of both extractants and proposed 1:3 stoichiometry between the metal and organic ligands. However, the origin of synergism in the systems with TODGA and TBP in IL and the exact stoichiometry of the extracted complexes remains unclear.

Herein, a synergistic extraction system with a mixture of two well-known neutral extractants, TBP and TODGA, in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$, a well-characterized hydrophobic room-temperature ionic liquid with low aqueous solubility, (Gaillard et al., 2012; Vranes et al., 2012) is investigated. The present work aims to examine the extraction behaviour of Ln(III) in this system and elucidate the underlying extraction mechanism that is key to the rational design and control of new extraction systems. The findings of this study contribute to the development of novel highly efficient separation systems for lanthanides for nuclear fuel reprocessing and metal recycling.

2. Experimental section

2.1. Materials

TODGA (> 97% purity) was prepared, purified, and characterized according to the published method (Sasaki and Choppin, 1996). TBP and 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide were purchased from Sigma-Aldrich. Ln(III) salts were of chemical grade and used as supplied. Analytical grade concentrated nitric acid (HNO_3 , Merck, 65 wt%) was used. Molecular diluents, nonane and 1,2-dichloroethane (DCE), were of chemical grade and used without further purification. All aqueous acidic solutions were prepared using distilled water and concentrated acid.

2.2. Solvent extraction procedure

In this study, all solvent extraction batch experiments were carried out at room temperature (20–25 °C).

A stock Ln(III) solution was prepared by dissolving metal nitrate salt. The initial aqueous concentration of the metal ions was 2×10^{-6} M. The organic phase was prepared by dissolving measured quantities of TODGA and/or TBP in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$, DCE, or nonane. All extraction samples were prepared using precisely weighed aliquots of each phase in centrifuge tubes equipped with sealing plugs. Generally, a 1:1 volume ratio of organic and aqueous phases was employed. The biphasic mixtures obtained by combining the aqueous and organic phases were shaken vigorously using a rotor mixer at a rate of 60 rpm for 1 h. It was checked in the preliminary trials if this time of phase contact was sufficient to achieve the equilibrium. To promote phase separation, the extraction tubes were centrifuged, and the aliquots of each phase were sampled for further analysis. The values of the metal (M) distribution ratio D_M were calculated as the concentration of the metal ion in the organic phase to that in the aqueous phase, $[\text{M}]_{\text{org}}/[\text{M}]$. The subscript “org” denotes the metal species in the organic phase and its omission represents the species in the aqueous phase. Duplicate experiments showed that the reproducibility of the D_M measurements was within 10%.

The concentration of the metal ions in the aqueous phase was determined using inductively coupled plasma mass spectrometry (ICP-MS) using an X-7 mass spectrometer (Thermo Electron, USA) according to the previously described procedure (Turanov et al., 1996).

3. Results and discussion

In the present study, a room-temperature hydrophobic IL is employed, with commonly used 1-butyl-3-methylimidazolium cation ($[\text{C}_4\text{mim}^+]$) and *bis*(trifluoromethanesulfonyl)imide anion ($[\text{Tf}_2\text{N}^-]$) as a diluent for organic ligands (extractants). For comparison, a conventional molecular solvent, nonane (C_9H_{20}), is also investigated. The chemical structures and abbreviations of the IL and extracting agents employed are shown in Fig. 1 and S1. In this study, some distribution experiments were performed with only Eu(III) as a representative trivalent lanthanide, whereas the selectivity study was conducted with trivalent Ln.

3.1. Eu(III) extraction by TODGA and/or TBP

The extraction behaviour of individual lanthanide, Eu(III), with TODGA and/or TBP diluted in the molecular solvent or IL was investigated at a fixed nitric acid concentration of the aqueous phase (3 M HNO_3) solutions, as many studies were conducted using TODGA at this acidity because of nuclear fuel reprocessing, and their results were useful for comparative studies. For the lanthanides, nitrate complex formation is an important factor in solvent extraction studies. In the aqueous solutions, Eu is known to form two successive complexes with nitrate ions, $\text{Eu}(\text{NO}_3)_2^{2+}$ and $\text{Eu}(\text{NO}_3)_2^+$ (stability constants are 1.86

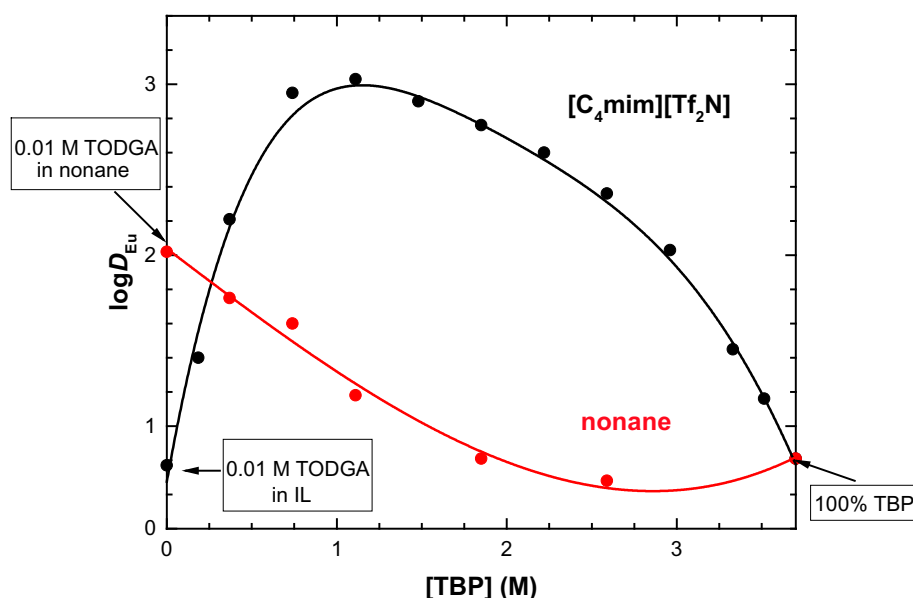


Fig. 2. Effect of TBP concentration on the distribution behaviour of Eu(III) between 3 M HNO_3 solution and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ or nonane containing 0.01 M TODGA. The lines are added for clarification.

and 0.23, respectively) (Sofie et al., 2006).

As expected, the distribution of Eu(III) ions between 3 M HNO_3 solution and the organic phase containing only TODGA is high, i.e., 0.01 M TODGA diluted in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ IL or nonane yields D_{Eu} values of 5.9 or 104.7, respectively (Fig. 2). This result is consistent with the prior observations, which also show that the Eu(III) extraction with TODGA is much more efficient in the extraction system with molecular diluent, in comparison to that with the IL at a high acidity of the aqueous phase (Mincher et al., 2012; Shimojo et al., 2008). According to Mincher et al., this result can be explained by the suppression of the extraction of cationic lanthanide-nitrato species, $[\text{Ln}(\text{L})_n(\text{NO}_3)]^{2+}$ and $[\text{Ln}(\text{L})_n(\text{NO}_3)_2]^+$ (L = diglycolamide ligand, n = number of L), into the IL phase at a high acidity. High nitrate concentration favours the formation of neutral metal complexes that are readily extracted into the molecular solvent, but are less efficiently extracted into the IL (Mincher et al., 2012). This difference in the Eu(III) extraction behaviour in the IL and nonane systems will be discussed in detail in Section 3.3.

Notably, the dissolution of only 1.1 M TBP in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ IL yields a negligible distribution value for Eu(III) ions at 3 M HNO_3 (D_{Eu} value is close to 0.045).

However, 0.01 M TODGA dissolved in TBP affords a distribution ratio value of ~ 6.5 for Eu(III) under these experimental conditions (Fig. 2). This D_{Eu} value is significantly greater compared to that reported for Eu(III) extraction from 3 M HNO_3 solutions using neat TBP (D_{Eu} is ~ 0.46 (Scargill et al., 1957)). This finding implies that TODGA molecules bind to Eu(III) more efficiently than the TBP ligand, resulting in good extraction efficiency. This result is consistent with that of a previous study which reported that Eu(III) and Am(III) extraction was performed by TODGA molecules instead of TBP (Brown et al., 2010).

Furthermore, a comparison of the D values for the extraction of Eu(III) by 0.01 M TODGA into two different molecular diluents reveals that D_{Eu} value strongly depends on the organic solvent properties (D_{Eu} is 104.7 or 6.5 for TODGA dissolved in nonane or TBP, respectively). The different extractabilities were previously observed for the extraction of Eu(III) and Am(III) ions with TODGA diluted in five molecular solvents of different polarities (dichloroethane, octanol, chloroform, toluene, and dodecane) (Sasaki and Rao, 2007). The authors of this investigation suggested that the enhanced extraction into the solvent phase containing a diluent with low dielectric constant such as dodecane was associated with high metal-TODGA stoichiometry in the

extracted complex. In addition, two molecules of HNO_3 could probably be involved in the metal extraction that resulted in more stable M $(\text{TODGA})_{3-4}(\text{NO}_3)_3(\text{HNO}_3)_2$ species.

To evaluate the potential synergistic effect between the two neutral organic ligands and determine the optimal ratio between TBP and IL in the solvent phase in terms of D_{Eu} , the Eu(III) extraction behaviour using 0.01 M TODGA was studied as a function of TBP concentration diluted in the IL or benchmark solvent, i.e., nonane. TBP concentration was varied in the range of 0–3.7 M (i.e., 0–100%, v/v). The experimental results plotted as $\log D_{\text{Eu}}$ versus $[\text{TBP}]_{\text{org}}$ are shown in Fig. 2. The addition of TBP solvating molecules synergistically enhances the extraction efficiency for trivalent Eu ions from the aqueous nitric acid solutions by TODGA dissolved in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ IL. In other words, the use of binary mixtures of TODGA and TBP in the IL-based extraction system leads to distribution values that are greater than the sum of those obtained for individual extractants. Fig. 2 shows that the curve for D_{Eu} in the TODGA/TBP/IL extraction system passes through a maximum at approximately 1.1 M TBP. To evaluate the magnitude of the synergic effect, the synergistic factor is calculated as a ratio of D_{Eu} in 0.01 M TODGA/1.1 M TBP/IL and the sum of the D_{Eu} values in 0.01 M TODGA/IL and 1.1 M TBP/IL. The synergistic factor S_{Eu} for 0.01 M TODGA/1.1 M TBP/IL system is close to 180.

As observed in Fig. 2, the system comprising TODGA, TBP, and nonane differs from the IL-based system. No synergism is observed in this case. When nonane is used as a diluent, Eu(III) extractability decreases rapidly with an increase in the TBP concentration in the organic phase and passes through a minimum at approximately 2.6 M TBP ($D_{\text{Eu}} = 4.8$), after which it increases slightly. As discussed above, a possible explanation for this can be the change in the speciation of the metal extracted species and its stability with and without HNO_3 in the complex composition, due to a change in the polarity of the extraction solvent with an increase in TBP concentration (Sasaki and Rao, 2007) and the competition between TODGA and TBP molecules. This outcome is supported by the results of a previous study on the uranium(VI)-TODGA-TBP system using infrared spectroscopy, which showed that the addition of TBP to the U/TODGA solution in odourless kerosene led to a gradual displacement of the coordinated TODGA molecules resulting in free TODGA and U-TBP species. However, the presence of mixed U-TODGA-TBP complexes could not be confirmed (Brown et al., 2010).

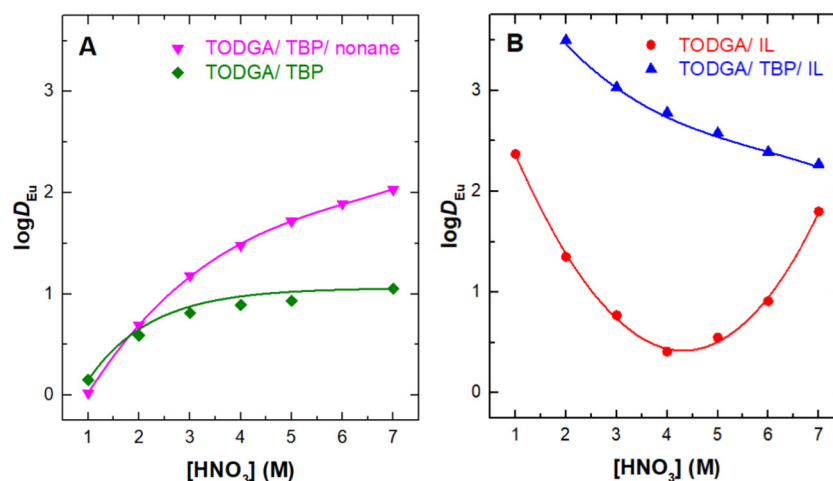


Fig. 3. Effect of initial HNO_3 concentration (aqueous) on Eu(III) extraction with 0.01 M TODGA dissolved in (A) pure TBP or 1.1 M TBP/nonane mixture and (B) pure IL or 1.1 M TBP/IL mixture ($V_o:V_a = 1:10$).

3.2. Effect of HNO_3 concentration on Eu(III) extraction by TODGA and/or TBP

To further elucidate the metal extraction equilibria between an aqueous and organic phase composed of TODGA and TBP extractants diluted in the IL or molecular solvent, the distribution behaviour of Eu (III) ions was studied as a function of the initial nitric acid concentration in the aqueous phase. The extraction performances of these two binary extractant systems, TODGA/TBP/IL and TODGA/TBP/nonane, were compared with the system comprising TODGA and IL (TODGA/IL) and TODGA dissolved in pure TBP (TODGA/TBP) (Fig. 3).

When pure TBP or a mixture of TBP and nonane is used as a diluent for TODGA molecules, the $\log D_{\text{Eu}}$ values increase with an increase in the initial HNO_3 concentration in the aqueous phase (Fig. 3A). This result indicates that the nitrate anions and/or nitric acid molecules play an important role in this type of extraction system. Prior studies on the conventional extraction systems have also reported a strong and positive acid dependence for metal extraction with TODGA or TBP, i.e., for Ln and An (Rama et al., 2016; Sasaki et al., 2001). As observed in Fig. 3A, the Eu(III) distribution ratio values are considerably higher with aqueous $[\text{HNO}_3] > 2$ M for ternary mixtures of 0.01 M TODGA, 1.1 M TBP, and nonane. This counterintuitive result that the metal extraction efficiency decreases with an increase in the TBP concentration in the solvent phase can be explained based on the lower polarity of the organic phase comprising TBP and nonane. Importantly, prior research has established that Eu(III) forms identical complexes in different diluents such as n-dodecane, toluene, and octanol (Pathak et al., 2009). For the trivalent ions, the inner coordination sphere is completed by $\text{Ln}(\text{TODGA})_x(\text{NO}_3)_y$, where $x + y = 3$ and $x = 2$ or 3 (Whittaker et al., 2018). Extended X-ray absorption fine structure studies of TODGA-extracted Pr(III), Nd(III), Eu(III), Yb(III), and Lu(III) show that the inner coordination sphere of these lanthanide cations is saturated by the organic ligand; $[\text{Ln}(\text{L})_3]^{3+}$ species is predominant (Ellis et al., 2016). Thus, the extraction efficiency results from the combined effects of the interactions between the nitrate anions, nitric acid, and/or water molecules in the outer sphere of the extracted species.

In contrast, in the IL-based extraction system (Fig. 3 B), the efficiency of Eu extraction with mixtures containing 0.01 M TODGA and 1.1 M TBP declines steadily with an increase in the concentration of nitric acid in the aqueous phase. Moreover, TBP and TODGA mixture yields significantly higher distribution ratio values for Eu when it is dissolved in the IL instead of a molecular diluent (TODGA/TBP/nonane, Fig. 3A), where only the extraction of the neutral metal species with nitrate ions is possible. A similar cooperative effect of neutral organic

ligand and hydrophobic anions was previously observed for the extraction of Ln(III) from nitric acid solutions (Naganawa et al., 2001; Suzuki et al., 2003). Therefore, in the TODGA/TBP/IL system, the hydrophobic TF_2N^- anions probably act as counter ions resulting in more hydrophobic metal species compared to those with the nitrate anions. Moreover, in addition to solvation or ion-pairing mechanism, ion exchange can also occur in the system with IL as the diluent owing to its ionic nature, particularly, at low aqueous acidity.

To confirm our hypothesis regarding the cation-exchange mechanism in the TODGA/TBP/IL system, the extraction behaviour of Eu was investigated as a function of the concentration of water-soluble $[\text{C}_4\text{mim}]\text{Cl}$ salt at 3 M HNO_3 . As observed in Fig. 4, the distribution ratio values for Eu gradually decrease with an increase in the aqueous concentration of $[\text{C}_4\text{mim}^+]$ cations. A similar dependency was previously reported for the extraction of actinides and lanthanides from nitric acid medium with TODGA diluted in IL (Panja et al., 2012; Shimojo et al., 2008). The addition of IL common cations in the aqueous phase results in a shift of the extraction equilibrium, and suggests that Eu is extracted in the IL-based system via the cation-exchange mechanism:

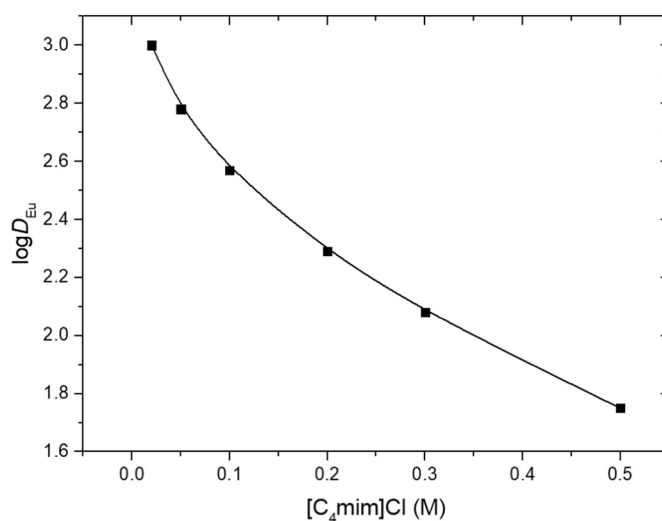
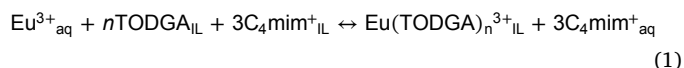


Fig. 4. Effect of aqueous $[\text{C}_4\text{mim}]\text{Cl}$ concentration on Eu(III) extraction from 3 M HNO_3 with 0.01 M TODGA dissolved in 1.1 M TBP/IL mixture ($V_o:V_a = 1:10$).



A more complex behaviour of Eu(III) extraction as a function of initial nitric acid concentration in the aqueous phase is observed when IL is used as diluent for only TODGA (Fig. 3B). At a low acidic concentration, the distribution ratio of Eu(III) decreases with an increase in the HNO_3 concentration and reaches a minimum value in 4 M HNO_3 . Thereafter, D_{Eu} increases as the concentration of HNO_3 in the aqueous phase increases from 4 to 7 M. The flexion point at 4 M HNO_3 indicates the modification of the extraction mechanism. Mincher et al. observed a similar acid dependency of the distribution ratio values for the metal ions and proposed the extraction mechanism (Mincher et al., 2012). At 1–4 M HNO_3 in the aqueous phase, the Eu extraction probably proceeds via the cationic exchange between lanthanide–organic ligand species and IL cations, or/and via the extraction of neutral complexes composed of Ln–organic ligand and nitrate and/or Tf_2N^- anions as counter ions. In our previous publications, the possible participation of hydrophobic Tf_2N^- anions as counterions in the extracted species encountered in the extraction systems with ILs was considered (Turanov et al., 2016; Turanov et al., 2017). At high aqueous acidity, the extraction of neutral metal complexes with nitrate ions is probably favoured.

3.3. Intra-lanthanide selectivity with TODGA and/or TBP extractants

To investigate the intra-lanthanide selectivity in the extraction systems under consideration in this study, a set of extractions of trivalent light (La–Nd), medium (Sm, Eu, and Gd), and heavy (Tb–Lu) lanthanides from 3.0 M HNO_3 solution were performed. Previous studies have shown that diglycolamide ligands diluted in the molecular solvents are selective within the Ln series and favour the extraction of heavy lanthanides (Narita et al., 1999; Sasaki et al., 2001; Shimojo et al., 2008) Baldwin et al. (Baldwin et al., 2018) suggested that the two TODGA extraction regimes defined across the lanthanide series resulted from the differences in the placement of the charge-neutralising nitrate counter ions.

First, the separation of Ln(III) ions with the solvent phase composed of two components is considered. The results of intergroup extractions with 0.01 M TODGA diluted in nonane or TBP, and with 1.1 M TBP in nonane or $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ are shown in Fig. 5A. These results are

compared with the data previously obtained for Ln(III) extraction using TODGA dissolved in IL or DCE (Turanov et al., 2017). As observed, the distribution ratio values for trivalent lanthanides follow an increasing trend across the lanthanide series for the solvent phases composed of TODGA in the molecular solvent (nonane, TBP, or DCE; Fig. 5A). This behaviour is generally observed in the solvent extractions with diglycolamides (Sasaki et al., 2001). Heavy lanthanides including Ho, Er, Tm, Yb, and Lu constitute the most efficiently extracted group in these systems. For instance, in the TODGA/TBP system, the separation factors of Lu(III) and La(III), Lu(III) and Sm(III), and Lu(III) and Tb(III) are 276, 28, and 5.3, respectively (Fig. 6) (Turanov et al., 2017). TBP diluted in either IL or nonane shows poor extractability and selectivity across the lanthanide series. TODGA dissolved in IL also exhibits low selectivity for Ln(III) extraction.

An increasing trend in the intergroup lanthanide extractions was observed for the extraction systems with ternary mixtures of TBP and TODGA dissolved in the IL or nonane (Fig. 5B). Notably, the addition of TBP as a co-extractant to TODGA leads to a significant enhancement of the extraction efficiency of metal ions, in particular for middle and heavy lanthanides (up to many orders of magnitude) in the IL-based system. The most striking finding of the present study is the significant enhancement of selectivity among Ln(III) ions in the TODGA/TBP/IL extraction system compared to that in the TODGA/IL binary mixture (Fig. 5). For instance, in the TODGA/TBP/IL system, the separation factors of Lu/La, Lu/Sm, and Lu/Tb are 1622, 45, and 4.8, respectively (Fig. 6). In the extraction system with nonane, the addition of TBP decreases the separation among the lanthanides compared to that in the TODGA/nonane system.

Thus, the solvent combination of TODGA/TBP/IL affords excellent separation among the Ln(III) ions in terms of efficiency and selectivity. The results of the present study regarding the intra-lanthanide selectivity using TODGA and TBP mixtures both in molecular and IL diluents are consistent with those of previous studies on the synergic extraction of lanthanides ions with TODGA and 0.01 M IL in DCE (Turanov et al., 2017). The authors suggested that the preferential complexation of heavy Ln(III) ions with TODGA- HNO_3 and/or TODGA- HTf_2N entities yielded high selectivity.

The low performing extraction systems in terms of Ln(III) ion selectivity constitute only TODGA dissolved in the IL or a mixture of IL and DCE (Fig. 5). This result is in line with those reported in other studies, which describe that the lanthanide patterns in the IL and

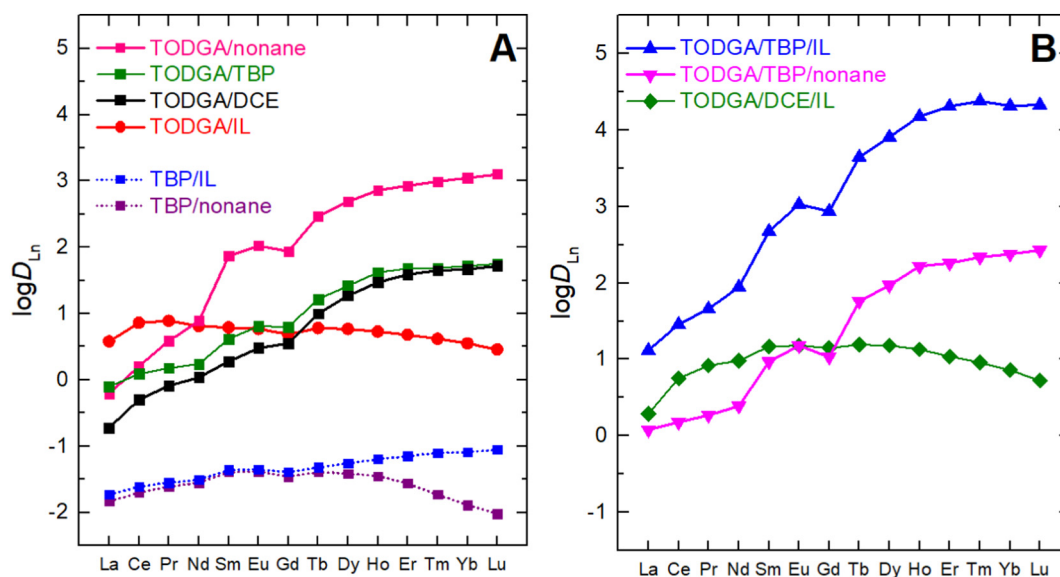


Fig. 5. Extraction and separation of Ln(III) ions from 3 M HNO_3 aqueous solution using (A) 0.01 M TODGA diluted in pure nonane, TBP, IL ($V_{\text{O}}:V_{\text{A}} = 1:10$), (Turanov et al., 2017) or DCE (Turanov et al., 2017) and with TBP in nonane or IL; (B) mixture of 0.01 M TODGA and 1.1 M TBP dissolved in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ($V_{\text{O}}:V_{\text{A}} = 1:10$) or nonane, and 0.01 M TODGA in a 7:3 (v:v) mixture of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and DCE (Turanov et al., 2017).

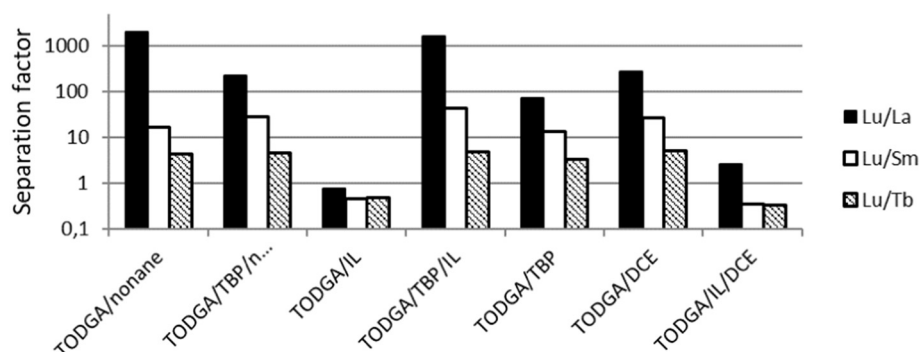


Fig. 6. Lu/La, Lu/Sm, and Lu/Tb separation factors in the extraction systems studied in the present work and ref. [5] (see text); aqueous phase: 3 M HNO₃.

conventional extraction systems with diglycolamide ligand show different features. The TODGA/IL system shows selectivity toward middle lanthanides, but lanthanide separation into individual metals is difficult (Mincher et al., 2012; Shimojo et al., 2008). The origin of this phenomenon is still not clearly understood.

3.4. Stoichiometry of extracted metal complexes with TODGA and TBP ligands

The extraction behaviours of several lanthanides using TODGA and TBP in the IL system were investigated through slope analyses. The effect of TODGA concentration at a fixed TBP concentration of 1.83 M in [C₄mim][Tf₂N] and 3 M HNO₃ in the aqueous phase on the distribution ratio of metals is displayed in Fig. 7.

The slope of logD_M versus log[TODGA] plot allows the interpretation of the stoichiometry of the extracted Ln(III) complexes from aqueous 3 M HNO₃ solutions. The number of TODGA molecules associated with light lanthanides is close to 2.5, i.e., 2.4, 2.5, and 2.6 for La, Ce, and Pr, respectively. This implies that the stoichiometry of TODGA with these metals is close to 2:1 and 3:1. For other metals, namely Nd, Eu, Tb, Ho, and Lu, the number of TODGA molecules is close to 3.0. These results are in line with those of previous studies employing conventional extraction systems (Baldwin et al., 2018; Ellis et al., 2016).

Thus, it is suggested that the higher extraction efficiencies and selectivities for lanthanides using TODGA and TBP extractants in the IL-based extraction system in comparison to those with TODGA/TBP/nonane (Fig. 5B) can be explained on the basis of two underlying

mechanisms, namely, exchange between cationic metal–organic ligand species and IL cations, and/or their ion pairing with Tf₂N[−] and/or NO₃[−] anions. The anionic components of IL, Tf₂N[−] ions, are very weak ligands owing to their low charge density. This implies that these lipophilic anions are not present in the inner-sphere of the Ln(III) ions in the extracted species. Moreover, in a study on the extraction behaviour of rare earth elements by TODGA in phosphonium-based ILs, Murakami et al. described that no Tf₂N[−] anions existed in the first coordination sphere of the extracted complex [Nd(TODGA)_(2–3)]³⁺, based on the Raman spectroscopic analysis (Murakami et al., 2016). The results of this study revealed the importance of the interactions in the outer-sphere of the extracted species, i.e., between the metal cations and organic ligands, as well as aqueous and organic solutes.

Further studies using complementary techniques such as synchrotron small-angle X-ray scattering, X-ray absorption fine structure spectroscopy, and molecular dynamics calculations can provide useful information regarding the inner and outer coordination environment of the extracted lanthanide species with TODGA and TBP mixtures to establish the origin of the synergistic effect in this binary extractant system. Moreover, it has been reported that the presence of solutes both in the aqueous and organic phases modifies the distribution of species (such as IL cations, anions, water, and protons) in the IL/water biphasic systems (Dietz and Stepinski, 2008; Gaillard et al., 2015; Turanov et al., 2016). A detailed investigation of the IL solubility product should be also undertaken to understand the underlying metal extraction mechanism.

4. Conclusions

In the present study, Ln(III) ions were extracted from nitric acid solutions using a mixture of two electrically neutral extractants, tri(*n*-butyl)phosphate (TBP) and *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA), dissolved in hydrophobic [C₄mim][Tf₂N] IL.

The results reveal that the addition of TBP as a co-extractant to TODGA in the molecular solvent results in a decrease in the extraction efficiency and selectivity toward heavy Ln(III). In contrast, TODGA dissolved in IL instead of the molecular solvent shows a significantly higher extraction efficiency of Ln(III) ions, while the selectivity is suppressed. Furthermore, TBP added to TODGA in the IL medium not only significantly enhances the metal extraction from acidic nitrate media, but also the intra-lanthanide ion selectivity. For TODGA/TBP/IL system, the separation factors of Lu/La, Lu/Sm, and Lu/Tb are 1622, 45, and 4.8, respectively. Thus, a combination of TODGA/TBP/IL can afford excellent separation of the Ln(III) ions. TODGA/nonane and TODGA/TBP/IL are the highest performing systems under study in terms of the lanthanide separation.

The findings suggest that the cationic exchange between metal–organic ligand species and IL cations as well as neutral complex extraction result in a more efficient extraction of Ln(III) with TODGA dissolved in the IL. Moreover, the hydrophobic anionic IL entities can be involved in

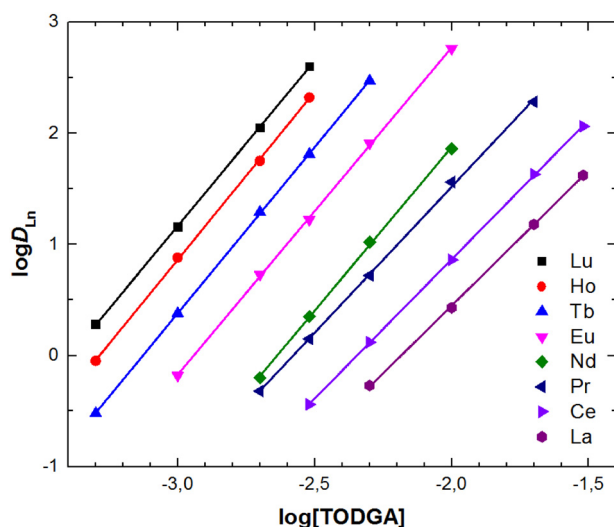


Fig. 7. Distribution ratio of lanthanide(III) ions extracted from 3 M HNO₃ aqueous solutions as a function of TODGA concentration at 1.83 M TBP diluted in [C₄mim][Tf₂N] ionic liquid.

the extraction mechanism resulting in higher amount of lipophilic Ln complexes in comparison to the complexes with nitrate ions as charge neutralising anions. The enhancement of TODGA performance upon TBP addition as a co-extractant in the IL media is probably due to the formation of complex lanthanide species with both organic extracting agents, and complex interactions between the counter anions, acids, and/or water molecules in the outer-sphere of the extracted species.

The findings of this study contribute to the development of novel highly efficient separation systems for lanthanides for nuclear fuel re-processing and metal recycling.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.hydromet.2020.105367>.

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