

Demonstration of extraction performance of Aliquat 336 for Europium (III) from nitrate medium

Sanghamitra Pradhan¹ , Nilam Swain¹ , Bhabanisankar Sarangi¹ , Sujata Mishra^{1,*} 

¹ Department of Chemistry, Institute of Technical Education and Research, Siksha'O'Anusandhan, Deemed to be University, Khandagiri Square, Bhubaneswar, 751030, Odisha, India

* Correspondence: drsujatamishra97@gmail.com/sujatamishra@soa.ac.in; Scopus ID: [57203777707](https://orcid.org/57203777707)

Abstract: Hydrophobic ionic liquid Aliquat 336, a quaternary ammonium salt in combination with 20% decanol and kerosene, was deployed to extract Europium(III) in the presence of salting-out agent by liquid-liquid extraction. This extraction system circumvents the problems associated with conventional molecular solvents. The extraction behavior has been analyzed as a function of phase contact time, extractant concentration, nitrate concentration, and temperature. With increasing the phase contact time between the aqueous and organic phase, the percentage of extraction gets enhanced from 8.4% to 40.1%. The increase in ionic liquid concentration has a positive influence on the Eu (III) distribution ratio. The dependence of extraction of Eu(III) on Aliquat 336 molarity has been assessed by regression analysis. Temperature shows an adverse effect on the extraction efficiency. The changes in heat content and degree of randomness have been calculated as $-13.52 \text{ kJ mol}^{-1}$ and $65.77 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The percentage extraction of Europium (III) increases with the rise in the carbon chain length of the modifier.

Keywords: Europium(III); Aliquat 336; Thermodynamics; Modifiers; Regression analysis.

Abbreviations: Aliquat 336-tricapryl methyl ammonium chloride; $[\text{C}_n\text{m}^+][\text{TF}_2\text{N}^-]$ - 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides; HTTA2-thenoyltrifluoroacetone; CMPO N,N-diisobutyl-2-(octylphenylphosphoryl)acetamide; $[\text{P66614}][\text{MA}]$ trihexyl(tetradecyl)phosphonium N,N,N',N'-tetra(2-ethylhexyl)Malonate; $[\text{P66614}][\text{NO}_3]$ trihexyl(tetradecyl)phosphonium nitrate; $[\text{P66614}][\text{Cl}]$ trihexyl(tetradecyl)-phosphonium chloride; DPObis(chlorophosphoryl)decahydro-2,4-di(2-hydroxyphenyl)benzo[d]; [1,3,6]oxadiazepine; DEHDGA bis(2-ethylhexyl)diglycolamic acid; $[\text{N8888}][\text{DS}]$ tetraoctylammonium dodecyl sulphate; OHA 4-oxaheptanediamide; $[\text{C}_n\text{mim}^+\text{PF}_6^-]$ 1-alkyl-3-methylimidazolium hexafluorophosphate.

© 2020 by the authors. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Owing to their excellent magnetic, electrical, optical properties, rare earth elements are used for various essential applications in the field of metallurgy, smart materials, electric motors, computer peripherals, nuclear medicine, etc. [1]. The vast demand for these elements and limited supply has created an imbalance in supply-demand statistics. Hence, the design of a sustainable and

MATERIALS INTERNATIONAL | <https://materials.international> | 256

Cite This Article: Pradhan, S.; Swain, N.; Sarangi, B.; Mishra, S. Demonstration of extraction performance of Aliquat 336 for Europium (III) from nitrate medium. *Mat Int* 2020, 2, 0256-0262.

<https://doi.org/10.33263/Materials23.256262>

Demonstration of Extraction Performance of Aliquat 336 for Europium (III) from Nitrate Medium



effective pathway for the recovery and separation of these elements is a significant challenge for the researchers working in this area. Solvent extraction is a very widely used separation technique that adopts a simple procedure to recover rare earth elements from various primary and secondary resources [2-5]. Europium is categorized as a very important element by the Department of Energy, United States. Europium is used in permanent magnets, phosphors, optical fibers due to its unique optical, luminescent properties. It occurs along with other rare earths in minerals like bastnaesite, monazite, and xenotime.

Usage of large quantities of volatile organic compounds as extractants results in environmental pollution. Ionic liquids are mostly the organic salt compounds composed of cationic and anionic moieties. These are unique in the sense that they have less volatility, non-flammability, low melting point, and thermal resistance [6]. These are good alternatives to the usual organic extractants since these are stable liquids in a wide temperature range of -70° to 400° C [7]. Being highly hydrophobic, they behave as good extractants at room temperature. Ionic liquids are potential extracting agents used in hydrometallurgical techniques for the separation of lanthanides from different aqueous medium [8]. Good regeneration capacity and low aqueous solubility have made the ammonium-based ionic liquids more popular extractants for solvent extraction [9]. Ionic liquids extract either charged or neutral metal species from the aqueous solution depending upon the nature of metal ion, the stability of the extracted complex as well as the nature of the aqueous medium. High viscosity is the only limiting factor in the use of ionic liquids on a large scale. Larsson et al. developed a process in chloride media, for the separation of La (III) and Ni (II) with Aliquat 336 [10]. This method is pertinent to recycle waste nickel-metal hydride batteries. The extraction and separation studies of rare earth elements like Sm-Gd and Eu-Gd have been carried out using mixtures of Aliquat 336-TBP from nitric solutions, and optimum condition for complete extraction was

achieved [11]. The extraction and separation of Sm (III) and Europium (III) using undiluted quaternary ammonium ionic liquid have been investigated [12]. A novel non-fluorinated ionic liquid ($[P_{66614}][MA]$ in $[P_{66614}][NO_3]$ as diluent) was employed for the extraction of Europium (III) and other lanthanides from acidic nitrate media [13]. The comparison between the extraction behaviors of $[P_{66614}][MA]$ in $[P_{66614}][NO_3]$ and $[P_{66614}][MA]$ in $[P_{66614}][Cl]$ reveals that nitrate media is preferred to chloride media. Europium (III) extraction was performed using HTTA as extracting agent in ionic liquid diluent (ionic medium) $[C_1C_nim^+][Tf_2N^-]$ and a synergistic mixture of HTTA and CMPO in $[C_1C_nim^+][Tf_2N^-]$ ($n = 4, 6, 8, 10$) [14]. Rout et al., [15] applied DEHDGA exploited in the non-fluorinated green solvent $[N8888][DS]$ for the extraction of Europium (III) from aqueous phase containing $NaNO_3$ as a salting-out agent. The comparative study of an extraction efficiency of DEHDGA and classical acidic extractants DEHPA or Cyanex 272 dissolved in $[N8888][DS]$ divulge that DEHDGA is a potential extractant for Europium (III) loading. Europium (III) extraction has been carried out exploiting OHA in ionic liquid $[C_nmim^+PF_6^-]$ as diluent where $n = 4, 6$, and 8 [16]. Previous literature survey reveals that in most of cases, undiluted ionic liquids have been used, which may lead to a lot of extractant loss and, therefore, not viable from the economic point of view.

In this present investigation, liquid-liquid extraction of Europium (III) from nitrate feed solution applying room temperature ammonium-based ionic liquid, Aliquat 336, has been systematically scrutinized. Kerosene as a diluent and 20% decanol as a modifier have been used for the study. The influence of various extraction parameters like contact time, ionic liquid concentration, temperature, salting-out agent molarity has been studied in detail. The role and influence of different modifiers on the extraction system have also been investigated.

2. Materials and Methods

Aliquat 336 (triprlyl methyl ammonium chloride) procured from Sigma Aldrich was used without purification. Commercially available kerosene was used as diluent. The organic phase modifiers purchased from Merck were used.

Europium nitrate, $Eu(NO_3)_3$, purchased from Loba Chemie, was used for preparing metal stock solution by dissolving in double-distilled water. The desired dilution was done from the stock solution.

All other chemicals of AR grade were used in this work.

For the preparation of the organic phase, an appropriate amount of Aliquat 336, 20% decanol, and kerosene were mixed and appropriately shaken for perfect blending. The aqueous phase containing 0.325g/L Europium (III), NaNO_3 at desired pH, and organic phase with extractant in diluent and modifier were stirred using a thermostat shaker for the requisite time period in order to achieve equilibrium. Then phases were allowed to separate. Aqueous phase solution and raffinate were taken for analyzing the Europium (III) content using a double beam UV-Vis spectrophotometer (SYSTRONICS 2202) by Arsenazo (III) method [17]. The pH of the aqueous feed was measured using Systronics pH meter.

3. Results and Discussion

3.1. Influence of phase contact time.

The influence of aqueous and organic phase contact time on the extraction of 0.325g/L Eu (III) from aqueous feed containing 3M NaNO_3 using Aliquat 336 + 20% decanol + kerosene has been investigated at pH 3 by varying it from 30-75 minutes. The results show that the percentage extraction of Eu (III) enhances from 8.4 to 40.1% with rise in a contact time of both aqueous and organic phase and then reaches a plateau after the stirring time of 60 minutes Figure 1. Therefore for all further experimental studies, an equilibration time of 60 minutes has been selected.

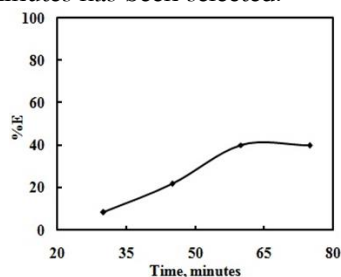


Figure 1. Influence of shaking time for the percentage extraction of 0.325g/L Eu (III) from 3M NaNO_3 at pH 3 employing 1.5M Aliquat 336 + 20% decanol + kerosene at 298K and 1:1 O/A ratio.

3.2. Variation of aqueous feed nitrate concentration.

The extraction dependency of Eu (III) on nitrate ion strength has been examined by varying the concentration ranging from 2.5 to 5M in the

2.1. Extraction efficiency.

In liquid-liquid extraction, distribution coefficient (D) and percentage of extraction (%E) are the two significant parameters to measure the extraction efficiency. Here, the extraction efficiency of Europium (III) has been determined under the investigated experimental conditions as follows.

The distribution ratio was calculated as

$$D = \frac{[\text{Eu (III)}]_I - [\text{Eu (III)}]_F}{[\text{Eu (III)}]_F} \quad (1)$$

Where $[\text{Eu (III)}]_I$ and $[\text{Eu(III)}]_F$ are concentrations of Eu (III) ion in the aqueous feed and raffinate, respectively.

The percentage of extraction (%E) was calculated using the equation

$$\%E = 100 * \frac{\frac{[\text{Eu (III)}]_I - [\text{Eu (III)}]_F}{[\text{Eu (III)}]_F}}{\frac{[\text{Eu (III)}]_I}{[\text{Eu (III)}]_F}} \quad (2)$$

aqueous feed along with 0.325g/L Europium (III) at pH 3. The organic phase used for this study contained 1.5M Aliquat 336, 20%decanol, and kerosene. It was noticed that the percent of extraction of Europium (III) rose from 30.5 to 60.2 when sodium nitrate concentration enhances from 2.5M to 5M depicted in Figure 2. This may be because of the salting-out effect. The presence of more nitrate salt in the aqueous solution resulted in an increase in ionic strength, which led to a decrease in the number of water molecules nearby the hydration sphere of Europium (III), thereby making it more hydrophobic [12] which enhanced its transfer into the organic phase.

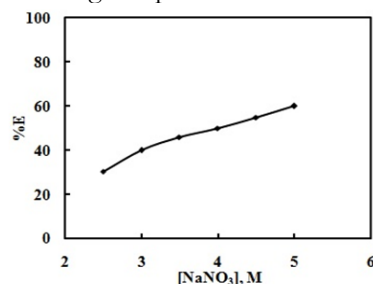


Figure 2. Variation of percentage extraction of 0.325g/L Eu (III) with respect to the concentration of nitrate ion at pH 3 employing 1.5M Aliquat 336 + 20% decanol + kerosene at 298K and 1:1 O/A ratio.

3.3. Variation in Aliquat 336 molarity.

The highly viscous extracting agent, Aliquat 336, has been found to form the third phase while used for extraction studies of Europium (III). This

Demonstration of Extraction Performance of Aliquat 336 for Europium (III) from Nitrate Medium

• • •

might be caused by less solubility of the extracted complex in the organic phase containing Aliquat 336 and kerosene. Therefore, 20% of decanol was used as a modifier in the organic phase. It was observed that the extraction of 0.325g/ L Europium (III) at pH 3 from 3M NaNO₃ increased from 8.3% to 40.1% in an increase in Aliquat 336 concentration from 0.8M to 1.5M, Figure 3. This was probably due to the formation of more complex Europium (III) in the presence of more Aliquat 336. The plot of log D versus log [Aliquat 336] gives a linear one with a slope of 3.137 ~3. This confirms that 3 moles of Aliquat 336 are involved in the extraction equilibrium.

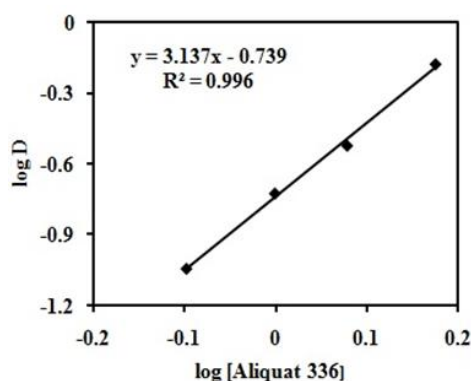
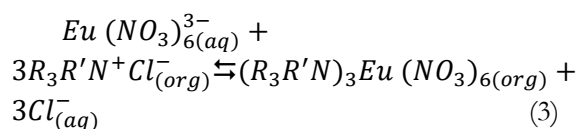


Figure 3. Plot of logD versus log[Aliquat 336] in the extraction of 0.325g/L Eu (III) from 3M NaNO₃ with 1:1 O/A ratio at pH 3 and 298K.

3.4. Extraction mechanism.

The slope (3.137) obtained from the plot of the variation of the log-log plot of distribution ratio against Aliquat 336 concentration describes the extraction mechanism in which 3 moles of Aliquat 336 are participating in the extraction process. This shows that the organic phase got loaded with negatively charged Europium (III) nitrate complex, and the extraction equilibrium has been proposed as follows:



Europium (III) form hexa or pentanitrato complex in an aqueous phase containing nitrate ions. The hexanitrato complex of Europium (III) has been isolated by Onghena et al., [18]. The interaction of Aliquat 336 with anionic Europium (III) complex is electrostatic in nature and m

3.5. Regression analysis of extraction data.

In order to clarify the correlation between experimental and estimated values of log D, linear regression analysis was operated with the aid of regression analysis software present in MS-Excel Figure 4. Experimental log D values were acquired from the Aliquat 336 variation study for the extraction of 0.325g/L Europium (III) from 3M NaNO₃ without disturbing the aqueous phase pH 3. Using the experimental and predicted log D values (Table 1), standard deviation (σ) was calculated, and Table 2 enumerates the regression statistics. The value of the standard deviation represents a good correlation between the results. A lower p-value, i.e., less than 0.05, clearly indicates that the percentage of extraction of Europium (III) is governed by Aliquat 336 concentration.

Table 1. Experimental and predicted log D values for the extraction of 0.325g/L Europium (III) from 3M NaNO₃ using 1.5M Aliquat 336 blended in 20%decanol and kerosene at pH 3, 298K with 1:1O/A ratio.

[Aliquat336],M	logD _{Experimental}	logD _{Predicted}
0.8	-1.043	-1.043
1	-0.723	-0.753
1.2	-0.491	-0.411
1.5	-0.174	-0.225

Table 2. Regression data for the extraction of 0.325g/L Europium (III) from 3M NaNO₃ using 1.5M Aliquat 336 blended in 20% decanol and kerosene at pH 3, 298K with 1:1 O/A ratio.

Regression statistics	
Standard deviation (σ)	0.050
Standard error	0.070
p-value	0.003
R squared value	0.975

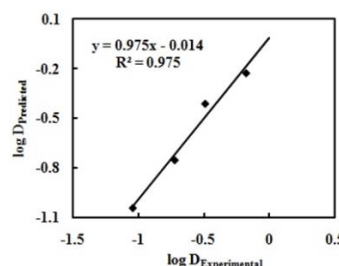


Figure 4. Graph showing the correlation between log D_{Predicted} and log D_{Experimental} for the extraction of 0.325g/L Eu (III) from 3M NaNO₃ using Aliquat 336 at pH 3, 298K with 1:1 O/A ratio.

3.6. Dependence on temperature.

Aliquat 336 is highly viscous, and anticipation regarding the effect of temperature on the extraction using this ionic liquid as an organic phase

is quite apparent. In this context, the extraction of 0.325g/L Europium (III), 3M NaNO₃ at aqueous phase pH 3 was carried out with the help of 1.5M Aliquat 336 + 20% decanol + kerosene in the temperature range 298K to 328K. It has been found that the extraction percentage of Europium (III) adversely affected by temperature as cleared from the extraction behavior, which decreased from 40.1% to 20.8% with an increase in temperature. This extraction behavior is very similar to the previous study executed by Acharya and Mishra [19]. All experiments were performed at 298K. Figure 5, i.e. plot of log D vs. 1000/T, the slope corresponds to standard enthalpy change (ΔH^0), and the value of standard entropy (ΔS^0) values has been predicted from the intercept and were figured out as -13.52 kJmol⁻¹ and 65.77J K⁻¹mol⁻¹, respectively.

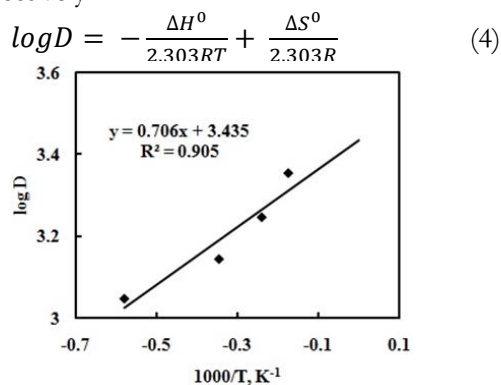


Figure 5. Plot of logD versus 1000/T for the extraction of 0.325g/L Eu (III) from 3M NaNO₃ at pH 3

employing 1.5M Aliquat 336 + 20% decanol + kerosene with 1:1 O/A ratio.

The values of ΔH^0 and ΔS^0 suggest that the extraction is a heat releasing process with an increase in randomness. The positive value of entropy reveals that Europium (III) forms the inner-sphere complex with Aliquat 336, expelling the water of hydration.

3.7. Role of modifiers.

Modifiers play a crucial role in the extraction system by making the extracted complex congenial with the organic phase and hence, remove the third phase, which is formed during the extraction due to the immiscibility of the extracted complex in the organic phase. To know the influence of modifiers, the extraction of Europium (III) was executed with four different aliphatic alcohols having different chain lengths, i.e. C₃ (propanol), C₆ (hexanol), C₈ (octanol), C₁₀ (decanol) as modifiers in the organic phase. The low dielectric constant and enhanced chain length of the modifiers witness a higher rate of extraction. This is worthwhile that an increase in the number of C-atoms in the alkyl chain of modifier increases the hydrophobicity of extracted complex, and hence, it solubilizes the metal complex more and thereby speeds up the extraction process. Modifiers with low dielectric constant exhibit less contact with the extractant resulting enhancement in the recovery process. The variation of percentage extraction of Europium (III) with a chain length of modifier is demonstrated in Table 3.

Table 3. Role of modifiers on percentage extraction of 0.325g/L Europium (III) from 3M NaNO₃ at pH 3 using 1.5M Aliquat 336 in kerosene at 298K and 1:1 O/A ratio.

Modifier	Dielectric constant (ϵ) (Dean, 1998)	D	%E
Propanol	20.80	0.14	12.4
Hexanol	13.03	0.31	23.8
Octanol	10.30	0.49	32.7
Decanol	8.10	0.67	40.1

4. Conclusions

In this investigation, ionic liquid Aliquat 336, a conventional green solvent, has been tested to extract Europium (III) from nitrate medium under varying conditions of phase contact time, temperature, nitrate ion molarity and Aliquat 336 molarity. The extraction efficiency of Europium (III) was observed to enhance with a rise in nitrate ion molarity in the aqueous feed. The extractant concentration had

a positive influence on the percent extraction due to an increase in the amount of extractable metal complex. The extraction was studied at pH 3, and decanol was used as an organic phase modifier along with diluent kerosene. The temperature variation experiments provide information regarding changes in enthalpy and entropy. The increase in temperature went contrary to the extraction process in this case.

Demonstration of Extraction Performance of Aliquat 336 for Europium (III) from Nitrate Medium



The modifier with less polarity (decanol) was observed to be the best one for Europium (III) extraction.

Funding

This research received no external funding.

Acknowledgments

The authors express their heartfelt gratefulness to authorities of Siksha 'O' Anusandhan Deemed to be University for the inspiration to pursue this research work.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Balaram, V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers* **2019**, *10*, 1285-1303, <https://doi.org/10.1016/j.gsf.2018.12.005>.
2. Sui, N.; Huang, K. Separation of rare earths using solvent extraction consisting of three phases. *Hydrometallurgy* **2019**, *188*, 112-122, <https://doi.org/10.1016/j.hydromet.2019.06.012>.
3. Hidayah, N.N.; Abidin, S.Z. Extraction of light, medium and heavy rare-earth elements using synergist extractants developed from ionic liquid and conventional extractants. *Comptes Rendus Chimie* **2019**, *22*, 728-744, <https://doi.org/10.1016/j.crci.2019.10.006>.
4. Ismail, N.A.; Aziz, M.A.A.; Yunus, M.Y.M.; Hisyam, A.; Selection of extractant in rare earth solvent extraction: A review. *Int. J. Recent Technol. Eng.* **2019**, *8*, 728-743.
5. Al-Nafai, I.; Kim, H.; Osseo-Asare, K. Estimation of the Standard Free Energy of Formation of Bastnasite, REFCO₃. *Mining, Metallurgy & Exploration* **2019**, *36*, 227-233, <https://doi.org/10.1007/s42461-018-0041-7>.
6. Sun, X.; Waters, K.E. Synergistic Effect between Bifunctional Ionic Liquids and a Molecular Extractant for Lanthanide Separation. *ACS Sustainable Chemistry & Engineering* **2014**, *2*, 2758-2764, <https://doi.org/10.1021/sc500493d>.
7. Fredlake, C.P.; Crosthwaite, J.M.; Hert, D.G.; Aki, S.N.V.K.; Brennecke, J.F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *Journal of Chemical & Engineering Data* **2004**, *49*, 954-964, <https://doi.org/10.1021/jc034261a>.
8. Rout, A.; Binnemans, K. Solvent Extraction of Neodymium(III) by Functionalized Ionic Liquid Trioctylmethylammonium Dioctyl Diglycolamate in Fluorine-free Ionic Liquid Diluent. *Industrial & Engineering Chemistry Research* **2014**, *53*, 6500-6508, <https://doi.org/10.1021/ie404340p>.
9. Rout, A.; Kumerasan, R.; Venkatesan, K.A.; Antony, M.P. Separation of Am(III) from nitric acid medium by phosphonium ionic liquid-hydroxyacetamide mixture. *Journal of Radioanalytical and Nuclear Chemistry* **2017**, *313*, 505-513, <https://doi.org/10.1007/s10967-017-5340-9>.
10. Larsson, K.; Binnemans, K. Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling. *Green Chemistry* **2014**, *16*, 4595-4603, <https://doi.org/10.1039/C3GC41930D>.
11. Shulin, S.S.; Galieva, G.N.; Chighevskaya, S.V.; Pletuhina, J.V.; Saveliev, N.S. Extraction separation of rare earth elements of the medium group with isomolar mixture of Aliquat 336-TBP and Cyanex 572-TBP from nitric solutions. *Inorganic Materials* **2018**, *54*, 515-519, <https://doi.org/10.1134/S0020168518050126>.
12. Van de Voorde, M.; Van Hecke, K.; Binnemans, K.; Cardinaels, T. Separation of samarium and europium by solvent extraction with an undiluted quaternary ammonium ionic liquid: towards high-purity medical samarium-153. *RSC Advances* **2018**, *8*, 20077-20086, <https://doi.org/10.1039/C8RA03279C>.
13. Rout, A.; Binnemans, K. Liquid-liquid extraction of europium(III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid. *Dalton Transactions* **2014**, *43*, 1862-1872, <https://doi.org/10.1039/C3DT52285G>.
14. Atanassova, M.; Kurteva, V. Synergism in the Solvent Extraction of Europium(III) with Thenoyltrifluoroacetone and CMPO in Methylimidazolium Ionic Liquids. *Journal of Solution Chemistry* **2019**, *48*, 15-30, <https://doi.org/10.1007/s10953-019-00844-8>.
15. Rout, A.; Souza, E.R.; Binnemans, K. Solvent extraction of europium(III) to a fluorine-free ionic liquid phase with a diglycolamic acid extractant. *RSC Advances* **2014**, *4*, 11899-11906, <https://doi.org/10.1039/C3RA48045C>.
16. Niu, Y.N.; Ren, P.; Zhang, F.; Yan, Z.Y. Solvent extraction of Eu³⁺ with 4-oxaheptanediamide into ionic liquid system. *Separation Science and Technology* **2018**, *53*, 2750-2755, <https://doi.org/10.1080/01496395.2018.1471507>.
17. Savvin, S.B. Analytical use of arsenazo III: Determination of thorium, zirconium, uranium and rare earth elements. *Talanta* **1961**, *8*, 673-685, [https://doi.org/10.1016/0039-9140\(61\)80164-1](https://doi.org/10.1016/0039-9140(61)80164-1).



18. Onghena, B.; Papagni, E.; Souza, E.R.; Banerjee, D.; Binnemans, K.; Vander Hoogerstraete, T. Speciation of lanthanide ions in the organic phase after extraction from nitrate media by basic extractants. *RSC Advances* **2018**, *8*, 32044–32054, <https://doi.org/10.1039/C8RA06712K>.
19. Acharya, S.; Mishra, S. Studies on solvent extraction of La(III) using [A336][NO₃–] and modeling by statistical analysis and neural network. *Separation Science and Technology* **2017**, *52*, 1660–1669, <https://doi.org/10.1080/01496395.2017.1296870>.