Solvent Extraction of Neodymium(III) by Functionalized Ionic Liquid Trioctylmethylammonium Dioctyl Diglycolamate in Fluorine-free Ionic Liquid Diluent

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ABSTRACT: The extraction behavior of neodymium and other rare earths from nitric acid media by the functionalized ionic liquid trioctylmethylammonium dioctyl diglycolamate, [A336][DGA], was investigated. The nonfluorinated ionic liquid trioctylmethylammonium nitrate, [A336][NO$_3$], was used as diluent. The extraction behavior of neodymium(III) in this ionic liquid solution was carried out as a function of various parameters such as the pH, concentration of the extractant, type of acidic media, temperature, concentration of salting-out agent, and concentration of the aqueous feed. The extraction behavior of [A336][DGA] in [A336][NO$_3$] was compared with that of [A336][DGA] in the chloride-containing ionic liquid diluent [A336][Cl] (Aliquat 336). The distribution ratios obtained in [A336][DGA] were compared with those observed in molecular extractant N,N-dioctyl diglycol amic acid (HDGA), from which the anion of the ionic liquid extractant was prepared. The distribution ratio for extraction of neodymium(III) by [A336][DGA] in [A336][NO$_3$] was higher than that for extraction by HDGA in [A336][NO$_3$], at pH values >2. The effects of thermodynamic parameters, the stripping of neodymium(III) from the ionic liquid, and the reusability of the functionalized ionic liquid were studied in detail. The general applicability of the extraction system was illustrated by the extraction of lanthanide(III) ions other than neodymium(III).

■ INTRODUCTION

Neodymium is an important technological metal due to its widespread use in neodymium–iron–boron permanent magnets (NdFeB magnets or neomagnets).[1] The ever-increasing use of NdFeB magnets and possible supply risk of neodymium makes recycling of neodymium from end-of-life NdFeB magnets an important economic issue.[2] Given the relatively low abundance of neodymium compared to cerium and lanthanum in rare-earth ores such as bastnäsite, recycling of neodymium is also important from the point of view of the so-called "balance problem".[3] The development of sustainable recycling schemes for neodymium is a technological challenge. An important technique for the recovery of neodymium and other rare earths is solvent extraction (SX), because this technique allows the separation of rare earths from other metals as well as the separation of mixtures of rare earths into the individual elements.[4,5]

Ionic liquids (ILs) are of particular interest for the development of environmentally friendly solvent extraction systems[6–13] and for other applications in hydrometallurgy.[14–16] Room temperature ionic liquids (RTILs) are finding applications as novel solvents for liquid–liquid extraction and separation of metal ions, due to their favorable properties such as negligible vapor pressure, low flammability, and high thermal stability.[17] Ionic liquids can function not only as diluents in solvent extraction systems but also as extractants, and both functions can even be combined in one ionic liquid. New solvent extraction systems with undiluted ionic liquids are being developed, so that the use of volatile molecular diluents can be prevented.[18–20] It is even possible to design ionic liquid extraction systems with two mutually immiscible ionic liquids.[21] The ionic nature of the ionic liquid phase enables the efficient extraction of metal ions through different mechanisms such as

ion exchange (cation or anion exchange) and a neutral solvation mechanism.[22–26] Ionic liquids that are used as extractants are known as *task-specific ionic liquids* (TSILs) or as *functionalized ionic liquids* (FILs).[27–34] Functionalized ionic liquids with the functional moiety as part of the anion are enjoying a strong interest as novel extractants for solvent extraction of metal ions. Mehdi et al. synthesized a new family of ionic liquids containing a β-diketonate anion combined with an 1-alkyl-3-methylimidazolium cation.[35] They studied the coordination chemistry of neodymium(III) and cobalt(II) extracted by these ionic liquids. Similarly, Sun et al. synthesized bifunctionalized ionic liquids (bi-FILs) and discovered that inner synergism plays a dominant role when these bi-FILs are used as extractants as compared to a mixture of their corresponding precursors.[34,36] Rout et al. synthesized two ionic liquids derived from Aliquat 336: trioctylmethylammonium bis(2-ethylhexyl)phosphate, [A336][DEHP], and trioctylmethylammonium bis(2-ethylhexyl)diglycolamate, [A336]-[DGA].[37] They emphasized the unusual miscibility with solvents used in the nuclear industry, such as n-dodecane and its higher homologues. These ionic liquids were applied to the separation of europium(III) from americium(III). The same research group also used β-diketonate ionic liquids with ammonium and imidazolium cations for the extraction of plutonium(IV) from acidic media and highlighted the change in extraction mechanism in ionic liquid media, compared to extractions in conventional molecular diluents.[38] However, the main concern of most of the ionic liquid extraction systems is

that they make use of fluorinated anions such as hexafluorophosphate (PF_6^-) or bis(trifluoromethylsulfonyl)imide (Tf_2N^-). Ionic liquids with fluorinated anions are more expensive than their nonfluorinated counterparts, and they are persistent. In addition, ionic liquids with the hexafluorophosphate anion are susceptible to hydrolysis. A general observation for many of the ionic liquid extraction systems reported in the literature is that the metal complexes are extracted at the expense of the ionic liquid cation or anion, leading to contamination of the aqueous phase and losses of ionic liquid.[25,39] This extraction mechanism hampers the general application of ionic liquids in solvent extraction processes. Although the loss of ionic liquid can be reduced by structural variation of the ionic liquid, for example, by increasing the alkyl chain length of the cation or fluorination of the alkyl chain of the anion, these modifications often have a negative effect on the distribution ratios and extraction efficiency.[39,40] However, there are some ionic liquids such as trioctylmethylammonium chloride (Aliquat 336), trioctylmethylammonium nitrate, and trihexyl(tetradecyl)phoshonium chloride (Cyphos IL 101) that are nonfluorinated and exhibit no cation exchange with the aqueous phase during extraction.[18,19,37,41−46] Use of these types of ionic liquids could solve several of the issues associated with the fluorinated ionic liquids.

In this paper, the extraction of neodymium(III) by a nonfluorinated ionic liquid system, consisting of the ionic liquid extractant trioctylmethylammonium dioctyl diglycolamate, [A336][DGA], in the ionic liquid diluent trioctylmethylammonium nitrate, [A336][NO_3], is described. The structure of [A336][DGA] is shown in Figure 1. The [A336][DGA]/
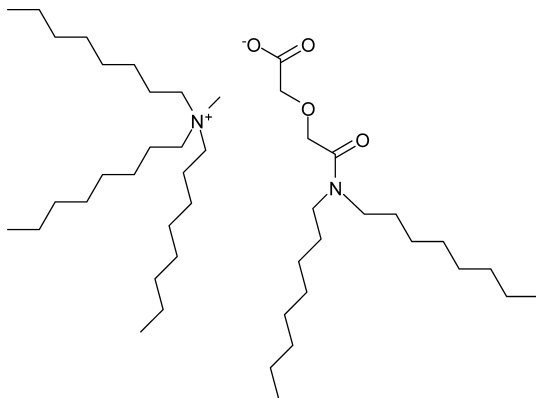
Figure 1. Structure of the functionalized ionic liquid [A336][DGA].

[A336][NO_3] extraction system is studied in detail, and different extraction parameters such as the pH, concentration of the ionic liquid extractant, temperature, concentration of salting-out agent, and concentration of the aqueous feed are described. The stripping of neodymium from the loaded ionic liquid phase is investigated as well as the recycling and reusability of the ionic liquid phase. The extraction of rare earths other than neodymium is investigated as well.

■ EXPERIMENTAL SECTION

Materials/Reagents. All of the chemicals and reagents used in this study were of analytical grade. The chemicals nitric acid (Sigma-Aldrich), dichloromethane (Sigma-Aldrich), Aliquat 336 (Sigma-Aldrich), sodium nitrate (99%, Sigma-Aldrich), diglycolic anhydride (99%, Sigma Aldrich), dioctyl-

amine (99%, Sigma-Aldrich), and sodium hydroxide (Alfa Aeser) were used as received. Trioctylmethylammonium nitrate was synthesized following a literature procedure.[47] Neodymium(III) nitrate hexahydrate (>99%) and other metal nitrates (purity ≥ 99%) were purchased from ACROS Organics (Geel, Belgium) or Sigma-Aldrich (Diegem, Belgium). A 1000 ppm gallium standard was purchased from Merck (Overijse, Belgium). Dioctyl diglycol amic acid (HDGA) was synthesized as described elsewhere.[48] Aliquat 336 is considered here as trioctylmethylammonium chloride or tricaprylmethylammonium chloride. However, this technical product consists of a mixture of compounds with octyl chains (major component) and decyl chains (minor component). For this reason, products derived from Aliquat 336 by substitution of other anions for chloride consequently contain mixtures of different cations.

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 in small vials in a temperature-controllable compact benchtop turbo thermo-shaker (model TMS-200, Hangzhou Allsheng Instrument Co. Ltd., China). After 1 h of equilibration, part of the aqueous phase was removed and a gallium internal standard with an appropriate concentration was added in a 1 mL sample tube to prepare the sample solution for analysis. 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) to bind the sample droplet by its polar sites. Then, the sample carriers were dried for 5 min in a hot air oven at 60 °C, followed by the addition of 5 μL of the sample and a drying process of 20 min at the same temperature. The samples were measured for 200 s in the TXRF spectrometer. All samples were diluted with Milli-Q50 water, if necessary. A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of the samples after extraction. ^{1}H NMR and ^{13}C NMR spectra of ionic liquids were recorded on a Bruker Avance 300 spectrometer, operating at 300 MHz for ^{1}H. CDCl$_3$ was used as the solvent for recording the NMR spectra, and the data were analyzed with the SPINWORKS software package. The viscosities of the ionic liquids were 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 Slimtrode (Hamilton) electrode. The water content of the ionic liquid phase before and after extraction was determined with a Mettler-Toledo DL 39 coulometric Karl Fischer titrator.

Synthesis of Trioctylmethylammonium Dioctyl Diglycolamate, [A336][DGA]. The first step of the synthesis of [A336][DGA] involved the ion exchange of chloride ions present in Aliquat 336, [A336][Cl], by hydroxide ion to form [A336][OH]. This was done by equilibrating a 0.5 M solution of Aliquat 336 in chloroform with an aqueous 4–5 M NaOH solution for 1 h. The aqueous phase was removed, and the organic phase was equilibrated again with a fresh NaOH solution. This procedure was repeated at least 8–10 times until the chloride content in organic phase was negligible (checked with an acidified AgNO$_3$ solution and by TXRF). Then, the organic phase was washed with distilled water, followed by removal of chloroform in vacuo. The subsequent step involved refluxing the solution of the intermediate product [A336][OH] in dichloromethane with the solution of HDGA in dichloro-

methane in a 1:1 mol ratio for 10−12 h. The solvent was removed by using a rotary evaporator and the final product was dried completely at 75−80 °C at reduced pressure on a Schlenk line for about 4−5 h. A slightly yellowish viscous liquid was obtained in a yield of 90%. The viscosity of the ionic liquid was 165 cP (at 60 °C), the density was 0.83 g cm^{-3} (at 25 °C), and the water content was 0.21 wt %. FT-IR (ν/cm^{-1}): 2962−2854 (CH$_2$), 1742 (−CO in −COO$^-$), 1647(−CO in −CON), 1466, 1331 (C−N in [A336]$^+$ ion), 1061, 1040 (C−O ether linkage). ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si, δ): 4.38 (s, 2H, −OC−C$\underline{H}_2$O−), 4.21 (s, 2H, −OC$\underline{H}_2$−CO−), 3.47−3.41 (m, 6H), 3.33 (t, 2H, −NC$\underline{H}_2$− of [DGA]$^-$ ion), 3.30 (s, 3H), 3.10 (t, 2H, −NC$\underline{H}_2$− of [DGA]$^-$ ion), 1.66−1.55 (m, 24H, N−CH$_2$−(C$\underline{H}_2$)$_6$−CH$_3$), 1.36−1.29 (m, 36H), 0.91−0.86 (m, 15H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 171.86 (−$\underline{C}$OO$^-$), 170.41(−$\underline{C}$ON), 72.71 (−O$\underline{C}$H$_2$−), 71.07 (−$\underline{C}$H$_2$O−), 61.35 (3 × $\underline{C}$H$_2$N of [A336]$^+$ ion), 46.88 (2 × $\underline{C}$H$_2$N of [DGA]$^-$ ion), 46.78 ($\underline{C}$H$_3$N), 31.83, 31.77, 31.71, 31.62, 29.41, 29.36, 29.28, 29.20, 29.14, 29.01, 28.65, 27.43, 26.95, 26.82, 26.33, 22.65, 22.62, 22.58, 22.41 (various −CH$_2$− groups), 14.10, 14.05 (CH$_3$ groups).

Equilibration Procedure. The extraction experiments were performed at 300 K with a temperature-controllable thermo-shaker. Various solutions of [A336][DGA] in [A336][NO$_3$] were prepared. It was observed that emulsions were easily formed at low salt concentrations of the aqueous phase, so that it was difficult to get a good phase separation under these conditions. 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 neodymium(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 neodymium(III) solution (7 × 10^{-4} M) at the required pH value. The pH of the aqueous phases ranged from 1 and 6.6, and the pH was adjusted by adding a 1 M HNO$_3$ or a 1 M NaOH solution. Extractions were performed by intensive stirring (1800 rpm) of the extraction mixture for 1 h. After the extraction, separation of the phases was obtained by centrifugation for 5 min at 3000 rpm. The concentrations of Nd(III) and other Ln(III) distributed between the ionic liquid and the aqueous phases were measured by TXRF. The *distribution ratio* (*D*) was determined using the following equation:

$$D = \frac{[Ln]_{IL}}{[Ln]_{aq}}$$
$$= \frac{C_i - C_f}{C_f} \tag{1}$$

C_i and C_f are the concentrations of the metal ions in the aqueous phase before and after extraction, respectively. Ln is a trivalent rare-earth ion. Because the volume of the aqueous phase (V_{aq}) is equal to that of ionic liquid phase (V_{IL}), the *extraction efficiency* (%E) is given by the following equation:

$$\%E = \frac{D}{D+1} \times 100\% \tag{2}$$

The stripping percentage (%S) is given by

$$\%S = \frac{[Ln]_{aq}}{[Ln]_{IL}} \times 100 \tag{3}$$

The effect of the concentration of [A336][DGA] in the organic phase was studied by varying the concentration from 0.005 to 0.1 M.

RESULTS AND DISCUSSION

Extraction of Neodymium(III) by [A336][DGA]/ [A336][NO$_3$]. It was observed that the distribution ratio increased with increase in pH for the extraction of Nd(III) by [A336][DGA] diluted in [A336][NO$_3$] (Figure 2). This trend
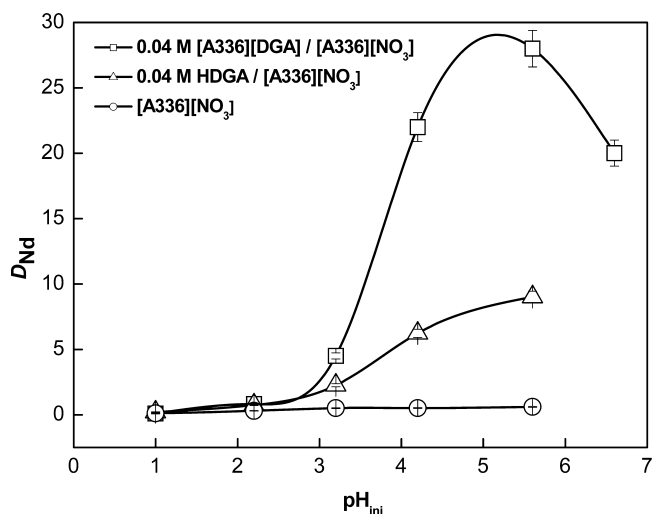
Figure 2. Variation of the distribution ratio of Nd(III) as a function of the (initial) pH of the aqueous phase. Organic phase, 0.04 M [A336][DGA]/[A336][NO$_3$] or 0.04 M HDGA/[A336][NO$_3$] or [A336][NO$_3$] alone; aqueous phase, pH between 1 and 6.6 and 7 × 10^{-4} M Nd(III).

is similar to the characteristic of any acidic extractant system, including HDGA in molecular diluents.[48−52] The increase in *D* values with decrease in acid strength is due to the lesser competition of HNO$_3$ extraction with Nd(III) extraction. Because the pK_a value of the molecular HDGA is about 5.08, the extraction trend is strongly dependent on the experimental pH.[53] There is a sudden drop of D_{Nd} at pH values >5.6 because of hydrolysis of Nd(III) at these pH values, resulting in the formation of oligomeric hydrolysis products.[54] One can note that D_{Nd} at pH values >2 is remarkably higher for the ionic liquid extractant [A336][DGA] than for the molecular extractant HDGA, although the functional moiety is the same in both compounds (Figure 2). This observation indicates that there exists an inner synergism between [A336]$^+$ and [DGA]$^-$ ions upon coordination of [DGA]$^-$ to Nd(III). Such behavior has been reported by Sun et al. and by Rout et al. for the extraction of Eu(III).[34,37] For the sake of comparison, the extraction of Nd(III) by the diluent [A336][NO$_3$], without added extractant, has also been investigated (Figure 2). The distribution coefficients for extraction of Nd(III) by [A336][NO$_3$] are very small, at all pH values. It has been reported that [A336][NO$_3$] in molecular diluents is able to extract rare-earth ions from aqueous nitrate media.[55−63] However, for extraction of rare-earth ions by [A336][NO$_3$], the nitrate concentration of the aqueous phase needs to be quite high (several mol L^{-1}), which is much higher than the

nitrate concentration in our experiments. From Figure 2, it is evident that there is little difference in distribution ratios for the [A336][DGA] and HDGA extracting agents at pH values <2. This can be attributed to the fact that below pH 2, [A336][DGA] is converted into [A336][NO$_3$] and HDGA by reaction with HNO$_3$ and, hence, the system behaves like HDGA/[A336][NO$_3$]. As a consequence, the inner synergism is lost. On the basis of this observation, eq 4 can be proposed for the conversion of [A336][DGA] at pH values <2. However, the extent of conversion is not known.

$$\overline{[A336][DGA]} + HNO_3 \Leftrightarrow \overline{[A336][NO_3]} + \overline{[HDGA]} \quad (4)$$
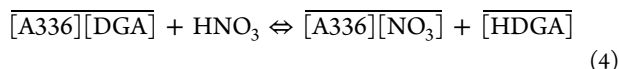
The bar in eq 4 indicates the components in the organic phase (ionic liquid phase).

Extraction Kinetics. In a study of a solvent extraction system, it is always important to pay attention to the extraction kinetics, that is, the time necessary to reach equilibrium conditions. The kinetics depend on physical parameters such as the viscosity, density, and hydrophobicity of the extracting phase. Because the system [A336][DGA]/[A336][NO$_3$] contains molecules with long alkyl chains, the viscosity of the dry ionic liquid system is high (1050 cP at 300 K, water content = 0.2 wt %). However, after presaturation of the ionic liquid phase with the aqueous phase, the viscosity of the ionic liquid phase drastically decreased to 103 cP, due to the uptake of a considerable amount of water (7 wt %). Although a viscosity of 103 cP is low enough for conveniently carrying out extraction studies, this value is still quite high compared to the viscosity of conventional diluents such as n-dodecane (about 2 cP). Thus, with these high viscosities in mind, the extraction was carried out as the function of equilibration time, and it was observed that it takes about 1 h to achieve the equilibrium state. Figure 3
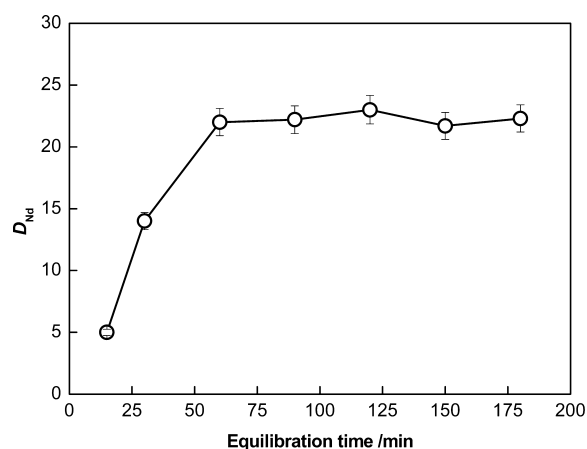
Figure 3. Variation of the distribution ratio of Nd(III) as a function of equilibration time. Organic phase, 0.04 M [A336][DGA]/[A336]-[NO$_3$]; aqueous phase, pH 4.2 and 7 × 10^{-4} M Nd(III).

shows the variation of distribution ratio of Nd(III) as a function of equilibration time. It was observed that $D_{Nd(III)}$ remains almost constant after 60 min, which indicates that 60 min of equilibration time is sufficient to achieve the equilibrium state.

Extraction Stoichiometry. The distribution ratio increases with an increase in the concentration of the ionic liquid (Figure 4). A linear regression analysis of the extraction data resulted in a straight line with a slope of 0.91, which suggests the involvement of one molecule of [A336][DGA] during the
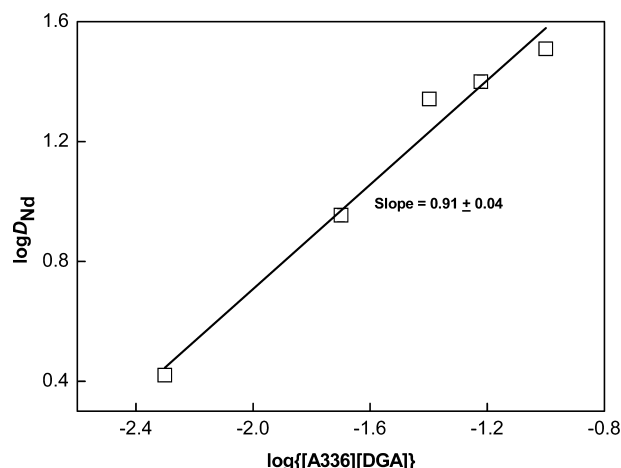

Figure 4. Variation in the plot of logD_{Nd} as a function of the logarithm of the initial concentration of ionic liquid [A336][DGA]. Organic phase, 0.005−0.1 M [A336][DGA]; aqueous phase, pH 4.2 and 7 × 10^{-4} M Nd(III).

extraction process. In molecular diluents, such an ionic liquid gives a straight line with a slope of 3, indicating the participation of three molecules during complex formation.[37] This shows that the extraction mechanism in a system with the ionic liquid diluent [A336][NO$_3$] is clearly different from that of extraction systems with molecular diluents. Therefore, a plausible mechanism for the extraction of Nd(III) by [A336][DGA] dissolved in [A336][NO$_3$] in the range of pH 2−5 with 0.1 M salting-out agent in the feed phase is

$$Nd^{3+} + 3NO_3^- + \overline{[A336][DGA]}$$
$$\Leftrightarrow \overline{Nd(NO_3)_3 \cdot [A336][DGA]} \quad (5)$$
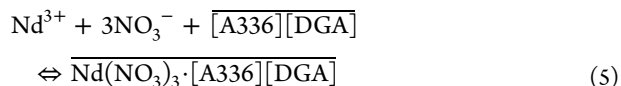
The bar indicates the species present in the ionic liquid phase. The involvement of nitrate ions in the complex formation and the extraction mechanism at high nitrate ion concentration is discussed in the next section on the effect of the concentration of salting-out agents. Therefore, it would be more appropriate to state that the extraction mechanism shown in eq 5 is only valid in the pH range from pH 2 to 5 and 0.1 M salting-out agent in the feed phase. [A336][DGA] is a so-called *binary extractant* or *mixed ionic solvent*.[64−68] Binary extractants are quaternary ammonium or phosphonium salts of acidic extractants. Such an 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 trioctylmethylammonium cation is very hydrophobic due to the long alkyl chains, and hence it has a very low solubility in the aqueous phase (the precursor Aliquat 336 is highly insoluble in the water phase and a well-known hydrophobic ionic liquid). Thus, one can conclude that the loss of the ionic liquid cation to the aqueous phase is negligible, unlike in the case of imidazolium ionic liquids with short alkyl chains and fluorinated anions, such as 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C$_4$mim][Tf$_2$N].[10,22] As far as the ionic liquid diluent [A336][NO$_3$] is concerned, there will be no loss of nitrate ions to the aqueous phase because the aqueous phase contains nitrate ions, and due to the common-ion effect, the nitrate ion prefers to be in the organic phase. Hence, the ionic liquid [A336][NO$_3$] remains intact

after equilibration. The diglycolamide anion is a very hydrophobic anion (derived of a well-known acidic extractant, dioctyldiglycolamic acid) 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 $[A336]^+$ cation. The change in the distribution ratio of Nd(III) with respect to the concentration of the ionic liquid $[A336][DGA]$ is shown in Figure 5. It is
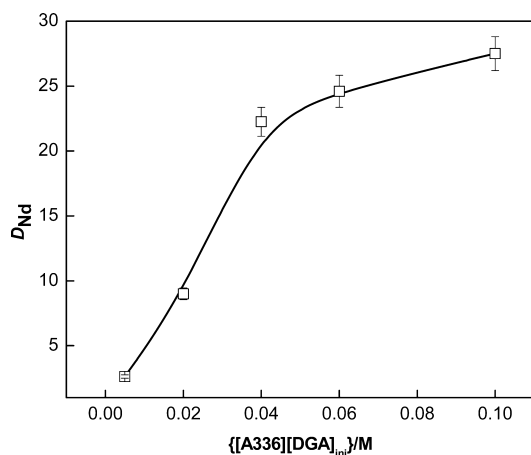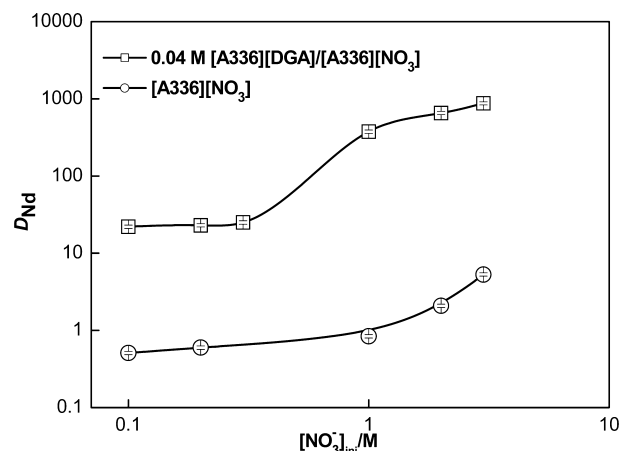

Figure 5. Variation in the distribution ratio of Nd(III) as a function of the concentration of $[A336][DGA]$ in the ionic liquid phase. Organic phase, 0.005−0.1 M $[A336][DGA]/[A336][NO_3]$; aqueous phase, pH 4.2 and 7×10^{-4} M Nd(III).

observed that D_{Nd} increases sharply with increase in the ionic liquid concentration up to 0.04 M followed by a slow increase with further increase in the extractant concentration. D_{Nd} increases from 22.3 to 27.5 when the extractant concentration changes from 0.04 to 0.1 M, respectively. Although there is an increasing trend in the D values, the extraction efficiency remains virtually the same (~96%) over the extractant concentration investigated (from 0.04 to 0.1 M). This indicates that 0.04 M $[A336][DGA]$ is more than enough to get maximum recovery of the metal ion under the studied experimental conditions.

Effect of the Concentration of Salting-out Agent. Salting-out agents play a vital role in the present extraction system. To have a detailed insight into the effect of the salting-out agent on the distribution ratio of Nd(III), the concentration of NaNO_3 in the aqueous feed solution (pH 4.2) was varied (Figure 6). There was an increase in D values when the concentration of NaNO_3 was increased from 0.1 to 3 M. This increase in distribution ratio with an increase in the concentration of nitrate ions in the aqueous phase clearly indicates that nitrate ions are coextracted during the equilibration and that they are present in the metal-solvate formed. Thus, this result supports the proposed mechanism (eq 5) and satisfies the characteristics of a binary ionic liquid extractant (they extract metal salts rather than metal ions).[64−68] From Figure 6, it can be seen that there are remarkably high extraction factors at high nitrate concentration (1−3 M). This could possibly be due to the occurrence of an anion exchange mechanism by the involvement of the diluent $[A336][NO_3]$ in the extraction along with $[A336][DGA]$, as a result of which the distribution ratio increases altogether. To confirm this, the extraction of Nd(III) was carried out in pure $[A336][NO_3]$ at high nitrate concentrations (Figure 6), and this experiment showed that D_{Nd} increases with an increase in nitrate ion
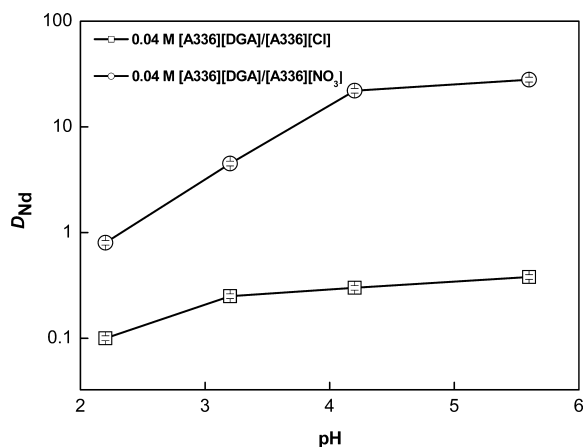

Figure 6. Variation in the distribution ratios of Nd(III) as a function of the nitrate ion concentration in the aqueous phase. Organic phase, 0.04 M $[A336][DGA]/[A336][NO_3]$ or $[A336][NO_3]$ alone; aqueous phase, pH 4.2, 7×10^{-4} M Nd(III), and varied concentrations of NO_3^- ion (in the form of NaNO_3).

concentration in the aqueous phase and that about 82% of Nd(III) is extracted at 3 M NO_3^- ion present in the feed solution ($D_{Nd} = 44$). At very high nitrate concentrations, the extraction of Nd(III) is mainly driven by both anion exchange and complex formation by the functionalized ionic liquid $[A336][DGA]$. Therefore, it is justified to state that Nd(III) is extracted through the complex formation mechanism at low nitrate concentrations but that an anionic complex is formed at high nitrate concentrations (eq 6):

$$Nd^{3+} + 3NO_3^- + x\overline{[A336][NO_3]}$$
$$\Leftrightarrow \overline{[A336]_x[Nd(NO_3)_{3+x}]} \qquad (6)$$
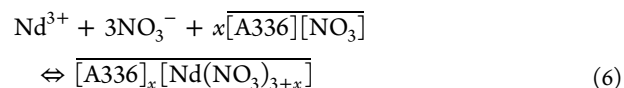
In eq 6 $1 \leq x \leq 3$. At low nitrate concentrations, the extraction is solely due to the complex formation mechanism, because the amount of nitrate ions present in the aqueous phase is not sufficient to extract Nd(III) in the form of $[Nd(NO_3)_{3+x}]^{x-}$ complexes.

Extraction in Chloride Media. The distribution ratios of Nd(III) in a solution of $[A336][DGA]$ in the ionic liquid $[A336][Cl]$ were measured at different pH values to determine the differences in the extraction behavior compared to that from nitrate media. Figure 7 shows that Nd(III) is not extracted efficiently from chloride media, unlike what is observed for the extraction from nitrate media. The distribution ratio is very low for extraction of Nd(III) by the ionic liquid system $[A336]-[DGA]/[A336][Cl]$ ($D_{Nd} < 1$). The poorer extractability of Nd(III) from chloride media can be attributed to the less efficient uptake of Nd^{3+}/Cl^- compared to Nd^{3+}/NO_3^-, which could be due to a difference in the hydration energy of Cl^- and NO_3^- ions. The poor extractability of Nd(III) by $[A336][Cl]$ is in agreement with what has been observed for the separation of Nd(III) and Fe(III) by extraction of Fe(III) with trihexyl-(tetradecyl)phosphonium chloride.[19] Figure 8 indicates that the distribution ratio increases at high chloride ion concentrations (1−3 M) in the aqueous phase (in the form of NaCl) while extraction from chloride media is carried out. It is interesting to observe from Figure 8 that there is hardly any increase in the distribution ratio in the presence of $[A336][DGA]$, unlike the trend observed in Figure 6 for the extraction from nitrate media. This could be attributed to a difference in the hydration
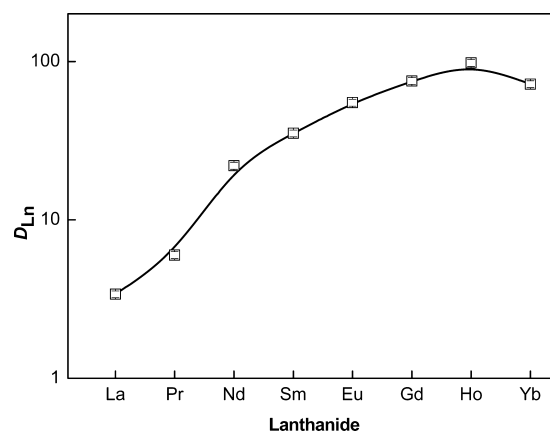
Figure 7. Comparison of the distribution ratio of Nd(III) in nitrate and chloride media. Organic phase, 0.04 M [A336][DGA]/[A336][NO$_3$] (or 0.04 M [A336][DGA]/[A336][Cl]); aqueous phase, pH 4.2 and 7 × 10^{-4} M Nd(III).
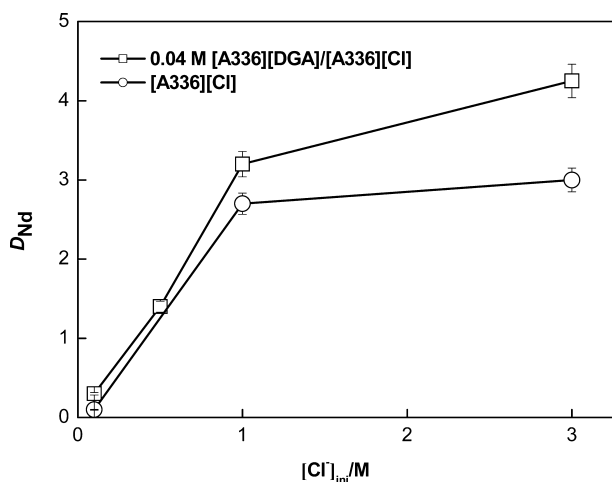
Figure 8. Change of the distribution ratios of Nd(III) as a function of the chloride ion concentration in the aqueous phase. Organic phase, 0.04 M [A336][DGA]/[A336][Cl] or [A336][Cl] alone; aqueous phase, pH 4.2, 7 × 10^{-4} M Nd(III), and varied concentrations of Cl$^-$ ion (in the form of NaCl).

energy of Cl$^-$ ions in NaCl and NO$_3^-$ ions in NaNO$_3$. Chloride ions are more strongly hydrated than nitrate ions. As a result, the salting-out capacity of medium for pushing Nd(III) to the organic phase for the formation of the neodymium(III) complex is hindered. On the other hand, it was observed that D_{Nd} increases to some extent at very high chloride concentration in the aqueous phase. However, the distribution ratios for extraction from chloride media are much lower than those for extraction from nitrate media, even at the highest chloride concentrations.

Extraction of Other Lanthanides. The extraction performance of the diglycolamate-based functionalized ionic liquid [A336][DGA] was explored for trivalent lanthanide ions other than Nd(III). The distribution D_{Ln} increases with increase in atomic number of the lanthanide, and it reaches a maximum at Ho(III) and then slightly decreases toward Yb(III) (Figure 9). This behavior, with a maximum in the curve of the distribution ratios as a function of the atomic number is, is similar to what is observed for extraction of rare earths with dimethylheptyl methyl phosphate (P350).[69] However, in the

Figure 9. Variation of the distribution ratio across the lanthanide series. Organic phase, 0.04 M [A336][DGA]/[A336][NO$_3$]; aqueous phase, pH 4.2 and 7 × 10^{-4} M Ln(III).

case of the extractant P350, the maximum in the curve is reached in the middle of the lanthanide series.

Effect of Temperature. The extraction of Nd(III) by [A336][DGA] in [A336][NO$_3$] was performed at temperatures ranging from 300 to 333 K to determine the influence of the temperature on the extraction process (Figure 10). It was noted
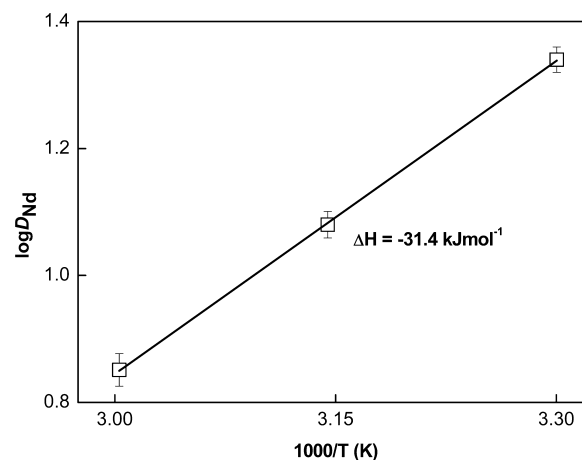
Figure 10. Effect of temperature on the distribution ratio of Nd(III). Organic phase, 0.04 M [A336][DGA]/[A336][NO$_3$]; aqueous phase, pH 4.2 and 7 × 10^{-4} M Nd(III).

that D_{Nd} decreases with increase in temperature. The enthalpy of the extraction was derived from the slope obtained in the plot of log$D$ versus $1000/T$ (K^{-1}) using the van't Hoff equation:

$$\Delta H_{total} = \frac{-2.303R \ \Delta \log D}{\Delta(1/T)} \quad (7)$$

The enthalpy change during the extraction was found to be −31.4 kJ mol^{-1}, showing that the extraction process is exothermic. The overall enthalpy change (ΔH_{total}) during mass transfer in the solvent extraction process is a combination of several factors, including (i) dehydration of the metal ion, (ii) complex formation of the metal ion with the extractant, (iii) dissolution of the metal solvate in the organic phase, and (iv) rearrangement of the organic phase to attain stable configuration. In the solvent extraction process, during formation of the metal−extractant complex, the metal-solvate

needs space in the organic phase to be dissolved and stabilized. Therefore, the previous molecular arrangement of the organic phase gets distorted in the presence of the metal complex and it rearranges to have a stable configuration at the expense of some enthalpy change. The magnitude of enthalpy change is governed by one of these factors. Due to the strong complexation of Nd(III) with [A336][DGA] and the high organophilicity of the Nd(III)−[A336][DGA] complex in the diluent phase [A336][NO₃] (equivalent structure of both [A336][DGA] and [A336][NO₃] with respect to the cation), the ΔH_{total} value of −31.4 kJmol⁻¹ is determined mainly by factors ii, iii, and iv, and hence it is an "enthalpy-driven" solvent extraction system. The change in Gibb's free energy (ΔG) can be calculated from eq 8:

$$\Delta G = -2.303RT \log K_{ex} \qquad (8)$$

The value of $\log K_{ex}$ was obtained from Figure 4. The value of ΔG was found to be −14.1 kJ mol⁻¹. This indicates that the process is energetically favored and spontaneous. The change in entropy (ΔS) at a fixed temperature can be evaluated using eq 9:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (9)$$

The value of ΔS was determined to be −57.7 J K⁻¹ mol⁻¹. The negative ΔS value could be attributed to the fact that there is hindrance of the C−C bond rotation in the ionic liquid, due to the more crowded octyl chains, so that fewer degrees of freedom are allowed during the complex formation process. Moreover, the negative entropy value suggests the existence of an outer-sphere complex formed between Nd(III) and [A336][DGA], because the process is "enthalpy-driven" and the dehydration from the inner-sphere is less efficient than the metal−ligand interaction.

Stripping and Reusability Studies. It is always important to study the stripping (back-extraction) of the metal ions under investigation from the loaded ionic liquid phase, because stripping is of equal importance as extraction in a separation process. A stripping study was carried out from the loaded ionic liquid phase. It was observed that complete stripping of Nd(III) was possible with a 0.5 M nitric acid solution, without the need of adding any complex-forming agent such as EDTA or DTPA to the aqueous phase (Table 1). This is an extra advantage of

Table 1. Variation of Back-Extraction Percentage (Stripping Percentage) as a Function of the Number of Stripping Stages[a]

no. of stages	% back extraction[b]
1	69.5
2	25
3	4.5
4	1

[a]Stripping solution = 0.5 M nitric acid. Loaded ionic liquid phase = 0.04 M [A336][DGA]/[A336][NO₃]. [b]Total percentage of back stripping after four stages is 100%.

the present ionic liquid extraction system because the presence of an aqueous complex former requires an additional cleanup step after stripping to decompose the complex and to recover the metal nitrates. The ionic liquid system [A336][DGA]/[A336][NO₃] is environmentally friendlier than solvent extraction systems with fluorinated ionic liquids or with volatile

organic solvents. After the back-extraction step, the ionic liquid phase was scrubbed four to five times with a 0.5 M NaOH solution to deprotonate the HDGA molecules, which are formed by interaction between [DGA]⁻ and HNO₃ in the stripping solution. The recycled ionic liquid was then washed thoroughly with Milli-Q water, followed by equilibration with an aqueous solution at the desired pH, before the next extraction step was carried out. An extraction efficiency of about 96.5% was obtained by using the recycled ionic liquid phase, which is very similar to the initial value (95.7%). This confirms that there is no loss of ionic liquid to the aqueous phase and that it can comfortably be reused. The same observations about the stability and reusability of ionic liquids for solvent extraction purposes have been made for phosphate- and carboxylate-based functionalized ionic liquids with the Aliquat 336 cation.[70−73]

CONCLUSION

A new ionic liquid extraction system was designed for the separation of neodymium(III) from aqueous solutions. The extraction system consists of the functionalized ionic liquid [A336][DGA] diluted in the ionic liquid [A336][NO₃]. This ionic liquid system has the merit of a simple synthesis and easy recyclability. Under the experimental conditions investigated, nearly 100% extraction of neodymium(III) was possible, despite the relatively high viscosity of the ionic liquid diluent [A336][NO₃]. Extraction from nitrate media was found to be far superior to extraction from chloride media. The presence of a salting-out agent has a dramatic effect on the distribution ratios, as well as on the phase separation. The distribution ratios of trivalent lanthanide ions increase with increasing atomic number. Nd(III) extraction was found to be exothermic in nature. The negative values of ΔG and ΔS confirm the spontaneity of the extraction process and the formation of an outer-sphere complex. The extraction stoichiometry indicates the formation of a 1:1 complex between [A336][DGA] and Nd(III). Complete stripping of Nd(III) from the pregnant ionic liquid solution was possible under relatively mild conditions (three washing steps with a 0.5 M HNO₃ solution) without the need of using a complex-forming agent in the aqueous phase. The ionic liquid extraction system could be regenerated and reused for the next extraction system without loss of extraction efficiency.

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Notes
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