

Deep Eutectic Solvents and Rare Earth Elements

Subjects: **Others**

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The boosted interest in the use of rare earth elements (REEs) in modern technologies had also increase the necessity of their recovery from various sources, including raw materials and wastes. Though Hydrometallurgy plays a key role in these recovery processes, some drawbacks (apparent or not) of these processes (including the use of aggressive mineral acids, harmful extractants and diluents, etc.), had led to the development of a *more environmental friendship subclass* named Solvometallurgy, in which non-aqueous solvents substituted to the aqueous media of the hydrometallurgical processing. Together to ionic liquids (ILs), the non-aqueous solvents chosen for these usages are the chemicals known as Deep Eutectic Solvents (DEEs). The utilization of DEEs included the leaching of REEs from the different sources containing them, and also in the separation-purification steps necessary for the yielding of these elements, normally as oxides or salts, in the most purified form.

deep eutectic solvents

rare earth elements

leaching

separation

purification

1. Introduction

Rare earth metals (REEs) are a group of elements of the Periodic Table consisting of seventeen chemical elements including fifteen lanthanides plus scandium and yttrium. Moreover, this group is commonly divided into two subgroups: i) light rare earth elements consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium and europium, and ii) heavy rare earths elements which include gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and yttrium.

From the XXI century, the uses of rare earth elements are gaining an extreme importance along the industrialized countries. This is undoubtedly due by the development of the more sophisticated technologies that nowadays make *life easier*. With respect to their utility, these elements are key components in various markets, including, magnets and permanent magnets, catalysts, metallurgy, phosphors, ceramics, glass and polishing. Also, they are of the utmost importance in the military field and in the production of clean energy. As its name tends to indicate, rare earth elements are not evenly distributed along the world, in fact, REEs availability has China as the leader with 70% of worldwide production, followed by USA (14.33%), Australia (6%), Myanmar (4%), Thailand (2.37%), Vietnam (1.43%), India (0.97%), Russia (0.87%), Madagascar (0.32%), and 0.03% for the rest of the world ^[1]. Reserves (in million MT) of these valuable metals are located in eight countries: China (44), Vietnam (22), Brazil and Russia (each 21), India (6.9), Australia (4.2), USA (2.3) and Greenland (1.5) ^[2].

Not all the rare earths have the same price, with terbium and dysprosium being the ones with the higher price, and lanthanum and cerium the cheapest. The current projects to recover these REEs are distributed along the world, but just one in Europe: Lovozersky (Russia, included in the top 30 REEs projects by estimated total value), and significantly, four advanced projects in Western Europe: one in Norway (Fen), two in Sweden (Norra Karr and Olserum) and one in Spain (Matamulas) [3].

The wide uses of REEs, joined to its relative scarcity and local accumulation of its reserves, has led to that its recovery from raw and secondary materials is gaining, day after day, a critical and strategic importance. Due to its operational characteristics (using of low temperatures, possibility to operate under pressure conditions, treatment of materials with low metal concentrations, possibility of purification of complex materials and solutions, etc.) Hydrometallurgy can be a major key for the recovery and purification of these strategic metals [4]. However, several environmental issues tend to consider traditional Hydrometallurgy as less environmental friendly than the use of Solvometallurgy in the recovery of valuable metals. In Solvometallurgy, the utilization of aqueous medium is displaced by non-aqueous systems, even in the leaching step, though and despite the advantageous characteristics and performance, the implementation of non-aqueous solvents in metal leaching processes at a pilot or industrial scale is still very limited [5].

The utility of Solvometallurgy has led to develop investigations about the use of ionic liquids (ILs) and deep eutectic solvents (DESSs) in the recovery of metals, and the consideration of these two types of chemicals as the future to a new green chemistry; however, as it will be further mentioned, these chemicals are not as green as they are considered. Having similar characteristics, DESSs and ILs are two differentiate group of chemicals [6].

It is often considered that DESSs can assist to the develop of cleaner processes due to its properties: good thermal and chemical stability, low melting point, easy synthesis, low vapor pressure and low or practically negligible toxicity, and probably one of the most important characteristics: tunability to meet specific applications [7][8][9]. Also often, most of them are biodegradable solvents, showing themselves to be candidates to be considered as *green* solvents [10]. Against the consideration of the greenish character, it is indicated [11], that there is an increase number of evidences about the non-greenness character of these chemicals precisely due to some of their characteristics, including instability, volatility, toxicity, flammability, and difficult regeneration.

In any case, besides its application in solvometallurgical processing, DESSs are used in catalysis, electrolytic processes, and other processes, which are applicable to a series of process industries like food, pharmaceutical, cosmetics, oil, gas, etc., [9][12][13][14].

What are DESSs?. Further to the first approach to understand the nature of this class of chemicals [15], the concept of DESSs where developed and expanded. This *deep* nature was first explained the preparation of different melts using metal chlorides (MCl_2 , $M = Zn$ y/o Sn) with quaternary ammonium salts of formula $[Me_3NC_2H_4Y]Cl$ ($Y = OH, Cl, OC(O)Me, OC(O)Ph$) and abbreviated as *liquid ionic Lewis acids* [16][17].

As a general rule, DESs are obtained from the mixture of two or three substances with a given composition where the melting points of each of the individual components are higher than that of the mixture, consisting of the appropriate combination of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBA) [18][19]. Accordingly, DESs are cataloged into five types:

1. i) TYPE I: the general formula for these DESs is $\text{Cat}+\text{X}-\text{x}(\text{MCl}_n)$, where, X^- and x refer to a Lewis base and the number of MCl_n in the DES unit, respectively.
2. ii) TYPE II: these DESs are obtained from the same HBA but the metallic chloride is hydrated ($\text{MCl}_n \cdot z\text{H}_2\text{O}$), where z represents the number of water molecules in the unit cell of salt. The general formula for this type of chemicals is $\text{Cat}+\text{X}-\text{x}(\text{MCl}_n)z\text{H}_2\text{O}$.
- iii) TYPE III: this subgroup is formed from the combination of quaternary ammonium salts such as HBA and HBD (carboxylic acid, alcohols, amides and carbohydrates, etc.).
1. iv) TYPE IV: formed from transition metallic salts or hydrated metal salts and the corresponding hydrogen bond donor.
2. v) TYPE V: in this class of DESs, both donors and acceptors of hydrogen bonds are non-ionic molecular substances, i.e 1 thymol:2 menthol in molar ratio. Thus, they are not ionic in nature but they have the characteristics of the melting point presented by the other types of DEEs. This is attributable to the large number of hydrogen bonds present in this type V of DESs [20].

Besides the above, it was reported [21] a new type of eutectic solvents, i.e., natural deep eutectic solvents (NDESS), containing natural basic metabolites, including sugars, sugar alcohols, carboxylic acids, amino acids and amines [22].

A novel DES formulation formed by dimethylthetin (DMT), oxalic acid dihydrate and water, serving as chelating, reducing, and leaching agents, respectively, is used in the recycling of waste Li-ion batteries [23].

Following the preparation of new DESs, it is described [24], the preparation of DES based on imidazole and monoethanolamine.

Also recently [25], it is reported the implications of using different approaches (no bond, generic bond, or single bond) to model the electrovalent or ionic interactions present in a hydrogen-bond acceptor molecule utilized in the synthesis of DEEs. It is concluded that in the system formed by choline chloride and urea, the use of the above different approaches for modeling the ionic or electrovalent bonds in the acceptor molecules, does not differentiate between the levels (PM3, HF, and DFT) of calculation utilized in the investigation. Moreover, the interaction of three H-atoms present in the alcohol functions of glycerol, as HBD, with the chloride ion of choline chloride, as HBA, is the thermodynamically feasible path for the choline chloride:glycerol compound formation.

Recently, the role of DESs (also ILs) in Extractive Metallurgy processes had been reviewed [26]. Despite the amply leadership given to these chemicals, at the present time (2024 year) still there are not commercial implantations using these *green* reactives. The above is attributed to a series of points, including: i) not high chemical stability

under the working conditions of metallurgical processes, ii) their high viscosity, which hindered phases disengagement (this lead to dissolve them in traditional organic solvents), iii) lack of pilot scale demonstrations of proposed flow-sheets, and thus iv) an interrogation about the cost of large-scale operations, etc.

Within more or less the same opinion, it was stated that in liquid-liquid extraction DESs has not any significant improvement over the use of conventional solvents [27].

In another review [28], the usefulness of DESs in Extractive Metallurgy is not as controversial as above, exploring a new generation of DESs and its uses on the actual research in this frontier area.

Despite all the controversy associated to these DESs, recent publications informed about the use of choline chloride-based DESs in the recovery of valuable metals (mainly lithium and cobalt) from spent batteries [29][30].

The present review described the most advanced data (2023 year) about the use of DESs on the recovery of REEs, moreover, the association of DESs and REEs to fabricate products of further use it is described.

2. Utilization of DESs in the Recovery of REEs

2.1. DESs as Non-Aqueous Leachants of REEs

Being monazite one of the raw material for REEs, a process to dissolve this raw material using DESs as environmental replacement to conventional acids (sulphuric and hydrochloric acids) was developed [31]. Various DESs (Table 1) were synthesized and utilized as non-aqueous leachant reagents of monazite.

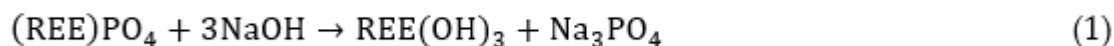
Table 1. DESs formulations used in the dissolution of monazite.

HBA	HBD	Molar ratio HBA:HBD
PEG-400	PTSA	1:1
Choline chloride	PTSA	2:1
Choline chloride	Urea	1:2
Choline chloride	EG	1:2
Choline chloride	Urea:EG	2:4:1
NaOH	PEG-200	1:44

NaOH	PEG-400	1:44
Choline chloride	PTSA:EG	2:1:1
Choline chloride	PTSA:PEG	2:1:1
Choline chloride	AA	1:2
Choline chloride	DLLA	1:2

PEG: polyethylene glycol. ChCl: choline chloride. PTSA: p-toluenesulfonic acid. EG: ethylene glycol. AA: acetic acid. DLLA: DL-lactic acid.

Experimental results indicated that no one of the above DESs recover REEs (Ce, La, Nd, Dy, Eu, Gd, Pr, Sm) from the phosphate phase under the next conditions: 2 hours 120° C and solid/liquid ratio of 1. Thus, the monazite material was roasted in NaOH medium at 500° C during two hours, and the resulting material was further leached with water. The roasting process transformed the phosphate salt to the corresponding hydroxide:



When the roasted process was performed at temperatures higher than 300° C, the next reaction occurred:



and the oxide was the final product. The roasted material was treated with the different DESs at 100° C and 72 hours using a solid /liquid ratio of 10g/L, the resulting data showed that with the ChCl:PTSA (2:1), ChCl:PTSA:EG (2:1:1), and PEG-400:PTSA (1:1) formulations the highest extraction efficiencies (exceeding 80%) was obtained. No data about the recovery of the different REEs from the leach solution was given in the published manuscript.

2.2. DESs as a Medium to Separate REEs

2.2.1. Electrodeposition

Having DESs, besides other characteristics, a wide electrochemical window presented an opportunity to be used in electrodeposition. Thus, a choline chloride-urea based DES was proposed as a medium for electrodeposition of yttrium, samarium and terbium [32]. All three metals were deposited in the DES by cyclic voltammetry and potentiostatic procedures. The results indicate that the electrodepositions of yttrium, samarium and terbium in the DES were governed by diffusion, being the diffusion coefficients of yttrium, samarium and terbium in DES at 60° C of $7.37 \cdot 10^{-13}$, $1.10 \cdot 10^{-12}$, and $9.29 \cdot 10^{-13}$ cm²/s, respectively. The three rare earth elements were deposited in the

form of two-dimensional nanonetwork structures, which were obtained when cyclic voltammetry or potentiostatic procedures.

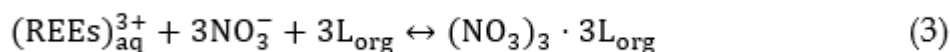
A DES formed by betaine-ethylene glycol (Bet-EG) and Nd_2O_3 was utilized for the electrodeposition of the rare earth at various working temperatures in the 80-100° C range [33]. The electrochemical behavior of Nd_2O_3 dissolved in Bet-EG DES was researched by cyclic voltammetry, potentiodynamic polarization and chronoamperometry methods. Cyclic voltammograms (CVs) manifest that Nd(III) reduction in Bet-EG is an irreversible process with diffusion-controlled, and the reduction overpotential of Nd(III) decreases with the increase of the temperature. The temperature has an impact on the diffusion coefficient of Nd(III) species, obeying the Arrhenius equation. The activation energy is estimated to be 36.78 kJ mol⁻¹. The cathodic polarization analysis shows that the rise of temperature promotes the reduction of Nd(III) . The UV-Vis and ESI-MS analyses show that $[\text{Nd}_2(\text{bet})_8(\text{H}_2\text{O})_4]^{6+}$ complex anions are formed as Nd_2O_3 is dissolved in Bet-EG DES. Electrodeposited neodymium with various morphologies were characterized and analyzed by EDX, XPS, XRD and SEM. It is found that the electrodeposition temperature has a great effect on the morphology of Nd electrodeposits. Depending on the deposition temperature, metallic Nd with submicron particles or porous structures were obtained.

2.2.2. Membranes

This reference used a NDES formed by betaine and lactic acid (1:2 molar ratio) in the formulation of a polymer inclusion membrane to separate Nd, Sm and Dy [34]. The preparation of the membrane also included the use of Cyanex 272 (phosphinic acid derivative) extractant. The use of NDES induced that the pores on the surface were much larger and abundant, and the migration of P-O and P[dbnd]O groups to the lower epidermal layer of the membrane assisted to increase the hydrophilicity of the surface layer. Of the various formulations, the membrane containing 5 wt% NDES presented the best overall permeability and separation performances. Using EDTA (0.15 M) as strippant or receiving phase, a maximum permeation flux of 4.5 μmol/m²·s was obtained, being the transport order Dy>Sm>Nd after 25 hours. No data about how these REEs were separated one to another from the stripping phase was given in the manuscript, also, the role of Cyanex 272 in the membrane formulation was not mentioned.

2.2.3. Solvent Extraction

A number of REEs (La, Ce, Pr, Nd, Eu, Gd, Y and Lu) in the REEs³⁺ oxidation state plus Ce^{4+} were extracted by a mixture of decanoic acid and trioctylphosphine oxide under different experimental conditions: extractant formulation, nitric acid concentration, and temperature [35]. It was described that the REEs³⁺ were extracted by trioctylphosphine oxide dissolved in toluene by the next equilibrium:



where L represented to the phosphine oxide and the subscripts aq and org to the respective aqueous and organic phases.

The various REEs were co-extracted (**Table 2**), though the extraction of the various elements was dependent on the aqueous phase acidity, and as a general rule, the extraction efficiency decreased at nitric acid concentrations in the 4-6 M range.

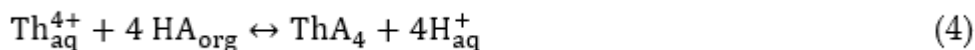
Table 2. Distribution ratios of the various REEs at different nitric acid concentrations.

Element	0.1 M HNO ₃	1 M HNO ₃	6 M HNO ₃
La(III)	0.59	1.0	0.19
Ce(III)	0.63	1.90	0.05
Ce(IV)	12.0	11.0	6.52
Pr(III)	2.77	3.47	0.02
Nd(III)	1.49	3.16	0.19
Eu(III)	6.56	8.16	0.51
Gd(III)	3.93	4.94	0.36
Y(III)	1.60	6.38	1.18
Lu(III)	2.98	6.72	1.90

From the data presented in the above Table, it was clear that Ce(IV) was much better extracted by the decanoic acid+phosphine oxide formulation than the other REEs investigated in the present work. The manuscript did not give data about how the extracted REEs were stripped from the organic phase.

A DES based on trioctyl phosphine oxide and thenoyl trifluoroacetone was used in the extraction of europium and actinides: UO₂²⁺, Pu⁴⁺ and Am³⁺ from aqueous nitric acid medium [36]. At higher molarity of nitric acid (>5 M) the extraction becomes insignificant only for trivalent metal ions and open up the possibility to selectively strip trivalent metal ions from tetravalent and hexavalent ions. This DES was also used for dissolution of uranium oxide (UO₃). The dissolution kinetics was studied and it was shown that oxide was dissolved within an hour at 80 °C. The maximum solubility of UO₃ in DES was measured and found to be 130±5 mg/mL which is one of the highest reported solubility of UO₃ in ILs and DES. The species of uranium which is formed in situ in DES was ascertained to be UO₂(TTA)₂.TOPO after dissolution of UO₃ as supported by FTIR and NMR (1H and 31P) investigations.

2-hexyldecanoic acid and thymol were used to formulate DESs for the extraction of thorium from radioactive waste leach solution [37]. It was described that thorium extraction (exceeding 98%) was due to a cation exchange reaction with the acid:



where HA represented the organic acid molecule, thus, the extraction of the metal released protons in the raffinate, the authors claimed that this raffinate, after adjusting the pH to 4, can be used to the further recovery of the other REEs present in it. Thorium stripping was accomplished by the use of 0.2 M HCl solution. Over five cycles, there was not any apparent loss of thorium extraction efficiency. Based on the separation factors ($\beta_{\text{Th/M}}$, M= accompanying metal) values (Table 3), defined as the ratio of the distribution ratios:

$$\beta_{\text{Th/M}} = \frac{D_{\text{Th}}}{D_{\text{M}}} \quad (5)$$

the system appeared to be highly selective with respect thorium.

Table 3. Separation factors in the extraction of Th(IV) from other elements present in the waste leachate.

La(III): $1.9 \cdot 10^5$	Gd(III): $2.5 \cdot 10^4$	Tm(III): $2.6 \cdot 10^4$
Ce(III): $1.2 \cdot 10^5$	Tb(III): $1.7 \cdot 10^4$	Yb(III): $2.5 \cdot 10^4$
Pr(III): $5.5 \cdot 10^4$	Dy(III): $2.3 \cdot 10^4$	Lu(III): $1.4 \cdot 10^4$
Nd(III): $5.1 \cdot 10^4$	Ho(III): $2.5 \cdot 10^4$	Mg(II): $2.9 \cdot 10^6$
Sm(III): $8.7 \cdot 10^3$	Y(III): $5.3 \cdot 10^4$	Al(III): $1.5 \cdot 10^5$
Eu(III): $1.9 \cdot 10^4$	Er(III): $2.8 \cdot 10^4$	Ca(II): $1.3 \cdot 10^6$

The next reference used a DES as a medium to purify Gd^{3+} by the extraction of the impurity (Al^{3+}) present in GdCl_3 solutions [38]. Using various formulations, in all the cases Gd extraction was less than 20% whereas aluminium extraction exceeded 70% except in the case of the amide:genifibrozil (4:1) mixture. From these DESs, N,N-diethyldodecanamide:ibuprofen (3:1) formulation presented better separation performance, with separation factor Al/Gd value greater than 400. Using a feed solution of near 854 mg/L Al(III) and 5.5 g/L Gd(III) and three continuous counter-current extraction stages, experimental results showed that the above 3:1 formulation quantitatively extracted Al^{3+} (99 %) from the feed GdCl_3 solution. The rare earth element was slightly extracted (about 2.4%), resulting in a gadolinium raffinate of 99.9% purity. The extraction mechanism responsible for aluminium extraction was defined as an ion exchange mechanism, moreover, a saponification degree (0.03-0.085

mol/L) was beneficial to improve the extraction performance. The extraction circuit was closed with a scrubbing stage at pH 3 and aluminium stripping in HCl medium. The system presented a good stability over five continuous extraction-scrubbing-stripping cycles.

The solvent extraction of Am(III) and Eu(III) by the use of DESs were modeled [39]. In this case, DESs formed by TOPO:oxalic acid and TOPO:maleic acid as HBA:HBD in a 1:1 molar ratio was used to extract Am(III) from nitric acid media. In the extraction of Am(III) and Eu(III), a DES formed by choline acetate:glycolic acid (as HBA:HBD also in 1:1 molar ratio) was used as an organic medium of the extractant phase formed by CyMe₄BTBP (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2'-bipyridine)) in 1-octanol. The model predicted reasonably well the experimental data for the systems involving the extraction of Am(III) with TOPO:organic acids, however, severe deviations occurred in the systems involving the extraction of Am(III) and Eu(III) in choline acetate:glycolic acid medium. Moreover, in these last two systems the DES was solubilized in the raffinate.

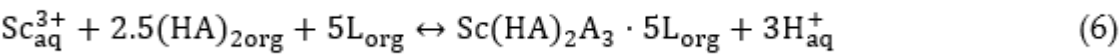
The quaternary ammonium salt Aliquat 336 and glycerol mixture diluted in kerosene was used for investigate the separation of Nd/Fe and Sm/Co from nitrate medium [40]. In the Nd/Fe system, the rare earth (near 94% extraction) was separate from iron(III) under the next experimental conditions: organic to aqueous phase volume ratio of 2, pH 2, extractant concentration of 0.2 M, 25° C, and with the feed solution also containing 3.5 M sodium nitrate. In the case of the Sm/Co system, samarium was extracted best (near 94%) under: O/A phases ratio of 4, pH 2, 0.2 M DES, and 25° C, in this case the presence of the nitrate salt improved metal extraction. Quantitative Nd(III) or Sm(III) was achieved using 0.6 M HCl. It should be noted that though iron(III) was slightly extracted, cobalt(II) was not extracted in any experimental condition. This reference demonstrated that the used of an organic diluent was necessary to perform metal extraction, moreover, the manuscript presented data of how the variation in the diluent influenced the REE extraction (Table 4).

Table 4. Approximate distribution ratio values using various diluents.

Diluent	Nd(III)	Fe(III)	Sm(III)	Co(II)
Heptane	20	<0.5	1.5	no extraction
Hexane	3	<0.5	1.75	no extraction
Carbon tetrachloride	5	<0.5	2	no extraction
Kerosene	6.5	0.5	2.5	no extraction

Also note the use of a forbidden diluent (carbon tetrachloride) due to cancer issues. Reviewers and Editor of this manuscript should never have allowed the publication of the data relative to the use of this harmful diluent.

Tri-octylphosphine oxide and isostearic acid (1:1 molar ratio) formed a DES utilized to investigate its performance in the extraction of scandium in the presence of yttrium, iron and aluminium [41]. The extractant was diluted in toluene, being scandium extracted into the organic phase by the next equilibrium:



where HA represented to the acid molecule and L to the phosphine oxide molecule. Thus, the extraction responded to a cation exchange mechanism, in which one mol of scandium extracted to the organic phase released three mol of protons to the raffinate. Accordingly, the stripping reaction occurred by shifting the equilibrium to the left, and scandium can be stripped by the use of 2 M HCl or sulphuric acid solutions. Though the authors claimed that the extractant can separate scandium from the other elements present in the feed solution, the manuscript did not present clear data about these separations. Also, the recovery of scandium from these highly acidic stripping solutions it was not contemplated in the manuscript. Lastly, this investigation is another example about the use of an ordinary diluent to dissolve DESs.

3. Miscellaneous DESs and REEs Uses

A DES, formed by tetra-butyl phosphoniumbromide and various organic acid as hydrogen bond donors, was coated with cerium oxide nanoparticles to investigate its performance on CO₂ capture [42]. The DES formed by the phosphonium salt and formic acid (1:1 molar ratio) presented the best CO₂ uptake of 0.056 mmol/g, whereas the DES containing butyric acid was the formulation with the lower CO₂ capture (0.041 mmol/g). The better CO₂ capture of the phosphonium salt:formic acid formulation was attributable to the high density of carboxylic functional groups, which led to improve the physisorption capture process due to the enrichment of binding energies. The manuscript did not presented data about the recyclability of the adsorbent.

Choline chloride and urea in a 1:2 molar ratio formed a DES utilized in the synthesis of praseodymium vanadate nanoparticles [43]. These nanoparticles were fabricated by a solvothermal procedure using praseodymium nitrate and ammonium vanadate dissolved in the above DES as precursors. The PrVO₄ nanoparticles were used as an electrochemical sensor for furaltadone (FLD) detection. A maximum in the peak current occurred when the pH of the electrolyte solution reached the value of 7 (Table 5).

Table 5. Influence of the electrolyte pH on current.

pH	Current, μA
3	-16
5	-21

7	-24
9	-16

During the furaltaldone reduction process, the amount of FLD^+ in the electrolyte increased resulting in a decrease of FLD^- species, thus, a maximum in the current is reached due to the influence of hydrogen bonding and electrostatic interactions. Moreover, at this pH of 7 the PrVO_4/GCE nanocomposite has greater electron mobility due to its contributed excited electrons.

Various DESs were fabricated by the use of choline chloride and different salts of various REES (lanthanum, cerium, europium and samarium) in the 1:0.5-1.3 ratio [44]. Further, these mixtures were used to form the vanadium phosphorous oxide (VPO) catalyst used to investigate its catalytic performance in n-butane selective oxidation to produce maleic anhydride. The presence of the REE-DESs tuned the structural modifiers and electronic promoters during the catalysts synthesis, and thus, tuned the physicochemical properties of the VPO catalysts. Though the different REE-DES improved n-butane conversion and MA selectivity, Ce-DES-VPO formulation presented the best results to respect the above points of conversion and selectivity.

Another DES, formed by cetyl trimethylammonium bromide:urea:glycerol in the molar ratio 1:2:5 together with yttrium nitrate hexahydrate and WO_3 nanoparticles were used to fabricate a $\text{WO}_3:\text{Y}_2\text{O}_3$ nanocomposite [45]. The use of the DES promoted changes in the porous nature, size and morphology of the nanocomposite. Using this nanocomposite, it was shown that the frequency dependent ac and dc conductivities were temperature dependent, increasing with the increase of this variable from 30° C to 150° C. From GCD curves was observed that the highest capacitance of 460 Fg^{-1} was obtained at a current density of 2 Ag^{-1} and the cycling stability was found to be around 79% up to 3050 cycles.

Different complexes of cerium(III) salt dissolved in a DES formed by choline chloride, urea, and water, with different molar hydration ratios (w) of 2, 5, and 10, were measured using neutron diffraction with isotopic substitution and the various structures were modeled using empirical potential structure refinement (EPSR) [46]. These various structures depended on the molar hydration ratio presented by the DES (**Table 6**).

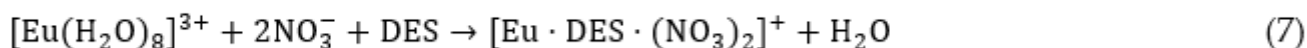
Table 6. Cerium(III) complexes as a function of the molar hydration ratio of the DES.

Molar hydration ratio	Complex
2w	$[\text{CeCl}_6\text{H}_2\text{O}]^{3-}$
5w	$[\text{CeCl}_5(\text{H}_2\text{O})_2]^{2-}$
10w	$[\text{CeCl}_5(\text{H}_2\text{O})_3]^{2-}$

This rare earth element formed highly charged complexes with coordination numbers of 7-8, in which the shell contained chloride and water. Cluster information highlighted the trace presence of percolating water clusters ($25 \leq n \leq 2$) in 5w and 10w DES formulations.

The self-aggregation process of three surfactants, anionic sodium dodecylsulfate (SDS), cationic cetyltrimethylammonium bromide (CTAB), and nonionic Triton X-100 (TX-100), dissolved in DESs composed of a lanthanide salt ($\text{Ln} = \text{La(III)}$ or Ce(III)) and urea was investigated [47]. The self-assembly process was comparable to that in water, being energetically favorable. The type of lanthanide element did not affect largely to the aggregation efficiency, however, the concentration of urea in the DES did. The increase of urea in the DES decreased the self-aggregation of both anionic and cationic surfactants, this was attributable to the different thermodynamic parameters involved in the aggregation process. This type of aggregation using these DESs may improved the applications of these systems in several fields: material synthesis, nanoreactors/nanocarriers, etc.

A DES formulated with heptyltriphenylphosphonium bromide:decanoic acid (1:2 ratio) and europium(III) were used to investigated its luminescent and electrochemically properties [48]. The Eu-DES complex was formed by the next reaction:



Electrochemical results showed that the redox reaction of $\text{Eu(III)}/\text{Eu(II)}$ in DES has a quasi-reversible behavior, and that the reaction rate increased with the use of higher temperatures.

Electrolytes based on a mixture of choline chloride and ethylene glycol, both forming a DES nicknamed ethaline, containing dissolved LaCl_3 and NiCl_2 were used as a source for the electrodeposition of Ni-La coatings [49]. The presence of lanthanum in the nickel matrix served to increase the electrocatalytic activity due to i) the presence of lanthanum in the (II) and (III) oxidation states and ii) to the synergistic interaction between both metals. These types of materials probably will be of utility in the production of green hydrogen by electrolytic procedures.

Very close to the previous reference, an electrolyte based on a DES formed by a mixture of choline chloride and urea, named reline, was used for electrodeposition of coatings containing Ni-Ce [50]. An increase of the electrocatalytic activity was found to occur when the concentration of cerium in the coating increased. In systems containing cerium(III), reline-based electrolytes formed coatings with a greater activity towards hydrogen evolution reaction than coatings formed by the utilization of electrolytes based in the DES formed by choline chloride and ethylene glycol.

A 1:2 M solution of choline chloride and ethylene glycol formed a DES from which LaF_3 was added in order to deposit the lanthanum salt on the pore walls of porous silicon, and investigate the photoluminescence properties of this LaF_3 -passivated porous silicon structures [51]. In the synthesis of the final material, firstly, the LaF_3 -DES phase

was spin-coating deposited on the pore wall of the porous silicon, and annealed to evaporate the DES and leaving the lanthanum salt on the pore wall forming passivating layer. Experimental results indicated that the passivated material presented a higher luminescence than the pristine porous silicon, these results were attributable to a unique chemical process involving the DES, and that this process was improved by the regulation of the spin coater speed.

Mixed matrix membranes used to investigate the permeation of CO₂ were fabricated from ceria nanoparticles-DES which acted as filler of the membrane [52]. The DES used in the investigation was formed by cetrimonium bromide and acetic acid in 1:1 ratio. Further to the casting process, it was demonstrated that the filler was dispersed in a uniform form in the polysulfone and that the polymer and the ceria-DES filler did not react between them. Experimental results indicated that the mixed matrix membrane performed better, to respect CO₂ permeation, than the pristine polysulfone membrane (Table 7). Also, CO₂ selectivity against the presence of CH₄ or N₂ in the gas stream was improved by the use of the present mixed matrix membranes.

Table 7. CO₂ permeation (Barrer units) using both types of membranes.

	CO ₂ pure	CO ₂ /CH ₄	CO ₂ /N ₂
Pristine membrane	6.7	6.06	6.36
Mixed matrix membrane	17.2	16.3	16.9

4. Conclusions

Deep eutectic solvents are being used in the recovery of REEs from different sources, both to dissolve them from the different solids containing them and in the separation operations aimed to recover pure products. This is because solvent extraction operation presented most of the publications related to these separations.

These applications and the term *green* attached to the name of DESs, sometimes became overshadowed by the utilization of traditional organic diluents, most probably due to the high viscosity presented from DESs which increases as these chemicals become loaded by REEs (metals in general), making of these processes not environmentally friendly, as in the first instance they appear to be. It is also amazing that some authors used today carcinogenic diluents (i.e. CCl₄) in its experimentations.

Besides the limitations of viscosity, another odd feature of using DESs in these separations systems is that, in some of the proposed processes of REEs recovery, the regeneration of DESs is not fully understood and even unexplained or unresolved.

Though the future of using DESs in leaching and separation operations is still open, some of the limitations must be resolved i.e. loss of the cationic moiety to the aqueous phase, and the own solubilization of DESs in water. These resolutions must be done first at the laboratory scale, prior to its scaling up to a pilot plant or demonstration plant and before to be an industrial process, which at present time seems to be a chimera.

It is of a positive interest to note how DESs are using as a medium or taking part in the fabrication of materials, involving REEs, with a wide field of applications in different disciplines.

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