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Recent Uses of Ionic Liquids in the Recovery and Utilization of Rare Earth Elements

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Abstract: The importance of rare earth elements as the basis in the development of new technologies or the improvement of the used ones, made of a necessity its recovery, besides that from raw materials, from waste materials. In this recovery, Hydrometallurgy and its derivative Solvometallurgy, play a key role due to its operational characteristics, which are emphasized with the use of ionic liquids. The manuscript reviewed the most recent advances (2023 and 2024 years) about the use of ionic liquids in the unit operations (leaching and separation technologies) aimed to the recovery of these valuable and strategic metals. Moreover, a comprehensive review about the use of these chemicals in the development of advanced materials containing some of these rare earth elements is presented.

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1. Introduction

The elements named rare earths (in which yttrium and scandium are included) consisted of seventeen elements presenting similar and unique properties that from recent times had gained enormous interest in world. Traditionally, these elements are divided in light rare earths (lanthanum, cerium, praseodymium, neodymium, promethium, samarium and europium) and heavy rare earths (gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and yttrium). Against other metals, this group of elements can not be found in nature in its zero valent form, but forming compounds such as phosphates, silicates, carbonates, oxides and halides. Their total abundance in Earth's crust is about 169 ppm, which divided in near 138 ppm for light rare earth elements, and 31 ppm of heavy rare earth elements. Thus, they are not *as rare* since its abundance is comparable to that of other metals (copper, tin, nickel, etc.). It was described [1], that the concept of *rare* emerged due to that the deposits containing them are distributed along the world in low concentrations.

The strategic importance of these elements is due to these unique properties, which are the key factor in the development of different high-tech fields (military affairs), such as electronics, permanent magnets, extremely powerful magnets (holmium), medical, technological and renewable energy applications, etc. These various uses had led to consider the recovery of these valuable metals not only from raw materials but also from secondary resources, and thus, to the recycling of these metals; among these secondary resources, phosphogypsum, e-wastes, red mud, coal, coal fly ash and mine tailings were included.

It is worth to consider that not all the world concerning rare earth elements is as smooth as it seemed, and in real terms there are serious, though still scarce, concerns about environmental problems and health issues related to rare earths mining and processing [2].

As it is mentioned above, the recovery of REEs (rare earth elements) included the treatment of raw materials as well as secondary or waste materials. It is their high demand and utilization in smart technologies that the recovery of these elements from these secondary and waste resources had gained interest during the last years. The recovery of these strategic metals from one of another resource is accomplished either by hydrometallurgical or pyrometallurgical processes, though in some cases, both types of processing are coupled to fulfil the task. Solvometallurgy, which can be considered a third type of processing, has evolved from Hydrometallurgy. In the former, conventional aqueous medium is substituted by solvents with *green label*, even, traditional extractants and diluents used in solvent extraction are substituted by these green chemicals in order to reach a more environmental friendship technology, and it is here when ionic liquids (ILs) enter in the field of the recovery of metals.

Ionic liquids are chemicals exclusively composed by a cation and an anion, both types of ions can be of organic or inorganic nature, though the common features are ILs formed by an organic cation and organic anion or organic cation and inorganic anion. Other properties of these chemicals included to be liquids at temperatures below 100º C (mandatory), low vapor pressure, thermal and radioactive stability, non-flammability, etc., whereas their uses encompass a wide spectrum of applications: additives in lubricants, drug design, wastewater treatment, adsorbents for gases, etc. Despite its characteristics, the green label has been questioned from time ago [3-8], since it can be demonstrated that ionic liquids are harmful to living organisms [9].

Thus, the use of these ILs has known a widespread use in the recovery of REE and other metals [10], and recent reviews [11-13] describing the utilization of ILs on hydrometallurgical processes as an alternative to classical extractants for solvent extraction. In a description of the different methodologies aimed to the recovery of REEs from magnets used on wind generators [14], several ILs alone (Cyphos IL101, a phosphonium salt) or mixed with traditional extractants (Cyanex 923, a phosphine oxide) are used for the recovery of dysprosium or neodymium. Other procedures using polyamides or epoxy derivatives dissolved in ILs are also mentioned in the work. Some ILs based in the next groups are available for REE extraction [15]: carbamoylmethylphosphine oxide (CMPO), diglycolamides (DGAs), phenantroline-dicarboxamides, hydroxypyridine, etc., and whereas most of these ILs extracted REEs by a cation exchange mechanism, some (ammonium+DHDGA (dihexyldiglycoamide) or ammonium+carboxylate) responded to an ion-association mechanism. These two last systems necessitated the use of diluents as hexane or sulfonated kerosene plus n-octanol, respectively.

Important secondary sources for REEs recovery are electronic-wastes, and here ILs also play a key role in the processing of these, otherwise, pollutant residues [16]. Another wastes of interest about its recyclability are spent Ni-MH batteries which contained about 10 wt% of rare earth elements (La, Ce, Nd, and Pr), showing the potential of ILs to recover La and Ce from different aqueous (real and synthetic) solutions [17]. A third source for REEs recovery are NdFeB scraps, and though a recent review does not mention the utilization of ILs in the dissolution or separation steps, it claims about the use of ILs in the electrochemistry of these scraps.

Liquid membranes in its various configurations (supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs)) are used to recover rare earths elements from various sources [19]. These liquid membranes contained different ionic liquids which act both as sole carriers (Cyphos IL104, phosphonium salt) or in combination with other extractants to form synergic mixtures to aid REEs transport: TOPO (tri-octyl phosphine oxide), DEHPA (di-(2-ethylhexyl) phosphoric acid), and TBP (tri-n-butil phosphate). Mixtures of the ionic liquid $[C_6mim^+][NTf_2^-]$ (1-hexyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide) with DEHPA or TBP, TOPO and TBP, DEHPA and TBP are used to investigate the transport of Ce, Nd or Pr, Gd or Y, respectively.

Despite all the green properties associated to ILs and the benefits of their usage, it is recently stated [20], that there are very few examples in which ILs performed better than conventional aqueous systems. As it is mentioned above, a first drawback about the utilization of ILs is that an important number of ILs systems needs traditional organic diluents, to decrease its inherent viscosity, which increases as the IL phase becomes loaded by the extracted metal. Thus, the pair extractant+diluent of the traditional solvent extraction is not completely avoided with the use of ILs. The solubility of these ILs due to the mechanisms involved in the extraction of metals must be consider and odd point about its practical uses. Very often, these extraction mechanisms closely resembled these showed by conventional extractants [21]. As it is cleverly described in about using

ILs to recover metals, there is a complete mismatch between what scientists investigated and proposed and what the industry needs

Nevertheless, the interest in the utilization of ILs in the various steps involved in the recovery of REEs (and metals in general) from primary and secondary sources still maintains alive proposals about the use of these chemicals, thus, this work reviewed very recently published investigations about the involvement of ILs in the various steps of REEs dissolution-separation-purification. Also, recent references about the use of ILs and REEs to develop some materials of interest are reviewed.

2. Using ionic liquids in the recovery of rare earth elements

2.1. Leaching

Betaine hydrochloride ($[Hbet^+]Cl^-$) solution was used to dissolve permanent magnet waste containing Ce, Nd, Gd, Pr plus Fe, Al, B [22]. Results indicated that the best leaching conditions were: time 8 hours, temperature 200º C, ionic liquid concentration 0.1 M and solid- liquid relationship 1 g-150 mL. Under these conditions, the percentage of REEs leached was 56.24 Ce, 97.05 Nd, 95.51 Gd, 99.81 Pr, and 0.20 Fe, remaining iron oxide in the residue. The REEs dissolved by the next reaction:

$$RE_2O_3 + 8[Hbet^+]Cl^- + H_2O \rightarrow [RE_2(bet)_8(H_2O)_4]^{6+} + 2H^+ + 8Cl^- \quad (1)$$

Once the REEs were disolved, they were extracted with N,N-di-2-ethylhexyl diglycolamic acid (D2EHDGAA) at pH 2.57. The percentage of extraction for these elements was shown in Table 1 using two media: HCl and $[Hbet^+]Cl^-$.

Table 1. Approximate percentage of REEs extraction with D2DEHDGAA.

Medium	Ce	Nd	Gd	Pr
HCl	45	82	99	68
$[Hbet^+]Cl^-$	44	95	99	69

From [22].

It can be seen that the change of the medium hardly affect to the extraction of the metals, except in the case of neodymium. The authors claimed that the REEs can be separate using the extractant, however, data presented in Table 1 showed that in both media all the REEs were co-extracted. Moreover, no data about the stripping step were given in the published manuscript.

An ionic liquid also based in betaine, such as betainium bis(trifluoromethylsulfonyl)imide $[Hbet^+][Tf_2N^-]$ and wáter in a 1:1 ratio was used to recover the REEs from end-of-life mobile phone speakers [23]. The experiments carried out under various experimental conditions utilized binary (Nd_2O_3-Pr_2O_3) or ternary (Nd_2O_3-Pr_2O_3-Fe_2O_3) systems, being the oxides of light REEs selectively leached by the IL. In this case, the dissolution reaction was expressed as:

$$RE_2O_3 + 6[Hbet^+][Tf_2N^-] \rightarrow 2[RE(bet)_3][Tf_2N]_3 + 6H_2O \quad (2)$$

with optimum leaching conditions as: 1 M $NaNO_3$, 60º C, 250 rpm and 30 min. In the binary system, Nd_2O_3 was leached preferably to the praseodymium oxide, and together with the above oxides, the oxides of La, Eu and Gd were disolved, whereas Y_2O_3, Tb_4O_7 and Yb_2O_3 did not. A complete hydrometallurgical process for the recovery of REEs, as oxides, from as-received waste speakers was developed, this process included: pre-treatment, leaching, precipitation, and calcination.

The same ionic liquid as in the previous reference was use for the recovery of REEs from various coal fly ash (CFA) solids [24]. In this case the leaching reaction was described as:

$$REE^{3+} + 3[Hbet^+][Tf_2N^-] \rightarrow [REE(bet)_3][Tf_2N]_3 + 3H^+ \quad (3)$$

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The REEs in the organic phase was remove as dissolved salt using a mild acid stripping step, which regenerated the IL. It was described that an alkaline preteratment converted the REEs in the CFA to their respective oxides, and after, the complete recovery sequence consisted of seven steps:

1. leaching at 85º C (IL:aqueous phase mass ratio 1:1, 1 M NaCl, solid/total liquid ratio 15 mg/g, 3 hours),
2. cooling at 25º C,
3. removal of CFA residue and addition of ascorbic acid plus betaine (25 mM ascorbic acid/g aqueous phase and 10 mg betaine/g aqueous phase),
4. heating at 85º C during 1.5 hours,
5. cooling at 25º C and keep at 4º C overnight, and separation of aqueous and IL (containing REEs) phases,
6. addition of 1.5 M HCl and heating at 85º C (IL:HCl mass ratio of 1, 1.5 hours),
7. cooling at 25º C and keep at 4º C overnight, followed by separation of an acidic phase containing the REEs and an IL regenerated phase. In all the steps, the different aqueous phases were located above the IL due to the higher density of this phase. The recovery of total REEs varies in the 44%-66% range, with Sc, Y, Nd, Sm, Gd, Dy, and Yb extracted preferably into the IL phase, with recovery efficiencies in the 53.8%-66.2% range, while the recovery of other REEs greatly depends on the different CFA sample used in the investigation.

It was described the recovery of REEs and Sc either by direct leaching through H_2SO_4 and ion exchange or by direct leaching with task-specific ionic liquids, i.e. betainium bistriflimide and subsequent stripping with acidic HCl solutions.

The next reference investigates the separation of Nd and Pr by the selective dissolution of Nd_2O_3 from their oxide mixtures (Nd_2O_3+Pr_6O_{11}) using as leaching medium a mixture of the ionic liquid 1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide ([C_{4mim}^+][NTf_2^-]), 2-thenoyltrifluoro acetate (HTTA) and 0.1% water. The procedure allowed to yield a separation factor ($\beta_{Nd/Pr}$)>500, demonstrating that Pr_6O_{11} remains practically undissolved. Nd was stripped with 0.5 M nitric acid solution and precipitate as Nd_2O_3.

2.2. Electrodeposition

It was shown that the electrodeposition of Nd(III) in ionic liquids media is dependent of the presence of water in the system. In fact, the presence of water catalyzed the electrodeposition of the rare earth, thus, the introduction of water into the coordination sphere of the complex formed by this REE and bis(trifluoromethanesulfonyl)imide [NTf_2^-] anions and its influence on the metal deposition was investigated [27]. The addition of water produced various effects in the Nd^{3+} [NTf_2^-] complexes affecting the Nd^{3+} electrochemical reduction, these effects can be summarized as: cis/trans transformation of the anion, change from bidentate to monodentate forms in the coordination mode of the anion and preferably coordination of water with the transition metal.

This reference investigated the electrochemical (co)deposition of La and Fe-group transition metals from solutions in 1-butyl-1-methyl-pyrrolidinium dicyanamide [BMP^+][DCA^-] with controlled water content [28]. The presence of Fe-group metals produced a positive shift in the onset potential of La^{3+} reduction, being lanthanum codeposited with the respective Fe-group metal. This electrodeposition occured at room temperature and $E \leq -1.75$ V, however the ionic liquid tended to degrade. Also, the presence of water up to 3.092 M produced a positive shift of La^{3+} electrodeposition. This ionic liquid containing the [BMP^+] group had better stability against cathode degradation when compared with ILs having imidazolium-type cations. Lanthanum was deposited both as zero valent and oxidized states.

2.3. Ion exchange resins

The performance of different ion exchange resins (tetra-n-alkyl diglycolamide) in [C_{4mim}^+][Tf_2N^-] ionic liquid on the uptake of. La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) from nitric acid solutions was investigated [29]. Experimentation was carried out both in batch and continuous (column) operations. The ion exchange resins contained different n-alkyl groups (Table 2), and the uptake order was Dy>Gd>Sm>Nd>Pr>Ce>La, increasing this uptake from 0.3 M to 3 M nitric acid, with little variation in the 3-6 M nitric acid concentration range. Table 2 showed the máximum and minium uptakes of the resins.

Table 2. Composition and maximum and mínimum uptakes (mg/g) of the resins.

Resin	Maximum	Minimum
TPDGA: n-pentyl	Dy: 41.7	Sm: 36.8
THDGA: n-hexyl	Dy: 40.9	Pr: 33.1
TODGA: n-octyl:	Dy: 38.4	Pr: 29.2
TDDGA: n-decyl	Dy: 32.6	La: 19.6

From [29].

It is show that with allresins maximum uptake occurred in the case of dysprosium, and that uptake decrease with the increase of the length of the alkyl chain. As it was somewhat expected, for all the resins the breakthrough volume followed the same order than above. Prior to the elution step (0.05 M EDTA in 1 M guanidine carbonate), the column was washed with 3 M nitric acid solution. The presence of the ionic liquid enhanced the lanthanides uptake.

2.4. Membranes

PVDF or chitosan based membranes were investigated for the extraction of lanthanides (Yb, Er, Dy, Sm, Gd, Nd, Ce) from 10^{-4} M Ln solutions [30]. The ionic liquids used in the investigation were; 1-n-Butyl-3-methylimidazolium hexafluorophosphate $[Bmim^+][PF_6^-]$, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide $[P_{66614}^+][NTf_2^-]$, Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_{4mim}^+][NTf_2^-]$, 1-Butyl-3-methylimidazolium-di(2-ethylhexyl)-oxamate $[C_{4mim}^+][DEHOX^-]$. In the case of PVDF membranes, best extraction was produced when the membrane was soaked in $[C_{4mim}^+][DEHOX^-]$, with an extraction order as Yb>Er>Dy=Sm>Gd>Nd>Ce; when the membrane was soaked with the other three ionic liquid, the lanthanides were not extracted. In the case of chitosan membranes, all the membranes containing the above ionic liquids extracted in an appreciable form all the REEs, though the chitosan membrane formulated with $[C_{4mim}^+][DEHOX^-]$ presented the best results. In any case, the best extraction results were obtained when the chitosan membranes contained sucrose/citric acid and irradiated at 5kGy. In all the above experiments, the stripping phase was a 0.5 M nitric acid solution.

2.5. Liquid-liquid extraction

Two ionic liquids, derived from N,N-dioctyl diglycol amic acid DODGA and quaternary ammonium salts, where fabricated and formulated as $[N_{1888}^+][DODGA^-]$ and $[N_{4444}^+][DODGA^-]$, were used in the separation of europium from an europium-uranium binary system [31]. Maximum Eu(III) extraction was obtained at 4-5 M nitric acid, with N_{4444}-based IL performing better than N_{1888} as their respective distribution ratios assesed: 13 versus 9. Also the europium(III)/uranium(VI) separation factors were better in the case of N_{4444} IL: 60.35 versus 55.44. Despite these results, there was a continuous loss of extraction efficiency under continuous use: 85% (1st cycle) to 45% (5th cycle) and 95% (1st cycle) to 65% (5th cycle) for N_{1888} and N_{4444}-based ILs, respectively. This work uses a kinetics investigation approach: pseudo-first and pseudo-second kinetics model, which were inadequate for a solvent extraction investigation but for adsorption or ion exchange with adsorbents/resins investigations. Thus, the published manuscript never should have included these data, it is responsability of the authors, but also of the reviewers and Editor of the Journal to allow the publication of such manuscript in this form.

Real scrap NdFeNi magnet from computer hard disks was used to investigate the recovery of Nd(III) [32]. Using Aliquat 336 (quaternary ammonium salt) and Cyanex 572 (phosphonic acid), an ionic liquid formulated as $[R_4N^+][Cy^-]$ and diluted in kerosene was used for solvent extraction studies in order to separate Nd(III) from Ni(II). Nd(III) extraction was maximum at 0.1 M acidic concentrations (HCl, HNO_3, or H_2SO_4), decreasing the extraction as the acid concentration increased from 0.1 to 1 M in the aqueous phase. Nd(III) extraction performed better in the nitric acid medium, however, the highest (26.3) Nd/Ni separation factor was obtained at 0.2 M HCl. Thus, a process was defined using 0.2 M HCl solution to leach the magnets, and the extraction occurred at pH 1.23, accordingly with the equilibrium:

$$\mathrm{Nd^{3+}_{aq} + 3Cl^-_{aq} + 3(R_4N^+Cl^-)_{org} \leftrightarrow NdCl_3 \cdot 3(R_4N^+Cy^-)_{org}} \quad (4)$$

The extraction of nickel(II) responded to the formation in the organic phase of a compound with $NiCl_2{\cdot}2(R_4N^+Cy^-)$ stoichiometry. Both Nd(III) and Ni(II) were extracted by a solvation mechanism. Stripping was accomplished in 0.5-2 M HCl medium, and after stripping, Nd was precipitated with oxalic acid followed of calcination to produce Nd_2O_3.

An industrial solution containing Ho, Er, Tm, Yb, Lu and Y was use to investigate the separation of yttrium from the rest of the REEs [33]. The separation was carried out by solvent extraction with the ionic liquid trioctylmethylammonium (2,6-dimethylheptyl propionate ($[N_{1888}^+][POPA^-]$) dissolved in sulfonated kerosene. The extraction of yttrium responded to the next equilibrium:

$$\mathrm{Y_3Cl^-_{aq} + 3[N^+_{1888}][POPA^-]_{org} \leftrightarrow [N_{1888}]_3Y[POPA]_3Cl_3} \quad (5)$$

Best extraction results were reached at pH 5, whereas stripping was performed in HCl medium. The use of this ionic liquid had selectivities for Y against the presence of heavy rare earths (Ho–Lu), which can be stripped from the organic phase by the use of deionized water. A countercurrent experimentation consisting of nine extraction stages and six scrubbing stages allowed to yield a solution in which yttrium was purified near 99 wt%.

The extraction performance of the task-specific ionic liquid trihexyltetradecylphosphonium 3-hydroxy-2-naphthoate against the presence of La, Ce (IV), Nd, Ho and Lu was investigated [34]. Using single-bearing solutions it was demonstrated that the extraction was pH-dependent, with best results yielded at pH 2.5, 23º C and 6 hours of contact between both aqueous and organic phases. The extraction of these elements responded to the equilibrium:

$$\mathrm{Ln(NO_3)_{5aq} + 2[P^+_{66614}][HNA^-]_{org} \leftrightarrow [P_{66614}]_2[Ln(NO_3)_5]_{\mathit{org}} + 2HNA^-_{aq}} \quad (6)$$

where Ln= La, Nd, Ho, Lu. Cerium(IV) was extracted by a similar reaction, but the extracted species presented the $[P_{66614}]_2[Ce(NO_3)_6]$ stoichiometry. Metals loaded onto the organic phase can be stripped with a 0.5 M nitric acid solution. Despite the apparent good characteristics of the ionic liquid, extraction experiments showed that the ionic liquid dissolved in the raffinate, and during the stripping stage also to the acidic strippant solution. It is worth to notice here, that the authors of this investigation considered *leaching* to the process of IL dissolution into the different aqueous phases.

Tri-n-octylamine (R_3N] and octanoic acid (HA) were the precursors of an ionic liquid $[R_3NH^+][A^-]$ which disolved in n-octanol was used for the extraction of REEs (Eu, Y, Tb, Gd) from nitrate medium [35]. Two types of equilibria were responsible for REEs extraction: i) when the initial IL concentration in the organic phase versus the REEs concentration in the organic phase was 3, the reaction was:

$$\mathrm{Ln^{3+}_{aq} + 3NO^-_{3aq} + 3R_3NH^+Cl^-_{\mathit{org}} \leftrightarrow LnA_{3org} + 3R_3NHNO_{3org}} \quad (7)$$

and ii) when the above relationship was 2, the equilibrium responded to the reaction:

$$\mathrm{Ln^{3+}_{aq} + NO^-_{3aq} + 2R_3NH^+Cl^-_{org} \leftrightarrow Ln(NO_3)A_{2org} + 2R_3NHNO_{3org}} \quad (8)$$

These REEs were best extracted at pH 5 and in the presence of $NaNO_3$ in the aqueous solution. At this pH value, the extraction order was Tb=Eu>Gd>Y. Stripping can be accomplished with the use of distilled water, and under five extraction-stripping cycles the extraction efficiency slightly decreased but the stripping one remained almost constant.

The ionic liquid formed by trihexylamine di-2-ethyl hexyl phosphate ($[TAHAH^+][DEHP^-]$) was utilized in the solvent extraction of yttrium(III) from nitrate solutions [36]. As in other studies, the ionic liquid was dissolved in an organic diluent, being n-hexane the diluent used here. Best extraction results were obtain using 0.1 M ionic liquid concentration in the organic phase, 0.2 M sodium nitrate in the aqueous phase, and pH 3, being the yttrium extraction represented by the next equilibrium:

$$Y^{3+}_{aq} + 3NO^{-}_{3aq} + 2[THAH^{+}][DEHP^{-}]_{org} \leftrightarrow Y(NO_3)_3 2[THAH][DEHP]_{org} \quad (9)$$

Yttrium stripping from the Y-loaded organic phase was carried out with 0.1 M nitric acid solution. The extraction of this metal was greatly dependent on the organic diluent used to dissolve the ionic liquid (Table 3). After continuous cycles, this IL also lost its extraction performance: 100% in the first cycle versus 29% in the fifth cycle.

The same ionic liquid than in the previous reference was diluted in kerosene and used in the solvent extraction of Nd(III) [37]. Under different experimental conditions, results indicated that the extraction was pH-dependent, and increased with the increase of the pH value from 1 to 3, and also in the presence of a salt (i.e. $NaNO_3$) in the aqueous feed phase. Neodymium extraction responded to the formation of species with $Nd(NO_3)_3{\cdot}3IL$ stoichiometry in the organic phase. Stripping was best performed with diluted ($2{\cdot}10^{-3}$ M) sulphuric acid solutions. The extraction ability of this ionic liquid also changed with the different diluents used to dissolve it (Table 3). After four cycles of continuous use, the extraction performance of the ionic liquid considerably decreased: 100% in the first cycle and 45% in the fourth cycle.

Table 3. Influence of the organic diluent on the percentages of Y(III) or Nd(III) extraction by trihexylamine di-2-ethyl hexyl phosphate.

Diluent	[a]Y	[b]Nd
n-hexane	73	81
n-heptane	13	86
chloroform	76	41
carbón tetrachloride	96	35
kerosene	97	99

[a]In 0.2 M $NaNO_3$. [b]In 2 M $NaNO_3$. Other experimental conditions: 0.1 M IL in the respective diluent and pH 3. From [36,37].

From results presented in this Table, it is worth to be mention about the use of two toxic (cancerigenous) diluents as chloroform and carbon tetrachloride are. Beside the responsabilities of the respective authors, reviewers of these two references and the corresponding Editor never had allowed the publication of these unsense data.

The ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_{4mim}^{+}][Tf_2N^{-}]$) was used to dissolve tri-n-octylphosphine (TOPO) extractant and used in the solvent extraction of Nd(III) [38]. The extracted species presented a 1:6 Nd:TOPO stoichiometry, with a 45% increase of the extraction percentage, in the presence of the IL, with respect to extractions performed only with TOPO. No stripping data were found in the published manuscript.

This reference presented a system in which Zr(IV) can be separate from Eu(III)/Am(III) as elements representatives of lanthanides and actinides, respectively [39]. The ionic liquid tri(hexyl)tetradecylphosphonium nitrate ($[P_{66614}^{+}][NO_3^{-}]$ was used as extractant, whereas nitric acid solutions formed the feed phase. Zr(IV) was extracted preferably to Eu(III) adn Am(III) in the 1-5 g/L initial metal concentrations range and 3 M nitric acid medium. It was mentioned that 1,3-diisopropyl benzene (another toxic diluent) was used to dilute the ionic liquid, unless the Abstract of the manuscript did not mention this. Another bad praxis of authors, reviewers and Editor of the Journal to allow the publication of a system usign a harmful chemical.

This reference investigated the separation of Th(IV) from uranium and REEs using the ionic liquid tetraphenylethane-1,2-diylbis(phosphoramidate diluted in chloroform [40]. Thus, this is another manuscript that never should have been authorized to be published due to the utilization of this toxic organic diluent in the experimentation.

Nd(III) extraction was investigated by the use of P204 (DEHPA) extractant and the IL tributylhexylphosphonium bis(trifluoromethanesulfonyl)imide $[P_{4446}^{+}][NTf_2^{-}]$ [41]. Under the various experimental conditions used, it was found that the extraction in nitric acid medium favoured metal extraction over the use of HCl solutions; the extraction rate increased with the increase of the aqueous pH value, reaching a maximum efficiency at pH 4; an increase of the temperature also increased the extraction percentage, reaching maximum at 60º C. The apparent role of the IL was to combine with the protons generated during the metal extraction process allowing the continuity of the extraction process. The manuscript did not present stripping results, and some contradictions appeared: i.e. authors concluded that at pH 4, molar ratio (P204:Nd(III)) greater than 5:1 and 20º C, the extraction rate of the system in both HCl and HNO_3 media reached 99.99%, whereas previous results indicated against the above.

The separation of thorium(IV) from cerium(III), (IV) and lanthanum(III) in nitrate solutions was investigated using the quaternary ammonium chloride salt Cyphos® IL-101 [42]. Experimental results showed that at 50 mg/L of the metals in the aqeuous solution and pH 2, the extraction order was Th(IV)>La(III)>Ce(III) with Th/Ce and Th/La separation factors of >5000 and >1000 for the respective systems. At 110 mg/L metals concentration, the extraction order was Th(IV)>Ce(III)>La(III). Cerium(IV) was extracted much better than Ce(III), with results comparable to that of Th(IV). Both Th(IV) and Ce(IV) were extracted by formation of species with $[PR_4^+]\cdot(M(OH)_3(NO_3)_2)^-$ stoichiometry in the organic phase. The extracted metals can be stripped using an EDTA+0.5 M NaCl solution. Experiments carried out on a simulated REEs solution demonstrated that the extraction order was Th>>>Sm>Eu>Nd>Gd>La>Ce(III). The extractant suffered a considerable loss of thorium(IV) extraction efficiency after continuous use: 99% in the first cycle and 46% in the fifth cycle.

The next reference also used solvent extraction with ionic liquids as a procedure to eliminate impurities from REEs solution [43]. In this case, the impurity was aluminium, and the REEs were: La, Ce, Pr, Nd. Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y. The composition of the ILs and some of the results derived from this investigation were shown in Table 4.

Table 4. Composition of the ILs and Al and REEs percentages of extraction and separation factors (SF).

Ionic liquid	Al	REEs	$SF_{Al/REEs}$
Methyltrioctylammonium-neodecanoic acid $[N_{1888}^+][NDA^-]$	80	<1	250
Methyltrioctylammonium-decanoic acid $[N_{1888}^+][DA^-]$	65	<1	175
Methyltrioctylammonium-palmitic acid $[N_{1888}^+][PA^-]$	50	<1	50
Methyltrioctylammonium-lauric acid $[N_{1888}^+][LA^-]$	50	<1	100

The ILs were disolved in n-hexane. From [43].

Best aluminium separation from the REEs reached at an equilibrium pH value of 4.8. After the extraction step, the organic phase was stripped with sulphuric acid solutions, being aluminium completely stripped with the use of a $7\cdot10^{-2}$ M sulphuric acid aolution at O/A ratio of 1. Further, the IL phase was regenerated with a 1 M NaOH solution. The process was demonstrated on a real leach solution (REEs+Al+Ca+Mg).

Cyanex 272 extractant (bis(2,4,4-trimethylpentyl)phosphinic acid) was utilized together with Alamine 336 and Aliquat 336 extractants (trioctylamine and N-methyl-N,N-di-octyloctan-1-ammonium chloride, respectively) to form ionic liquids $[ALA336^+][C272^-]$ and $[Ali^+][C272^-]$, which disolved in a kerosene type diluent, were used to extract Tb(III) from HCl solutions and containing organic acids (see Table 5) [44]. The presence of these organic acids served to complex terbium(II) and help to buffer the solution. In all the case, the percentage of terbium extraction increased with the increase of the pH of the feed solution, reaching best extraction results at pH 5 (Table 5).

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Table 5. Percentages of Tb(III) extraction in the presence of organic acids by [ALA336$^+$][C272$^-$] and [Ali$^+$][C272$^-$] ILs.

Organic acid	[ALA336$^+$][C272$^-$]	[Ali$^+$][C272$^-$]
Formic acid	80	10
Lactic acid	100	10
Fumaric acid	75	75
Maleic acid	90	90

From [44].

As it can be seen from these results, the presence of formic or lactic acids in the aqueous solution had different influence on Tb(III) extraction, since with the IL derived from the quaternary ammonium salt (Aliquat 336), metal extraction was greatly reduced with respect to the presence of fumaric or maleic acids in the solution, effect which was not found when the IL derived from the tertiary amine Alamine 336 was used to extract the rare earth. In fact, with this last IL, maximum Tb(III) extraction was yielded when lactic acid was present in the aqueous solution. These results can be attributed that besides the metal, the organic acids can be extracted by the ILs, and whereas the extraction of formic and lactic acids was less than 10% by [Ali$^+$][C272$^-$], these acids were extracted at an approximate rate of 80% in the case of [ALA336$^+$][C272$^-$]; against the above, fumaric and maleic acids were extracted at 90% or higher rates by both ILs. It was evident, that the co-extraction of the organic acids increased the extraction of terbium(III). At 0.5 M initial acids concentrations and for both ILs, the acids extraction efficiency followed the sequence: maleic>fumaric>lactic>formic. Again, the published manuscript did not include data about the terbium stripping step.

Several ILs ([N_{118H}^+][DEHP$^-$] (N,N-dimethyloctylamine bis(2-ethylhexyl)phosphate), [N_{1110H}^+[DEHP$^-$] (N,N-dimethyldecylamine bis(2-ethylhexyl)phosphate) and [N_{1112H}^+][DEHP$^-$] (N,N-dimethyldodecylamine bis(2-ethylhexyl)phosphate) were formulated and used to separate Nd(III) from Pr(III), La(III) and Ce(III) from aqueous solutions [45]. Prior to the extraction step, the Ils were presaturated with water to decrease the risk of their solubilization in the aqueous phases. Best Nd(III) extraction efficiency was reached at pH 4, ten minutes of contact between the organic and aqueous phases and 30º C; at this pH value, optimal Nd-REEs separation can be reached (Table 6).

Table 6. REE distribution coefficients (D) and Nd/REEs separation factors (SF).

REE	D	SF
Nd(III)	768	-
Pr(III)	286	2.7
Ce(III)	111	6.9
La(III)	56	13.7

Extractant: [N_{118H}^+][DEHP$^-$]. O/A ratio: 1/3. From [45].

It was described, that the extraction of Nd(III) responded to the next equilibrium:

$$\mathrm{Nd}^{3+}_{\mathrm{aq}} + 3\mathrm{Cl}^{-}_{\mathrm{aq}} + 3[\mathrm{N}^{+}_{118\mathrm{H}}][\mathrm{DEHP}^{-}]_{\mathrm{org}} \leftrightarrow [\mathrm{N}^{+}_{118\mathrm{H}}]_3\,\mathrm{Nd}[\mathrm{DEHP}^{-}]_3\mathrm{Cl}_{3\mathrm{org}} \tag{10}$$

Quantitative Nd(III) stripping from metal-loaded organic phases can be reached using a 0.16 M HCl solution. The extractant maintained an extractant efficiency of about 98% after eight cycles.

This reference investigated the same problem, the separation of Nd(III) from La(III)-Ce(III)-Pr(III), that the previous one, but using different ionic liquids [46]. In this case they were based on bis(2-ethylhexyl)phosphate moiety, but here named as [DOP$^-$], whereras the cation moiety was based on 1-methyl-3-ethylhexylimidazole [O_{min}^+], 1-methylpyrrole [H_{mpy}^+] and the previously used N,N-dimethyloctylamine [N_{118H}^+]. Using feed solutions containing 0.017 M $NdCl_3$, 20 min of contact time, 20º C and a IL/aqueous phases volume ratio of 1/5, results indicated that at pH 4, Nd(III) extraction efficiency followed the sequence: O_{mim}>H_{mpy}>N_{118H}. Thus, rare earth was extracted by formation of [O_{mim}^+]$_3$Nd[DOP$^-$]$_3$Cl$_3$ species into the organic phase, whereas the distribution coefficients were D(Nd)= 369, D(Pr)= 48, D(Ce)=27, D(La)= 19, leading to separation factor values of 7.7, 13.7 and 19.4

for the Nd/Pr, Nd/Ce and Nd/La pairs. Stripping can be accomplished by HCl solutions; at 0.3 M HCl, the stripping order was La=Ce>Pr>Nd, but at 0.6 M HCl the stripping efficiency was almost equal (100%) for the four REEs. The ionic liquid showed an extraction efficiency of about 97% after seven cycles. No data were included about what to do with the stripped solution, in order to recover Nd(II). and the purity of the final product.

A waste generated by ion-adsorbed rare earth ore (IATREO) separation plants contained thorium(IV), which needed to be eliminated due to environmental implications, thus, different ionic liquids (Table 7) dissolved in kerosene were used for the elimination of this rare earth from the waste residue leaching solution [47].

Table 7. Ionic liquids used in the extraction of Th^{4+} from waste residue leaching solution.

Ionic liquid	Acronysm
Bis(3,3-dimethyl-2-oxobutyl)dioctylammonium sec-octyl-phenoxyacetate $[OB2DTA^+][CA12^-]$	IL1
Bis(1-ethoxy-1-oxooct-2-yl)dioctylammonium sec-octyl-phenoxyacetate $[EO2DTA^+][CA12^-]$	IL2
(3,3-dimethyl-2-oxobutyl)trioctylammonium sec-octyl-phenoxyacetate $[OBTA^+][CA12^-]$	IL3
(1-ethoxy-1-oxooct-2-yl)trioctylammonium sec-octyl-phenoxyacetate $[EOTA^+][CA12^-]$	IL4

From [47].

In a simulated solution of pH 3, Th^{4+} extraction followed the IL1=IL2>IL3>IL4 order, it was also noted that the addition of tributylphosphate (TBP) or isoocty alcohol to the system improved phase separation. A 0.2 M HCl solution stripped thorium, and again, the presence of the above two modifiers improved the stripping efficiency in the case of IL1 and IL 2 extractants. From the real waste leach solution, thorium was separated after two extraction stages with minimal loss of the rest of REEs of about 15 mg/L. From the raffinate, these REEs can be recored by oxalate precipitation to form $RE_2(C_2O_4)_3$ salts, whereas from the stripped solution and after pH adjustement, thorium was recovered by precipitation as $Th(OH)_4$.

Thorium(IV) was again the target to be extracted by solvent extraction in this case using dimethyl distearyl ammonium chloride $[DMDSA^+][Cl^-]$ (and ionic liquid itself) and N,N-dialkyl-succinamide acid (R-SCA, alkyl chains: n-butyl, n.hexyl or n-octyl)), which formed different $[DMDSA]^+[R\text{-}SCA]^-$ ionic liquids [48]. These ILs were dissolved in different diluents and the extraction of Th^{4+} followed the next sequence: n-hexadecane>n-tetradecane>n-dodecane>n-decane>kerosene>n-decylalcohol. Also, the presence of sodium nitrate in the aqueous solution improved the extraction of the rare earth. After the extraction at 8 M nitric acid, near 99% of thorium (IV) immediately aggregated into self-assembly solid at the interface between the ionic liquid and raffinate phases, though apparently, in the extraction process some thorium was released to the raffinate as $Th(NO_3)_5^-$. The extraction mainly responded to the formation of $[SCA\cdot Th(NO_3)_4^-]$ species, and using a 0.01 M $[DMDSA^+][DOSCA^-]$ (dimethyl distearyl ammonium N,N-dioctyl-succinamidate) in n-hexadecane solution and 8 M HNO_3 concentration in the aqueous feed phase, the separation factor values of 2516, 1885, 558 and 1512 were experimentally found for the Th/U, Th/La, Th/Lu an Th/Eu pairs. No mention of how thorium was recovered from the solid and what was the fate of the ionic liquid in this recovery.

The purification of Gd(III) from Al(III) impurities is of interest, and solvent extraction was used to perform this purification [49]. In this case, different ionic liquids, diluted in sulfonated kerosene, and based on the methyltrioctylammonium ($[N_{1888}^+]$ cation and various carboxyl groups (Table 8) as counter-ions were investigated to perform this task.

Table 8. The various carboxylic acids used in the extraction of Al(III) from Al/Gd solutions.

Carboxylic acid	Derived anion	[a]Al	[a]Gd
Cyclopentaneacetic acid	$C_7H_{11}O_2^-$	75	11
Heptanoic acid	$C_7H_{13}O_2^-$	60	18
3-cyclopentylpropionic acid	$C_8H_{13}O_2^-$	60	10
n-octanoic acid	$C_8H_{15}O_2^-$	55	25
3-cyclohexanepropionic acid	$C_9H_{15}O_2^-$	57	30
Nonanoic acid	$C_9H_{17}O_2^-$	58	20

[a]Percentages of extraction. From [49].

The above Table also presented some results relative to the extraction of these elements from the binary Al/Gd solution. At the initial conditions of 0-1 M ionic liquid, 0.01 M (each) Al and Ga, pH 1.50, and 25º C, highest Al/Gd separation factor was obtained with $[N_{1888}^+][C_7H_{11}O_2^-]$ ionic liquid, though the increase of the temperature in the 25-75º C range was accompanied by a decrease in the separation factor value. Both elements (M) were extracted by the same speciation of 1:3.3:3 ($M:N_{1888}:C_7H_{11}O_2:Cl$). Stripping was accomplished by the use of HCl solutions. It is worth to note here, that after all this investigation a subsection in the published manuscript mentioned about the formation of a third phase (or second organic phase) in the system, this third phase was eliminated by addition of iso-octanol to the organic phase, however, this addition sharply decreased aluminium extraction efficiency (5% alcohol resulted in 36% efficiency, 15% alcohol in 9.55% efficiency). The authors of the manuscript did not mention if all the previous investigations were perform in the presence of this alcohol. If not, and all the experimentation were carry out in conditions of third phase formation, the data has not any value because a solvent extraction system presenting a third phase is simply useless, sic*: its (third phase) presence must to be avoided like the plague* [50]. Thus, this manuscript is doubtful, and again the reviewers and the Editor has their responsabilities to allow the publication of the manuscript in its present form.

Gd(III) was extracted by 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) using $[C_1C_nim^+][NTf_2^-]$ (n= 4 or 10) ionic liquid [51]. The investigation compared conventional solvent extraction procedure (aqueous and organic phases) with the use of two inmiscible organic phases. Under this system, Gd^{3+} appeared in the more polar phase (MP, ethylen glycol), whereas the phase containing the ligand and the ionic liquid formed the less polar phase (LP). In this system, the extraction of the REE at an initial pH value of 3.3 responded to the equilibrium:

$$Gd^{3+}_{MP} + \frac{1}{2}HP_{LP} + n[NTf_2^-]_{LP} \leftrightarrow Gd(P)^{2+}_{\frac{1}{2}} \cdot (NTf_2^-)_{nLP} + H^+_{MP} \quad (11)$$

with no transfer of $[C_1C_nim^+]$ to the ethylen glycol phase. If the extraction occurred in a conventional Gd(III)-aqueous and organic phases solvent extraction system, the extraction equilibrium responded to the formation of $GdP^{2+}\cdot(NTf_2^-)_n$ species in the organic phase, releasing protons and $[C_1C_nim^+]$to the aqueous phase or raffinate. In the ethylen glycol medium, neither La(III) nor Ce(III) were extracted into the organic phase, whereas Lu(III) was extracted with an efficiency greater than 50%, and Eu(III and Gd(III) only in the presence of the ionic liquid in this LP phase. In the system involving aqueous and organic phases, Ce(III) was not extracted, La(III) with an efficiency lower than 50% and in the presence of the ionic liquid, and Eu(III, Gd(III), and Lu(III) with efficiencies greater than 50%. No stripping data were included in the published manuscript. .

Europium(III) was extracted by mixtures of the acidic chelating compounds thenoyltrifluoroacetone (HTTA), 4-benzoyl-3-methyl-1-phenyl-pyrazol-5-one (HP) or 4-bemzoyl-3-phenyl-isoxasol-5-one (HPBI) and *meso*-hexamethylpropyleneamine oxime (HM-PAO) or its bis-imine precursor (pre-HM-PAO) [52]. Also the effect of the presence of the presence of different ionic liquids as $[C_1C_nim^+][NTf_2^-]$ (n= 4,6,8,10) or $[C_1C_4pyr^+][NTf_2-]$ (1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide) on the extraction of the REE was investigated. When the organic phase contained HTTA a strong synergism effect on Eu(III) extraction was observed, and HM-PAO was more effective than pre-HM-PAO. Using HPBI ligand, the nature of the IL favoured the extraction of the metal in the series: $n=10>8>6>4>C_1C_4pyr^+$. The manusript did not include stripping data.

The amide derivative 4-chloro-N-(1-methyl-1H-pyrazol)-3-yl)picolinamide (L) dissolved in two ionic liquids: 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_{6mim}^+][NTf_2^-]$) or 1-hexyl-3-methylimidazolium bromide ($[C_{6mim}^+][Br^-]$) was used to extract Eu^{3+} from nitric acid solutions [53]. Preliminary tests showed that in the presence of the ionic liquid containing $[NTf_2^-]$ anion the ligand L was more effective with respect to the extraction of the rare earth element, thus, further investigation used only this IL to dissolve the amide derivative. This rare earth was extracted by a cation exchange mechanism and formation of $Eu(L)_3(NO_3)_2^-$ species in the organic phase, and the same species also coordinated with one water molecule. In the extraction process, the ionic liquid cation ($[C_{6mim}^+]$ was transfered to the aqueous solutions for charge compensation. The increase of the temperature decreased the IL viscosity but extraction efficiency also decreased. Stripping was accomplished by 0.05 EDTA and 1 M guanidine carbonate solutions. The manuscript did not mention how the IL was regenerated and what to do with the europium-loading stripped solution.

These series of references [54-56] investigated the extraction of lanthanides using the extractants showed in the next Table 9. Studying these references, it can be concluded that the data has not practical interest since the diluent used in the investigation is highly toxic, the same can be extended to the results derived from the utilization of nitrobenzene, chloroform and 1,2-dichloroethane using TODGA plus ILs in the extraction of the lanthanides. In the case of the system formed by 0.1 M TODGA plus 0.01 M $[N1888^+][NTf_2^-]$ best extraction results, in comparison with the n-nonane plus TBP mixture, were obtained when 1-octanol was used as diluent of the organic phase, being the extraction sequence as Er,Tm,Yb,Lu>Ho>Dy>Th>>Eu=Gd>Sm>Nd>Pr>Ce>La. The extraction responded to a cation exchange mechanism with formation of $Ln(TODGA)_6(NTf_2)_3$ species in the organic phase and releasing of $N1888^+$ ions to the aqueous phase. It was mentioned that stripping was performed with 0.1 M 1-hydroxyethane-1,1-diphosphinic acid aqueous solution, though no more data were given in the manuscript, also it was not mentioned how the lanthanides were recovered from the stripped solution.

Table 9. Several ligands used in the extraction of lanthanides.

Ligand	IL	Remarks	Reference
1,2-bis(diphenylphosphinyl)-ethane or 1,2-bis(diphenylphosphinyl)benzene	$[C_{4mim}^+][NTf_2^-]$	Use of toxic H_2CCl_2 as diluent	54
tetraoctyldiglycolamide	$[N_{1888}^+][NTf_2^-]$	[a]Use of 1-octanol or n-nonane and 1.1 M TBP as diluents	55
tetraoctyldiglycolamide	$[TOAH^+][NTf_2^-]$	[b]Use of dodecane:1-octanol (9:1 %v/v) mixture as diluent	56

$[C_{4mim}^+][NTf_2^-]$: 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide. $[N_{1888}^+][NTf_2^-]$: methyltrioctylammonium bis(trifluoromethanesulfonul)imide. $[TOAH^+][NTf_2^-]$: {trioctylammonium bis[(trifluoromethyl)sulfonyl]imide. [a]Other diluents used: nitrobenzene, chloroform, 1,2-dichloroethane. [b]Other diluents used: chloroform, 1,2-dichloroethane. From [54-56].

In the case of the system using TODGA and $[TOAH^+][NTf_2^-]$, the extraction sequence was the same that showed above. In this system, the extraction responded to the formation of $Ln(TODGA)_3(NO_3^-)(NTf_2^-)_2$ species in the organic phase and formation of $[TOAH^+][NO_3^-]$ ionic liquid in this same phase. At high nitric acid concentrations the formation of this new ionic liquid was favoured and the extraction of all the lanthanides, but luthetium decreased with respect to the values obtained from dilute nitric acid solutions. The role of TBP and 1-octanol in the respective previous references was to act as modifiers to avoid the formation of the undesirable third phase after phase disengagement in the extraction step. No stripping data were included in this last reference. As we are repeating along this work, the reviewers and Editors of the respective references never should allowed the +

Column experiments were developed to investigate the influence of an ionic liquid on the extraction of dysprosium [57]. The organic phase was formed by 1% *v/v* D2EHPA (di-(2-ethylhexyl) phosphoric acid) in tri-butylphosphate (TBP) and the ionic liquid. $[C_{6mim}^+]$ $[NTf_2^-]$. The presence of the ionic liquid in the organic phase enhanced the physical properties of the system in comparison to when this ionic liquid was not present in the organic phase. Furthermore, the presence of the ionic liquid diminished the interfacial tension, resulting in a decrease in Sauter mean diameter and an increase in the holdup of the dispersed phase, as well as the extraction of dysprosium. The most effective conditions for extracting Dy(III) ions from an aqueous solution were observed at a rotation speed of 359 rpm, with a solvent stream rate (Qd) of 30 L/h and an aqueous solution stream rate (Qc) of 28 L/h. Dysprosium was extracted by a cation exchange reaction with D2EHPA.

Utilizing trihexylammonium octonoate and trioctylammonium myristrate pseudo-protic ionic liquid as extractants, this investigatin showed the impact of the Hofmeister effect and the Van 't Hoff – LeChatelier effect on the extraction of cobalt and neodymium from aqueous phases [58]. A high driving force is required from the Hofmeister effect or from both effects simultaneously to successfully increase the extraction of cobalt (more than tenfold). Lower driving forces are sufficient to the increase the extraction of neodymium (up to 100 %). No stripping data included in the work.

Quaternary ammonium based ILs (QA-ILs), i.e., $[N_{333}MeOAc^+][NTf_2^-]$ (N,N,N,-tripropyl-1-methylacetate ammonium bistriflimide) and $[N_{444}MeOAc^+][NTf_2^-]$, (N,N,N,-tributyl-1-methylacetate ammonium bistriflimide) have been synthesized and dissolved in chloroform for selective Sc(III) extraction from other REEs [59]. Both ILs are selective respect to the separation of Sc(III) from other REEs, though, the selectivity Sc/Lu and Sc/Yb is greater when $[N_{444}MeOAc^+][NTf_2^-]$ is used. Specifically, at pH 4.5 and 5, the extraction efficiency of Sc(III) using $[N_{333}MeOAc^+][NTf_2^-]$ was 73.6 % and 83.4 %, respectively, while it was high up to 90.5 % and 95.9 %, respectively, using the former extractant. These ILs can be recycled with a high stripping efficiency up to 86 % using 4 M H2SO4 solution. The above information has not value since the ILs are dissolved in harmul chloroform. Thus, the manuscript should not have been published.

An organic phase containing N,N,N′,N′-tetra-(2-ethylhexyl)diglycolamide (T2EHDGA) diluted in the ionic liquid trihexyl(tetradecyl)phosphonium nitrate (Cyphos nitrate: $[P_{66614}^+][NO_3^-]$) was used to investigate the extraction of Eu(III) from aqueous solutions [60]. Results showed an increasing in the REE extraction with an increase in the aqueous acidity followed by the attainment of a plateau region at higher acid concentration (Table 10).

Table 10. Effect of nitric acid concentration in the feed phase on Eu(III) extraction.

$[HNO_3]$, M	% Extraction
0.5	50
1	85
3	95
5	99
6	99
8	99

Feed phase: nitric acid spiked with $^{(152+154)}$Eu(III) tracer. Organic phase: 0.1M T2EHDGA and Cyphos nitrate. Equilibration time: 1 hour. Temperature: 25º C. O/A ratio: 1. From [60].

In the absence of T2EHDGA, the ionic liqud did not extract the rare earth, thus, the extraction of europium(III) was due to the next equilibrium:

$$\mathrm{Eu_{aq}^{3+} + 3NO_{3aq}^{-} + 2T2EHDGA_{org} \leftrightarrow Eu(NO)_3 \cdot 2T2EHDGA_{org}} \quad (12)$$

The mixture of T2EHDGA/$[\mathrm{P}_{66614}^{+}][\mathrm{NO}_3^{-}]$ was implemented on the extraction of Fast Reactor Simulated High Level Liquid Waste (FR-SHLLW) solution spiked with Am(III) and the results were promising with respect to efficacy of the proposed IL phase. All the trivalent Ln(III) and Am(III) were selectively separated from some of the co-extracting fission products using a suitable holding agent in the feed phase. The present investigation uses dilute nitric acid (pH 2) as the stripping agent.

Two hydrophobic carboxylic acid ionic liquids, namely, lauryl betaine bis(trifluoromethanesulphonyl)imide ($[\mathrm{Laur}^{+}][\mathrm{NTf}_2^{-}]$) and cocamidopropyl betaine bis(trifluoromethanesulphonyl)imide ($[\mathrm{Coca}^{+}][\mathrm{NTf}_2^{-}]$), were synthesized and used in the extraction of Sc(III) [61]. The best extraction conditions were 40 min (equilibrium), initial Sc(III) concentration of 0.001 M, sodium nitrate concentration of 0.5 M, and pH of 3. The extraction efficiency for the above ILs could even exceed 98.7% and 96.0%, respectively. Both ILs extracted Sc(III) why a cation exchange mechanism, though the stoichiometry of the extracted species differed from one IL to the other:

$$\mathrm{Sc}^{3+}_{\mathrm{aq}} + 3([\mathrm{Laur}^{+}][\mathrm{NTf}_2^{-}])_{\mathrm{org}} \leftrightarrow \mathrm{Sc}([\mathrm{Laur}^{+}][\mathrm{NTf}_2^{-}])_{3\mathrm{org}} + 3\mathrm{H}^{+}_{\mathrm{aq}} \tag{13}$$

$$\mathrm{Sc}^{3+}_{\mathrm{aq}} + 2([\mathrm{Coca}^{+}][\mathrm{NTf}_2^{-}])_{\mathrm{org}} \leftrightarrow \mathrm{Sc}([\mathrm{Laur}^{+}][\mathrm{NTf}_2^{-}])_{2\mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}} \tag{14}$$

From the respective organic phases (eqs. (13) and (14), Sc(III) is completely stripped with 0.1 M and 0.2 M $\mathrm{HNO_3}$ solutions. The extraction differences at different pH levels made it possible to separate Sc(iii) from other rare earths using both ionic liquids. Best Sc/Lu separation factor (238) is obtained with the lauryl betaine-bearing IL and pH 2, whereas in the case of the pair Sc/La, this IL also presented the best separation since La(III) is not extracted into the organic phase. Comparatively, the separation factors using $[\mathrm{Coca}^{+}][\mathrm{NTf}_2^{-}]$ are 30.5 an 41.4 for the pairs Sc/Lu and Sc/La, respectively.

A series of bifunctional ionic liquids with methyltrioctylammonium as the cation and o-alkoxybenzoic acetate as the anion were synthesized [62], and dissolved in sulfonate kerosene, to investigate the separation of rare earth and transition metal for NdFeB waste recycling. It was found, that 0.12 M methyltrioctyl ammonium o-octyloxybenzoic acetate ($[\mathrm{N}_{1888}^{+}][\mathrm{OOB}^{-}]$) solutions in kerosene could preferentially extract rare earths in preference to Fe and Co. The extraction sequence being: Dy>Nd>Pr>>Fe>Co, and whereas the extraction increased with the increase of the initial pH value in the 2.02-2.92 range (equlibrium pH values in the 4.20-4.96 range), at the limiting pH value of 2.92, the extractability follows the sequence: Dy>>Nd>Pr>Co>Fe. The extraction mechanism of rare earth with the IL responded to an ion association in a molar ratio of 2:1 (IL:RE):

$$\mathrm{RE}^{3+}_{\mathrm{aq}} + 3\mathrm{Cl}^{-}_{\mathrm{aq}} + 2\mathrm{IL}_{\mathrm{org}} \leftrightarrow \mathrm{RECl}_3 \cdot 2\mathrm{IL}_{\mathrm{org}} \tag{15}$$

The rare earth loaded onto the organic phase is selectively stripped with deionize water. Against it was mentioned in the title of the published manuscript, all the investigation was carried out using synthetic solutions, and not solutions from NdFeB magnet.

Various functionalized ionic liquids were formulated to investigate its performance in the separation of yttrium from heavy rare earth elements [63]. Extractions were carried out dissolving the ionic liquid in kerosene. The results show that [N16MOP][HDA] is the best extractant to separate Y from the other REEs, achieving a Ho/Y separation factor of 2.82. The formation of a third phase (or second organic phase9 makes it necessary the use of a modifier. Both iso-octanol and tri-butylphosphate are investigated in this role, and whereas the presence of the alcohol tends to decrease metal extraction, the presence of the phosphoric ester derivative in the organic phase, eliminated the third phase and enhanced the metal extraction. This enhancement is attributable to a synergistic effect. Taking Ho(III) as example, the extraction mechanism responded to an ion pair association:

$$\mathrm{Ho}^{3+}_{\mathrm{aq}} + 3\mathrm{Cl}^{-}_{\mathrm{aq}} + 2([\mathrm{N}_{16}\mathrm{MOP}^{+}][\mathrm{HDA}^{-}]_{\mathrm{org}} \leftrightarrow ([\mathrm{N}_{16}\mathrm{MOP}^{+}][\mathrm{HDA}^{-}])_2\mathrm{HoCl}_{3\mathrm{org}} \tag{16}$$

Complete stripping of the loaded rare earth elements (REEs) can be achieved using 0.1 M HCl solution. An industrial solution containing: La-Dy (23 mg/l), Y (1 g/L), Ho (35.8 mg/L), Er (0.11 g/L), Tm (27.2 mg/L), Yb (0.16 g/L), Lu (19 mg/L), Fe (0.4 mg/L), Cu (0.6 mg/L), Ca (0.2 mg/L) (adjusted at pH 4) was extracted with an organic phase of 0.013 M of the ionic liquid + 15% *v/v* TBP in kerosene, the values of the separation factors of 2.52, 3.31, 4,22, 6.43 and 5.05 were obtained for the respective pairs Ho/Y, Er/Y, Tm/Y, Yb/Y and Lu/Y.

An ionic liquid ($[N_{1888}^{+}][NA^{-}]$) was synthesized from methyltrioctylammonium chloride ($[N_{1888}^{+}]Cl^{-}$) and industrial naphthenic acid (NA) for the purification of Al^{3+} from $GdCl_3$ solution [64]. Under the experimental conditions, the extraction properties of diluted ionic liquid in kerosene, diluted NA and saponified NA were comparatively investigated and the separation factors Al/Gd were 23.0, 3.5 and 1.3, respectively. In the case of the ionic liquid, the extraction responded to the next equilibrium:

$$\mathrm{M_{aq}^{3+} + 3Cl_{aq}^{-} + IL_{org} \leftrightarrow MCl_3 \cdot IL_{org}} \tag{17}$$

Near quantitative aluminium stripping efficiency is obtained using 0.3 M NaOh or HCl solutions as strippants. On an industrial $GdCl_3$ feed, aluminium impurity was lowered from 889 mg/L to 5 mg/L. The removal efficiency of Al was 99.4%, and the purity of Gd was 99.998%.

The separation of Nd from Co and Ni using a pseudo-protic ionic liquid formed from the reaction of lauric acid (LA) and the primary amine N1923 (RNH2) was investigated [65]. This ionic liquid ($[RNH_3^{+}][RCOO^{-}]$) was diluted in sulfonated kerosene, and again the use of a modifier (iso-octanol) was mandatory to avoid the formation of a third phase. The increase in iso-.octanol concentration in the 5-25% *v*/*v* range slightly decreased the extraction of the rare earth element. Effective separation of Nd from Co and Ni can be achieved, with separation factors of 1503 and 2762 for the pairs Nd/Co and Nd/Ni, respectively. The next equilibrium was responsible of neodymium extraction:

$$\mathrm{Nd_{aq}^{3+} + 3Cl_{aq}^{-} + 2IL_{org} \leftrightarrow NdCl_3 \cdot 2IL_{org}} \tag{18}$$

$Na_2C_2O_4$ and water were used as strippants in respective first and second steps, respectively, Further, the Nd-oxalate solid was roasted, yielding a product of 99.97% wt% Nd purity. In the treatment of a leachate (1 g/L La, 92.9 mg/L Ce, 18.8 mg/L Pr, 0.3 g/L Nd, 0.25 g/L Co, 1.9 g/L Ni and 0.21 g/L Mn) derived from the treatment of NiMH battery alloy, REEs are extracted preferably to base metals (Table 11).

Table 11. Metal distribution ratios (D) in the extraction of a NiMH battery alloy leachate with $[RNH_3^{+}][RCOO^{-}]$.

Element	D
La	15
Ce	quantitative extraction
Pr	quantitative extraction
Nd	125
Co	0.049
Ni	0.070
Mn	0.028

From [65].

The ionic liquid [N-methyl-N,N-dioctyloctan-1-aminium][2-(bis(2-ethylhexyl)amino)-2-oxoacetate] ($[N_{1888}^{+}][DEAO^{-}]$) dissolved in kerosene was used to investigate the separation of thorium from a series of rare earth elements [66]. Best separation Th/REEs was achieved at a pH of 2.4 and in absence of a salt (NaCl) in the feed solution. With a maximum loading capacity of 1.02 g/L Th in a 0.04 M ionic liquid in kerosene organic phase, the extraction equilibrium was represented by the equation:

$$\mathrm{Th_{aq}^{4+} + 4Cl_{aq}^{-} + 4([N_{1888}^{+}][DEAO^{-}]_{org} \leftrightarrow ThCl_4 \cdot ([N_{1888}^{+}][DEAO^{-}]_{4org}} \tag{19}$$

A mixture of saturated NaC_2O_4 and 1.5 M NaOH solution was used as strippant.

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3. Using ionic liquids and rare earth elements in the development of advanced materials

Different investigations used the properties of the ILs as a medium, or taking part, in the manufacturing of REEs materials with diverse uses. Next, some of these recent usages are reviewed.

The couple formed by Er(III) and 1-Butyl-methylimidazolium trifluorometahne sulfonate ionic liquid ($[B_{mim}^+][TFO_-]$) was used to the separation of the pair ethane/ethylene (C_2H_6/C_2H_4) [67]. However, the system needed the addition of dimethylformamide (DMF) to decrease both the density and the viscosity of the IL, at the same time this DMF not only served as diluent but also it was found that there was a strong interaction between Er^{3+} ions and DMF resulting in a greater amount of Er^{3+} to be complexed with ethane. Best ethane/ethylene separations was obtained in the $[B_{mim}^+][TFO^-]/Er(TFO)_3$ plus 20 wt% DMF system at 1+1 molar ratio. Gas-desorption was carried out at 30º C and 0.1 KPa during one hour, and continuous use showed a constant ethane adsorption after five cycles.

Lanthanum doped-graphene oxide functionalized with imidazole- or imidazolium-based benzothiadiazole ligands were use as fluorescent biosensors to the detection of cholesterol by colorimetric procedures [68]; for the above task, ChOx (cholesteroloxidase) enzyme was immobilize onto the various materials. Results showed that not all the compositions performed equally, summarizing Table 12 the limiting detections yielded by some of these derivatives.

Table 12. Response in cholesterol detection of GO-La based biosensors.

Response	Biosensor+ChOx	Sensitivity, a.u.dL/mg
Best	GO-La:BTDIm (1:1)	0.0649
Poor	GO-La:BTDAc (1:1)	<0.0602

Linear range of detection: 0.06-5.83 mg/dL range of colesterol concentrations: BTDIm: 4,7-Bis-(imidazol-1-yl)-2,1,3-bezothiadiazole. BTDAc: 4,7-bis-[1-carboxymethyl-(imidazol-3-ium)]-2,1,3-benzothidiazole chloride. From [68].

The next reference investigated about the formation of neutral betaine species during the formation of protonated betaine bis(trifluoromethylsulfonyl)imide ($[HBet^+][[NT_2^-]$) ionic liquid [69]. This IL was widely used in the extraction of metals (including REEs), being synthesized by anion exchange reaction between $[HBet^+][Cl^-]$ and $[Li^+]$ $[NTf_2^-]$ (two ionic liquids themselves); during this synthesis, the next reaction occurred:

$$\mathrm{HBet}_{\mathrm{aq}}^{+} + \mathrm{H_2O} \leftrightarrow \mathrm{Bet}_{\mathrm{aq}} + \mathrm{H_3O^+} \qquad (20)$$

and thus, a neutral zwitterionic betaine was formed due to the deprotonation of the carboxylic group of betaine. The above resulted in a loss of effectiveness to extract metals. It was concluded that due to the reaction showed in eq.(12), acid must be added after the ion exchange process responsible for the formation of the IL, this acid addition served to promote the complete protonation of betaine allowing to reach maximum REEs (and metals) extraction.

Al_2O_3/FeAl coatings doped with Er_2O_3 were prepared on CLAM steel by an electrochemical deposition in ionic liquids and ion injection [70]. The procedure to fabricate these materials was based in that CLAM steel samples working as anodes were electrochemically etched and being aluminium coating deposited in 1-ethyl-3-methylimidazolium chloride ionic liquid and aluminium chloride (1:2 molar ratio) medium. After, the erbium atoms were injected into the aluminium layer at room temperature. Following the corrosion experiments in liquid Pb-15.7Li at 550º C and treatment during a thousand hours, and against the results observed from the steel without the presence of the rare earth, it was found that the steel with the surface of the coating doped with erbium oxide was smooth and uniform with a minor quantity of corrosion products.

In all-solid-state lithium-ion batteries with high energy densities, the substitution of the organic liquid electrolytes by perovskite-type $Li_{0.33}La_{0.56}TiO_3$ (LLTO) presented a series of advantages [71]. To improve the properties of this LLTO, 1-butyl-3-methylimidazolium tetrafluoroboarte ionic liquid ($[BMIM^+][BF_4^-]$) was used. The presence of the ionic liquid enhanced the total conductivity of the hybrid electrolyte, with a maximum $4\text{-}7{\cdot}10^{-4}$ S/cm at an IL concentration of 12.5 wt%. This characteristic was attributable to the coupling of the ionic liquid with Li^+ improving patwhays for the migration of these ions across the boundaries resulting in a decrease of the activation energy.

Ring-opening-copolymerization (ROCOP) of epoxydes and cyclic anhydrides to produce aliphatic polyesters needed of i.e. carboxylic salts to actuate as active catalysts [72]. The presence of lanthanides salts improved the actuation of these catalysts, thus, from the use of trihexyltetradecylphosphonium chloride ionic liquid $[H3DP^+][Cl^-]$ several compositions IL-$LnCl_3$ (Ln= Gd, Nd, Ho, Y) were tested. Two routes for the synthesis of these products were followed: i) at 95º C and wet formation of $LnCl_3{\cdot}6H_2O{\cdot}4[H3DP^+][Cl^-]$, and ii) at room temperature and using water and dichloromethane with dry formation of $LnCl_3{\cdot}4[H3DP^+][Cl^-]$. After the sysnthesis, all the products were dried at 50º C prior to its use. Best results, with respect to the cycloaddition process, were obtained when dry-dichloromethane monomers were used and in the presence of YCl_3.

Several lanthanide-bearing paramagnetic ionic liquids, $[C_1C_nim^+]_3[LnCl_{3\times3}^{3-}]$ (n = 4, 6, 8; Ln = Dy, Gd, and Ho; X = Cl or Br), were sinthesized and characterized [73]. All of these PILs presented the properties expected to their conditions of ILs plus significant magnetic susceptibility (Table13).

Table 13. Volume magnetic susceptibility of some of the synthesized PILs.

PILs	$X{\cdot}10^{-4}$	PILs	$X{\cdot}10^{-4}$
$[C_1C_8im^+]_3[HoCl_6^{3-}]$	1.759	$[C_1C_4im^+]_3[HoCl_3Br_3^{3-}]$	1.752
$[C_1C_8im^+]_3[DyCl_6^{3-}]$	1.425	$[C_1C_4im^+]_3[DyCl_3Br_3^{3-}]$	1.650
$[C_1C_8im^+]_3[GdCl_6^{3-}]$	1.014	$[C_1C_4im^+]_3[GdCl_3Br_3^{3-}]$	1.011

From [73].

As a general rule, susceptibilities followed the order Ho>Dy>Gd, whereas in the case of $LnCl_3Br_3^{3-}$ bearing PILs the corresponding susceptibility depended on the alkyl chain of the PIL cation and decreased in the $C_4>C_6>C_8$ order. These PILs presented potential applications in diverse areas including, biomedicine, mass transfer, magnetic resonance imaging, and environmental remediation.

A β-diketone, (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD)), was used to investigate its coordination with Ln(III) (Ln= Nd, La, and Eu) in the presence of different methylimidazolium-based ionic liquids $[C_nmim^+][NTf_2^-]$ (n=4,6,8) [74]. Two complexes were formed with $Ln(HFOD)_2^+$ and $Ln(HFOD)_4^-$ stoichiometries (Ln= Nd, Eu) and characterized, further, density functional theory calculation was carried out to optimize the structural parameters such as bond angles and distances, and energies associated with the formation of the respective complexes. The investigations concluded that the formation of the complexes responded to an anion exchange reaction which released NTf_2^- species to the aqueous phase.

A series of phosphors doped with REEs, $Lu_7O_6F_9$ (REEs= Eu,Gd,Yb,Er) were synthesized in 1-octyl-3-methylimidazolium tetrafluoroborate ($[O_{mim}^+][BF_4^-]$) ionic liquid medium [75]. In the process of growth of the precursors, water penetrated in the IL and BF_4^- hydrolized according to:

$$BF_4^- + H_2O \rightarrow BF_3 \cdot H_2O + F^- \tag{21}$$

and fluoride ions reacted with the REEs to form $REEF_3$ compounds. It was described that the role of the ionic liquid was to act as solvent, fluorine source, shape control agent and cristal phase regulator. $Lu_7O_6F_9{:}10\%Yb^{3+},1\%Eu^{3+}$ phosphors presented intense pure red luminiscence, whereas Gd^{3+}, Eu^{3+} co-doped phosphors showed bright emissions, high thermal stability and paramagnetic properties.

Using as precursors $[C_nmim^+][NO_3^-]$ and RE nitrate salts (RE= Ho,Er,Tm,Yb,Lu), several ionic liquids with $[C_nmim^+]_2[RE(NO_3)_5^{2-}]$ formulation was formed, also it was described the formation of $C_{12}H_{22}N_9O_{15}RE$ crystals [76]. These various ionic liquids presented properties which can be used in the development of soft materials with tunable optical transparency and light scattering.

In this reference [77], 1,3-bis(1-dicarboxylatoethyl)imidazolium bromide ($[H2bcei^+][Br^-]$ ionic liquid was used for the formulation, *via* a solvothermal procedure, of two lanthanide metal organic frameworks (LnMOFs): $Er_2[(C_9N_2O_4H_{11})_3(H_2O)Br]Br{\cdot}Cl\}_n$ and $Yb_2[(C_9N_2O_4H_{11})_3(H_2O)_{2]}Br{\cdot}Cl_2\}_n$. The synthesis of these compounds was dependent on the amount of NaOH used, temperature, type of organic solvents and their volume ratios, these variables influenced the morphology and the single cristal growth of the corresponding MOF. [bcei$^+$] ligand adopted one bridging bidentate coordination mode to bond to Er and Yb. At 700º C both MOFs decomposed and Er_2O_3 and Yb_2O_3 were formed. These two MOFs possesed stability, water solubility and various properties, which made of them candidates to be used in i.e. catalysis and biomedicine. Moreover, the,Yb-MOF presented antiferromagnetic interaction.

In order to improve a sustainable chemical industry, the direct synthesis of dimethyl carbonate (DMC) from renewable carbon dioxide (CO_2) and methanol (MeOH) is studied using CeO_2 nanoparticles modified with the ionic liquid (IL) 1-butyl-3-methylimidazolium hydrogen carbonate ([BMIm$^+$][HCO_3^-]) [78]. The synthesized CeO_2@IL catalyst presented various DMC yields and methanol conversions depending of the temperature and pressure (Table 14), with the optimal conditions described as: pressure of CO2 of 5 MPa; temperature of 130 °C).

Table 14. Effect of temperature and pressure on MeOH conversion and DMC yield.

Temperature, ºC	%conversion	%yield	Pressure, MPa	%conversion	%yield
80	3	2	1	2	<1
100	8	5	2	6	2
120	15	8	4	11	7
130	16	10	5	16	10
140	16	10	6	16	10

Operational conditions: 50 mg catalyst. 26.5 mM methanol. 6 hours. Temperature experiments at 5 MPa CO_2. Pressure experiments at 130º C. From [78].

The catalytic behavior of CeO_2@IL] suggests that the synergy between the two catalytic components originating from an increased surface oxygen vacancies boosts the overall catalytic performance. After several recycling tests, the catalyst demonstrated no significant reduction in DMC yield and methanol conversion.

One approach to enhance the catalytic activity of metal organic frameworks (MOFs) in CO_2 cycloaddition reactions is to create open metal sites within MOFs [79]. Thus, the amino-functionalized rare earth Gd-MOF (Gd-TPTC-NH_2) and its ionic liquid composite catalysts (Gd-TPTC-NH-[B$_{MIM}^+$][Br$^-$]) were synthesized using 2′-amino-[1,1′:4′,1″-terphenyl]-3,3″,5,5″-tetracarboxylic acid (H_4TPTC-NH_2) as the ligand. Under the optimized reaction conditions of temperature and catalyst dosage, Gd-TPTC-NH-[B$_{MIM}^+$][Br$^-$] can effectively catalyze the cycloaddition reaction of a variety of epoxide substrates with promising yields of cyclic carbonate products. Comparatively, epichlorohydrin and epibromohydrin, which possess halogen substituents, promote higher yields of cyclic carbonates due to the electron-withdrawing nature of Cl$^-$ and Br$^-$ substituents.

CeO_2 (a widely used abrasive) can be synthesized via coprecipitation, hydrothermal, and solvothermal methods. To overcome some issues encountered within these syntheses, an ionothermal synthesis approach for high-quality CeO_2 particles using different ionic liquids without a template was investigated [80]. The ionic liquids used in the investigation were: 1-ethyl-3-methylimidazolium tetrafluoroborate ([E$_{mim}^+$][BF_4^-]), 1-butyl-3-methylimidazolium tetrafluoroborate ([B$_{mim}^+$][BF_4^-]), and 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ([HOEt$_{mim}^+$][BF_4^-]). Based on the scanning electron microscopy and particle size distribution, CeO_2 spherical and crystalline particles synthesized at a reaction temperature of 210° C for 16 hours displayed sizes ranging between 0.1 and 0.3 μm. The results of chemical mechanical polishing (CMP) experiments indicated that the abrasives could reduce the surface roughness from 1.63 to 0.29 nm (scanning area is 5 μm × 5 μm). The obtained synthesized CeO_2 particles demonstrated promising performance in Si polishing, achieving removal rates of up to 255.5 nm/min.

In the next reference [81], a terbium based ionic liquid, vinylimidazolium tetranitroterbium ([V$_{im}^+$][$Tb(NO_3)_4^-$]), and the corresponding polymer, poly(vinylimidazolium tetranitroterbium) (P[V$_{im}^+$][$Tb(NO_3)_4^-$]), are synthesized by introducing terbium into counterions. Magnetic property tests show that the monomer and polymer are paramagnetic, and the susceptibility of $P[V_{im}^+][Tb(NO_3)_4^-]$ is higher than that of the former. The magnetic monomer and polymer show bright fluorescence under ultraviolet excitation, while there is no color under sunlight. $[V_{im}^+][Tb(NO_3)_4^-]$ exhibits stronger fluorescence than the polymer form in solution, while pure $P[V_{im}^+][Tb(NO_3)_4^-]$ exhibits stronger fluorescence than pure monomer, thus, the polymer seems to be more suitable for anti-counterfeiting applications and droplet manipulation.

Zerovalent scandium, zirconium, hafnium, and manganese nanoparticles are prepared by reduction of $ScCl_3$, $ZrCl_4$, $HfCl_4$, and $MnCl_2$ with lithium or sodium naphthalenide in a one-pot, liquid-phase synthesis [82]. Small-sized monocrystalline nanoparticles are obtained with diameters of 2.4 ± 0.2 nm (Sc), 4.0 ± 0.9 nm (Zr), 8.0 ± 3.9 nm (Hf) and 2.4 ± 0.3 nm (Mn). Thereof, Zr^0 and Hf^0 nanoparticles with such size are shown for the first time. To probe the reactivity and reactions of the as-prepared zero valent REEs nanoparticles, they arey reacted in the liquid phase (e.g., THF, toluene and ionic liquids: ethylmethylimidazolium chloride ($[EMIm^+][Cl^-]$) or butylmethylimidazolium chloride ($[BMIm^+][Cl^-]$)) with different sterically demanding, monodentate to multidentate ligands, mainly comprising O-H and N-H acidic alcohols and amines. These include isopropanol (HOiPr), 1,1′-bi-2-naphthol (H2binol), N,N′-bis(salicylidene)ethylenediamine (H2salen), 2-mercaptopyridine (2-Hmpy), 2,6-diisopropylaniline (H2dipa), carbazole (Hcz), triphenylphosphane (PPh3), N,N,N′,N′-tetramethylethylenediamine (tmeda), 2,2′-bipyridine (bipy), N,N′-diphenylformamidine (Hdpfa), N,N′-(2,6-diisopropylphenyl)-2,4-pentanediimine ((dipp)2nacnacH), 2,2′-dipydridylamine (Hdpa), and 2,6-bis(2-benzimidazolyl)pyridine (H2bbp). As a result, 22 different compounds are obtained, which frequently exhibit a metal center coordinated only by the sterically demanding ligand. Though sometimes the final compound did not contain the REE:

$$4Sc^0 + 12([EMIm^+][Cl^-]) + 12LiCl \rightarrow 3([Li_4(C_6H_{10}N_2)_4Cl_4]) + 4ScCl_3 + 6H_2 \quad (22)$$

the majority of compounds show the metal coordinated by the sterically demanding ligand:

$$Sc + 5([BMIm^+][Cl^-]) + 3AlCl_3 \rightarrow [BMIm^+]_5[AlCl_4^-][ScCl_6^{4-}] + Al^0 \quad (23)$$

$$3Zr^0 + 3([BMIm^+][Cl^-]) + 4AlCl_3 + 3NaCl \rightarrow 3([BMIm^+][NaZrCl_6^-]) + 4Al^0 \quad (24)$$

Options and restrictions for the liquid-phase syntheses of novel coordination compounds using the oxidation of base-metal nanoparticles near room temperature are evaluated.

Garnet composites with ionic liquid dispersion have been prepared for electrolytic applications. Various ionic liquids in small amounts were added to garnet type $Li_{6.75}Al_{0.25}La_3Zr_2O_{12}$ (LALZO) to improve its ionic conductivity and electrode-electrolyte interfacial compatibility [83]. The optimal composition having near 6 wt% $[EMIm^+][BF_4^-]$ in LALZO showed a high ionic conductivity of 6×10^{-4} $\Omega^{-1}cm^{-1}$ at room temperature, which is almost two orders of magnitude higher than the pristine garnet pellet. Such a high conductivity is attributed to the alteration of the ionic liquid-garnet interface by a weak non-uniform chemisorption. It is concluded that these materials can be used for energy storage applications.

The luminescent amphiphilic polyoxometalates (POM) complex, namely surfactant-encapsulated POM hybrid (SEP), was prepared mainly through electrostatic interaction from polyanionic lanthanide-containing POM, $Na_9(EuW_{10}O_{36})\cdot32H_2O$ (EuW10) and cationic surfactant, 1-octadecyl-3-methylimidazolium bromide ($[C_{18}mim^+][Br^-]$ (OB)) [84]. Next, highly luminescent lamellar micro-fiber aggregates were assembled by SEP in a polymerizable imidazolium-IL solvent, i.e. 1-vinyl-3-butyl imidazolium terafluoroborate ($[Vbim^+][BF_4^-]$). After morphology and structure characterizations for soft aggregates in detail, a lamellar aggregation arrangement mechanism was proposed. Further, and through in situ photopolymerization for such aggregate matrices, the flexible and organized films with enhanced luminescent properties were obtained. The investigation showed that the rational design of polymerizable organized aggregate matrices in the ionic liquids improves the photophysical properties of such luminescent soft materials and broadening their practical applications. These results indicated that hybrid co-assembly from lanthanide-containing polyoxometalates and surfactants optimize the formed aggregate luminescent properties and structural diversity. Moreover, compared to conventional solvents, aprotic ionic liquids are useful as assembly media and acted as remarkable solvents for luminescent lanthanide compounds.

A strategy of lanthanum manganese mixed metal oxides (LMMO) regulated via an ionic liquid--assisted hydrothermal method was proposed to yield multifunctional catalysts, which exhibited excellent catalytic performance in the selective aerobic oxidation of cyclohexane [85]. Up to seven different ionic liquids were tested, having LMMO-$[B_{mim}^+][HSO_4^-]$-1.0 wt% the highest cyclohexane conversion (8.9%) and 90% KA oil selectivity, against the above, LMMO-$[B_{mim}^+][BF_4^-]$-1.0 wt% presented the lowest values of conversion (4%) and selectivity (59.2%). The investigation indicated the structure-directing and template effect of the ionic liquids on the multifunctional catalysts.

Ascorbic acid (AA) is widely used as an antioxidant in several industries, i.e. food. The concentration of this essential chemical can be influenced by different factors: time, temperature, and pH value during food preparation and storage, leading to its instability in content. Thus, the accurate detection of AA content is of paramount importance to avoid health issues. Based in the above, and using the ionic liquid 1-aminopropyl-3-methylimidazolium bromine ($[APMIm^+][Br^-]$, it was investigated the formulation of an imidazole-based ionic liquid functionalized carbon dots (CDs) hybrid APM-CDs [86]. A photo functional hybrid probe Eu^{3+}@APM-CDs was obtained via an ion-exchange reaction between APM-CDs and lanthanide complex $Eu(DPA)_3$. (DPA= 2,6-pyridinedicarboxylic acid). The results show that the fluorescent intensity of Eu3+@APM-CDs has a good linear response to AA concentrations in the range of 25–500 μM, with a detection limit of 80 nM. The fluorescence probe is highly selective respect to ascorbic acid and in the presence of analogs such as aspartic, glutamic and citric acids, glycine, threonine, alanine, arginine, lysine and fructose.

As it was mentioned in the Introduction section, the green label for ionic liquids is under controversy, thus investigations about the degradation compounds of these chemicals mast be of interest. In the next reference [87], La and Ce-codoped TiO_2@PAM (polyacrylamide) composite microspheres were formed to investigate the degradation of three imidazole ionic liquids. The experimental results show that the composite La (0.25%) and Ce (0.15%)-codoped TiO_2@PAM composite microspheres with calcination temperature of 450° C presented a photocatalytic activity of 97.4%, 91.2% and 88.5% for 1-butyl-3-methyl imidazolium hexafluorophosphate, 1-hexyl-3-methyl imidazolium hexafluorophosphate, and 1-octyl-3-methyl imidazolium hexafluorophosphate, respectively and using a concentration of 10 mg/L and 90 min of reaction time. In all the three cases, the various intermediates finally degraded to CO_2 and water. Though the catalyst degrades with the number of cycles (1-6), this degradation is less than that showed by TiO_2P25 catalyst (Table 15). In all the three cases, the various intermediates finally degraded to CO_2 and water.

Table 15. Photodegradation of imidazolium-based ionic liquids at various cycles.

Catalyst	1-butyl	1-hexyl	1-hexyl-3-methyl
La/Ce-based	1st(95%)-6th(90%)	1st(90%)-6th(80%)	1st(85%)-6th(80%)
TiO_2P25	1st(70%)-6th(50%)	1st(55%)-6th(40%)	1st(50%)-6th(35%)

Temperature: 25º C. Dosage: 40 mg of the catalyst. Experiments under xenon lamp irradiation. From [87].

Again in relation with the food industry, determination of bispheno A is of the utmost necessity in order to safeguarding food safety. The next reference developed an electrochemical sensor based on modified carbon paste electrode (CPE) to measure this bisphenol A. The sensor was developed using CeO_2 nanoparticles and the ionic liquid 1-butyl-3-methylimidazolium hexafluoro phosphate $(BMI^+][PF_6^-]$ to modify the carbon pas electrode. Under the optimum detection conditions, the CeO2/IL/CPE sensor showed good linearity in the detection of bisphenol A within range 0.02–460.0 μM with a limit of detection (LOD) of 0.01 μM. There was not observed important interferences in the presence of a number of metal ions (Pb^{2+}, Li^+, Ag^+, Zn^{2+}), anions (CN^-, SO_4^{2-}, SCN^-), and other chemicals (ascorbic acid, glucose, urea, fructose, sucrose).

Next investigation [89], combined use of europium-doped diamond-like carbon (Eu-doped DLC) with varying atomic concentrations of the dopant element (1.7 at. % and 2.4 at. %) and gadolinium-doped diamond-like carbon (Gd-doped DLC) with different atomic concentrations of the dopant element (1.7 at. % and 2.3 at. %), together a pure DLC coating and incorporating of an ionic liquid (1-ethyl-3-methylimiazolium diethylphosphate) additive in a tribological block-on-ring system. In the investigation, solutions at 1% wt% of the ionic liquid in polyalphaolefin 8 were used. With respect to the tribological properties of these systems, the lubricant based in europium presented the best results., it was demonstrated that the solution of the ionic liquid in polyalphaolefin 8 induced to a significant reduction in wear for all the investigated coatings. A composite lubricating system that combines solid and liquid lubrication created a synergistic system that takes advantage of the strengths of both types of lubricants.

Since anhydrous rare earth elements chlorides have a series of practical applications in various fields (organic metallic chemistry, catalysts, etc.), it is of interest investigate approaches to the established synthesis methods. This reference uses the reaction of RE_2O_3 in $[BMIm^+][Cl^-]\cdot nAlCl_3$ at 175° C to fabricate pure anhydrous $RECl_3$, where $[BMIm^+][Cl^-]$ stands for 1-butyl-3-methylimidazolium chloride. The synthesis procedure allowed to the obtaining of these pure salts in the case of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy.

4. Conclusions

Ionic liquids are used to accomplish various roles in the recovery of rare earth elements from raw or secondary (wastes) resources. They are used in the various unit operations involved in the hydrometallurgical processing aimed from these recoveries: leaching, exchange operation with solid ion exchange resins and electrodepositon, even a laboratory operation as supported liquid membranes used this type of compounds. However, as it is somewhat expected due the *green* tendency that we are living today, most of the investigations are related with the use of these chemicals in solvent extraction studies. But the reality shows that in many cases, the use of the ILs is accompanied with the use of classical organic diluents, thus, the apparent *green* advantage of the utilization of these ILs versus traditional solvent extraction is lost. It is worth to note that a series of scientists uses and proposed applications of ILs in systems which utilized highly toxic (and forbidden) organic diluents, and that the corresponding reviewers (and Editors) do not realize and critics about this issue.

This review also shows that in a series of this proposals, researchers do not present data about the recovery of REEs from stripped solutions and being solvent extraction a two steps operation: extraction and stripping. Moreover, some publications do not present data of how these REEs are finally recovered from the solutions.

Also, in a series of systems, ILs take part in active form in the recovery of REEs from the solutions, sometimes releasing part of the organic moiety from the IL to the corresponding raffinate, and causing a probable environmental problem, besides the destruction of the ILs, with little attention from the authors to the above and to the regeneration of the IL

At present time, the industrialization or even scaling up, from laboratory to pilot plant, of technologies using ILs is far to be real, being requiring more fundamental data on the efficiency of the involved processes and investigations about the recovery and separation of REEs from real wastes.

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