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# Extraction of Lanthanides(III) from Aqueous Nitric Acid Solutions with Tetra(*n*-octyl)diglycolamide into Methyltrioctylammonium Bis(trifluoromethanesulfonul)imide Ionic Liquid and Its Mixtures with Molecular Organic Diluents

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**Abstract:** The extraction of lanthanides(III) from aqueous nitric acid solutions with tetra(*n*-octyl) diglycolamide into methyltrioctylammonium bis(trifluoromethanesulfonul)imide ($[N_{1888}][Tf_2N]$) ionic liquid and its mixtures with molecular organic diluents is investigated in this study. This study also investigates the effect of $HNO_3$ concentration in the aqueous phase on the extraction of Ln(III) ions. Subsequently, the stoichiometry of the extracted complexes is determined, and the mechanism of Ln(III) extraction in a system with $[N_{1888}][Tf_2N]$ is discussed. It is shown that the intragroup selectivity of the extraction of Ln(III) ions is significantly higher when using $[N_{1888}][Tf_2N]$ than when using the imidazolium-based ionic liquid $[C_4mim][Tf_2N]$.

**Keywords:** solvent extraction; separation; ionic liquids; tetra(*n*-octyl)diglycolamide; lanthanides(III)

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## 1. Introduction

Individual rare earth elements (REEs) and their compounds are widely used in various modern industries, as well as for the production of radiopharmaceuticals. The growing consumption of rare earth elements and their compounds necessitates the processing of mineral raw materials with a low content of rare earth elements, as well as industrial end-of-life wastes [1–3]. The separation of REEs is a difficult task because of the closeness of the physicochemical properties of these elements. In the hydrometallurgy of REEs, various methods are used for their extraction, separation, and purification from impurities, such as fractional precipitation and crystallization, selective redox, adsorption, ion exchange, membrane processes, solvent extraction, and others. Compared to other methods, solvent extraction has a number of advantages, such as the ability to carry out the extraction process in a continuous, multi-step mode, which is easy to automate and has high productivity. Extraction methods with the use of organophosphorus and carboxylic acids, neutral mono- and polydentate organophosphorus compounds, are widely used to extract, concentrate, and separate REEs [4–7]. Nevertheless, the search for new effective and selective extractants continues.

In recent decades, interest in the use of alkylsubstituted diglycol-amides (DGA) as extractants has increased. These compounds exhibit high extraction ability with respect to lanthanide and actinide ions in nitric acid medium [8–16]. They act as tridentate ligands since they contain three oxygen atoms. The advantages of DGA as compared to bidentate-neutral organophosphorus compounds are ease of synthesis, milder requirements for stripping, and the harmless chemical composition of completely incinerable elements.

The hydrophobicity of DGA extractants is controlled by the length of the alkyl radicals linked to the amidic N atoms. The octyl chains of N,N,N,N′,N′-tetraoctyldiglycolamide (TODGA) give the molecule sufficient lipophilicity to dissolve in various organic diluents. The efficiency of Ln(III) extraction with TODGA largely depends on the nature of the organic diluent [11]. A significant disadvantage of DGA is its tendency to aggregate in solutions of non-polar organic solvents, which leads to the formation of a third phase during the extraction of metal ions from nitric acid solutions. This seriously complicates the process of REE extraction. To eliminate this phenomenon, various modifiers such as high-molecular-weight alcohols, tributyl phosphate, and others are added to the organic phase [14].

In recent years, ionic liquids (ILs), due to their extremely low volatility, noncombustibility, and excellent solvating properties, have been considered a possible replacement for conventional molecular organic diluents in various extraction areas, including spent nuclear fuel reprocessing [17–31]. In addition, it has been found that the simple replacement of traditional molecular solvents with IL increases the extraction efficiency of many known neutral extractants. Nakashima et al. [19] showed that the extractability and selectivity of the lanthanide cations with octylphenyl-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO) dissolved in [$C_4$mim][$PF_6$] or [$C_4$mim][$Tf_2N$] significantly increased compared to CMPO solutions in conventional organic diluents. The undoubted advantage of using IL as a solvent is the absence of the formation of a third phase in the extraction of actinides and REEs from nitric acid solutions with TODGA [14].

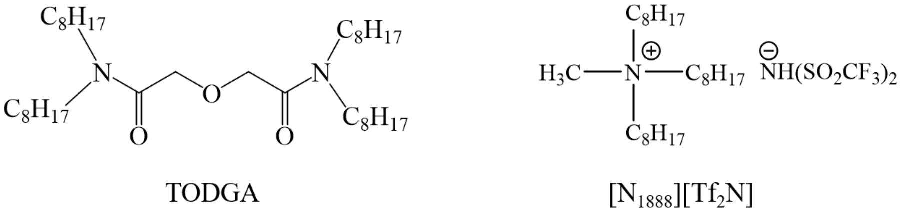
A number of studies have studied the extraction behavior of actinides and lanthanides in DGA-IL systems [32–36]. DGA extractant solutions in [$C_n$mim][$PF_6$] and ([$C_n$mim][$Tf_2N$] ($n$ = 4, 6, 8, and 10) efficiently extract lanthanides and actinides from aqueous solutions under reduced acidity, while traditional organic solvents such as chloroform show insignificant extraction. However, in DGA-[$C_n$mim][$Tf_2N$] systems, low intragroup selectivity was observed, which greatly hindered their application for the separation of rare earth elements in nitric acid media [33].

The addition of even small amounts of ILs to a solution of neutral extractants in conventional molecular diluents leads to a significant increase in the extraction efficiency of metal ions. In the extraction of alkaline earth cations, actinides, and lanthanides from aqueous nitric acid solutions in the presence of a small amount of IL in the organic phase containing DGA ligands [37–39], CMPO-type ligands [40], and a pillar[5]arene-based phosphine oxide [41], a significant synergetic effect was observed. A large number of possible "extractant—IL—molecular diluent" mixtures enable the development of new extraction systems for separating and preconcentrating metal ions. This allows for maintaining the high efficiency and selectivity of extraction processes with IL and eliminates significant cost increases.

In a number of studies, the effect of the nature of the cation and anion of ILs on the efficiency of the extraction of metal ions was studied. It was established that an increase in the hydrophobicity of the IL anion enables an increase in the extraction efficiency [20]. On the contrary, an increase in the hydrophobicity of the IL cation is accompanied by a decrease in the extraction of metal ions. It was shown that an increase in the length of the alkyl substituent in the [$C_n$mim]$^+$ cation leads to a sharp decrease in the extraction of Am(III) and Eu(III) by CMPO solutions in IL [42]. Hence, only when using IL diluents with relatively short alkyl chain radicals attached to the cationic part of the ILs, a significant increase in the extraction efficiency of neutral donor ligands with respect to metal ions is observed. However, because of their appreciable solubility in aqueous solutions, IL ions contaminate the aqueous phase. This disadvantage, as well as the high cost and viscosity of ILs, significantly complicates their wide-scale use as diluents. Therefore, a very urgent task is to find ways to minimize the loss of IL to the aqueous phase.

Recently, the use of alkylammonium ILs for metal ion extraction has attracted increasing attention. These ILs are more hydrophobic than imidazolium-based ILs due to the presence of alkyl radicals that are attached to the cationic N atom [43]. In addition, the alkylammonium ILs are easy to prepare and cheaper than imidazolium-based ILs. The extraction of Eu(III) with N,N,N′,N′-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) into [$N_{1444}$][$Tf_2N$] was studied [44]. However, there are no data on the selectivity of Ln(III) extraction in systems with alkylammonium ILs. In addition, there are no data on the effect of these ILs on the extraction of Ln(III) with solutions of DGA in molecular organic diluents.

This paper describes the results of our studies on the simultaneous extraction of lanthanides(III) with TODGA into methyltrioctylammonium bis(trifluoromethanesulfonul)imide ([$N_{1888}$][$Tf_2N$]) ionic liquid and its mixtures with molecular organic diluents. Scheme 1 shows the structures of TODGA and [$N_{1888}$][$Tf_2N$].



**Scheme 1.** The structure of TODGA and [$N_{1888}$][$Tf_2N$].

## 2. Materials and Methods

All starting materials for the synthesis of the extractants TODGA and methyltrioctylammonium bis(trifluoromethanesulfonul)imide ionic liquid were purchased from Sigma-Aldrich (St. Louis, MO, USA) and were used without further purification. Chemical and analytical grade nitrobenzene, 1-octanol, chloroform, n-nonane, tri-n-butyl phosphate, and 1,2-dichloroethane were purchased from Vekton (Saint Petersburg, Russian Federation). Stock aqueous solutions of lanthanides(III) were prepared from single-element standard solutions (High Purity Standards, North Charleston, SC, USA). High-purity nitric acid (65%) was purchased from Merck, Germany. Deionized water after the NANOPURE purification system (Thermo Scientific, North Charleston, SC, USA) with a specific resistivity of 18 MΩ was used to prepare all aqueous solutions.

N,N,N′,N′-tetra(*n*-octyl)diglycolamide (TODGA) N,N,N,N′,N′-tetra(*n*-octyl)diglycola mide (TODGA) was synthesized and then purified according to the method described in [45]. Trioctylmethylammonium *bis*(trifluoromethylsulfonyl)imide was obtained by the procedure given in [46].

The Ln(III) concentration in the initial and equilibrium aqueous solutions was determined by inductively coupled plasma mass spectrometry (ICP-MS) on an XSeries II mass spectrometer (Thermo Scientific, Waltham, MA, USA). The $Tf_2N^-$ anion concentration in equilibrium aqueous solutions was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an iCAP-6500 spectrometer (Thermo Scientific, Waltham, MA, USA). The concentration of $HNO_3$ in the equilibrium aqueous phase was determined by potentiometric titration of $H^+$ with a standard NaOH solution.

### *Extraction Procedure*

Extractant solutions were prepared using precisely weighed portions. Initial aqueous solutions of Ln(III) were prepared by diluting stock aqueous solutions with water and adding $HNO_3$ to the desired concentration. All lanthanides(III) (except for Pm) were presented in the initial aqueous phase. The initial concentration of each Ln(III) was 2 μM.

Metal ion extraction experiments were performed in plastic tubes at room temperature (21 ± 2 °C) and a volume ratio of aqueous vs. organic phases of 1:1. The organic and aqueous phases were mixed on a rotary mixer at 60 rpm for 1 h. To separate the phases, the tubes with the extract were centrifuged, and then aliquots of each phase were sampled for further analysis.

The Ln(III) concentration in the initial and equilibrium aqueous solutions was determined by ICP-MS. The content of lanthanides(III) in the organic phase was determined as the difference between the initial ($[Ln]_{init}$) and equilibrium ($[Ln]_{aq}$) concentrations of metal ions in the aqueous phase. Since this difference was very small in some cases, the concentration of metal ions in the organic phase ($[Ln]_{org}$) was determined by ICP-MS after the stripping of Ln(III). In this work, an aqueous solution of 0.1 M of 1-hydroxyethane-1,1-diphosphonic acid was used as a stripping agent. It is known that this reagent forms very stable complexes with Ln(III) ions in aqueous solutions [47]. The Ln(III) stripping was carried out at a volume ratio of organic and aqueous phases of 1:1. It was found that the sum of the metal ion concentrations in the aqueous phases after extraction and back-extraction was well in agreement with the initial concentration of metal ions. Consequently, virtually total Ln(III) stripping has been achieved. The values of the distribution coefficient ($D_{Ln}$) were calculated as $[Ln]_{org}/[Ln]_{aq}$. At least three replicate measurements were carried out. The measurement error of $D$ usually does not exceed 10%.

## 3. Results and Discussion

### 3.1. Solubility of $[N_{1888}][Tf_2N]$ in Aqueous $HNO_3$ Solutions

In order to evaluate the transfer of $[N_{1888}][Tf_2N]$ components into an aqueous phase during the extraction of metal ions, the distribution of $Tf_2N^-$ ions between IL and aqueous solutions of nitric acid was considered. An increase in the $HNO_3$ concentration in the aqueous phase leads to an increase in the $Tf_2N^-$ concentration in the aqueous phase, meaning an increase in the IL transition into the aqueous phase (Figure 1, Table S1). This may be due to the formation of IL with nitrate ions, which have a significantly lower hydrophobicity than $Tf_2N^-$ ions. In the case of IL $[N_{1888}][Tf_2N]$, the process of equilibrium can be described by the equation

$$H^+ + NO_3^- + [N_{1888}][Tf_2N]_{(org)} \rightleftharpoons [N_{1888}][NO_3]_{(org)} + Tf_2N^- + H^+ \quad (1)$$

where components with the index (org) and those without an index refer to the organic and aqueous phases, respectively.

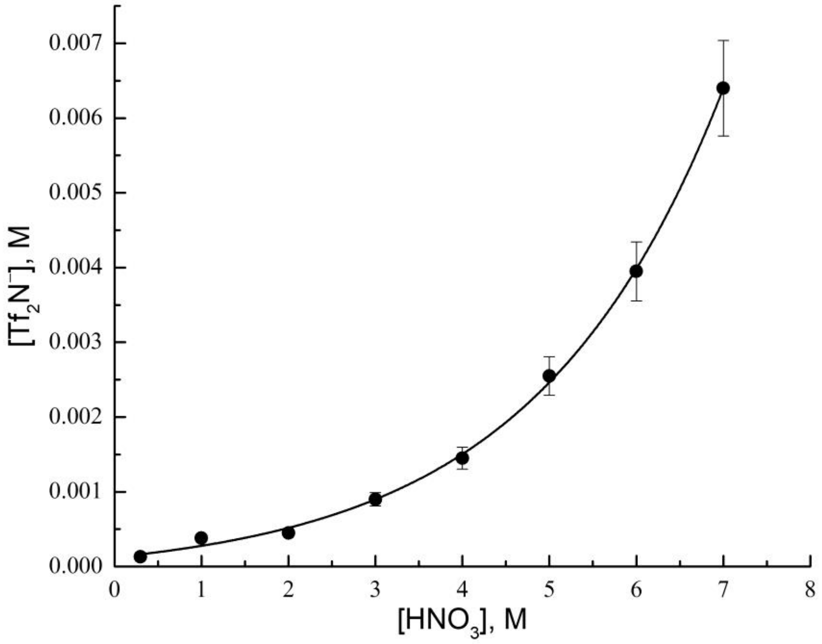


**Figure 1.** The effect of $HNO_3$ concentration in the aqueous phase on the transfer of $Tf_2N^-$ ions into the aqueous phase.

It should be noted that in the system with $[N_{1888}][Tf_2N]$, the transfer of $Tf_2N^-$ ions into the aqueous phase occurs to a much lesser extent than in systems with imidazolium ILs used in the solvent extraction of metal ions. Thus, during extraction from the 3 M $HNO_3$

solution, the concentration of the $Tf_2N^-$ ion in the aqueous phase when using $[N_{1888}][Tf_2N]$ is 0.0009 M, and when using IL $[C_4mim][Tf_2N]$, it is 0.047 M [48].

### *3.2. Effect of the Composition of the Aqueous Phase on the Ln(III) Extraction with TODGA into $[N_{1888}][Tf_2N]$*

The composition of the aqueous phase has a significant effect on the extraction of metal ions with neutral donor extractants. At the extraction of Ln(III) with TODGA solutions in low-polarity organic solvents, an increase in $D_{Ln}$ is observed with an increase in the concentration of $HNO_3$ in the aqueous phase [8]. It was found that both the unbound TODGA (L) and its complex $HNO_3L$ take part in the complexation with Ln(III) ions when polar organic diluents are used [40]. In this case, the extraction of Ln(III) with TODGA into the organic phase from the nitric acid solution through the solvation mechanism can be described using the following equation:

$$Ln^{3+} + 3NO_3^- + (s\text{-}n)L_{(org)} + nHNO_3L_{(org)} \rightleftharpoons LnL_{s\text{-}n}(HNO_3L)_n(NO_3)_{3(org)} \quad (2)$$

where s is a solvation number equal to 2 or 3.

The nature of the $\log D_{Ln}$-$\log[HNO_3]$ dependence changes sharply upon extraction with DGA solutions in ILs. The effect of the $HNO_3$ concentration in the equilibrium aqueous phase on the extraction of Ln(III) ions with TODGA into $[N_{1888}][Tf_2N]$ is shown in Figure 2 (Table S2). An increase in the concentration of $HNO_3$ in the aqueous phase is accompanied by a decrease in the distribution ratios of Ln(III). A similar dependence of D on the acidity of the aqueous phase was previously observed during the extraction of Ln(III), alkaline earth metals, and U(VI) with neutral DGA extractants [32–35] dissolved in imidazolium ILs, as well as the extraction of Eu(III) with T2EHDGA into $[N_{1444}][Tf_2N]$ [44].

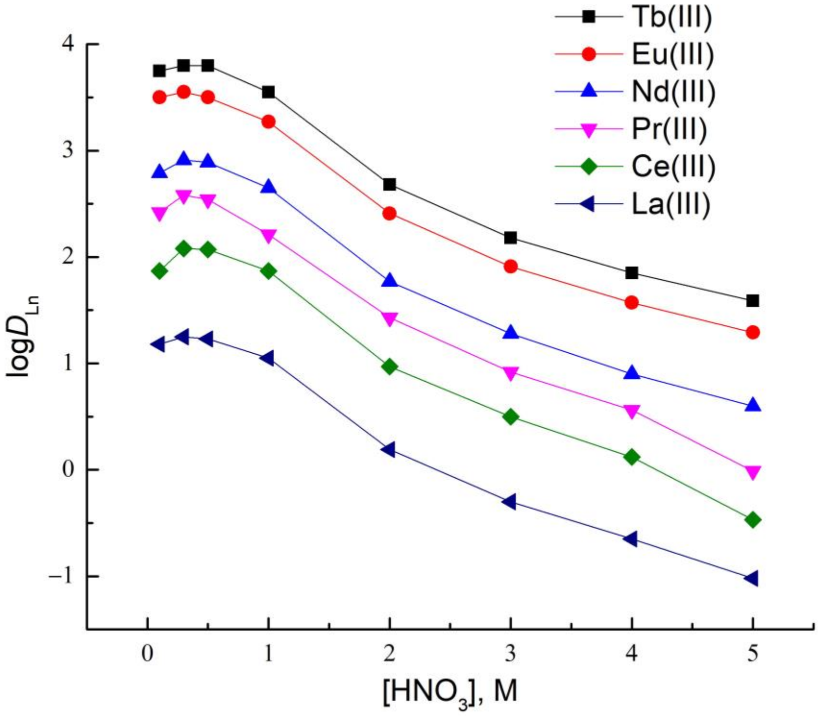


**Figure 2.** The effect of $HNO_3$ concentrations in the aqueous phase on the extraction of Ln(III) with 0.01 M solutions of TODGA in $[N_{1888}][Tf_2N]$. The sizes of the points represent error bars.

The extraction of Ln(III) ions into the organic phase containing the neutral ligand TODGA into $[N_{1888}][Tf_2N]$, according to the cation exchange mechanism, can be described by the following equilibrium:

$$Ln^{3+} + sL_{(org)} + 3[N_{1888}][Tf_2N]_{(org)} \rightleftharpoons LnL_s(Tf_2N)_{3(org)} + 3N_{1888}{}^{+} \quad (3)$$

It follows from this equation that, formally, the efficiency of the Ln(III) extraction does not depend on the concentration of $HNO_3$ in the aqueous phase. However, the effect of the concentration of $H^+$ and $NO_3{}^-$ ions in the aqueous phase is significantly different. As can be seen from the data in Figure 3 (Table S3), at a constant acidity of the aqueous phase, an increase in the concentration of $NO_3{}^-$ ions in the aqueous phase does not lead to a significant change in the Ln(III) distribution ratios. Some decrease in $D_{Ln}$ with an increase in the concentration of nitrate ions can be due to a shift in equilibrium (1) to the right, leading to an increase in the concentration of $[N_{1888}][NO_3]$ in the organic phase. Consequently, there will be an increase in the concentration of $N_{1888}{}^+$ ions in the aqueous phase, leading to a shift in equilibrium (3) to the left and, consequently, a decrease in $D_{Ln}$.

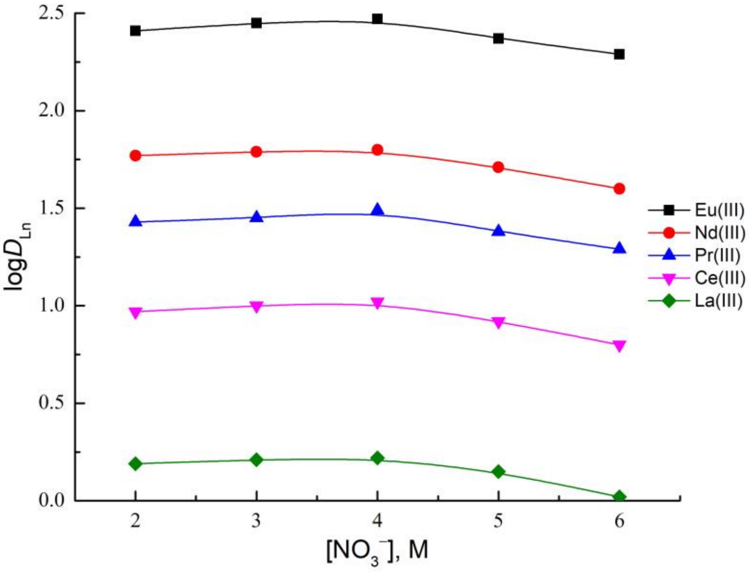


**Figure 3.** The effect of $NO_3{}^-$ concentrations in the aqueous phase on the extraction of Ln(III) with 0.01 M solutions of TODGA in $[N_{1888}][Tf_2N]$. $[H^+] = 2$ M. The sizes of the points represent error bars.

On the other hand, an increase in the acidity of the aqueous phase at a constant concentration of $NO_3{}^-$ ions is accompanied by a sharp decrease in the Ln(III) distribution ratios (Figure 4, Table S4). This may be due to the protonation of the TODGA molecule and the formation of TODGA complexes with $NO_3{}^-$ and $Tf_2N^-$ ions. Moreover, the molar fraction of the latter in the ionic liquid phase is significantly higher since TODGA interacts more actively with $HTf_2N$ than with $HNO_3$. This is indicated by the difference in the values of the extraction constants of these acids with TODGA into dichloroethane ($K_{HNO3} = 0.625$ [39], $K_{HTf2N} = 14{,}100$ [37]). Therefore, the process of extraction of Ln(III) ions by the cation exchange mechanism can be described by the following equilibrium:

$$Ln^{3+} + sLHTf_2N_{(org)} \rightleftharpoons LnL_s(Tf_2N)_{3(org)} + sH^+ \quad (4)$$

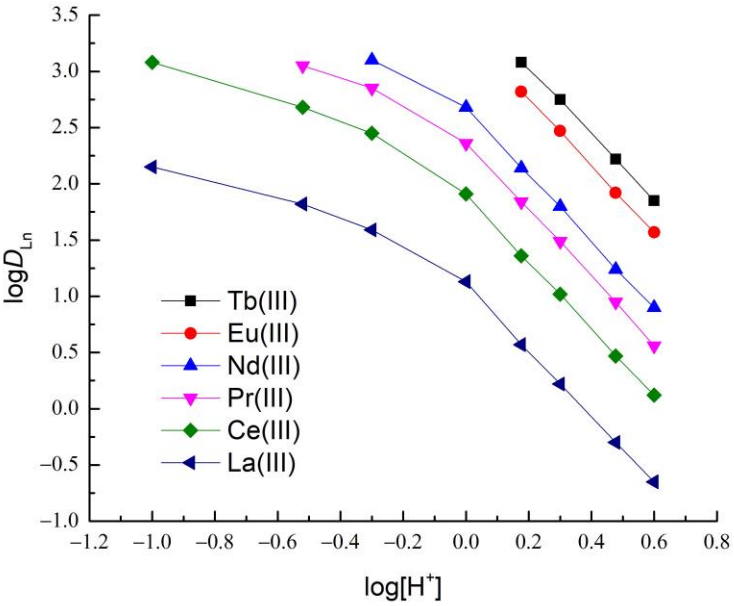


**Figure 4.** The effect of $H^+$ concentrations in the aqueous phase on the extraction of Ln(III) with 0.01 M solutions of TODGA in $[N_{1888}][Tf_2N]$. $[NO_3^-]$ = 4 M. The sizes of the points represent error bars.

### 3.3. Effect of TODGA Concentration in the IL Phase on the Extraction of Ln(III)

In order to determine the stoichiometric ratio of Ln(III): TODGA in the extracted complexes, the dependence of the distribution ratios of Ln(III) on the concentration of TODGA in IL during extraction from aqueous solutions with a constant concentration of nitric acid was studied. The plot of $\log D_{\mathrm{Ln}}$ vs. log[L] shows straight lines with a slope close to 3 (Figure 5, Table S5). This indicates that three TODGA molecules are coordinated to Ln(III) ions in the IL phase. Similar results were obtained for the extraction of Eu(III) with T2EHDGA into $[N_{1444}][Tf_2N]$ ionic liquid [44].

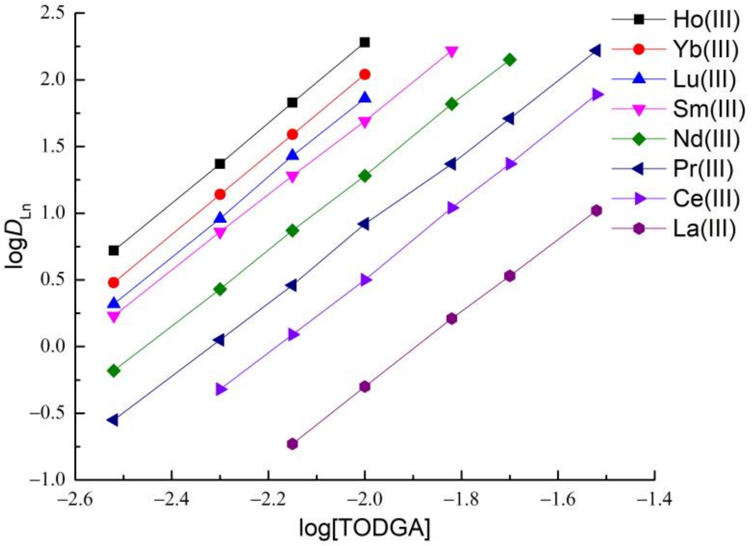


**Figure 5.** The effect of TODGA concentration in $[N_{1888}][Tf_2N]$ on the extraction of lanthanides(III) from 3 M $HNO_3$ solutions. The sizes of the points represent error bars.

Since $[N_{1888}][Tf_2N]$ itself does not extract Ln(III) from nitric acid solutions ($\log D < -2$), and increasing the concentration of nitrate ions in the aqueous phase has almost no effect on the efficiency of the Ln(III) extraction with TODGA into the IL phase, it can be assumed that Ln(III) are extracted in the Ln(III)-$HNO_3$-TODGA-IL system in the form of $LnL_3(Tf_2N)_3$

complexes. The inclusion of $Tf_2N^-$ anions into such complexes leads to the formation of extractable complexes of a more hydrophobic nature in comparison with the complexes formed with nitrate ions. Previously, Rao et al. based on luminescence spectroscopy studies, confirmed the coordination of T2EHDGA in the first coordination sphere of Eu(III) and the expulsion of water molecules from the coordination sphere [44]. We assume that the $Tf_2N^-$ anions, which have weak coordination ability [49], are located in the outer coordination sphere of the extracted complexes. Large $Tf_2N^-$ anions are incompatible with the strongly hydrogen-bonded structure of water in the aqueous phase, which makes their transfer to the organic phase more energetically favorable compared to smaller nitrate anions. However, the experimental extraction data in the present study do not allow us to characterize the exact structure of the extracted species. Further spectroscopic study would provide helpful information about the postulated extracted metal complexes.

### 3.4. Selectivity of Ln(III) Extraction with TODGA into [$N_{1888}$][$Tf_2N$]

At a moderate concentration of $HNO_3$ in the equilibrium aqueous phase, the extraction of Ln(III) with TODGA into [$N_{1888}$][$Tf_2N$] increases as the atomic number (Z) of lanthanides increases (Figure 6, Table S6). On the whole, this order of extractability in the series of lanthanides is typical for ligands of the DGA type [15] in nitric acid systems. The dependence of $\log D_{Ln}$ on Z trend was explained by an increase in the positive charge density of $Ln^{3+}$ ions as their ionic radii decreased with increasing Z.

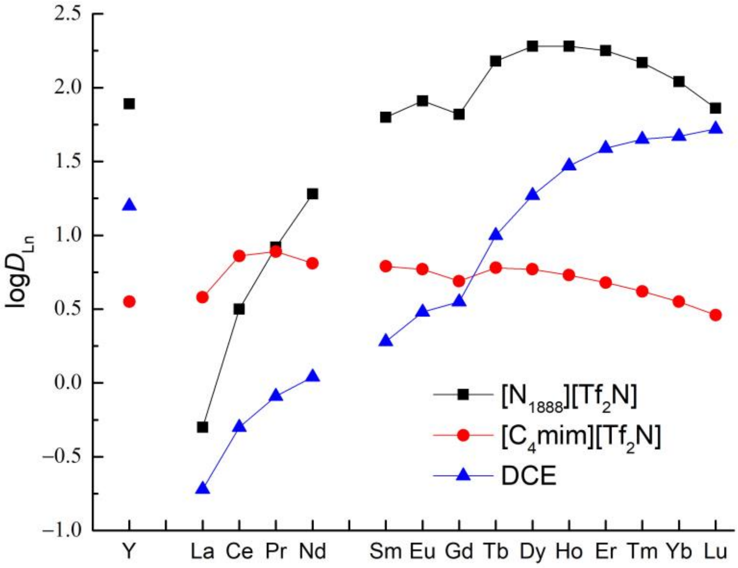


**Figure 6.** The extraction of lanthanides(III) from 3 M $HNO_3$ solutions with 0.01 M TODGA solutions in [$N_{1888}$][$Tf_2N$], [$C_4$mim][$Tf_2N$] [a], and dichloroethane (DCE) [a]. The sizes of the points represent error bars. [a] Data from ref. [40].

The selectivity of Ln(III) extraction with TODGA solutions can be characterized by the separation factor of Lu over La ($SF_{Lu/La} = D_{Lu}/D_{La}$). From the data on the Ln(III) extraction from 3 M $HNO_3$ solution with TODGA into ionic liquids [$N_{1888}$][$Tf_2N$] and [$C_4$mim][$Tf_2N$], as well as the molecular organic solvent 1,2-dichloroethane (DCE), it follows that the systems with imidazolium IL are characterized by low selectivity. The $SF_{Lu/La}$ value in systems with [$C_4$mim][$Tf_2N$] is 0.76, while in the DCE system the $SF_{Lu/La}$ is 275. Previously, it was shown that the selectivity of Ln(III) extraction from $HNO_3$ solutions with N,N,N′,N′-tetrabutyldiglycolamide into [$C_4$mim][$Tf_2N$] is significantly lower than when using octanol as a diluent [33].

The use of alkylammonium IL [$N_{1888}$][$Tf_2N$] as a diluent leads not only to an increase in the efficiency of Ln(III) extraction but also to an increase in the selectivity of their separation. The $SF_{Lu/La}$ value in the system with [$N_{1888}$][$Tf_2N$] is 144. Therefore, the use of alkylammonium IL [$N_{1888}$][$Tf_2N$] as a diluent not only leads to a significant decrease in the transfer of IL components to the aqueous phase but also to an increase in the efficiency and selectivity of Ln(III) extraction compared to imidazolium ILs.

### *3.5. Extraction of Lanthanides(III) from Aqueous Nitric Acid Solutions with Mixtures of TODGA and [$N_{1888}$][$Tf_2N$] in Molecular Organic Diluents*

It was previously established that the addition of even small amounts of [$C_4$mim][$Tf_2N$] to a solution of DGA ligands [37–39] in conventional molecular diluents leads to a significant increase in the efficiency of the extraction of Ln(III) ions. This effect was associated with the high hydrophobicity of the IL anions, $Tf_2N^-$, which are involved in the formation of extractable complexes as counterions. Therefore, in this work, we consider the effect of [$N_{1888}$][$Tf_2N$] on the extraction of Ln(III) ions with solutions of TODGA in molecular organic diluents.

It can be seen from Figure 7 (Table S7) that the addition of [$N_{1888}$][$Tf_2N$] to the organic phase leads to a significant increase in the extraction of Ln(III) with solutions of TODGA in DCE. Since the IL itself does not extract Ln(III) under these conditions, it can be said that this system exhibits a synergistic effect—a non-additive increase in the distribution ratios of metal ions, which is often used to increase the efficiency of the metal ion extraction [50,51]. The synergistic enhancement of the Ln(III) extraction produced by TODGA—[$N_{1888}$][$Tf_2N$] mixtures can be determined using synergistic coefficients (SC) calculated as

$$SC = D_{(L+IL)}/(D_{(L)} + D_{(IL)})^{+} \quad (5)$$

where $D_{(L)}$, $D_{(IL)}$, and $D_{(L+IL)}$ are the distribution ratios of the metal ion with TODGA and [$N_{1888}$][$Tf_2N$] taken separately and with their mixtures, respectively.

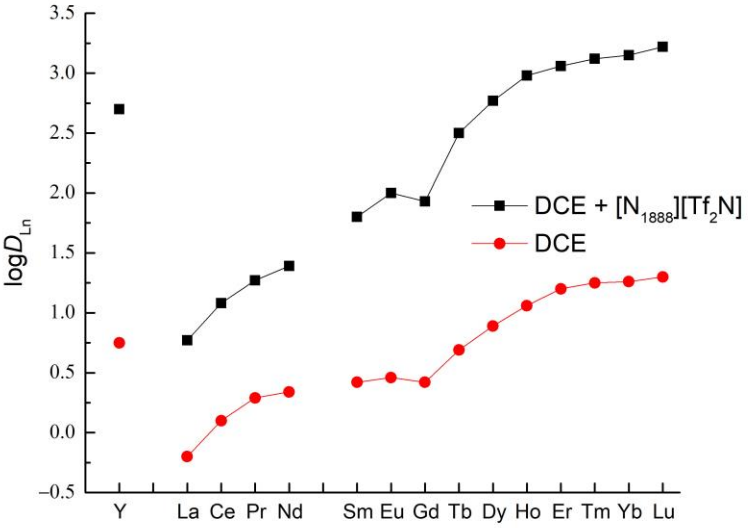


**Figure 7.** The extraction of lanthanides(III) from 4 M $NH_4NO_3$ solutions with 0.01 M TODGA solutions in DCE and DCE containing 0.01 M [$N_{1888}$][$Tf_2N$]. The sizes of the points represent error bars.

The SC values in the system with [$N_{1888}$][$Tf_2N$] increase from 9.5 for La(III) to 52.5 for Lu(III). It is obvious that the extraction of more hydrated heavy Ln(III) ions is most sensitive to the participation of hydrophobic $Tf_2N^-$ anions in the formation of the extracted Ln(III) complexes. In addition, the intragroup selectivity of Ln(III) extraction in the presence of IL increases significantly. The $SF_{Lu/La}$ values during extraction from the 4 M $NH_4NO_3$ solution with TODGA solutions in DCE without and with [$N_{1888}$][$Tf_2N$] are 31.6 and 174, respectively.

The effect of the nature of the organic diluent on the extraction of Ln(III) is considered. As can be seen from the data in Figure 8 (Table S8), the efficiency of Ln(III) extraction increases in the series chloroform < nonane–1.1 M TBP < DCE < octanol < nitrobenzene. The addition of TBP to nonane was carried out to prevent the formation of a third phase.

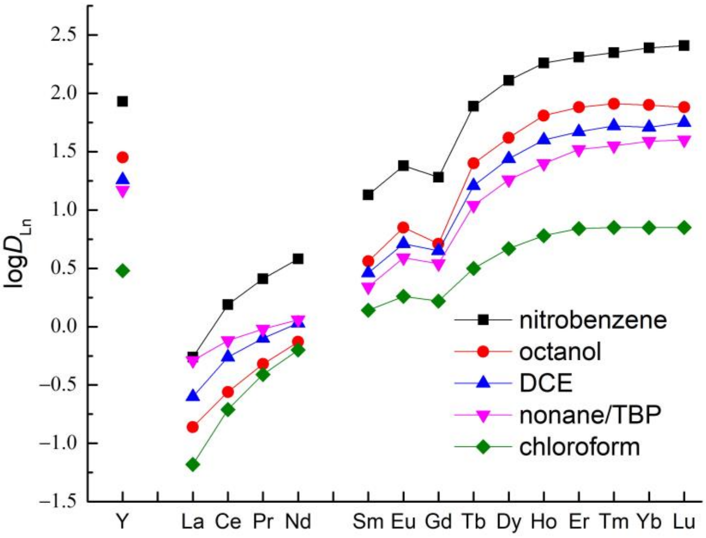


**Figure 8.** The extraction of lanthanides(III) from 1 M $HNO_3$ solutions with 0.01 M TODGA solutions in nitrobenzene, octanol, DCE, nonane, containing 1.1 M TBP, and chloroform in the presence of 0.01 M $[N_{1888}][Tf_2N]$. The sizes of the points represent error bars.

The effect of the $HNO_3$ concentration in the equilibrium aqueous phase on the extraction of Ln(III) ions with TODGA solutions in DCE and in the 1.1 M TBP solution in nonane containing the $[N_{1888}][Tf_2N]$ additive, as well as in these solvents without IL, is shown in Figure 9 (Table S9). The addition of $[N_{1888}][Tf_2N]$ to the organic phase leads to a significant increase in the extraction of Ln(III) with solutions of TODGA in DCE. In the case of using the 1.1 M TBP solution in nonane, the synergistic effect is less pronounced. An increase in the concentration of $HNO_3$ in the aqueous phase is accompanied by a decrease in the SC value. The same nature of the SC—$[HNO_3]$ dependence was observed earlier in the extraction of Ln(III) ions with TODGA in DCE in the presence of an $[C_4mim][Tf_2N]$ additive [38].

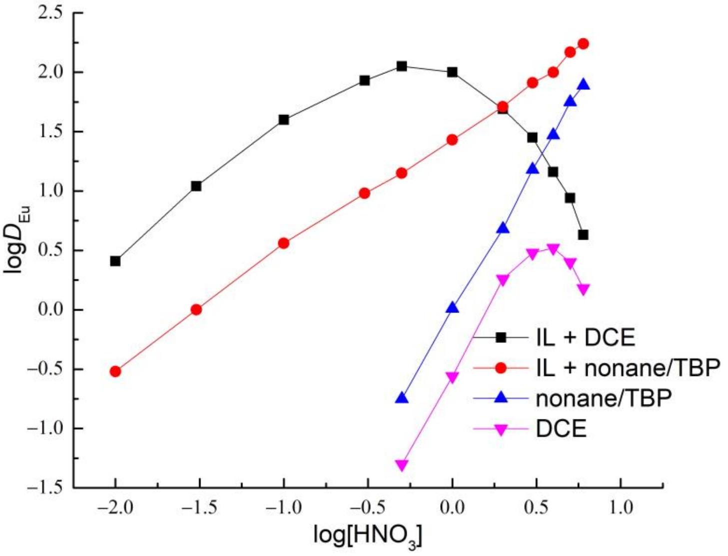


**Figure 9.** The effect of $HNO_3$ concentrations in the aqueous phase on the extraction of Eu(III) with 0.01 M solutions of TODGA in DCE, nonane, containing 1.1 M TBP, and in DCE, nonane, containing 1.1 M TBP in the presence of 0.1 M $[N_{1888}][Tf_2N]$. The sizes of the points represent error bars.

The data on the Ln(III) extraction from a 3 M acid solution with solutions of TODGA in DCE and nonane containing 1.1 M TBP in the presence of 0.1 M [$N_{1888}$][$Tf_2N$] are shown in Figure 10 (Table S10). It can be seen from these data that the distribution ratios of Ln(III) in these systems are higher than in the extraction of Ln(III) with TODGA in undiluted [$N_{1888}$][$Tf_2N$] (Figure 6). In addition, the selectivity of Ln(III) extraction with TODGA solutions in molecular solvents containing IL is higher than that of Ln(III) extraction with TODGA in undiluted [$N_{1888}$][$Tf_2N$] IL. The $SF_{Lu/La}$ values in the systems TODGA—DCE—IL, TODGA—nonane—TBP—IL, and TODGA—IL are 2630, 320, and 144, respectively.

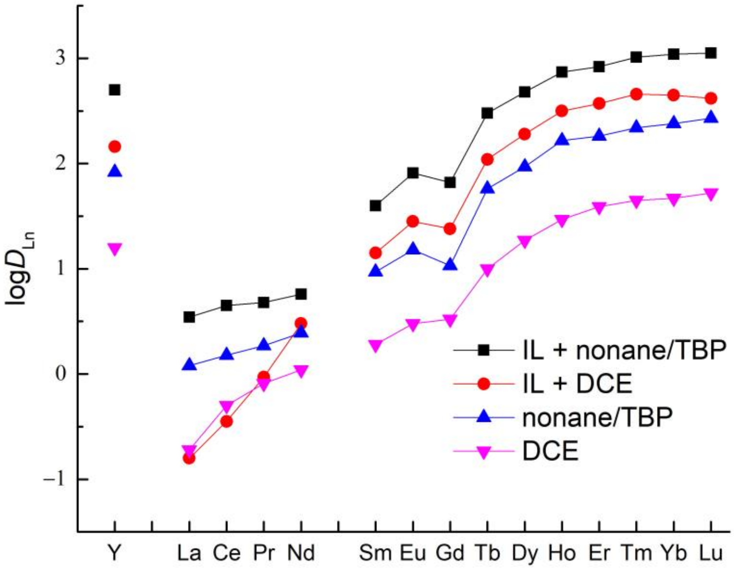


**Figure 10.** The extraction of lanthanides(III) from 3 M $HNO_3$ solutions with 0.01 M TODGA solutions in DCE, nonane, containing 1.1 M TBP, and in DCE, nonane, containing 1.1 M TBP in the presence of 0.1 M [$N_{1888}$][$Tf_2N$]. The sizes of the points represent error bars.

## 4. Conclusions

The Ln(III) extraction from aqueous nitric acid solutions with tetra(*n*-octyl)diglycolamide (TODGA) into methyltrioctylammonium bis(trifluoromethanesulfonul)imide ([$N_{1888}$][$Tf_2N$]) ionic liquid is studied. The high hydrophobicity of this IL leads to a significant decrease in the transfer of IL components into the aqueous phase compared to imidazolium-based ILs. The use of [$N_{1888}$][$Tf_2N$] as a diluent leads to a significant increase in the efficiency of lanthanides(III) extraction with TODGA compared to conventional organic solvents. This is due to the high hydrophobicity of IL anions, $Tf_2N^-$, which are involved in the formation of the extracted complexes as counter ions. The stoichiometry of the extracted complexes is determined, and the effect of the composition of the aqueous phase is studied. The use of alkylammonium IL [$N_{1888}$][$Tf_2N$] as a diluent leads not only to an increase in the efficiency of Ln(III) extraction but also to an increase in the selectivity of their separation. This study demonstrates a significant synergistic effect in the extraction of lanthanides(III) from aqueous $HNO_3$ solutions with TODGA dissolved in molecular organic diluents in the presence of [$N_{1888}$][$Tf_2N$]. In these systems, the distribution ratios of Ln(III) are higher than in the case of extraction of Ln(III) with TODGA into undiluted [$N_{1888}$][$Tf_2N$]. The results of this work can be used to develop technologies for the recovery and separation of rare earth elements from various objects, for example, industrial end-of-life wastes. This requires additional studies, including the determination of the capacity of the extractant solution, the study of the influence of accompanying metal ions, and a detailed study of the stripping stage and reuse of the extractant. We believe that solutions containing water-soluble complexing agents, such as ethylenediaminetetraacetic acid (EDTA) or diethylenetriamine pentaacetate (DTPA), can be used for the REEs stripping.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min13060736/s1, Table S1: The effect of $HNO_3$ concentration in the aqueous phase on the transfer of $Tf_2N^-$ ions into the aqueous phase; Table S2: The effect of $HNO_3$ concentrations in the aqueous phase on the extraction of Ln(III) with 0.01 M solutions of TODGA in $[N_{1888}][Tf_2N]$; Table S3: The effect of $NO_3^-$ concentrations in the aqueous phase on the extraction of Ln(III) with 0.01 M solutions of TODGA in $[N_{1888}][Tf_2N]$. $[H^+]$ = 2 M; Table S4: The effect of $H^+$ concentrations in the aqueous phase on the extraction of Ln(III) with 0.01 M solutions of TODGA in $[N_{1888}][Tf_2N]$. $[NO_3^-]$ = 4 M; Table S5: The effect of TODGA concentration in $[N_{1888}][Tf_2N]$ on the extraction of lanthanides(III) from 3 M $HNO_3$ solutions; Table S6: The extraction of lanthanides(III) from 3 M $HNO_3$ solutions with 0.01 M TODGA solutions in $[N_{1888}][Tf_2N]$, $[C_4mim][Tf_2N]$, and dichloroethane (DCE); Table S7: The extraction of lanthanides(III) from 4 M $NH_4NO_3$ solutions with 0.01 M TODGA solutions in DCE and DCE containing 0.01 M $[N_{1888}][Tf_2N]$; Table S8: The extraction of lanthanides(III) from 1 M $HNO_3$ solutions with 0.01 M TODGA solutions in nitrobenzene (NB), octanol (OC), dichloroethane (DCE), nonane containing 1.1 M TBP (N/TBP), and chloroform (CL) in the presence of 0.01 M $[N_{1888}][Tf_2N]$; Table S9: The effect of $HNO_3$ concentrations in the aqueous phase on the extraction of Eu(III) with 0.01 M solutions of TODGA (L) in DCE, nonane containing 1.1 M TBP, and DCE in the presence of 0.1 M $[N_{1888}][Tf_2N]$; Table S10: The extraction of lanthanides(III) from 3 M $HNO_3$ solutions with 0.01 M TODGA solutions in DCE, nonane containing 1.1 M TBP, and DCE in the presence of 0.1 M $[N_{1888}][Tf_2N]$.

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