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Recovery of metals from waste electrical and electronic equipment (WEEE) using unconventional solvents based on ionic liquids

Nicolas Schaeffer[a] (iD), Helena Passos[a] (iD), Isabelle Billard[b,c],
Nicolas Papaiconomou[b,c,d,e], and João A.P. Coutinho[a] (iD)

[a]Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal; [b]Université Grenoble-Alpes, LEPMI, Grenoble, France; [c]CNRS, LEPMI, Grenoble, France; [d]Université Savoie, LEPMI, Chambéry, France; [e]Institut de Chimie de Nice, Université Côte d'Azur, CNRS, Nice, France
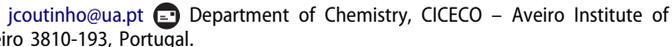
ABSTRACT

Waste electrical and electronic equipment (WEEE) is the fastest growing type of waste globally and is an important challenge due to its heterogeneity, intrinsic toxicity and potential environmental impact. However, WEEE also represents an important secondary source of critical and valuable elements and must be viewed as a resource within the context of a circular economy. The use of ionic liquids (ILs) to recover metals from WEEE is reviewed with a special emphasis on the use of ILs in leaching and solvent extraction processes. The advantages of ILs as a reaction medium compared to existing conventional solvents lies in their tuneability and potential environmental benefits. Many studies have used ILs for the selective extraction and purification of metals from WEEE, particularly from waste fluorescent lamp phosphor and batteries containing rare-earth elements with promising results. However, significant barriers remain to the commercial use of ILs for treating WEEE and key barriers to progress are identified. In particular more focus is required to improve upstream collection and separation of WEEE, as this would greatly increase the potential to use selective, more efficient, ILs for metal recovery.

1. Introduction

As organizations are looking for ways to mitigate the effects of human activity on the environment, recent global trends point towards a shift from the historically prevailing linear economic model, whereby goods are manufactured, consumed and disposed, to a circular economic model promoting reuse and recycling. The primary tenet of the circular economy is the concept of value recovery: all waste possesses an inherent value, which

if properly managed can be extracted. In this new context of global environmental remediation, sustainable, effective and affordable waste management is an issue of critical importance.

Waste electrical and electronic equipment (WEEE) is the fastest growing waste stream globally and is an important challenge due to inherent value, heterogeneity and potential environmental impact (Ye, Kayaga, & Smout, 2009; Ongondo et al., 2011). Essential constituents of many EEE products, in particular information technology (IT) and communication equipment, are base metals (Fe, Cu, Al, etc.) as well as important concentrations of precious metals (Au, Ag, Pd) and specialty metals (In, Sb, Te, Ta, rare earth elements (REE), etc.) all highly interlinked in a complex composition (Hagelüken, 2006). Many WEEE streams or components of WEEE contain higher concentrations of valuable metals than their primary ore and as such represent an opportunity as secondary 'ores'. This is especially true as metals are finite commodities with a limited availability for human use. Mining rates of most metals are at a historical maximum whilst the average ore grade has decreased over the last hundred years for both base and precious metals (Mudd, 2010; Northey, Mohr, Mudd, Weng, & Giurco, 2014). The reduced availability of minable deposits and the concentration of these deposits in a limited number of countries results in an imbalance between supply and demand, making the current practice unsustainable in the long term. In addition, there is a growing legislative pressure on the proper handling and recycling of WEEE, with the collection and recycling targets recently increased as part of the EU WEEE Directive (2012/19/EU) (European Commission, 2012).

Current processes to recover value from WEEE can be complex and involve high water and energy consumption and/or the production of large quantities of hazardous effluents (Cui & Zhang, 2008; Tuncuk, Stazi, Akcil, Yazici, & Deveci, 2012). WEEE recycling occurs in three major stages: (1) disassembly, (2) upgrading using mechanical and/or metallurgical processing to increase the desirable materials content of the waste, and (3) refining by purification of the upgraded material by metallurgical processing (Cui & Forssberg, 2003). A schematic flow-diagram of the major stages in WEEE processing is given in Figure 1.

Although both hydro- and pyro- metallurgy have advantages, hydrometallurgy is often favored over traditional pyrometallurgy by industry due to an ability to recover metals from a variety of challenging sources, including low grade ores, mixed metal ores and secondary sources such as WEEE. Furthermore, hydrometallurgy allows the use of low process temperatures and recycling of reagents (Wilson et al., 2014). Conventional industrial processing of WEEE requires extraction and separation techniques that use aggressive acid or alkali digestion, can involve multi-stage separation procedures, produce large aqueous waste streams which require further
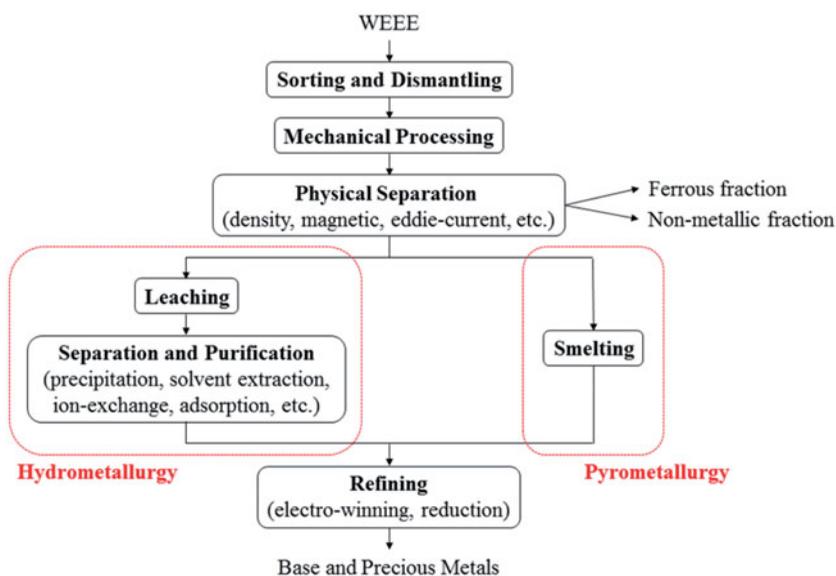
Figure 1. Simplified schematic of the major stages of WEEE recycling.

treatment, and in the solvent extraction process, make use of solvents which are potentially flammable, volatile and toxic.

Ionic liquids (ILs) are solvents composed of ions with properties intermediate between molten salts and organic solvents and are attracting significant interest due to potential environmental benefits and tailorability compared to conventional solvents (Earle & Seddon, 2000; Rogers & Seddon, 2003). They have been applied in a number of industrial processes and products (Plechkova & Seddon, 2008) and if properly selected, ILs could offer an environmentally friendly alternative to current hydrometallurgical WEEE recycling processes by minimizing waste generation and acid consumption whilst maintaining selective leaching. Since the proposal of ILs as environmentally friendly media compared to volatile organic solvents for liquid-liquid extraction (Huddleston, Willauer, Swatloski, Visser, & Rogers, 1998), the use of ILs for solvent extraction remains the most widely researched field in IL mediated metal processing. Solvent extraction (or liquid-liquid extraction) is the favored option for metal separation and involves the preferential two-phase distribution of a solute between mutually immiscible liquid phases usually consisting of an aqueous acidic solution and an aliphatic organic solvent.

Due to their versatility and growing popularity, the use of ILs for metal separation has been reviewed by previous authors (Dietz, 2006; Lee, 2006; Han & Armstrong, 2007; Abbott et al., 2011; Tian, Li, & Hua, 2010; Stojanovic & Keppler, 2012; Sun, Luo, & Dai, 2012; Kolarik, 2013) whilst the use of the immobilized IL in metal extraction was reviewed elsewhere (Stojanovic & Keppler, 2012; Vidal, Riekkola, & Canals, 2012). The use of
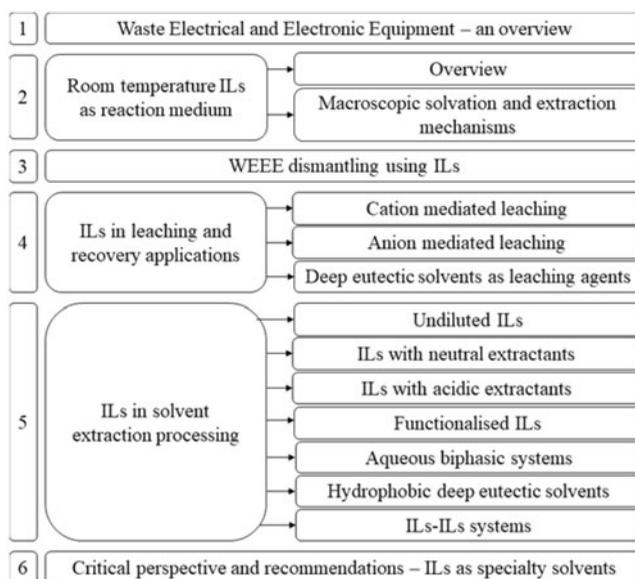
Figure 2. Schematic outline of the review.

ILs for the electro-deposition of metals was previously reviewed by multiple research groups (Abbott, Capper, Davies, McKenzie, & Obi, 2006; Endres, Abbott, and MacFarlane, 2008; Abbott et al., 2011; Abbott, Frisch, & Ryder, 2013; Smith, Abbott, & Ryder, 2014). Furthermore, a detailed description of the fundamental governing principles dictating metal extraction to IL (Katsuta, Watanabe, Araki, & Kudo, 2016; Svecova et al., 2016) as well as specific applications for certain classes of ILs such as acidic ILs (Amarasekara, 2016) or temperature responsive ILs (Qiao, Ma, Theyssen, Chen, & Hou, 2017) are also available. Nevertheless, there is currently no review focusing on the use of ILs for the recovery of value from WEEE despite the increasing number of publications on this field in the last five years.

This review is divided into six sections, with the schematic review outline presented in Figure 2. After an introduction of the current WEEE recycling and ILs, the discussion follows the typical sequence in WEEE processing, starting with dismantling, followed by leaching and finishing with solvent extraction. The first provides a brief overview of metal recycling from WEEE highlighting the metals of critical interest for recovery and the challenges to date. The second addresses the general properties of ILs as reaction medium with an emphasis on metal-ILs extraction mechanisms. The third and fourth sections present the application of IL-derived solvents to the solvato-metallurgical processing of electronic waste, namely their use for the dismantling and leaching of WEEE. In the case where the reviewed literature presents a recovery methodology, this will be presented in conjunction with its leaching to promote the application of a one solution for

the elective leaching and recovery of metals from WEEE. The fifth section reviews the use of unconventional solvents based on ILs in solvent extraction processes relevant to WEEE recycling. This section represents the largest body of reviewed works and covers both the use of traditional IL solvent extraction processes as well as non-conventional systems such as hydrophobic deep eutectic solvents (DES) and aqueous biphasic systems (ABS). Finally, a critical assessment on the use of ILs for metal extraction from WEEE is conducted with guidelines provided based on the reviewed literature to maximize its beneficial application. The focus is on recovery of metals from WEEE rather than plastic or glass components, with emphasis on ILs used in leaching and solvent extraction. In this review, the ILs are discussed according to their application. As such, one IL used both in leaching and in solvent extraction applications will be presented in two different section although care is taken to avoid overlap. Although not within the scope of this review, some relevant examples on the application of ILs for the recovery of metals from primary ores are presented to enrich the discussion. Current hydrometallurgical treatment of WEEE borrows heavily from principles developed by the mining industry; innovative techniques developed for the latter can be transferred to the extraction of value from WEEE.

2. Waste electrical and electronic equipment (WEEE)

Global WEEE generation is estimated at 20-50 million tonnes per year and is increasing at a 3–5% rate (Ongondo et al., 2011). In 2005, WEEE already represented approximately 8% of municipal solid waste (Widmer, Oswald-Krapf, Sinha-Khetriwal, Schnellmann, & Böni, 2005). Annual WEEE production in the European Union (EU) increased from 6.5 Mt in 2004 to 12 Mt in 2015 (Goosey, 2004; Baldé, Wang, Kuehr, & Huisman, 2015). An important distinction must be made between WEEE and e-waste. Although many authors use the terms interchangeably, Robinson (2009) describes WEEE as "discarded appliances that use electricity" including traditionally non-electronic goods such as refrigerators and ovens. WEEE designates any wastes that fall under the jurisdiction of the European WEEE Directive (2002/96/EC) as set out in Table 1. E-waste is a sub-fraction of WEEE that encompasses "waste electronic goods, such as computers, televisions and cell phones" (European Commission, 2003). These goods primarily fall under category 3 and 4 of the WEEE Directive.

Global WEEE is exponentially increasing due to (1) population growth, (2) economic growth and the resulting improvement in living standards, (3) decrease in product lifespan and (4) the increase in everyday commodities containing microprocessors. One consequence of increasing EEE on

Table 1. Classification of WEEE into ten categories according to the European WEEE Directive (2002/96/EC (European Commission, 2003)). The highlighted rows correspond to the e-waste subsection of WEEE.

No.	Category	Example
1	Large household appliances	Refrigerator, oven, washing machine
2	Small household appliance	Toaster, microwave, vacuum cleaner
3	IT and telecommunications equipment	Mobile phone, computer, computer screen
4	Consumer equipment	Television, radio, speaker
5	Lighting Equipment	LED, gas discharge lamps
6	Electrical and electronic tools	Power drill, electric screw driver
7	Toys, leisure and sports equipment	Treadmill, game console
8	Medical devices	MRI, dialysis
9	Monitoring and control instruments	Thermocouple, smoke detector
10	Automatic dispenser	Vending machine, cash distributor

the market is the blurring of the traditional borders between classical electrical equipment and electronic equipment. Over 98% of all programable microprocessors are now embedded in commodities that are not associated with computers (Hilty, 2005).

WEEE is a complex, heterogeneous waste stream containing over 1000 different substances (Ye et al., 2009) and is primarily composed of plastics (34.6 wt.%), electronic components (23.5 wt.%) and ferrous metals (15.6 wt.%) (Dimitrakakis, Janz, Bilitewski, & Gidarakos, 2009). Essential constituents of many EEE products, in particular IT and communication equipment, are base metals (Fe, Cu, Al, etc.), precious metals (Au, Ag, Pd) and speciality metals (In, Sb, Te, Ta, rare earth elements (REEs), etc.) (Hagelüken, 2006). Due to their significant metal concentration, EEE production has an important impact on global demand for metals and is an important driver of metal scarcity. Essential constituent of many EEE are metal with reserves often concentrated in a handful of countries creating a potential supply risk. This is exemplified by the substantial increase of most of rare earth oxides (REOs) prices in 2011 due to the implementation during the previous year in China of a REOs export quota policy (Tan & Zeng, 2015). Imbalances between metal supply and demand in conjunction with the importance of a metal for continued economic growth has inspired the concept of metal criticality (Graedel, Harper, Nassar, Nuss, & Reck, 2015). Multiple methodologies have attempted to assess the criticality of materials with widely varying results (Erdmann & Graedel, 2011; Buijs & Sievers, 2011).

A selection of previous studies assessing raw material criticality is presented in Table 2. These studies primarily focus on the criticality of materials from a European or U.S. perspective. It is important to remark that criticality varies geographically, and certain materials labeled as critical in EU are likely to change if other countries such as China are considered. The most comprehensive studies are those originating from the European Commission (2014) and from Graedel et al. (2012, 2015). These reports

Table 2. Selection of previous studies assessing raw material criticality.

Study	Critical Material
NRC (2008)	In, Mn, Nb, PGM, REE
Morley & Eatherley (2008)	Au, Rh, Pt, Sr, Ag, Sb, Sn
Buchert, Schuler, & Bleher (2009)	Te, In, Ga, REE, PGM, Ta, Li, Ge, Co
U.S. DoE (2010)	REE (Dy, Nd, Tb, Eu, Y), In
Erdmann & Graedel (2011)	REE, PGM, In, W
Graedel et al. (2012)	Results grouped by mineral family. *Eg.* for 'copper family': $As = Gd > Ag > Se \approx Cu > Te$
European Commission (2014)	Sb, Be, Co, fluorspar, Ga, Ge, graphite, In, Mg, Nb, PGM, REE, Ta, W
Graedel et al. (2015)	In, As, Tl, Sb, Ag, Se, Au, PGM, Mg, Cr, Mn, Rh, REE

include a temporal dimension (assessment of current and future criticality) and estimate material criticality based on multiple factors including (but not limited to) economic importance, supply risk, vulnerability to supply restriction, substitutability and environmental impact. Although material criticality is a fluid concept with temporal and geographical variations, certain metal groups appear in most of the presented studies, namely indium, antimony, REE, platinum group metals (PGM), magnesium, manganese and niobium. Recovery of these elements is of major importance to minimize their environmental impact and for the continued growth of the EEE industry and green industry.

In 2007, demand for indium, antimony, tin, copper, silver, cobalt and selenium for use in EEE accounted for an estimated 79.2, 50.0, 32.7, 30.0, 30.0, 19.0 and 17.1% of total production of these metals (Hagelüken & Buchert, 2008). Many WEEE streams and components of WEEE contain greater concentrations of valuable metals than the primary ore. It is estimated that the annual replacement value of the materials found in WEEE disposed of in the UK alone is ~£1.3bn, with £400 m either hoarded or landfilled (Haig, Morrish, Morton, & Wilkinson, 2012). The quantity of precious metal in WEEE generated solely in the UK is estimated at about 50 tonnes per year. For example, phosphor powders used in fluorescent lamps contains elevated concentration of REE including Eu. Binnemans et al. (2013) estimate that waste fluorescent lamps will contain up to 25,000 tons of REEs by 2020.

The primary factors influencing the recyclability of a metal from WEEE are the volume of the waste, the price of the metal and the purity of the element and ease of recovery. For many electrical products, innovation is associated with an increase in the number of elements used. In the 1980's, 11 elements were contained in Intel® printed circuit boards (PCBs), compared to ~60 in the 2000s (Johnson, Harper, Lifset, & Graedel, 2007). Additional elements are often present at low concentrations but have important specific functions. New high-strength permanent magnets or new alloys with enhanced physical and chemical properties are obtained using lanthanide elements (Graedel, 2011; Binnemans et al., 2013).
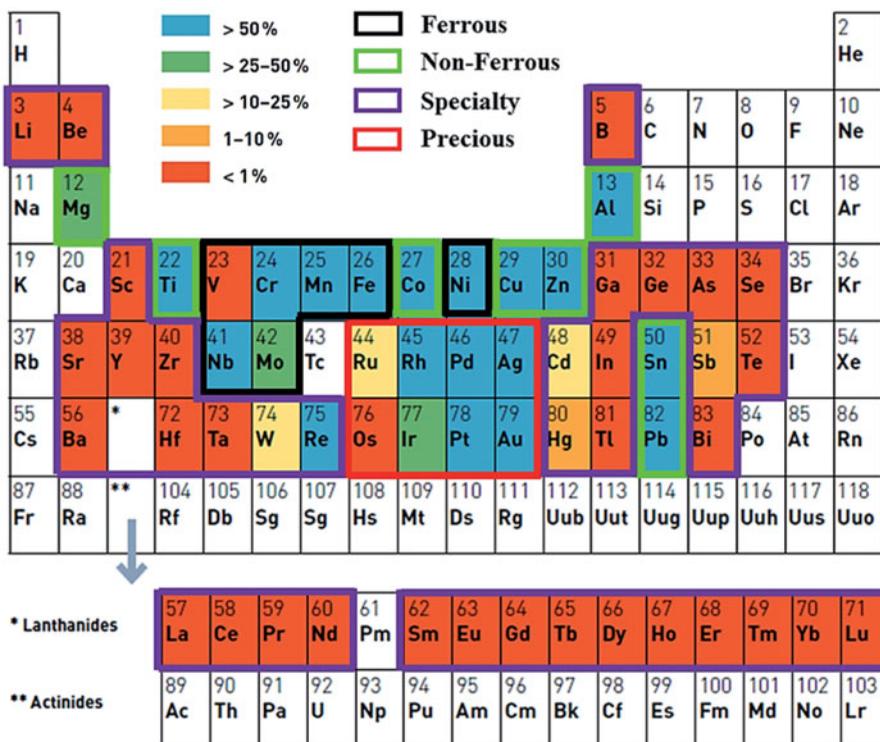
Figure 3. Global estimates of end-of-life recycling rates for 60 metals and metalloid in 2008 (adapted from UNEP, 2011).

Recovery of these metals from WEEE is seldom considered due to the technological and economic challenges involved (Reck & Graedel, 2012). A consequence of the rising number of elements in WEEE is that individual metal recycling rates can be divided into three categories. Recent global estimates of end-of-life recycling rates for 60 metals and metalloid (UNEP, 2011) are presented in Figure 3.

The first category of metal corresponds to 'base metals' (Fe, Cu, Sn, Ni, Zn, Al and Pb), with end-of-life recycling rates (EOL-RRs) at >50 wt.%. These are the main metals in WEEE, are often found in relatively pure elemental form and benefit from mature recycling infrastructure (Khaliq, Rhamdhani, Geoffrey Brooks, & Masood, 2014). The second category corresponds to 'precious metals' with EOL-RRs of ∼50–60 wt.%. This includes some platinum group metals, Au and Ag, which despite low concentrations have high economic value (UNEP, 2011; LME, 2016). The recycling rates are positively skewed due to the high recycling rates of industrial catalysts and jewelry. This significantly masks lower EOL-RR from WEEE in the EU (Chancerel, Meskers, Hagelüken, & Rotter, 2009; Hagelüken, 2012). Platinum group metal recycling rates from WEEE, such as Pd(II) from

PCBs were only 5–10 wt.% in 2011. EOL-RRs for other elements from WEEE are restricted by low collection rates due to export of WEEE to countries with primitive treatment technologies and disposal of WEEE in municipal solid waste (Hagelüken, 2012). The final category consists of 'specialty metals' that are characterized by low recycling rate, typically below <1 wt.% (UNEP, 2011). Many metals in this category are labeled as critical (see Table 2). These are used in low concentrations and extensively mixed making separation often economically unviable (Du & Graedel, 2011; Reck & Graedel, 2012). Recovery of these metals represents a major challenge to achieve a circular economy due to increasing use in EEE and the current linear management system.

Frustratingly, a significant portion of most strategic metals in e-waste is lost during the collection, sorting and mechanical separation stages. In turn, this decreases the financial viability of any recovery process through the dilution of precious metal content by commingling with other types of lower-value e-waste. Small high-value e-waste such as mobile phones suffer from low end-of-life recycling rate as they are often either improperly disposed in municipal waste bins or stored forgotten in a drawer. Mechanical treatment options suffer from the 'concentration dilemma', i.e. the recovery yield for a specific metal decreases with the rising purity of that metal in the output stream (Hagelüken, 2006). The unintended co-separation of minor metals during mechanical pretreatment unavoidably can lead to substantial losses before it ever reaches any hydrometallurgical processes. A substance flow analysis of a full-scale pre-processing facility shows that 60 wt.% of the Cu reach output fractions from which it may potentially be recovered. This decreases to 25.6 wt.% for Au and Pt and only 11.5 wt.% for Ag (Chancerel et al., 2009).

The ILs covered in this review are for the most part limited to the recovery of value from PCBs, waste fluorescent phosphor, nickel metal hydride batteries and permanent magnets. Research has focused on these waste types due to (i) their high inherent metallic value and (ii) their ease of procurement as an 'uncontaminated' waste. These e-wastes have well established collection and sorting processes, with some even separated at source due to legislative pressure. Fluorescent tubes, which contain rare-earth rich phosphor powder, are classified as a hazardous waste in the European Union due to their mercury content. As such, fluorescent lamps benefit from a dedicated collection and separation chain, ensuring a high content of REE, phosphorus and antimony. In contrast, indium and tantalum can be found in high concentration in indium-tin oxide film in flat screen and in capacitors respectively. However as these are small components of a larger waste, their current recycling barriers make the recovery of these metals from large scale WEEE treatment facilities difficult.
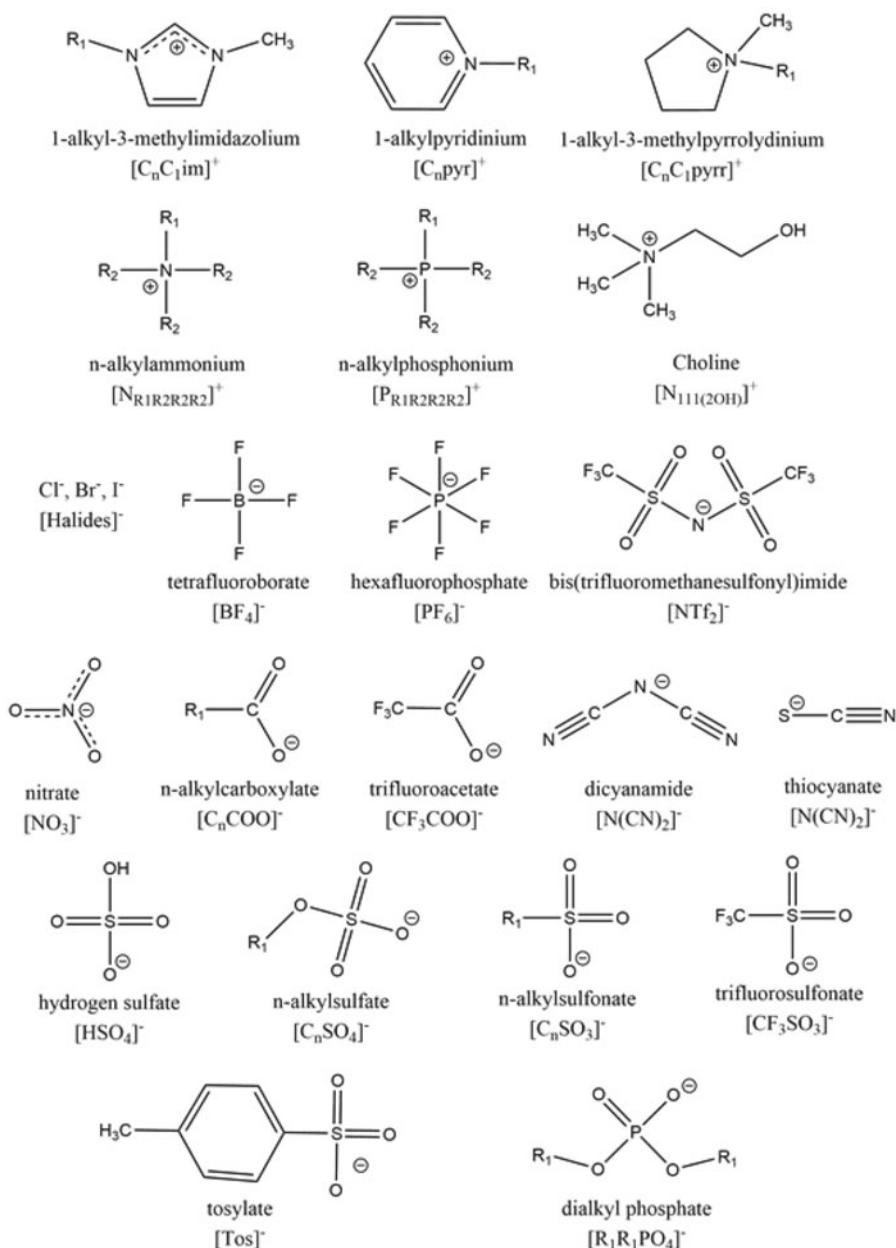
3. Room temperature ILs as reaction medium

3.1. Overview

Room temperature ILs are a class of solvents consisting of organic cations and organic or inorganic anions with melting points below 100 °C (Earle & Seddon, 2000). Due to their unique physical and chemical properties, ILs have generated considerable scientific interest over the last 20 years. In this section, solvation interactions within ILs are discussed prior to a more detailed assessment of ILs for the recovery of metals from WEEE with special emphasis on hydrometallurgical processes. The discussion is limited to second and third generation ILs and will not cover ILs based on chloroaluminate anions.

The majority of chemical reactions occur in solution, with the solvent properties influencing its suitability as a reaction medium. ILs are solvents composed exclusively of ions and as such their solvation behavior differs from that of neutral molecular solvents (hexane, acetone, DMSO, etc) and aqueous, or partially ionized, solvents. ILs (generally) consist of large asymmetrical cations and simple coordinating anions. The low degree of packing efficiency, induced by the size and lack of symmetry of the cation, in conjunction with a lower cationic (and occasionally anionic) charge density, caused by delocalization of the partial charge over the whole ion, drastically reduces the lattice energy of the salt resulting in lower melting points (Seddon, 1997). This low melting point distinguishes ILs from conventional molten salts like molten sodium chloride ($T_m \geq 801$ °C), which are characterized by a high charge density and packing efficiency. Commonly used cations and anions for ILs and their abbreviations are provided in Figure 4. For the sake of clarity and to enable meaningful comparisons between different systems, ILs will be refered according to their structure and not their commercial name. ILs comprised of the other anions listed in Figure 4 display varying degrees of hydrophobicity depending on the cation's alkyl chain length. The hydrophobicity of an IL is of particular relevance for its application as an extraction and separation media. It is important to state that all ILs are hygroscopic, regardless of their hydrophobicity, and water may make up a significant molar percentage of an IL.

Many solvent properties, including hydrophobicity, polarity and viscosity to name a few, are important to an IL's performance and applicability as a reaction medium. In ILs, these 'bulk properties' are altered by either varying the anion or the cation and this has led ILs to be labeled as 'designer solvents' (Freemantle, 1998; Huddleston et al., 2001). Many of these properties have been extensively reviewed elsewhere (Ohno, 2005; Koel, Linert, & Gärtner, 2007; Endres et al., 2008; Freemantle, 2009; Hallett & Welton, 2011) and will not be discussed here.

1-alkyl-3-methylimidazolium
$[C_nC_1im]^+$

1-alkylpyridinium
$[C_npyr]^+$

1-alkyl-3-methylpyrrolydinium
$[C_nC_1pyrr]^+$

n-alkylammonium
$[N_{R1R2R2R2}]^+$

n-alkylphosphonium
$[P_{R1R2R2R2}]^+$

Choline
$[N_{111(2OH)}]^+$

Cl^-, Br^-, I^-
[Halides]$^-$

tetrafluoroborate
$[BF_4]^-$

hexafluorophosphate
$[PF_6]^-$

bis(trifluoromethanesulfonyl)imide
$[NTf_2]^-$

nitrate
$[NO_3]^-$

n-alkylcarboxylate
$[C_nCOO]^-$

trifluoroacetate
$[CF_3COO]^-$

dicyanamide
$[N(CN)_2]^-$

thiocyanate
$[N(CN)_2]^-$

hydrogen sulfate
$[HSO_4]^-$

n-alkylsulfate
$[C_nSO_4]^-$

n-alkylsulfonate
$[C_nSO_3]^-$

trifluorosulfonate
$[CF_3SO_3]^-$

tosylate
$[Tos]^-$

dialkyl phosphate
$[R_1R_1PO_4]^-$

Figure 4. Schematic of selected cations and anions from common ILs and DES and their abbreviations.

3.2. Macroscopic solvation and extraction mechanisms

In this section, a brief synopsis of the fundamental governing principles dictating metal-IL interaction and extraction is given, particularly as no new extraction mechanisms were reported compared to older existing work. For an in-depth analysis, the reader is referred to the review of

Janssen et al. (2015). The overall solvation property of a system results from the sum of the possible solute-solvent interactions and depends on the cation and anion of the IL, as well as the solute. Charged complexes can be highly soluble in ILs, allowing for a wider range of metal speciation compared to molecular solvent in which generally only neutral complexes are soluble. The ionic nature of ILs results in metal extraction mechanisms from an aqueous phase that are not possible in conventional organic solvents such as ion-exchange mechanisms involving ions of the IL, which can lead to the degradation of the IL. Both charged and neutral metal complexes can be highly soluble in ILs (Jensen, Dzielawa, Rickert, & Dietz, 2002). The most conclusive method for the determination of metallic species in IL is single-crystal XRD analysis (Nockemann et al., 2010a,b). However, due to the low vapor pressure and melting point of ILs, acquisition of suitable crystal structure is often impossible and in-situ techniques are required. These are reviewed by Abbott, Frisch, & Ryder (2008) and will only be listed here. The most widely used technique to probe metallic complexes in ILs is extended X-ray absorption fine structure (EXAFS), with certain studies also using Raman, UV-vis and FAB-MS spectroscopic techniques.

When discussing metal-IL interaction, a distinction must be made between positively and negatively charge metal complexes. For positively charged metal complexes, typically the IL anion dictates the chemistry of the system because it interacts with the generally more Lewis acidic metal solute. Anion selection determines the Lewis acidity and coordination ability of an IL, with metal salts being poorly soluble in ILs with strongly Lewis acidic/practically non-coordinating anions. Chloride, nitrate and sulfate, are strongly Lewis basic/strongly coordinating anions whilst the fluorinated anions $[BF_4]^-$, $[PF_6]^-$ and $[NTf_2]^-$ are acidic and only weakly coordinating (Wasserscheid & Welton, 2008). ILs incorporating strongly coordinating anions exhibit significantly greater metal dissolution potential than those with acidic anions (Pereiro et al., 2012). Complexation of the metal with the IL anion controls the metal speciation and therefore its reactivity, solubility, redox potential and color (Abbott et al., 2011). The metal counter-anion also plays an important role in determining solubility in a particular IL. The Hofmeister series (or the lyotropic series) provides a general indication of the hydrophobicity of an anion. In ascending order, it reads: $[SO_4]^{2-} \leq Cl^- \leq Br^- \leq [NO_3]^- \leq I^- \leq [ClO_4]^- \leq [SCN]^- \leq [NTf_2]^-$ and reflects the charge density and hydration numbers of the different anions (Dupont, Depuydt, & Binnemans, 2015). Metal salts containing hydrophilic anions of high charge density are unlikely to dissolve in poorly coordinating hydrophobic ILs such as $[C_4C_1im][NTf_2]$. The solubility of inorganic salts in ILs with a common anion is greatly improved, both for hydrophilic and hydrophobic anions (Pereiro et al., 2012).

In many cases, metal ions, including the precious metals present in WEEE, form negatively charged complex species once dissolved in an acidic solution. For instance, Pt(IV) forms various polychloroplatinate(IV) complexes such as $PtCl_5(H_2O)^-$ or $PtCl_6^{2-}$ in aqueous solutions of HCl. Pt(II), Pd(II) and Rh(III) form similar polychlorometallate complexes, depending on the concentration of HCl in water. In such cases, ILs are much more efficient at extracting these ions. Precious metals are successfully extracted using undiluted ILs such as $[C_nC_1im][NTf_2]$ and their pyridinium or pyrrolidinium homologs (Papaiconomou, Vite, Goujon, Lévêque, & Billard, 2012; Papaiconomou, Génand-Pinaz, Leveque, & Guittonneau, 2013; Papaiconomou, Billard, & Chainet, 2014; Papaiconomou et al., 2015; Katsuta et al., 2016). Functionalized ILs, also known as task specific ILs (TSILs), are ILs with an added functional group covalently bonded to either the cation or anion which confer certain desired properties useful for selective metal extraction (Fagnant Jr., Goff, Scott, Rundell, & Brennecke, 2013). Derivatization of the IL cation to incorporate task-specific functionalities such as metal ligating groups provide an efficient way to maximize metal solvation (Visser et al., 2001). For example, substitution of the cationic alkyl chain in $[C_nC_1im][PF_6]$ with either urea-, thiourea-, and thioether- alkyl groups can result in an increase in the extraction of Cd(II) from aqueous solution by several orders of magnitude (Visser et al., 2002).

Major developments in the use of ILs in solvent extraction can be divided into three main categories: ILs used as the diluting hydrophobic phase in conjunction with a traditional extractant; selective extraction of metals through IL anion interaction; and task specific ILs (Abbott et al., 2011). Electroneutrality is the governing principle behind the multiple potential extraction mechanisms in ILs as the net charge of the aqueous and IL phases must remain constant (Janssen et al., 2015). A brief overview of the potential extraction mechanisms for a metal cation (M^{n+}) from an aqueous solution containing an anion (X^-) to an IL phase (C^+ – IL cation; A^- – IL anion) containing a ligand (L or HL if protonated) is described in Table 3. A commonly used category of hydrophobic ILs in solvent extraction are those incorporating the $[NTf_2]^-$ anion. These ILs often require the addition of an extractant to increase the hydrophobicity of the metal complex to facilitate the extraction of a hydrated metal cations. For example, many studies have reported enhanced extraction efficiency and selectivity for REEs on substitution of conventional organic diluents by hydrophobic ILs (Nakashima, Kubota, Maruyama, & Goto, 2004; Shimojo, Kurahashi, & Naganawa, 2008; Shen, Tan, Wang, & Wu, 2011). The structure and abbreviation for the main extractants discussed in this work are presented in Figure 5.

Table 3. Multiple extraction schemes for the transfer of metal cations from an aqueous phase to an IL phase.

Extraction mechanism	General extraction scheme	No.
ILs + extractants		
Neutral extraction	$M^{n+}_{aq} + nHL_{IL} \rightarrow [M \cdot (L)_n]_{IL} + nH^+_{aq}$	(1)
	$M^{n+}_{aq} + mL_{aq} + nX^-_{aq} \rightarrow [M \cdot (L)_m \cdot (X)_n]_{IL}$	(2)
Ion exchange	$M^{n+}_{aq} + mL_{aq} + nC^+_{IL} \rightarrow [M \cdot (L)_m]^{n+}_{IL} + nC^+_{aq}$	(3)
	$M^{n+}_{aq} + (n+1)HL_{aq} + [C][A]_{IL} \rightarrow [M \cdot (L)_{n+1}]^-_{IL} \cdots [C]^+_{IL} + (n+1)H^+_{aq} + A^-_{aq}$	(4)
	$M^{n+}_{aq} + mL_{aq} + (n+1)X^-_{aq} + [C][A]_{IL} \rightarrow [M \cdot (X)_{n+1} \cdot (L)_m]^-_{IL} \cdots [C]^+_{IL} + A^-_{aq}$	(5)
Neat ILs		
Ion pair	$M^{n+}_{aq} + mX^-_{aq} + (m-n)C^+_{aq} \rightarrow [C_{m-n}MX_m]_{IL}$	(6)
	$M^{n+}_{aq} + mX^-_{aq} + (m-n)CA_{IL} \rightarrow [C_{m-n}MX_m]_{IL} + (m-n)A_{aq}$	(7)
Anion exchange	$M^{n+}_{aq} + mX^-_{aq} + (m-n)A_{IL} \rightarrow [MX_m]_{IL} + (m-n)A_{aq}$	(8)
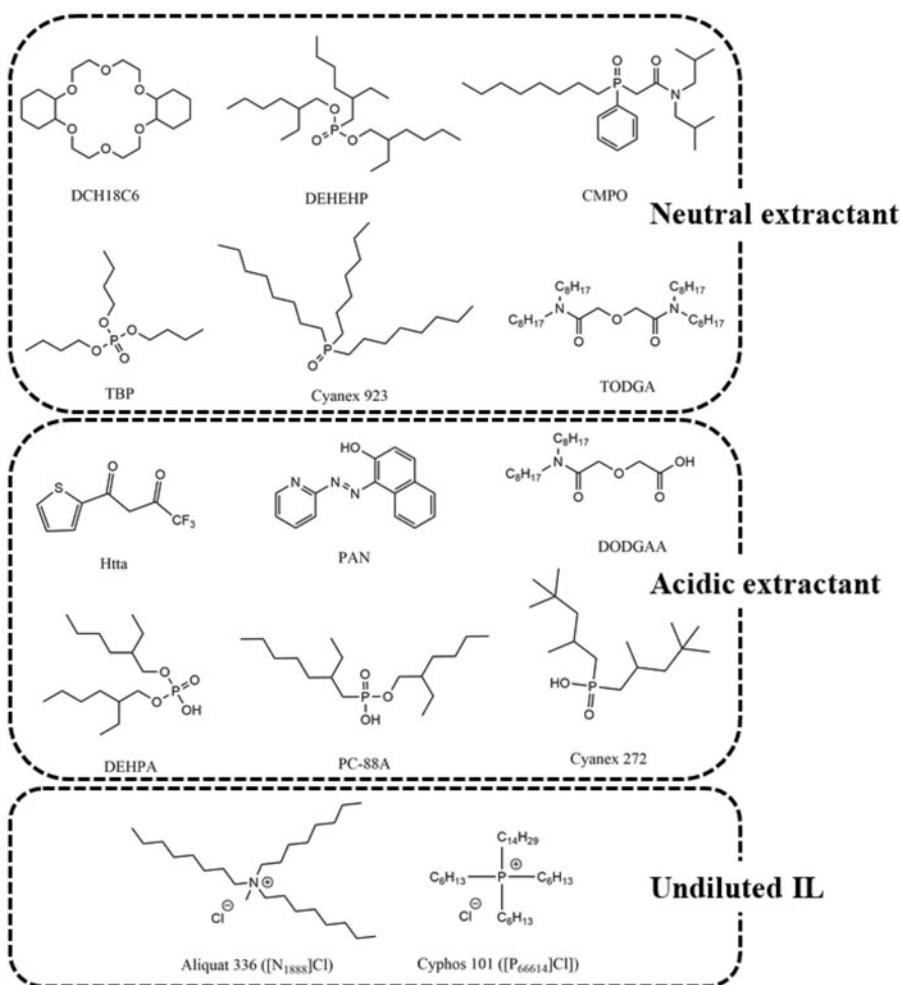
Figure 5. Schematic of selected neutral and acidic extractants and primary undiluted ILs presented in this work and their abbreviations.

These equations do not represent all potential extraction mechanisms in ILs but rather provide an overview of the various extraction schemes possible whilst preserving electroneutrality. The extraction mechanisms in

solvent extraction systems with a ligand dissolved in the IL can be broadly divided into two categories: neutral extraction and ion-exchange extraction. Neutral extraction can proceed through the formation of a neutral metal-ligand complex either via deprotonation of the ligand (Ext. 1), formation of a charge neutral complex with aqueous solution anions and extraction of a neutral metal-cation/anion ion-pair (Ext. 2). For metal extraction proceeding through an ion exchange mechanism, the IL cation is released to the aqueous phase to compensate for the incoming positive charge of the metal complex (Ext. 3–5). In the case of TSILs, the functionilized component of the IL acts as the ligand (Jensen, Neuefeind, Beitz, Skanthakumar, & Soderholm, 2003). It is possible for multiple extraction mechanisms to co-exist within similar solvent extraction systems. The factors determining the relative importance of an extraction scheme include hydrophobicity of the IL cation (Jensen et al., 2002) and anion (Jensen et al., 2003, 2012; Luo et al., 2006) and the hydration energy of the aqueous metal complex (Garvey, Hawkins, & Dietz, 2012; Wankowski & Dietz, 2016). The composition of the aqueous phase can also influence the extraction efficiency for a particular solvent extraction. The water miscibility of four hydrophobic ILs was found to increase with addition of the cations $NH_4^+ > K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}$ and anions $[ClO_4]^- > I^- > [NO_3]^- > Cl^- > F^- > [SO_4]^{2-}$ as predicted by the Hofmeister series (Dupont et al., 2015).

The most widely used solvent extraction systems involve use of either ion-exchange extractant classified into acidic (eg. carboxylates, sulfonates, phosphates) and basic extractant (primary to quaternary amines), solvating extractant (or neutral extractant) possessing ketone, ether, ester or alcohol functional groups and/or coordinating extractant (or chelating extractant) (Free, 2013). These will be discussed in the following section. Whilst a single extractant can often saturate the coordination sphere of a metallic cation as well as produce a charge neutral and hydrophobic complex, on occasion a combination of two extractants is required. If the resulting distribution ratio is greater for the combined extractant than the sum for the individual extractants employed, the system benefits from a synergistic extraction mechanism (Stepinski, Jensen, Dzielawa, & Dietz, 2005). In addition to increasing the extraction efficiencies, synergistic extraction systems can also improve the separation factors between two different metals. Such systems have been used effectively in conjunction with ILs, and the presence of two extractants can result in a change of extraction mechanism compared to when the extractants are individually employed (Zhu et al., 2015; Petrova, 2016).

In the case where no extractant is used and the metal ion forms negatively charged complex ions with anions present in the aqueous phase,

either originating from the acid used, or added on purpose in the solution, the extraction mechanisms can be discussed in a similar way as that detailed above. Because electroneutrality must be respected, two main possible extraction mechanisms, hydrophobic ion pair formation or anion exchange, occur (Ext. schemes 6 to 8). In the case of the formation of hydrophobic ion pairs, two versions exist in the literature, one using cations from the IL that are in the IL phase, and another one using cations that are dissolved in the aqueous phase (Ext. 6 and 7). Strikingly, even though anion exchange and ion pair formation were discussed as two distinct mechanisms, most recent studies show that these are actually linked together because a hydrophobic IL, as any salt, exhibits a limited, though non negligible, solubility in water. The typical solubility of $[C_8C_1im][NTf_2]$ is around $10^{-3} \, mol.L^{-1}$. In other terms, the solubility product of hydrophobic ILs is not negligible (Chapeaux, Simoni, Stadtherr, & Brennecke, 2007; Mazan, Billard, & Papaiconomou, 2014). In an anion exchange mechanism, an anion of the IL is transferred to the aqueous phase. Because the solubility of the IL is then exceeded, this necessarily yields the transfer of an IL ion pair initially dissolved in the aqueous phase towards the IL phase. This results as the co-extraction of a metal complex with a cation of the IL, that is, the formation of a hydrophobic ion pair (Ext. 8).

In the following sections, the use of ILs at different stages of WEEE recycling is reviewed, with particular emphasis on the use of ILs as solvents for leaching and liquid-liquid extraction processes. The use of IL for the electro-deposition of metals has previously been reviewed by Abbott et al. (Abbott & McKenzie, 2006; Abbott et al., 2011, 2013; Smith et al., 2014) and Endres et al. (2008) and will only be briefly addressed due to the potential for IL-based solvents as a medium for the 'one-pot' leaching and deposition of metals. It is important to note that not all reported studies use actual waste but often focus on simulated solutions or mixtures containing a few elements. The use of ILs covered in this review is for the most part focused on the recovery of value from PCBs, waste fluorescent phosphor, nickel metal hydride batteries and permanent magnets. From the literature reviewed, optimized process flowsheets are proposed for these wastes and are presented in Section 7.

4. WEEE dismantling using ILs

Current research on the use of ILs as WEEE dismantling agent is limited to the disassembly of electrical components and epoxy resin from waste PCBs. PCBs are complex and challenging materials due to their heterogeneous nature. PCBs are comprised of either: (1) an epoxy resin-based plastic reinforced with glass fibers coated with a copper layer (FR-4 type PCB)

or (2) a single layer of fiberglass or cellulose paper and phenolic resins coated with a copper layer (FR-2 type PCB). The resin board is overlaid with microelectronic components such as semiconductor chips and capacitors plus solder, which is a Pb-Sn alloy (Zeng, Li, Xie, & Liu, 2013; Zhu et al., 2012c).

Previous research focused on the separation of the electrical components from the waste PCBs and/or dissolution of the epoxy resin using the water soluble ILs $[C_2C_1im][BF_4]$ and $[C_4C_1im][BF_4]$. Separation of the electrical components from waste PCBs relies on the high thermal stability of the IL used. The welding point temperature for Pb and Pb-free solders is 215 °C (Zeng et al., 2013). By heating PCB chips in the IL at 240 to 250 °C for 10 to 30 minutes, at 45 to 150 rpm, the solder was melted and recovered from the board along with the previously attached electrical components. Under these conditions, over 90 wt.% of the electronic components were separated from the PCBs and XRD analysis of the recovered solder indicates no structural changes (Zhu et al., 2012b; 2012c; Zeng et al., 2013). The IL can be successfully recycled, and cost analysis of the process indicates that the process becomes financially viable for waste PCB amounts over 3 kt (Zeng et al., 2013). Heating of the bare board in $[C_2C_1im][BF_4]$ for 10 minutes results in the complete dissolution of the polymeric materials and the delamination of the glass and copper foils. H^1-NMR analysis indicates that H-bond formation plays an important role in the dissolution of the bromine epoxy resins by $[C_2C_1im][BF_4]$. The IL was successfully regenerated by the addition of water, resulting in the formation of a precipitate which was confirmed as bromine epoxy resin by FTIR (Zhu et al., 2012a; 2012c).

5. ILs in leaching and recovery applications

In this section, several methods for leaching metal ions and recovering them under a solid form (either as oxide or salts) will be detailed. The methods presented here will not deal with liquid-liquid extraction. The dissolution of metals and metal salts is the first step in hydrometallurgical processes (Figure 1). The state of elements in WEEE is diverse, with elements present as elemental metals, oxides, sulfates, phosphates, carbonates and others. The selection of an appropriate leaching agent depends on the waste matrix and value of the final product and should effectively act as a concentrating step by only selectively solubilizing elements of interest prior to further separation and recovery steps. Selection of a suitable leaching medium can help reduce the complexity and number of downstream processing steps. Research on metal dissolution using unconventional solvents based on ILs has focused on DES and ILs incorporating Brønsted acidic

functional groups and/or ILs based on strongly Lewis basic anions. However, some metal oxides including Ag_2O, NiO, CuO and ZnO were found to dissolve in imidazolium-based ILs with a hydrogen atom in the C^2 position of the imidazolium ring through the formation of carbene complexes (Wellens, Brooks, Thijs, Van Meervelt, & Binnemans, 2014b). Selected example of IL used in leaching and recovery applications are summarized in Table 4.

5.1. Cation mediated leaching

Many metal salts are insoluble in common hydrophobic ILs due to the hydrophilic nature of the metallic cation and the weakly coordinating nature of the anion; metals and metal oxides are only generally soluble in strong acidic or alkali aqueous solutions. First synthesized by Nockemann et al. (2006), $[N_{R11(2(O)OH)}][NTf_2]$ (R & imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium) are a group of betaine-based TSIL bearing a carboxyl group capable of selectively solubilizing REO, UO_2, ZnO, CdO, HgO, NiO, CuO, PdO, PbO, MnO, Ag_2O and some metal hydroxides. Insoluble or very poorly soluble oxides are Fe_2O_3, CoO, Al_2O_3 and SiO_2 (Nockemann et al., 2008a). The solubility of metal oxides in $[N_{R11(2(O)OH)}][NTf_2]$ is high due to the formation IL-RE stoichiometric compounds as indicated by single crystal XRD studies (Nockemann, Thijs, Van Hecke, Van Meervelt, & Binnemans, 2008b). Another interesting property of $[N_{111(2(O)OH)}][NTf_2]$ is the presence of an upper critical solution temperature (UCST) for the binary mixture of $[N_{111(2(O)OH)}][NTf_2]/H_2O$ (Nockemann et al., 2006). ILs with an UCST are said to exhibit thermomorphic behavior, with the two immiscible phases forming one homogeneous phases above the UCST. A two-phase system is reestablished by lowering the solution temperature to below the UCST. ^{1}H-NMR investigation attributes the presence of a UCST to the temperature-dependent hydration and hydrogen-bond formation between the carboxylic group of the $[N_{111(2(O)OH)}]^+$ cation and the nitrogen atom of the $[NTf_2]^-$ anion (Nockemann et al., 2008a). Conditions above the UCST reduce the viscosity of the solution and accelerate mass transfer, resulting in higher extraction efficiencies. Extracted metals were stripped from $[N_{111(2(O)OH)}][NTf_2]$ by contacting with an acidic aqueous solution, allowing the IL to be recycled for reuse.

The thermomorphic properties of $[N_{111(2(O)OH)}][NTf_2]$ were used for the recovery of Nd_2O_3, Dy_2O_3 and CoO from waste NdFeB magnets in a combined leaching-extraction step (Dupont & Binnemans, 2015a). After roasting in a microwave, waste NdFeB magnets were leached at 80 °C in a $[N_{111(2(O)OH)}][NTf_2]$-H_2O solution. The leach solution was cooled and returned to a biphasic system whereby the REE and Co were distributed in

Table 4. Selected example of ILs used in leaching and recovery applications of metals from WEEE and ores.

Waste matrix	Metals investigated	Ionic liquid/oxidant	Reference
Electric arc furnace dust	ZnO, PbO, Fe_2O_3, Al_2O_3	$[N_{111(2OH)}]Cl$:urea	Abbott et al. (2009)
Brass ash	ZnO, CuO, Cu^0	IL: $[C_4C_1im][HSO_4]$ Oxidant: H_2O_2 or $KHSO_5$	Kilicarslan et al. (2014)
Metals and alloys	Fe^0, Cu^0, In^0, Zn^0, Ga^0, Sb^0, Au^0, Pt^0, Ge^0, Ta^0, Sm^0, Dy^0, $GaAs$, $InAs$	$[P_{44414}][Cl_3]$	Li et al. (2018)
Ore	Sulfidic ore containing Au, Ag, Cu, Zn, Fe, Pb	IL: $[C_4C_1im][HSO_4]$ w/ thiourea Oxidant: $Fe_2(SO_4)_3$	Whitehead et al. (2004a)
Sulfidic ore/synthetic oxide ore	$CuFeS_2$, FeS_2, ZnS / SiO_2, $CaSO_4$, Fe_2O_3, Al_2O_3, MnO_2, TiO_2, AuO, AgO	IL: $\overline{[C_4C_1im]}[X]$ (X $=$ Cl$^-$,$[C_1SO_3]^-$, $[SCN]^-$, $[HSO_4]^-$) w./ thiourea Oxidant: $Fe_2(SO_4)_3$	Whitehead et al. (2007)
Ore	Sulfidic ore containing Au, Ag, Cu, Zn, Fe, Pb	IL: $\overline{[C_4C_1im]}[X]$ (X $=$ Cl$^-$, $[HSO_4]^-$) w./ thiourea, chloride, bromide or iodide Oxidant: $Fe_2(SO_4)_3$ or $KHSO_5$	Whitehead et al. (2009)
Ore	$CuFeS_2$, FeS_2, $ZnFeS$	IL: $\overline{[C_4C_1im]}[HSO_4]$ Oxidant: H_2O_2	Dong, Hua, Zhang, & Zhou (2009)
Fluoride ore/synthetic ore	$RECO_3F$, RE_2O_3, $RE_2(CO3)_3$	$[N_{11(2(OH))}]\overline{[NTf_2]}$ in $[C_4C_1im][NTf_2]$	Freiderich, Stankovich, Luo, Dai, & Moyer (2015)
Synthetic ore	Cu-Zn powder and crushed Ga-As wafer	IL: $[N_{111(2OH)}]Cl$:EG (1:2) Oxidant: Iodine	Abbott et al. (2015)
Ore	Sulfidic ore containing Au, Ag, Te, Fe	IL: $\overline{[N_{111(2OH)}]}Cl$:EG (1:2) Oxidant: Iodine	Jenkin et al. (2016)
Ore	Chalcopyrite	IL: $\overline{[C_nC_1im]}[HSO_4]$ (n $=$ 1,4) Oxidant: O_2	Carlesi, Cortes, Dibernardi, Morales, & Muñoz (2016)
Ore	Bauxite ore containing REE(III), Ti(IV), Si(IV), Al(III), Fe(III), Ca(II)	$[N_{111(2(O)OH)}][NTf_2]$	Davris et al. (2016)
Ore	Pyrite, arsenopyrite	$[N_{111(2OH)}]Cl$:EG (1:2)	Abbott et al. (2017)
PCB	Cu^0	IL: $[C_4C_1im][HSO_4]$ Oxidant: H_2O_2	Huang et al. (2014)
PCB	Cu^0, Zn^0, Pb^0	IL: $\overline{[(C_4SO_3H)C_1im]}[X]$ (X $=$ $[OTf]^-$, $[HSO_4]^-$), $[C_nC_1im][HSO_4]$ (n $=$ 1, 4) Oxidant: H_2O_2	Chen et al. (2015a,b,c)
PCB	Cu^0	IL: $\overline{[(SO_3H)C_4pyr]}[HSO_4]$ Oxidant: O_3	Zhang et al. (2018)
NdFeB magnets	Nd_2O_3, Dy_2O_3, CoO, Fe_2O_3	$[N_{111(2(O)OH)}][NTf_2]$	Dupont & Binnemans (2015a)
NdFeB magnets	CoO, Fe_2O_3, B_2O_3, Nd_2O_3, Dy_2O_3, Pr_2O_3, Gd_2O_3	$[N_{111(2OH)}]Cl$:lactic acid (1:2)	Riaño et al. (2017)
Synthetic phosphor mix	Y_2O_3:Eu^{3+} (YOX), $(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2$:$Sb^{3+}$,-$Mn^{2+}$ (HALO)	$[N_{111(2(O)OH)}][NTf_2]$	Dupont & Binnemans (2015b)
Synthetic phosphor mix and oxides	CuO, NiO, ZnO, MnO, MnO_2, Co_3O_4, Fe_2O_3, La_2O_3, Nd_2O_3, Dy_2O_3 $LaPO_4$:Ce_3^+,Tb_3^+ (LAP) $BaMgAl_{10}O_{17}$ (BAM)	$[N_{R1R2(H-SO3H)}][NTf_2]$	Dupont et al. (2016b)
Waste phosphor	Y_2O_3:Eu^{3+} (YOX), $(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2$:$Sb^{3+}$,-$Mn^{2+}$ (HALO)	$[HC_1im][HSO_4]$	Schaeffer et al. (2017)
Crude $In(OH)_3$	In(III), As(V), Ca(II), Cd(II), Fe(III), Pb(II), Zn(II), trace elements	$[N_{111(2(O)OH)}][NTf_2]$	Deferm et al. (2018)

RE: rare earth; EG: ethylene glycol.

the aqueous phase whilst Fe remained in the IL phase. Addition of oxalic acid to the solution precipitated the REE and Co while transferring Fe to the aqueous phase as a soluble oxalate complex. The REEs and Co were separated by selectively leaching Co from the oxalate precipitate using aqueous ammonia before calcining the RE oxalate to yield a 99.9% pure Nd_2O_3 and Dy_2O_3 mix. Dupont and Binnemans (2015b) also used $[N_{111(2(O)OH)}][NTf_2]$ for the recovery of yttrium and europium oxide from simulated waste phosphor powder yielding a 99.9% pure final $Y_2O_3{:}Eu^{3+}$ product after oxalate precipitation and calcination. The water content of the TSIL played a crucial role in the effectiveness and selectivity of the leaching process. Under water-poor conditions (<5 wt.% H_2O in the IL) YOX phosphor dissolves much more than HALO phosphor, but YOX leaching efficiency also decreases with decreasing IL water content. The leaching selectivity of water-poor $[N_{111(2(O)OH)}][NTf_2]$ was attributed to the inability of the IL to solvate anions due to the lack of suitable coordination mechanisms. As the dissolution of oxides generates no anions, YOX phosphor easily dissolves in $[N_{111(2(O)OH)}][NTf_2]$ whilst the phosphate and chloride metal salt of HALO phosphor do not. The selectivity of $[N_{111(2(O)OH)}][NTf_2]$ for REEs was also exploited for their recovery from bauxite residue containing the impurities Ti(IV), Si(IV), Al(III), Fe(III) and Ca(II) (Davris, Balomenos, Panias, & Paspaliaris, 2016). In addition, $[N_{111(2(O)OH)}][NTf_2]$ was shown to be an effective leaching agent for the purification of the critical element In(III) (Deferm, Luyten, Oosterhof, Fransaer, & Binnemans, 2018). At the optimal conditions of 3 hrs leaching time at 80 °C in a 1:1 $[N_{111(2(O)OH)}][NTf_2]{:}H_2O$ mixture, 99 wt.% of $In(OH)_3$ was leached and separated (D > 100) from Al(III), Ca(II), Cd(II), Ni(II) and Zn(II). Additional pre-hydrolysis and hydrolysis steps including the reduction of Fe(III) to Fe(II) were required to separate In(III) from the co-extracted Fe(III), As(V) and Pb(II). $MgCl_2$ was added as a salting-out agent to minimize the loss of the hydrophilic cation to aqueous phase during extraction but its addition was found to negatively impact the separation of In(III) from the other elements suggesting a compromise is required.

Three groups of zwitterionic, strongly Brønsted acidic TSILs with functionalized cations incorporating sulfonic acid groups (pKa $\sim$ −2.0), alkylsulfuric acid groups (pKa $\sim$ −3.5) and sulfamic acid groups (pKa $\sim$2.0) can solubilize large stoichiometric amounts for a wide range of metal oxides (Dupont et al., 2015; Dupont, Renders, & Binnemans, 2016a, Dupont, Renders, Raiguel, & Binnemans, 2016b). The general structure for these cations is presented in Figure 6. This includes the inert oxides CoO, Co_3O_4, Fe_2O_3, TiO_2, Al_2O_3, Cr_2O_3 and WO_3, which were not previously soluble in $[N_{111(2(O)OH)}][NTf_2]$. A 40 wt.% solution of the sulfamic IL

(a) $[N_{RRR(Cn(O)OH)}]^+$

(b) $[N_{RRR(CnSO3H)}]^+$

(c) $[N_{RRR(Cn(O)SO3H)}]^+$

(d) $[HN_{RR(SO3H)}]^+$
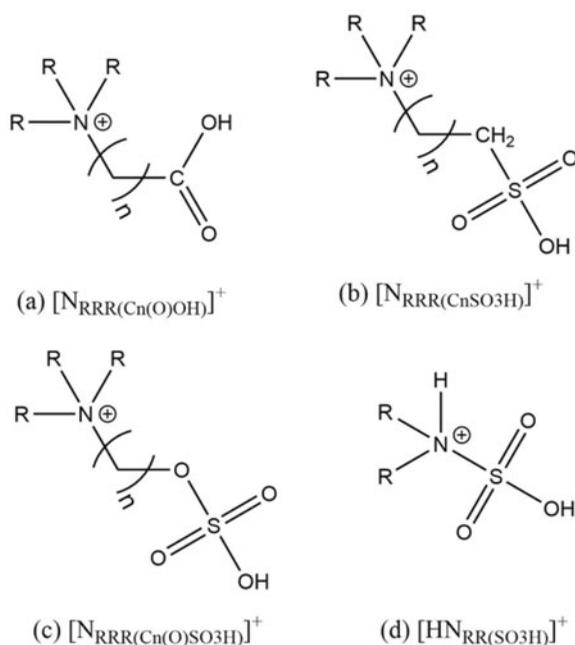
Figure 6. Structures of Brønsted acidic TSIL-derived from (a) betaine, (b) sulfonic acid, (c) sulfuric acid and (d) sulfamic acid.

$[HN_{22(SO3H)}][NTf_2]$ diluted in $[C_2C_1im]Cl$ was able to leach over 90 wt.% of the notoriously inert fluorescent lamp phosphors $LaPO_4:Ce^{3+}$, Tb^{3+} (LAP) and $BaMgAl_{10}O_{17}$ (BAM) (Dupont et al., 2016b). Similarly to $[N_{111(2(O)OH)}][NTf_2]$, metal extraction in these super-acidic TSIL with long alkyl chains is controlled by a proton exchange mechanism and is therefore pH sensitive. As the acidic proton is exchanged for the metal ion, the electronic balance is maintained, and extraction occurs generally without transfer of IL cations or anions to the water phase. Comparison of hydrophobic sulfonic and alkylsulfuric IL metal extraction shows that the extraction efficiency of the latter is intermediate between carboxyl-functionalized ILs such as $[N_{111(2(O)OH)}][NTf_2]$ (poor extraction for most metal ions), and sulfonic acid ILs which fully extract most studied metal ions from chloride solutions (>80%) (Dupont et al., 2016a). This trend follows the functional group charge density $R\text{-}COO^- < R\text{-}OSO_3^- < R\text{-}SO_3^-$. Interestingly in these systems, RE ions are extracted in the reverse order (La(III) > Nd(III) > Dy(III) > Lu(III)) than the one expected based on their charge density. This is attributed to the steric hindrance from the functional groups and long alkyl side chains which causes REEs with smaller radius to be less efficiently coordinated (Dupont et al., 2015). The doubly acidic task-specific pyridinium-based IL incorporating a sulfonic acid moiety $[(SO_3H)C_4pyr][HSO_4]$ was used to replace H_2SO_4 in a slurry electrolytic

system for the one step leaching and recovery of Cu(II) from waste PCBs (Zhang, Chen, Tan, Wang, & Chen, 2018). A 20% increase in Cu(II) recovery to 90.9 wt.% was obtained when 10% H_2SO_4 was replaced by $[(SO_3H)C_4pyr][HSO_4]$. However, a further increase in the IL concentration to 40 wt.% resulted in the decrease in the Cu(II) recovery rate and current efficiency due to the increase in solution viscosity. In addition, lower quality deposits were obtained at these high concentrations due to the strong competitive absorption of the IL cation at the cathode inhibiting deposition. The deposit was identified as a mixture of Cu^0, CuO and Cu_2O for a 10 wt.% concentration of $[(SO_3H)C_4pyr][HSO_4]$ with H_2SO_4 and O_3 as oxidant.

Although the hydrophobic IL trihexyl(tetradecyl)phosphonium chloride ($[P_{66614}]Cl$) is insoluble in water, $[P_{66614}]Cl$ can adsorb up to 13.5 wt.% of water at room temperature. $[P_{66614}]Cl$ saturated with concentrated HCl was used to dissolve CaO, NiO, MnO, CoO, CuO, ZnO and Fe_2O_3. Addition of HCl resulted in a large decrease in IL viscosity and allowed the solubilization of metal oxides. UV-Vis analysis indicated the presence of Ni(II), Cu(II), Fe(III), and Co(II) in $[P_{66614}]Cl$ as anionic tetrachlorometallate complexes, whilst Ca(II) is unable to form anionic complexes and remains as a hydrated calcium ion. Separation of the solubilized elements using a stripping HCl solution was based on the tendency of Ni(II) and Ca(II) to form aqua complexes regardless of HCl concentration and the partial stripping of Co(II) an Mn(II) at low HCl concentrations. Ni(II) and Ca(II) were first stripped using 6 M HCl before subsequent removal of Co and Mn from Fe, Zn and Cu by contacting the saturated IL with a water and ammonia solution (Wellens et al., 2014a).

5.2. Anion mediated leaching

$[HSO_4]^-$-based IL including $[C_4C_1im][HSO_4]$ were successfully used to recover Cu from waste PCBs (Huang, Chen, Chen, Chen, & Sun, 2014) and chalcopyrite ore (Dong et al., 2009; Chen, Huang, Ogunseitan, Zhu, & Wang, 2015a), Cu and Zn from brass ash (Kilicarslan, Saridede, Stopic, & Friedrich, 2014), leaching of Au, Ag, Cu and base metals from ores (Whitehead, Lawrance, & McCluskey, 2004a; Whitehead, Zhang, Pereira, McCluskey, & Lawrance, 2007; Whitehead, Zhang, McCluskey, & Lawrance, 2009) and YOX phosphor from waste fluorescent tubes (Schaeffer, Feng, Grimes, & Cheeseman, 2017).

The recovery of yttrium europium oxide from waste fluorescent tube phosphor by a simple efficient low-cost IL process was developed using $[H_4C_1im][HSO_4]$ (Schaeffer et al., 2017). The waste phosphor containing Y(III), Eu(III), Tb(III), La(III) and Gd(III) was first pretreated to

concentrate its rare earth content. Larger glass particles were removed by sieving through a 25 μm sieve whilst soluble Ca(II), Ba(II), Sr(II) were partially removed by contacting the phosphor with a dilute HCl solution for 1 hour. Leaching of REEs was optimized by systematically varying the leaching temperature, the $[H_4C_1im][HSO_4]:H_2O$ ratio, leaching time and solid to liquid ratio. Under the optimized conditions of 1:1 wt. $[H_4C_1im][HSO_4]:H_2O$ solution, a solid:liquid ratio of 5%, a mixing speed of 300 rpm, a leaching temperature of 80 °C and leaching time of 4 h, the percentage of Y, Eu and Ca leached is 91.6 wt.%, 97.7 wt.% and 24.9 wt.%, respectively. The low leaching efficiency of Tb(III), La(III) and Gd(III) compared to Y(III) and Eu(III) is due to the former being as highly stable phosphate salts whilst the latter are found as oxides. The REEs in the leachate were precipitated by the addition of oxalic acid at a molar ratio (OA:REE) of 1.5 and a solution pH of 0.9. Luminescence analysis of the recovered oxide product after calcination indicates that the recovered yttrium europium oxide has the potential to be directly reused as YOX phosphor. The stability and recyclability of the IL was demonstrated over four leaching/precipitation cycles.

A recent comparison of six ILs incorporating $[HSO_4]^-$ and $[CF_3SO_3]^-$ on the leaching efficiency of Cu, Zn and Pb respectively from waste PCBs found that greater leaching efficiency could be achieved using $[HSO_4]^-$ and that inclusion of an acidic group on the alkyl chain of the cation increased Cu and Zn leaching (Chen et al., 2015a; Chen, Wang, Huang, & Chen, 2015b). Leaching results indicate that all six IL acids could successfully recover Cu and Zn under the test conditions with almost 100 wt.% recovery except for $[C_1C_1im][HSO_4]$. Kinetic analysis of the dissolution process using the shrinking core set of equations indicates that in the case of Cu and Zn dissolution by $[HSO_4]^-$ and $[CF_3SO_3]^-$ ILs, the reaction rate is controlled by diffusion processes and not by the surface chemical reaction. However, the study of Pb is of minimal interest because of the aqueous insolubility of $PbSO_4$, with little to no recovery recorded for the $[HSO_4]^-$ and $[CF_3SO_3]^-$ ILs tested (Chen, Zhang, Huang, & Chen, 2015c). Quantitative Cu extraction from waste PCBs using $[C_4C_1im][HSO_4]$ was also achieved under the leach conditions: 1 g PCB powder (particle size of 0.1–0.25 mm), 25 mL 80% (v/v) $[C_4C_1im][HSO_4]$, 10 mL 30 wt.% H_2O_2, solid: liquid ratio of 1:25, 70 °C and 2 hours. Kinetic analysis of the leaching process determined that this was diffusion controlled with an activation energy of 25.4 kJ.mol^{-1} (Huang et al., 2014). None of these cited studies investigated the concomitant leaching of other elements or the recovery of Cu once in solution.

Many of the species of interest are present in their elemental form and must be oxidized prior to solubilization. The solubility of oxygen in ILs is

of crucial interest as it may determine the leaching rate and efficiency. The solubility of oxygen in neat imidazolium-based IL with $[HSO_4]^-$ anion is similar or even superior to that in water, decreases with increasing temperature, and is anion dependent. Larger anion-cation pairings leave larger 'holes' appropriate for oxygen residency compared to more compact ion-pairings. In addition, dipolar interactions between oxygen and the IL anion, influenced by the shape and surface charge density on the anion, are also likely to result in increased oxygen solubility (Whitehead et al., 2007). Common oxidants used with $[C_nC_1im][HSO_4]$ include hydrogen peroxide (H_2O_2), potassium peroxymonosulfate ($KHSO_5$) and Fe(III). Iron(III) is a mild oxidant and unlikely to affect the stability of the IL. However, none of the reported studies using $[C_nC_1im][HSO_4]$ as lixiviant have investigated the potential denaturalization of the IL after a leaching cycle in the presence of strong oxidants such as H_2O_2. Results from previous research suggest that $[C_nC_1im][HSO_4]$ is readily degraded by of H_2O_2 (Domínguez et al., 2014). The length of the alkyl chain has a dramatic effect on the stability of imidazolium-based ILs to degradation by stoichiometric amounts of H_2O_2, with greater resistance conferred by longer alkyl chains. Furthermore, ILs bearing methanesulfonate and methylsulfate anions are oxidized faster than those with chloride or acetate anions. A compromise between metal extraction and IL recovery is required under such circumstances

An innovative class of ILs containing trichloride anions (Cl_3^-) with oxidative properties capable of releasing chlorine was synthesized by bringing chlorine gas into contact with the corresponding chloride (Cl^-) ILs at room temperature (Li, Van den Bossche, Vander Hoogerstraete, & Binnemans, 2018). These were prepared with a range of cations with no degradation of the latter observed. An additional benefit from the conversion of the IL anion Cl^- to Cl_3^- is the accompanying reduction in the IL viscosity due to the lower electrostatic attraction between the cation and the Cl_3^- ion. Taking $[P_{44414}]Cl_3$ as a representative IL, dissolution experiments were performed for 12 metals and 2 alloys in solutions at 25 °C containing molar ratio of metal:IL of 1:8. Whilst the dissolution time was found to greatly vary between metals tested, 8 metals commonly found in WEEE Cu, Fe, In, Zn, Ga, Au, Ge and Sb along with the alloys InAs and GaAs could be dissolved in the tested IL. EXAFS analysis revealed that these metals exist as anionic chloride complexes in the IL.

5.3. Deep eutectic solvents (DES) as leaching agents

DES are usually composed of two chemicals, typically one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA), exhibiting high

melting points. Once combined in specific stoichiometric ratios, the mixture melts and forms a homogeneous liquid phase. The DES under consideration in this review are those based on at least one IL homologs, namely a quaternary ammonium salt, choline chloride ($[N_{111(2OH)}]Cl$) being the most common, and a HBD such as urea, carboxylic acids or polyols (Smith et al., 2014). DES exhibit unusual solvent properties that are dependent on the selection of the HBD and HBA and their respective molar ratio. The considerable attraction of DES stems from low synthesis cost, low environmental toxicity and solubility for a wide range of metal oxides (Abbott, Capper, Davies, Rasheed, & Tambyrajah, 2003; Abbott, Boothby, Capper, Davies, & Rasheed, 2004).

Metal oxide solubility in DES is influenced by the extent of H-bonding interactions, with compounds able to donate or accept electrons or protons to form H-bonds displaying high solubility (Abbott et al., 2004). The solubility of 17 metal oxides in the elemental mass series Ti through to Zn was reported, with $[N_{111(2OH)}]Cl$:malonic acid displaying the greatest solubility for the tested elements after HCl (Abbott et al., 2006). Most ionic transition metal oxides are soluble in DES whilst covalent metal oxides such as SiO_2 and Al_2O_3 are insoluble in all tested DES to date. Judicious selection of an appropriate HBD allows for the selective leaching of certain elements from a mixed oxide matrix. For example, Fe_3O_4 is soluble and CuO insoluble in $[N_{111(2OH)}]Cl$:oxalic acid eutectic whilst the opposite behavior is observed when the HBD is changed to phenylpropionic acid (Abbott et al., 2004). Furthermore, compounds that are known to form DES with choline chloride were successfully used for the leaching of Mn, Li, Co, and Ni using either L-tartaric acid (He, Sun, Mu, Song, & Yu, 2017) and lactic acid (Li et al., 2017) highlighting the untapped potential of DES as leaching agents. In addition to suitability for metal oxide leaching, a growing number of studies employ DES as electrolytes for metal electro-deposition, allowing for the development of a 'one pot' solvatometallurgical process. A large number of metals including Zn, Ni, Cu, Co, Sn, Se, In, Sm, Pd, Fe, Ag and Pb were successfully deposited from DES (Abbott et al., 2013; Smith et al., 2014; Zhang, Wang, Zhang, Lu, & Zhang, 2016).

The establishment of a comparable electrochemical series for 17 redox couples referenced to the $Fe(CN)_6^{3-/4-}$ couple in the DES $[N_{111(2OH)}]Cl$:urea and $[N_{111(2OH)}]Cl$:EG shows that some redox potentials shift considerably in DESs compared to aqueous solution, particularly the oxophilic p-block elements such as Ga and Sb, Cu and the chlorophilic late transition elements including Ag, Pd and Au. The high chloride concentration in DES electrolytes acts as an environmentally benign stabilizing ligand used to adjust metal speciation, thereby controlling solubility and deposition properties, making DES excellent separation and recovery media
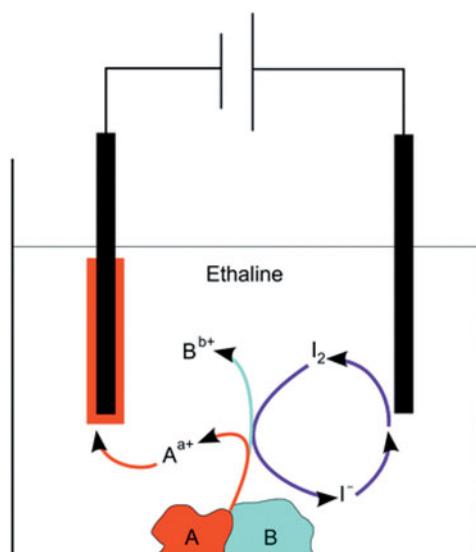
Figure 7. Schematic diagram of the separation and recovery of two elements, A and B, using iodine as an electrocatalytic oxidation agent in [N111(2OH)]Cl:EG. Reproduced from Abbott et al. (2015) with permission from The Royal Society of Chemistry.

(Abbott et al., 2011). The determination of the electrochemical series served as the basis for the recovery of value from synthetic wastes matrices and ores (Abbott et al., 2015; Jenkin et al., 2016). Iodine was selected as the electrocatalyst due to its fast electron transfer, reversibility, high rates of mass transport, high solubility in DES, and environmental compatibility in reduced form (Abbott et al., 2011, 2015). The redox potential of I_2/I^- in a $[N_{111(2OH)}]$Cl:EG DES was found to be more positive than that of most common metals. The developed system depicted in Figure 7 could oxidize Cu and Zn from 1:1 Cu-Zn powders, As and Ga from crushed Ga-As wafer and Au and Ag from gold-bearing ores (Abbott et al., 2015; Jenkin et al., 2016).

6. ILs in solvent extraction processing

Solvent extraction (or liquid-liquid extraction) is the favored option for metal separation and involves the preferential two-phase distribution of a solute between mutually immiscible liquid phases, usually consisting of an aqueous acidic solution and an aliphatic organic solvent. The ILs used in solvent extraction must be water immiscible to promote recovery of the metal and prevent the loss of the IL to the aqueous phase. Metal extraction from the aqueous phase results from the formation of hydrophobic M^{n+}-ligand complexes and their migration to the hydrophobic phase (Rydberg, Cox, Musikas, & Choppin, 2004). A schematic of the typical process steps in the recovery of metals from leach solutions using solvent extraction is presented in Figure 8.
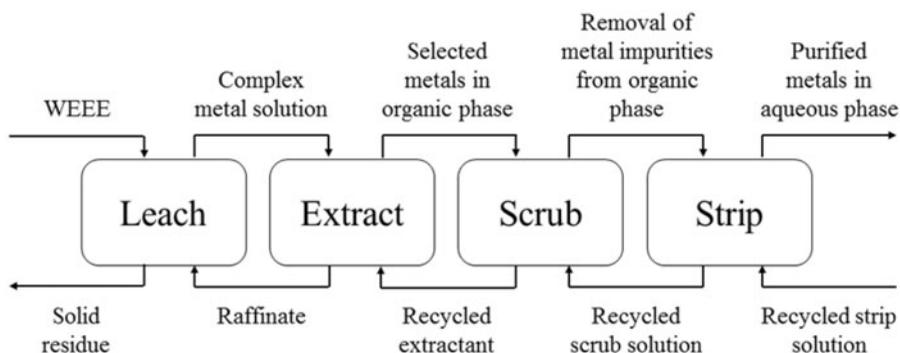
Figure 8. Schematic of the typical process steps in the recovery of metals from leach solutions using solvent extraction.

This section is divided according to the application of the IL-based solvent, with a division being made between traditional solvent extraction processes and more recent advances. First, the use of undiluted IL acting as both the extractant and hydrophobic phase in traditional solvent extraction is presented. Secondly, the application of IL as hydrophobic diluting phase in conjunction with neutral and acidic extractant is discussed. Finally, the application of TSIL in solvent extraction for the recovery of metals from WEEE is addressed. Following this review of more 'traditional' solvent extraction processes, the use of IL-based aqueous biphasic system applied to WEEE valorization is discussed as well as the developing field of hydrophobic DES and triphasic IL-IL systems for the simultaneous separation of different metal groups. Because of the large volume of publications on the topic, the discussion will be limited to a selected number of extraction systems directly addressing the recovery of metal from WEEE or the separation of critical metal groups relevant to recycling of WEEE. The major studies involving the use of ILs in solvent extraction processes for the recovery of metals from WEEE are summarized in Table 5.

6.1. Undiluted ILs

Recent research on the application of ILs in solvent extraction has focused on simple IL extraction systems without added complexing ligand. Hydrophobic ILs based on $[NTf_2]^-$ and cation imidazolium, pyrrolidinium or pyridinium have been shown to extract aqueous metal cations without the need for additional ligands (Kozonoi & Ikeda, 2007). Regarding metals found in WEEE, these ILs were found to be efficient at extracting precious metals such as Au(III), Pt(IV) or Ir(IV) from acidic aqueous solutions containing large amounts of HCl (Génand-Pinaz, Papaiconomou, & Leveque, 2013; Papaiconomou et al., 2012, 2014; Yang, Kubota, Baba, Kamiya, & Goto, 2014; Tong, Wang, Huan, & Yang, 2015; Kubota, Shigyo, Yoshida, &

Table 5. Reported IL used in solvent extraction processes for the recovery of metals from WEEE and ores (NMHB: nickel metal hydride battery; FLP: fluorescent lamp phosphor).

Waste substrate	Elements recovered	Extractant	Diluent	Reference
Synthetic NMHB leach solution	Co, Ni, Fe, Mn, Zn, K, Mg, REE	(1) $[P_{66614}]Cl$ (2) $[N_{1888}]Cl$ (3) Cyanex 923 (4) $[N_{1888}][SCN]$	(3) $[N_{1888}][NO_3]$ (4) $[N_{1888}]Cl$	Larsson & Binnemans (2014)
Synthetic NMHB leach solution	Co, Ni, Fe, Mn, Zn, REE	Cyanex 923	$[N_{1888}][NO_3]$	Larsson & Binnemans (2015a)
Synthetic NdFeB and SmCo magnet leach solution	Nd, Sm	$[(C_nCOOH)C_1im][NTf_2]$		Chen et al. (2015d)
NdFeB magnet	Pr, Nd, Dy	TBP	$[N_{1888}][NO_3]$	Kikuchi et al. (2014)
NdFeB magnet	Nd, Dy, Co, Cu, Fe, Mn	$[P_{66614}]Cl$		Vander Hoogerstraete et al. (2014)
NdFeB magnet	Nd, Sm, Fe, Co	$[P_{66614}][NO_3]$		Riaño & Binnemans (2015)
NdFeB magnet	Nd, Sm, Pr, Gd, Fe, Co, B	(1) $[N_{1888}][SCN]$ (2) Cyanex 923	Toluene Toluene	Riaño et al. (2017)
Simulated FLP solution	REE	$[N_{1888}][PC-88A]$ & $[N_{1888}][DEHPA]$		Yang et al. (2012)
FLP	La, Ce, Eu, Gd, Tb, Y	DODGAA	$[C_4C_1im][NTf_2]$	Yang, Kubota, Baba, Kamiya, & Goto, 2013
Commercial HALO phosphor	Sb, Ca	$[N_{1888}]Cl$		Dupont & Binnemans (2016)
Bastnäsite leach solution	Ce, F	DEHEHP	$[C_8C_1im][PF_6]$	Zuo, Liu, Chen, & Li (2009)
Bastnäsite and monazite	La, Ce, Nd, Th, Ca, Mn, Fe, Mg	$[N_{4444}][DEHPA]$	$[EtNH_3][NO_3]$ / $[C_2C_1im][SCN]$ / $[C_4C_1im][BF_4]$.	Azizi & Larachi (2018)
Salt Lake brine	Li, Mg	TBP	$[C_4C_1im][NTf_2]$	Shi, Jing, & Jia (2016)
Bauxite residue	Sc, Fe, Ti, Si, Ca, Al	$[N_{111(2(O)OH)}][NTf_2]$		Onghena, Borra, et al. (2017a)

Goto, 2017). Furthermore, separation of Au(III) from Pt(IV) and from Pt(IV) and Pd(II) is achieved using $[C_4C_1im][NTf_2]$ and $[C_8C_1im][NTf_2]$, respectively (Papaiconomou et al., 2012; Papaiconomou et al., 2014).

Linear quaternary ammonium ILs and quaternary phosphonium ILs have also been extensively studied and used in complete recycling processes of WEEE. ILs based on these cations and a wide variety of anions including chloride, bromide, dicyanamide (Papaiconomou et al., 2015; Svecova, Papaiconomou, & Billard, 2016), nitrate, dioctyl diglycolamate (Rout & Binnemans, 2014a), *N,N,N′,N′*-tetra(2-ethylhexyl)malonate, *N,N,N′,N′*-tetra(2-ethylhexyl)malonamide (Rout & Binnemans, 2014b) or oleate (Parmentier, Vander Hoogerstraete, Metz, Binnemans, & Kroon, 2015a) were studied. The hydrophobic fatty acid based IL tetraoctylphosphonium oleate ($[P_{8888}][C_{17}COO]$) displays a high affinity for first row transition

metals in chloride media (Parmentier et al., 2015a) and was employed in a continuous selective metal extraction process for the recovery of cobalt from two mixed salt solutions (Co/Na, Ca/Co/K) (Parmentier, Paradis, Metz, Wiedmer, & Kroon, 2015). The ammonium alternative to $[P_{8888}][C_{17}COO]$, tetraoctylammonium oleate ($[N_{8888}][C_{17}COO]$), was used in the solvent extraction of Co(II), Ni(II) and Zn(II) with success. Comparison of Co(II), Ni(II) and Zn(II) extraction with the IL as well as the IL precursors (sodium oleate and tetraoctylammonium chloride) indicates that Co(II) and Ni(II) at low chloride concentration are extracted via the IL anion whilst Zn(II) can be extracted both via the oleate anion and via the tetraoctylammonium cation of the IL. Slope analysis and EXAFS measurements reveal that Ni(II) and Co(II) are extracted via the formation of $[N_{8888}^+][M(C_{17}COO)_3^-]$ complexes with M being Co(II) or Ni(II). In contrast, Zn(II) was extracted via a different extraction mechanism, in which the Zn(II) ion was extracted by two IL moieties as $[N_{8888}^+]_2[MCl_2(C_{17}COO)_2^{2-}]$ (Parmentier et al., 2016). This example highlights the need to determine the dominant extraction mechanisms as this can shed light on the higher distribution ratio for one metal compared to another. Other interesting phosphonium- and ammonium-based ILs for the extraction of transition metals include those containing a thiosalycilate or thiocyanate anion (Leyma et al., 2016; Rout & Binnemans, 2016). The latter was used for the separation of transition metals from rare earth elements, a separation relevant for the recycling of permanent magnets, nickel metal hydride batteries and lamp phosphors. The extraction of metal ions from a chloride or nitrate solution with a thiocyanate IL is an example of "split-anion extraction", where different anions are present in the aqueous and IL phase. As per the Hofmeister series, the $[SCN]^-$ prefers the IL phase compared to the Cl^- and $[NO_3]^-$ ions and does not exchange to the aqueous phase, allowing it to preferentially coordinate the 3d transition metals.

Trihexyl(tetradecyl)phosphonium chloride ($[P_{66614}]Cl$) is a commercially available, non-fluorinated IL consisting of an organophosphorous-based cation with a chloride anion – *cf.* Figure 5. Due to the four long alkyl chains, $[P_{66614}]Cl$ has no reported surfactant properties, in contrast to some of the shorter alkyl chain quartenary phosphonium salts alternatives, thereby enhancing phase separation (Bradaric, Downard, Kennedy, Robertson, & Yuehui Zhou, 2003). $[P_{66614}]Cl$ functions by an anion exchange mechanism; and it can be used undiluted, eliminating the need for molecular solvents. The extraction experiments have primarily been conducted from aqueous chloride medium. $[P_{66614}]Cl$ IL shows great promise for the extraction of metal ions and has been studied for the extraction of Zn(II), Fe(II/III), Co(II) as well as REE(III), Au(III), Hg(II), Pd(II), Pt(IV), Bi(III), Re(IV) and U(IV). For example $[P_{66614}]Cl$, or $[P_{66614}]Br$,

extract almost quantitatively Pd(II) and Pt(IV) from aqueous solutions of HCl (Papaiconomou et al., 2015; Kubota et al., 2017). Distribution coefficients as high as 200 for Rh(III) are obtained in aqueous solution containing $1\,mol.L^{-1}$ HCl, while Rh(III) remains preferentially in the aqueous phases when the concentration of HCl exceeds $6\,mol.L^{-1}$ (Svecova et al., 2016). Aliquat 336 ($[N_{1888}]Cl$) is a well-established quaternary ammonium extractant capable of extracting a range of metal ions through anion exchange or formation of a neutral extraction complex (Černá, Volaufová, & Rod, 1992).

$[P_{66614}]Cl$ and its nitrate derivative trihexyl(tetradecyl)phosphonium nitrate were employed in separations relevant to the recycling of rare earths from permanent magnets and Co from Ni metal hydride batteries. Wellens, Thijs, and Binnemans (2012) demonstrated that Co(II) could be selectively separated from Ni(II), Ca(II) and Mg(II) in 8 M HCl aqueous chloride concentration using $[P_{66614}]Cl$ with a separation factor of ≥ 104. Co was extracted as the tetrahedral tetrachlorocobaltate complex, $[CoCl_4]^{2-}$. Co(II) was separated from the co-extracted Mn(II) by four stripping cycles with water. This process has been up-scaled to provide a proof-of-principle for the continuous IL separation process of Co(II) from Ni(II) (Wellens et al., 2013). A similarly high Co/Ni separation ratio was achieved using $[P_{66614}]Cl$ from sulfate media with the extraction proceeding via a split-anion mechanism. Co(II) present in the IL phase was stripped using water and the IL regenerated by contacting with $CaCl_2$ (Onghena, Valgaeren, Vander Hoogerstraete, & Binnemans, 2017b).

$[P_{66614}]Cl$ was also employed for the removal of Co(II) and Fe(III) from Sm(III) and Nd(III) respectively in chloride solutions (Vander Hoogerstraete, Wellens, Verachtert, & Binnemans, 2013). Separation factors of 5.0×10^6 and 8.0×10^5 were obtained for Nd/Fe and Sm/Co respectively at HCl concentrations of 8.5-9 M. The REE(III) remain in the aqueous phase while Co(II) and Fe(III) are extracted as anionic tetrachloro-complexes in the IL. The distribution of Co(II), Mn(II) and Fe(III) to the IL increased with increasing HCl concentration until 8.5–9 M while Zn(II) and Cu(II) decrease with increasing HCl concentrations. However, Al(III), Cr(III), Ni(II), Mg(II), and Ca(II) could not be separated from REEs. After extraction, Co was easily stripped from the IL with water although Fe could only be stripped by forming a water-soluble iron complex with ethylenediaminetetraacetic acid (EDTA). Using the IL trihexyl(tetradecyl)phosphonium nitrate, prepared from $[P_{66614}]Cl$, REEs were separated from Co(II) and Ni(II) (Vander Hoogerstraete & Binnemans, 2014). The separation of Sm(III) from Co(II) and La(III) from Ni(II) were studied. Extraction of the REEs is facilitated by an inner salting-out effect of a highly concentrated metal nitrate aqueous phase. After a scrubbing step using 7.5 M of NH_4NO_3, the purity of REEs in the loaded IL phase was 99.9%. Complete

stripping and regeneration of the IL was achieved using pure water. Extraction of REE by $[P_{66614}][NO_3]$ from nitrate solution occurs by formation of a neutral complex $Ln(NO_3)_{3+n}(P_{66614})_n$, while La and Sm exist as the anionic $[La(NO_3)_6]^{3-}$ and $[Sm(NO_3)_6]^{3-}$ complexes in the IL. The high negative charge of the extracted complexes and the resulting electrostatic interactions have a pronounced effect on the viscosity of the IL phase.

$[P_{66614}]Cl$ was used for the recovery of REEs from waste NdFeB permanent magnets in a seven-step process (Vander Hoogerstraete, Blanpain, Van Gerven, & Binnemans, 2014). This included (1) crushing and milling the magnet into coarse powder, (2) roasting to transform the metals into the corresponding oxides, (3) selective leaching of the REEs with HCl leaving Fe in the solid residue by raising the pH of the leach solution above 2, (4) extracting Co(II), Cu(II) and Mn(II) into $[P_{66614}]Cl$ 101 leaving the REEs in the aqueous phase, (5) precipitating the REEs by the addition of oxalic acid, (6) recovering the precipitate by filtration and (7) calcining the oxalate precipitate to yield rare-earth oxides. Roasting the waste magnet prior to dissolution was found to facilitate dissolution and reduces the HCl consumption, with ≥ 90 wt.% of Nd_2O_3 and Dy_2O_3 extracted compared to ≤ 25 wt.% of Fe_2O_3. A 3.5 M NH_4Cl was added to the leachate as a salting-out agent to prevent the extraction of the REEs into the IL. An alternative process for the extraction and separation of RE and other valuable elements from used NdFeB permanent magnets was proposed by Riaño and Binnemans (2015) using $[P_{66614}][NO_3]$. After roasting, the used magnets were dissolved in HNO_3. At the end of the leaching process, the solution pH was raised to 4 to remove Fe by precipitation. The remaining Nd(III) and Sm(III) were separated from Co(II) using $[P_{66614}][NO_3]$. Evaluation of the extraction parameters indicated that pH had little influence on the process selectivity, Co(II) extraction was supressed at high metal loading concentrations and addition of NH_4NO_3 salted in the REEs. After scrubbing Co(II) using NH_4NO_3, the loaded Nd(III) and Sm(III) were separated by stripping the IL phase using an EDTA and 10 M NH_4NO_3 solution. The preferential interaction of EDTA with Dy allowed for extraction to the aqueous phase whilst a high NH_4NO_3 concentration suppresses stripping of Nd. At 70 °C, 0.03 M EDTA and 10 M NH NH_4NO_3, 79.8% and 4.0% of Dy and Nd were stripped. Addition of concentrated HNO_3 to the stripping solution dissociated the weaker $[Nd(EDTA)]^-$ complex and facilitated its back extraction into the IL yielding a final Dy solution. All elements were precipitated as oxalate salts and calcined. Although this process is complicated due to the many steps involved, over 99% of Co, Nd and Dy are recovered as oxide with >99.5% purity.

Larsson and Binnemans (2014) attempted the selective recovery of metals from a synthetic nickel metal hydride battery leach solution using four IL
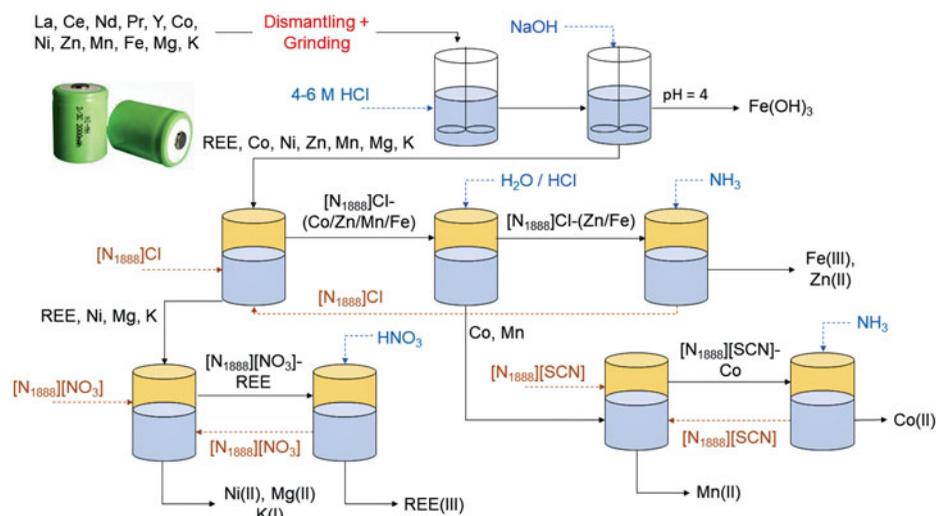
Figure 9. Flow-sheet describing recovery of metals from waste nickel metal hydride batteries using ILs (adapted from Larsson & Binnemans, 2014).

systems: $[P_{66614}]Cl$, $[N_{1888}]Cl$, 10% v/v Cyanex 923 (neutral extractant) in $[N_{1888}][NO_3]$ and 30% v/v $[N_{1888}][SCN]$ in $[N_{1888}]Cl$. A simplified process flowsheet is presented in Figure 9. This process clearly shows the potential of ILs to recover metals from complex aqueous solutions using careful selection of the ILs and understanding their influence on the metal extracted complex (chloride vs. nitrate, etc.).

The feasibility of an efficient solvent extraction process for the purification of the critical element indium from a chloride medium was demonstrated using $[P_{66614}]Cl$ and $[N_{1888}]Cl$. Results from single-element extraction studies indicate that the phosphonium IL $[P_{66614}]Cl$ outperformed $[N_{1888}]Cl$ with higher distribution ratio obtained across the entire HCl concentration range due to the greater hydrophobicity of $[P_{66614}]Cl$. Maximum extraction occurred at 5 M HCl for both ILs, with the extraction mechanism assigned to the evolution of indium speciation as a function of chloride concentration and the formation of anionic chlorindate complexes at high HCl concentration. A percentage stripping over 99% was reached for the 0.5 M HCl–$[P_{66614}]Cl$ system if 4.5 equivalents of NaOH were used. Two successive extraction/stripping cycles indicate that the IL can be recycled for reuse in liquid/liquid extraction of indium(III) without any loss of activity and with little loss of $[P_{66614}]Cl$. Multi-element extraction studies show $[N_{1888}]Cl$ is the preferred IL for the separation of In(III) from As(III), Mn(II) and Ni(II), taking advantage of the low affinity of these metals for the IL phase at lower HCl concentrations. However, In(III) could not be separated from cadmium(II), iron(III), lead(II), tin(IV) and zinc(II) in a single step and additional scrubbing and stripping steps appear necessary (Deferm et al., 2016).

[N_{1888}]-based ILs were used for the recovery of antimony and REEs from simulated waste phosphor from fluorescent lamps. Phosphor powder used in fluorescent lamps is a mixture of individual phosphors, namely HALO ($Ca_{4.86}Mn_{0.10}Sb_{0.04}Sr_{0.004}(PO_4)_3Cl_{0.10}F_{0.90}$), YOX ($Y_{1.92}Eu_{0.08}O_3$) and other constituents. Dupont & Binnemans (2016) considered the leaching and recovery of Sb from HALO phosphor only. Commercial HALO phosphor was completely leached using dilute HCl and extracted as the anionic tetrachloroantimonate(III) complex ($SbCl_4^-$) using [N_{1888}]Cl by an anion exchange mechanism. Quantitative extraction of Sb(III) was achieved from the leach solution containing Sr(II), Ca(II) and Mn(II) even in the absence of addition chloride ions. Mn(II) was only extracted at very high chloride concentrations ($\geq 4\,M$ NaCl), whilst Sr(II) and Ca(II) do not form anionic chloro-complexes under the tested experimental conditions and were therefore not extracted. The loaded IL phases was scrubbed with 1 M NaCl prior to Sb(III) stripping using a NaOH solution at pH 7. The residual Ca in the leach solution was precipitated by addition of NaOH to yield a valuable calcium phosphate apatite precipitate.

Yang and coworkers (2012) used "bifunctional IL extractants" (Bif-ILEs) prepared from [N_{1888}]Cl and the commercial organophosphorus acid extractants, di-(2-ethylhexyl)phosphoric acid (DEHPA) and di(2-ethylhexyl)orthophosphinate (PC-88A), to extract REEs from a simulated solution of a fluorescent powder containing a high concentration of $Al(NO_3)_3$. [N_{1888}][DEHPA] and [N_{1888}][PC-88A] possess binary functional groups, one each on the cation and anion, through which complexation can occur. The extraction performance of the synthesized [N_{1888}][DEHPA] and [N_{1888}][PC-88A] Bif-ILEs was compared to that of neutral organophosphorus extractants di(1-methylhepthl)methyl-phosphonate, TBP and Cyanex 923 in n-heptane. It was found that the sequence of extractability for REE(III) is Cyanex923 > [N_{1888}][DEHPA] = [N_{1888}][PC-88A] > di(1-methylhepthl)methyl-phosphonate > TBP. The extraction using [N_{1888}][DEHPA] and [N_{1888}][PC-88A] was thought to occur through the unshared electron pair of $P=O$ in the [PC-88A]$^-$ or [DEHPA]$^-$ groups and the N lone electron pair of the [N_{1888}]$^+$ group to form macromolecular extracted complexes (Figure 10).

The coexisting Al_2O_3 in the fluorescent powder was changed to a salting-out agent ($Al(NO_3)_3$) in the extraction process and this increased the extraction efficiency of REEs. Using a counter-current extraction process at a 4:1 organic to aqueous phase ratio and pH = 0.56, the REE recovery of 95.2 wt.% was achieved in stages 5–7. However, the use of Bif-ILEs had some drawbacks, namely the addition of 10% isopropanol modifier to prevent the formation of a third-phase on extraction and the important viscosity of the IL phase after extraction (Yang et al., 2012). Another study using
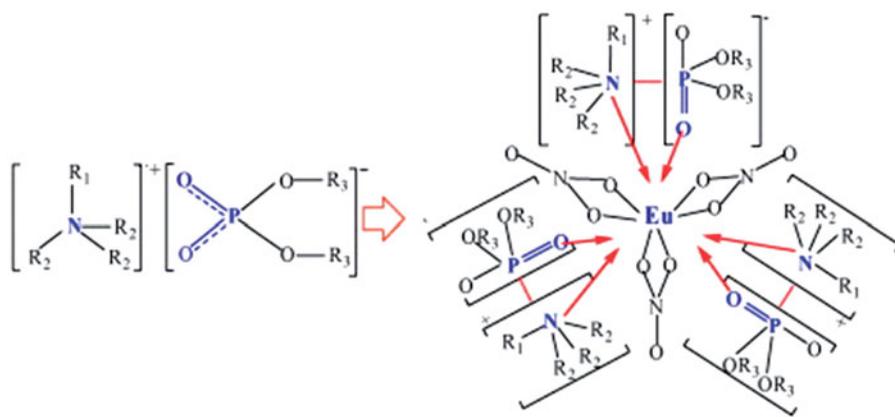
Figure 10. The proposed structure of [N1888][DEHPA] and its coordination environment with Eu(III) (Sun et al., 2010).

the same Bif-ILEs systems found that [N_{1888}][PC-88A] and [N_{1888}][DEHPA] were suitable for the separation of heavy REEs in nitrate medium and the separation of light REEs in chloride medium (Guo et al., 2014). EXAFS studies attributed the synergistic effect of bifunctional IL extractant [N_{1888}][DEHPA] for REE extraction to the greater stability and hydrophobicity of the metal complex formed. In addition, extraction was shown to proceed via co-extraction of the aqueous phase counter anion to produce a neutral complex in the IL phase (Sun et al., 2010).

6.2. Neutral extractants

The use of neutral extractant in conjunction with an IL diluent system for the recovery of aqueous metal complexes is the best studied extraction phenomenon involving ILs (Dai, Ju, & Barnes, 1999). Extraction using neutral extractant proceeds via an ion-exchange mechanism whereby to compensate for incoming positively charged metal cation into the IL, an IL component is released to the aqueous phase to maintain charge neutrality. This was reported for a wide range of neutral ligands including crown ethers (Jensen et al., 2002; Jensen et al., 2003; Stepinksi et al., 2005; Garvey et al., 2012; Hawkins, Garvey, & Dietz, 2012), phosphine oxide ligands (Kubota et al., 2009; Petrova, 2016), phosphate ligands (Billard et al., 2011; Zhu et al., 2015), diglycolamide ligands (Shimojo et al., 2008; Shen et al., 2011), calixarene ligands (Luo et al., 2004) and others (Figure 5). In addition, the stripping of loaded neutral extractants in IL is problematic and requires aggressive stripping solutions (Regel-Rosocka & Wisniewski, 2011). These factors have limited the application of IL containing neutral extractants for the recovery of value from aqueous streams.

One system, the neutral extractant Cyanex 923 dissolved in $[N_{1888}][NO_3]$, has been applied to recover of metals (Co, Ni, Fe, Mn, Zn, REE) from a synthetic Ni metal hydride battery leach solution (Larsson & Binnemans, 2015a). Cyanex 923 is a mixture of trialkylphosphine oxides with octyl and hexyl side groups. Addition of 15% Cyanex 923 (v/v) in $[N_{1888}][NO_3]$ increased the distribution ratio of the test metals and allowed higher extraction efficiencies and Co-Ni separation factors compared to direct application of $[N_{1888}][NO_3]$ alone. Over 98 wt.% of extracted Ni was scrubbed using a $MgCl_2$ solution prior to stripping Co and Mn from the IL phase using a 3 M $NaNO_3$ solution. In further stripping steps, REE were removed using a 1 M HCl strip before the remaining Fe and Zn were stripped using a 1 M HNO_3 solution. The separation of Co from Mn in the strip solution using $[N_{1888}][SCN]$ dissolved in $[N_{1888}][NO_3]$ (40% v/v) was also investigated. This research represents an example of "split-anion extraction", whereby the aqueous and organic phases possess different anions, allowing the use of a complexing anion in the organic phase that forms an extractable metal complex. This removes the necessity to add a significant concentration of complexing anion in the aqueous phase and facilitates metal stripping (Larsson & Binnemans, 2015b). Similarly, Kikuchi and coworkers (2014) extracted REE derived from NdFeB magnets from aqueous nitrate solution using TBP diluted in $[N_{1888}][NO_3]$. Aqueous nitrate added as $NaNO_3$, was found to salt-in the REE and increase the distribution of the latter to the IL phase. The presence of Fe(III) in solution has a negative effect on the overall REE extraction efficiency and selectivity. After removal of Fe from the system, the Nd(III) concentration in the IL phase reached $160\,g.L^{-1}$ after three loading cycles (Kikuchi, Matsumiya, & Kawakami, 2014).

The IL 1,3-dihexylimidazolium nitrate $[C_6C_6im][NO_3]$ was shown to preferentially extract light rare earth elements over 1st row transition metals and this was applied with moderate success to the separation of Sm(III)/Co(II) and La(III)/Ni(II) pairs from nitrate media, a separation relevant to the recycle of these metals from WEEE. Due to the high co-extraction of Co (30%) and to a lesser extent Ni (15%), successive scrubbing steps using 6 M $NaNO_3$ solution were required. Interestingly, $[C_6C_6im][NO_3]$ presents an UCST phase behavior, with the IL being fully miscible with water at temperature above 90 °C (Depuydt et al., 2017).

6.3. Acidic extractant

Acidic extractants are Brønsted acidic molecules containing a protonated functional group such as an alkylcarboxylic acid, alkylphosphoric acid or alkylsulfuric acid group. Coordination of an acidic extractant with a metal

cation usually proceeds via deprotonation of the ligand and formation of a charge neutral complex. The pKa of the extractant dictates the ability to deprotonate, thereby influencing the extraction behavior. By altering the pH of the aqueous solution, selectivity of metal ion extraction can be controlled. In comparison to neutral extractants, extraction behavior using acidic extractant is easier to predict and back-extraction of the loaded organic phase can be achieved by contacting with an acidic solution and regenerating the extractant (Cocalia et al., 2005; Free, 2013). The full potential of ILs to solvate charged species is properly utilized if neutral complexes are extracted. Acidic extractants commonly used in conjunction with ILs are shown in Figure 5.

Although widely tested on synthetic aqueous solutions, few studies have used acidic extractants diluted in ILs for the recovery of metals from WEEE. The only example consists of the recovery of lanthanides present in waste fluorescent lamps phosphor using N,N-dioctyldiglycolamic acid (DODGAA) in $[C_4C_1im][NTf_2]$ (Yang et al., 2013). DODGAA, is an anionic extractant possessing a carboxyl and carbamoyl group linked together by an ether chain reported to exhibit high selectivity for REEs, especially the lighter lanthanides (La(III) to Gd(III)) (Shimojo et al., 2014). In a 1st processing step, Y and Eu oxides were leached using a 5 M H_2SO_4 solution at 100 °C. The solid residue was leached a second time using 5 M HNO_3 solution for 6 hours at 100 °C to recover the difficult to extract RE phosphate (La, Ce and Tb). The extraction efficiency of DODGAA in $[C_4C_1im][NTf_2]$ was compared to that of the carboxylic extractant PC-88A in dodecane for the recovery of the REE present in both leach solutions. DODGAA in $[C_4C_1im][NTf_2]$ provided greater selectivity and extraction efficiencies for the REEs than PC-88A at similar pH. Y, Eu, La and Ce were separated from the metal impurities Fe, Al and Zn, although some Ca was co-extracted. Stripping was easily achieved using a dilute acidic solution, and UV spectroscopy of the aqueous phase confirmed minimal loss of the IL cation. The extractant-IL system was recycled and reused five times with no appreciable loss in efficiency (Yang et al., 2013). DODGAA has been shown by other researchers to extract REEs by deprotonation of three ligands and the formation of a charge neutral complex (Shimojo et al., 2014).

6.4. Functionalized ILs

Functionalized ILs, or TSILs, represent ILs incorporating a functional group on their anionic or cationic components that acts as metal complexation site, allowing ILs to function as a solvent and complexing agent. The cation is most often the functionalized moiety due to easier synthesis, which simply requires a quaternization reaction between a 'functionalized' alkyl halide
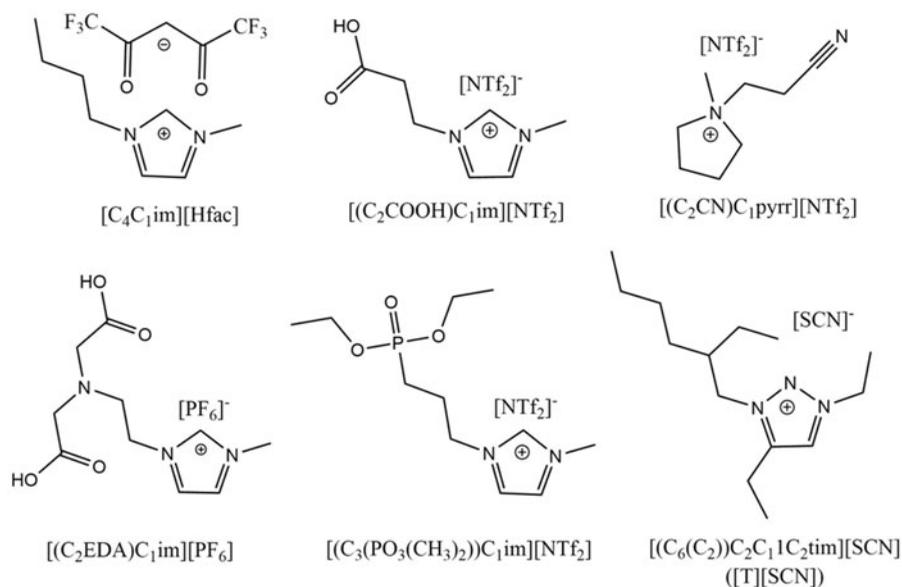
Figure 11. Selected examples of TSILs used in metal ion extraction.

and a nucleophile (tertiary amine, phosphine, etc.). The structure of the TSILs in this section are shown in Figure 11. TSILs with functionalized anions most often include strongly coordinating species such as alkylphosphate (Rout, Kotlarska, Dehaen, & Binnemans, 2013), alkyldiglycolamate (Rout, Venkatesan, Srinivasan, & Rao, 2012), β-diketonate (Mehdi, Binnemans, Van Hecke, Meervelt, & Nockemann, 2010), salicylate, thiosalicylate or benzoate (Stojanovic et al., 2010) anions. TSILs are covered in greater detail in the reviews by Lee (2006) and Chiappe and Silvio (2014).

The use of ILs as a simultaneous solvent and extraction media limits the ion-exchange extraction mechanism and prevents the unwanted partitioning of the IL components or extractant to the aqueous phase compared to extraction systems where the IL is solely used as a diluent. However, this is only valid for ILs with functionalized cations, as extraction with some IL containing functionalized anions proceeds on occasion via cation-exchange (Mehdi et al., 2010). The principal factors limiting the applicability of TSILs are their high viscosity, cost, complicated synthesis and unknown toxicity compared to conventional ILs (Visser et al., 2001; Visser et al., 2002). In addition, further understanding of the extraction mechanisms and characterization of the extracted complex are required, with crystal structure studies being a popular analysis method for TSIL-metal complexes (Harjani, Friscic, MacGillivray, & Singer, 2006; Mehdi et al., 2010; Nockemann et al., 2010a; Nockemann et al., 2010b).

TSILs incorporating a 'hard' base oxygen derived functional group such as a carboxylate, ketone or phosphonate are used in metal extraction and

separation processes. TSILs have been used to recover REE(III) from fluorescent lamps as well as REE(III) and Co(II) from waste permanent magnets. The use of $[N_{111(2(O)OH)}][NTf_2]$ for such applications was partially described in Section 5.1. In addition, $[N_{111(2(O)OH)}][NTf_2]$ was employed for the solvent extraction of scandium. A primary study showed that Sc(III) and Fe(III) could be selectively separated from La(III), Ce(III), Nd(III), Dy(III), Y(III), Al(III), Ti(IV), Ca(II) and Na(I) in chloride solutions using $[N_{111(2(O)OH)}][NTf_2]$ as the IL displays a poor affinity towards these elements (Onghena & Binnemans, 2015). The findings from this study were subsequently applied by the same authors to the recovery of scandium from 'sulfation-roasted' leachates of bauxite residue (Onghena, Borra, Van Gerven, & Binnemans, 2017a). The distribution ratio of Sc(III) found in this study was much lower than those reported from chloride media (Onghena & Binnemans, 2015). This was assigned to the high sulfate concentration in the leachate and the competing coordination between the sulfate and betaine ligands to Sc(III). As expected, the extraction of Sc(III) by $[N_{111(2(O)OH)}][NTf_2]$ is heavily pH dependent. At the following extraction conditions: pH = 2.4 and O/A = 1:5, 84 wt% of Sc(III) was extracted compared to 23 wt% for Al(III), 4.3 wt.% Fe(III) and 2.6 wt.% Ca(II). The co-extracted metals were scrubbed using dilute HCl solution prior to contacting the IL phase with 3 M H_2SO_4. The composition of the resulting strip solution is 90% Sc(III), 8% Al(III), 0.7% Fe(III) and the lanthanides with 0.5%. Finally, scandium was precipitated from the strip solution by addition of oxalic acid and calcined for a final oxide product with a purity of 98% (Onghena, Borra, et al., 2017a).

Chen, Wang, Pei, Ren, and Wang (2015d) assessed the recovery of Nd(III) from Fe(III) and Sm(III) from Co(II) from synthetic NdFeB and SmCo permanent magnet leach solutions using 1-alkylcarboxylic acid-3-methylimidazolium bis(trifluoromethylsulfonyl)imide IL $([(C_nCOOH)C_1im][NTf_2]$ ($n = 3$, 5, 7), (Figure 11). Separation of the REE from Fe(III) and Co(II) was found to be primarily pH dependent and the extraction efficiency of all the investigated metal ions increased with increasing aqueous phase pH, reaching as high as 99%. In addition, the extraction efficiency increased with a decrease in alkyl chain length at lower pH. By careful tuning of the aqueous solution pH, Sm(III) and Nd(III) could be selectively separated from Co(II) and Fe(III) respectively, with separation factors in the range $10^4–10^5$. Like the carboxy-functionalized $[N_{111(2(O)OH)}][NTf_2]$, REE extraction proceeds via de-protonation of the carboxylic group and formation of a 1:3 REE:IL charge neutral complex. The IL was easily stripped in a single step by dilute aqueous HCl or oxalic acid (Chen et al., 2015d).

Novel 1,2,3-triazolium ILs with $[SCN]^-$ or iodide anions (Figure 11) were synthesized for the extraction of transition metals and REEs from

HCl medium (Raiguel et al., 2017). These ILs exhibited better properties compared to imidazolium ILs, namely low viscosity, low solubility in water and high base stability. The ILs incorporating the 3,5-diethyl-1-(2-ethyl-hexyl)-4-methyl-1,2,3-triazolium ([T]) cation with an iodide anion displayed a high extraction efficiency for Cu(II), moderate extraction efficiencies towards Fe(III), Co(II), Ni(II) and La(III), Nd(III) and Dy(III). After substitution of the iodide anion for thiocyanate, close to quantitative extraction is obtained for the transition metals and low to medium extraction of the REE(III). EXAFS analysis of Cu(II) speciation in [T][I] after loading with $CuCl_2$ indicates its presence as the $[CuCl_2]^-$. Upon extraction, the redox-active Cu(II) is reduced to Cu(I) whilst I^- is oxidized to I_2 which in turn reacts with remaining I^- to form I_3^-. The high base stability of [T][I] was used in the separation of Cu(II), Zn(II) and Fe(III). Addition of Na_2CO_3 precipitated 98% of Zn(II) and Fe(III), leaving Cu(II) in the IL.

6.5. Aqueous biphasic systems for metal extraction

An alternative to traditional solvent extraction for the extraction metals is the use of ILs in aqueous biphasic system (ABS). ABS are mainly composed of water, and can be formed, when combining in the right proportions, an inorganic salt and a hydrophilic IL, which creates two immiscible – but reversible – aqueous phases (a salt-rich and an IL-rich phases). Since such systems are obtained with hydrophilic ILs, the range of potential compounds that can be explored for the extraction is significantly enlarged and unlocks the full potential of ILs as designer solvents. As the IL-rich phase consists of an aqueous solution of IL, a much lower amount of IL is required, thus reducing the overall process cost. In addition, the environmental impact of the use of ILs is diminished as less amounts are used and hydrophilic ILs are significantly less toxic and more biodegradable than their hydrophobic counterparts. Finally, ABS overcome the high viscosity of many ILs due to the presence of water thereby increasing the reaction kinetics and transport phenomena. The extraction of metals using poly-ethylene glycol-based ABS is well established (Rogers, Bond, & Bauer, 1993). One of the main limitations of ABS for metal extraction is the difficult handling of metal ions with high sensitivity to hydrolysis and/or precipitation as most reported ABS experiments were carried out using slightly acidic or alkaline solutions, with pH typically ranging from 5 to 13. A full review of metal extraction using ABS is available elsewhere (Billard, 2016).

An important development in the applicability of ABS extraction to the recovery of metals from acidic WEEE leachates is the recent proof-of-concept for acidic ABS (AcABS) in which the inorganic acid itself, in this case HCl, replaces the salt as the driver of ABS formation (Gras et al., 2018). The use of

the leachate solution itself as a salting-out agent allows for the simultaneous leaching and separation of critical metals, thereby simplifying the extraction and stripping processes. These systems display several advantages over other extracting solvents. Unlike classical systems based on an organic solvent and an extracting agent, the IL-based AcABS $[P_{44414}]Cl$-HCl-H_2O exhibits a thermomorphic behavior with a well pronounced LCST, i.e. the biphasic mixture becomes biphasic by heating above a certain temperature for a given HCl concentration. This system was applied to the extraction of Fe(III), Pt(IV) and Co(II) from concentrated HCl solutions and to the separation of the critical transition metal pair Co(II) from Ni(II). Extraction of Co(II), Fe(III) and Pt(IV) proceeds as in the traditional two-phased systems based on $[P_{66614}]Cl$ via anion exchange with the IL anion. An additional benefit of this AcABS is the poor miscibility of the IL in the HCl-rich phase, ensuring quantitative recovery of the IL after extraction. The traditional ABS also based on $[P_{44414}]Cl$ with NaCl was shown to selectively separate Co(II) and Ni(II) in chloride media (Onghena, Opsomer, & Binnemans, 2015). $[P_{44414}]Cl$ exhibits a large biphasic region, with just 5 wt% NaCl capable of inducing an ABS in a solution containing 40 wt.% IL. The $[P_{44414}]Cl - NaCl - H_2O$ system also displays a LCST phase behavior in water.

An interesting IL-surfactant-water microemulsion system based on the IL $[P_{66614}]Cl$ and the surfactant Triton 100 (TX100) was developed extraction and separation of Au(III), Pd(II), and Pt(IV) from acidic chloride media (Tu Nguyen et al., 2017). A number of factors were assessed including the microemulsion structure, temperature, surfactant concentration, IL concentration, extraction time, chloride concentration, and pH. Metal extraction was found to proceed through an anion exchange mechanism between the anionic chlorometallate complexes and the IL anion. A five-step methodology was elaborated for precious metal recovery consisting of (i) mixing the feed solution with the IL-based microemulsion, (ii) inducing TX100-$[P_{66614}]Cl$/aqueous phase splitting by heating to 90 °C, (iii) phase separation, (iv) stripping and (v) regeneration. Following this simple protocol, 99.9% of precious metals were selectively recovered at optimized condition. A two-step stripping process was successfully performed based on stripping of Au(III) using an aqueous solution of sodium thiosulfate followed by the recovery of Pd(II) and Pt(IV) with a thiourea-HCl solution. The performance of the system after five extraction-stripping cycles was found to decrease by approximately 9% for all three metals tested.

Similarly to the results reported using the hydrophobic $[P_{66614}][NO_3]$ (Vander Hoogerstraete & Binnemans, 2014), Nd(III) was selectively separated from Co(II) and Ni(II) using an ABS comprised of $[P_{4444}][NO_3]$ and $NaNO_3$ as phase former (Chen, Wang, Pei, & Wang, 2018) based on the ability of lanthanides to form anionic nitrate complexes. The extraction

efficiency was primarily influenced by the aqueous nitrate concentration, with the Nd(III) extraction efficiency increasing from less than 15% in aqueous solution containing no $NaNO_3$ to quantitative Nd(III) extraction for $NaNO_3$ greater than $0.3\,g.L^{-1}$. An increase in the $NaNO_3$ content of the aqueous phase also resulted in increased separation factors 10^3 and above when $[NaNO_3] = 0.6\,g.L^{-1}$. In contrast, IL concentration had little effect on the extraction yield: for a 1 mL feed solution containing $1\,g.L^{-1}$ of $Nd(NO_3)_3$ quantitative extraction of Nd(III) was obtained for all IL concentration tested (0.2-0.6 g). After separation of the IL rich phase, extracted Nd(III) was recovered by contacting with an aqueous solution of sodium oxalate such that the Nd(III) to oxalate molar ratio was of 1.5. However, a sharp drop in extraction efficiency over repeated cycles was observed with only 85.4% of extraction efficiency achieved after only three cycles. $NaNO_3$ was found to be a better salting out agent than NH_4NO_3 whilst $[N_{4444}][NO_3]$ has a smaller biphasic region compared to $[P_{4444}][NO_3]$, in accordance with the more hydrophobic nature of phosphonium cations over ammonium ones. As with the $[P_{44414}]Cl$ system previously described, a strong LCST-type temperature dependent behavior of the binodal curve was observed as the temperature was increased from 15 °C to 35 °C.

The ABS composed of the carboxyl-functionalized phosphonium IL $[P_{444(C1OOH)}]Cl$ (80 wt.%) and a 16 wt.% NaCl solution was employed as the salting-out agent for the selective extraction of Sc(III) (Depuydt, Dehaen, & Binnemans, 2015). Whilst the viscosity of the pure IL was over 20000 cP at room temperature, the viscosity of the IL-rich phase in the employed ABS was drastically decreased to 400 cP. REEs do not form anionic chloride complexes, the extraction of Sc(III) was shown to proceed via deprotonation of three IL-cations (pKa = 2.32) to form zwitterionic compounds that can coordinate scandium(III) ions in a 3:1 ratio. The pH was varied from 3.33 to 0 in the aqueous feed solution containing $5\,mmol\,kg^{-1}$ of Sc and 16 wt % of NaCl to determine the influence of the pH on the solubility of the IL cation in the water-rich phase. ^1H NMR analysis of the aqueous phase indicates that the solubility of the IL cation increases with decreasing pH from approximately 5.8 wt.% at pH = 6.8 to 10.5 wt.% at pH = 0. The zwitteronic form of the $[P_{444(C1OOH)}]^+$ is more hydrophobic than its protonated counterpart, thus, a lower solubility is observed at higher pH values since low pH values prevent deprotonation of the cation. Quantitative stripping of IL-rich phase was achieved after addition of oxalic acid at a molar ratio of 1.5.

6.6. Hydrophobic deep eutectic solvents (DES)

Whilst the use of hydrophilic DES is well documented at the laboratory scale for many applications, the use of hydrophobic DES for the

liquid-liquid extraction of metals is relatively recent and opens the possibility for the substitution of expensive hydrophobic ILs.

A hydrophobic DES composed of a x:1 ($x = 2$–4) molar ratio of decanoic acid and lidocaine was investigated for the extraction of the transition and alkaline metals Co(II), Zn(II), Ni(II), Cu(II), Fe(II), Na(I), Li(I) and K(I) from chloride media (Van Osch et al., 2016). The physical properties of the DES are described, and single element extraction studies show that most transition metal cations are extracted with high efficiencies although some Fe(II) was found to precipitate and the DES phase forms a gel after extraction of Mn(II). The loading capacity of the DES is higher than that of corresponding ILs composed of fatty acids and quaternary ammonium salts. The higher the decanoic acid to lidocaine ratio, the higher the decrease in the distribution ratio because of the greater hydrophobicity of the DES. The majority of the chloride remains in the aqueous phase. This is reasoned through the interaction between the protonated lidocaine and the chloride anion: it is likely that lidocaine hydrochloride is formed, which has a higher water solubility in comparison to lidocaine itself. Thus, metal extraction proceeds via an ion-exchange reaction in which upon extraction of the metal ion to the DES phase, protonated lidocaine is transferred simultaneously to the water phase. The loaded DES phase was stripped using sodium oxalate, and the regenerated DES was recycled. Due to the loss of lidocaine upon metal extraction, the DES cannot be recycled indefinitely. Although the 3:1 and 4:1 molar ratio decanoic acid to lidocaine DES could be reused a second time without any drop in Co(II) distribution coefficient, a drastic drop in D for the 2:1 DES was observed. In addition, the water phase became turbid for all DES ratio.

Quaternary tetraheptylammonium- and menthol-based hydrophobic DES containing carboxylic acids, lauric acid, decanoic acid, oleic acid and ibuprofen, were investigated for the recovery of indium from chloride and oxalate media (Tereshatov, Boltoeva, & Folden, 2016). DL-menthol:lauric acid based DES were found to be ineffective extracting agents. However, all $[N_{7777}]^+$ based DES were successful in extracting In(III), with the $[N_{7777}]$:ibuprofen (7:3 molar ratio) DES displaying the highest distribution ratio. Furthermore, all $[N_{7777}]$ based DES display the same extraction behavior in HCl and oxalate solution respectively, suggesting that the fatty acid alkyl chain does not influence In(III) extraction. In both media, In(III) extraction is dictated by its speciation. Similarly to In(III) extraction in the IL $[P_{66614}]Cl$ (Deferm et al., 2016), the DES preferentially extracts the anionic complexes $[InCl_4(H_2O)_2]^-$ and $[In(C_2O_4)_2]^-$ in chloride and oxalate solution respectively (Tereshatov et al., 2016) through ion-pairing with the $[N_{7777}]^+$ cation as deprotonation of the carboxylic acid is assumed to be suppressed at the experimental pH used. Diethylene triamine pentaacetic acid was used to strip the loaded DES.
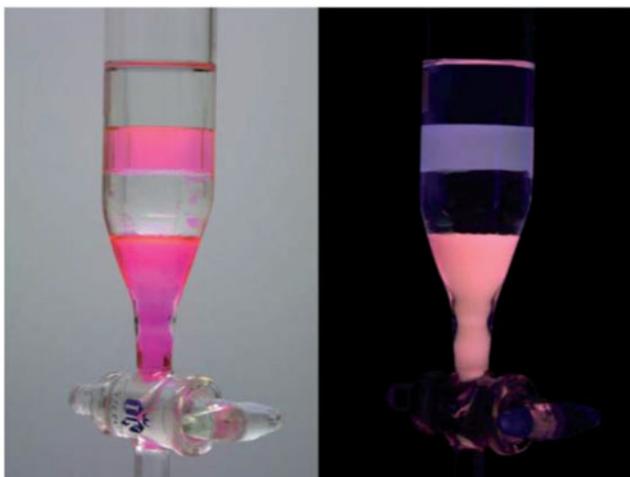
Figure 12. A stable tetraphasic mixture of (from top to bottom): pentane, [P66614][NTf2], water and [C2C1im][NTf2]. The pink coloration is due to rhodamine B dye, which is soluble in the ionic layers. The figure on the left was taken in daylight and the figure on the right was taken under illumination from UV light (254 nm). Reproduced from Arce et al. (2006) with permission from The Royal Society of Chemistry.

6.7. Ionic liquid – ionic liquid solvent extraction

Systems composed of two different immiscible ILs allow for the development of new separation processes and the potential for the formation of ternary or quaternary IL systems for extraction as exemplified in Figure 12.

Arce, Earle, Katdare, Rodríguez, and Seddon (2006) and Neves, Silva, Fernandes, Coutinho, and Freire (2017) demonstrated that if large enough structural or chemical differences exists between two ILs, then this ion mixture may yield a biphasic mixture at room temperature. For example, mixtures of $[P_{66614}]Cl$ and $[C_nC_1im]Cl$ were found to be 'immiscible' in the temperature range 298 to 458 K, where the n was smaller or equal to 5, with only approximately 10 mol% of imidazolium ion salt dissolved in the phosphonium phase for $[C_2C_1im]Cl$ (Arce et al., 2006). These findings were expanded upon by Neves et al. (2017) for systems with 4 ions showing that six pairs of cholinium- and phosphonium-based aprotic ILs ($[N_{111(2OH)}][NTf_2]$ and $[P_{66614}][X]$ where $X = [Cyanex272]^-$, $[C_9COO]^-$, $[NTf_2]^-$, $[N(CN)_2]^-$, Br^- and Cl^-) were able to form biphasic systems. The formation of an IL liquid-liquid system is cation driven: only mixtures of two ILs with significantly structurally different IL cations or of highly different hydrogen-bond acidity can undergo liquid-liquid demixing. The IL anion does not have a significant impact on the creation of a binary systems but plays an important role in defining the mutual solubility magnitude, which was suggested to linearly depend on the volume of the IL anion. In all cases except for systems formed by ILs with a common anion,

significant ion exchange occurs, the extent of which correlates with the ILs cohesive energy (Neves et al., 2017).

This principle was successfully used to separate cobalt from nickel and REEs from nickel respectively using the biphasic system $[C_2C_1im]Cl$ and $[P_{66614}]$-bis(2,4,4-trimethylpentyl)phosphinate (Wellens et al., 2013; out et al., 2014). A solubility of 9.2 wt% (or 31 mol%) of $[C_2C_1im]Cl$ in $[P_{66614}][P_{RROO}]$ was determined from ^{1}H-NMR peak analysis peaks. The solubility of $[P_{66614}][P_{RROO}]$ in $[C_2C_1im]Cl$ was found to be below the detection limit (Wellens et al., 2013).

Vander Hoogerstraete and coworkers (2015) demonstrated a proof of principle for the separation of tin(II), scandium(III) and yttrium(III) using the ternary IL system composed of $[N_{111(2(O)OH)}][NTf_2]$-H_2O-$[P_{66614}][NTf_2]$. A ternary system was required for this separation as tin(II) and scandium(III) extraction by carboxylic ligands display the same pH dependent behavior. $[N_{111(2(O)OH)}][NTf_2]$ was selected over $[N_{111(2OH)}][NTf_2]$ as one of the phases due to its significantly larger triphasic region. Initial biphasic tests showed that Sc(III) and Sn(II) could be separated from Y(III) in the $[N_{111(2(O)OH)}][NTf_2]$-H_2O system at pH 1.0 whilst 80% of Sn(II) was extracted to the IL phase in the $[P_{66614}][NTf_2]$-H_2O in the presence of the neutral tributylphosphate (TBP) ligand whilst the REEs remained mainly in the aqueous phase. A pH below 1, along with the addition of 1 M $MgCl_2$ to the aqueous phase, was required to suppress tin hydrolysis and prevent $[P_{66614}][NTf_2]$-TBP emulsions. In the ternary system, the best separation was obtained at low chloride concentrations without pH adjustment and at high TBP concentration in the $[P_{66614}][NTf_2]$ phase. Under these conditions (20 wt.% TBP, 0.25 M $MgCl_2$), 89% of Sn(II) was extracted to the $[N_{111(2(O)OH)}][NTf_2]$ phase, 89% of Y(III) remained in the aqueous phase and 85% of Sc(III) was extracted to the $[P_{66614}][NTf_2]$ phase. Although not conclusive, these encouraging results underline the versatility of ILs and the possibilities available for IL-IL liquid-liquid extraction.

The IL-IL mineral separation of rare-earth minerals (bastnäsite and monazite) from Ca, Mn, Fe and Mg rich samples (ankerite, dolomite and calcite) was attempted (Azizi & Larachi, 2018). Specifically, $[N_{4444}][DEHPA]$ was added as a droplet phase in three different ILs used as a continuous phase, ethylammonium nitrate ($[EtNH_3][NO_3]$), $[C_2C_1im][SCN]$ and $[C_4C_1im][BF_4]$. These ILs were selected as i) $[N_{4444}][DEHPA]$ displays a far superior affinity for the REEs compared to the other ILs, ii) the droplet phase viscosity is lesser than that of the continuous phases and iii) the droplet phase and continuous phase must display minimal solubility with one-another. The optimal system of $[N_{4444}][DEHPA]$ dispersed in $[C_2C_1im][SCN]$ was shown to outperform froth flotation and traditional liquid-liquid mineral separation for the

recovery of RE minerals. DFT analysis found that anionic moiety of $[N_{4444}][DEHPA]$ directly interacts with the metal cations on the mineral surfaces through covalent bonds resulting in very favorable interaction energies compared to the other ILs.

Although not technically an IL-IL extraction system, the solvent extraction of Co, Fe and B from waste NdFeB magnets in DES $[N_{111(2OH)}]$ Cl:lactic acid using $[N_{1888}][SCN]$ was successfully achieved and scaled-up over multiple mixer-settlers (Riaño et al., 2017). The dissolution of Co, Fe, B, Nd, Dy, Pr and Gd oxides from crushed and roasted rare-earth permanent magnets (NdFeB) was attempted using three different DES: $[N_{111(2OH)}]$Cl:urea (1:2), $[N_{111(2OH)}]$Cl:EG (1:2) and $[N_{111(2OH)}]$Cl:lactic acid (1:2). At a liquid to solid ratio of $20\,mL.g^{-1}$, $70\,°C$ leaching temperature and 24 hour leaching time, over 80 wt.% of all the target elements were lixiviated using $[N_{111(2OH)}]$Cl:lactic acid and little to no dissolution occurred in $[N_{111(2OH)}]$Cl:urea and $[N_{111(2OH)}]$Cl:EG. This contrast in leaching efficiency was assigned to the ability of the lactic acid moiety to deprotonate and form the metal complex $M(CH_3CHOHCOO)_{n,DES}$ (where n is the metal oxidation state). Interestingly, whilst the water content had no influence on the leach efficiency of the non-roasted magnet, it does have an important influence on the leaching of the roasted oxides with a decrease in leaching efficiency with increasing water content. Almost no Fe and Co are recovered at 80 wt.% ($L/S = 12.5\,mg.L^{-1}$, $70\,°C$, and 24 hour) water content due to their hydrolysis. Recovery of the target metals from the DES $[N_{111(2OH)}]$Cl:lactic acid (1:2) without water is achieved using a two-stage solvent extraction procedure. In this procedure, the DES phase was employed as the more polar phase for solvent extraction and the IL $[N_{1888}][SCN]$ diluted in toluene as the less polar phase. Co(II), Fe(III) and B(I) were separated from the REE(III) in an initial solvent extraction stage using $[N_{1888}][SCN]$. EXAFS analysis indicates that cobalt is extracted as the complex $[Co(SCN)_4]^{2-}$ in $[N_{1888}][SCN]$ whilst iron is extracted as $[N_{1888}][FeCl_4]$. In a second stage, Nd was separated from Dy using the acidic extractant Cyanex 923 in toluene. Cyanex 923 was selected ahead of D2EHPA due to the difficulty in stripping Dy(III). The less polar phases were recycled and reused a second time with little loss in efficiency although boron extraction declined due to presence of chloride anion in $[N_{1888}][SCN]$ resulting from anion-exchange.

7. Critical perspective and recommendations – ILs as specialty solvents

7.1. Ionic liquids – the case for application-specific solvents

The publications reviewed here demonstrate the growing application of ILs for the treatment of WEEE. Despite these promising results, few studies
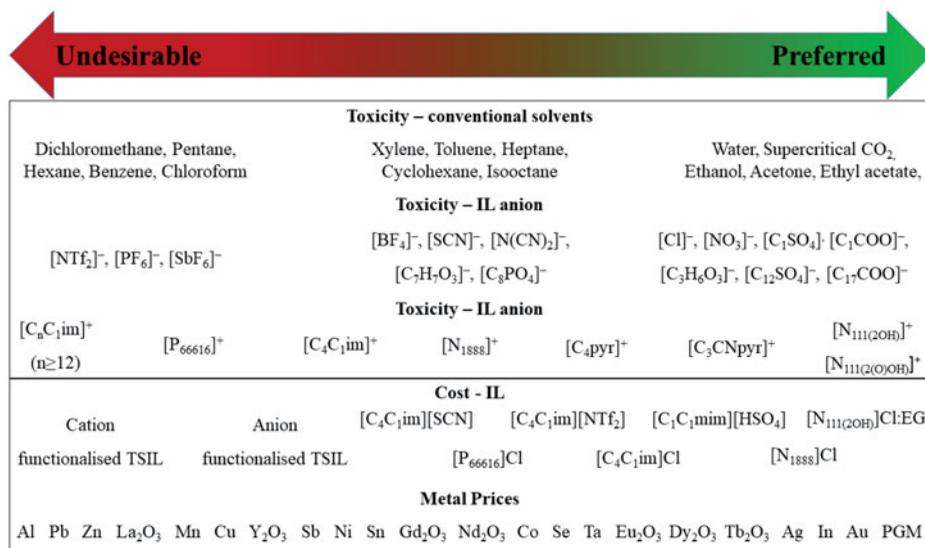
Figure 13. Qualitative toxicity and cost scale for the judicious selection of ILs for metal extraction.

have made the jump from laboratory to industrial scale. In this section, the major obstacles currently preventing the use of ILs in metal extraction processes are highlighted. The selection of ILs is usually justified based on their green credentials, namely their tunability, low vapor pressure, non-flammability and high stability. However, ILs also suffer from some important disadvantages preventing their industrial application such as their high viscosity, corrosiveness, hygroscopicity, toxicity and their higher cost compared to molecular solvents. As such, a more nuanced perspective is required when considering the use of an IL and the following issues must be addressed prior to any successful application. The discussion is summarized in Figure 13. All data here presented is qualitative and should be used just as a guideline. Based on the guidelines presented in Figure 13 and the literature reviewed in the previous Sections, optimized process flowsheets are proposed for the valorization of the inherent metallic value in fluorescent lamp phosphor waste (Figure 15) and nickel metal hydride battery waste (Figure 16).

- How to design ILs more environmentally benign than currently used molecular solvents?

The structural modifications that confer hydrophobicity to ILs are the same that increase their toxicity. Thuy Pham and coworkers (2010) reviewed the toxicity of common ILs across multiple trophic levels and found that toxicity seemed to be determined mainly by the cationic component and that it correlates directly with the length of the cationic alkyl-chain(s). In addition,
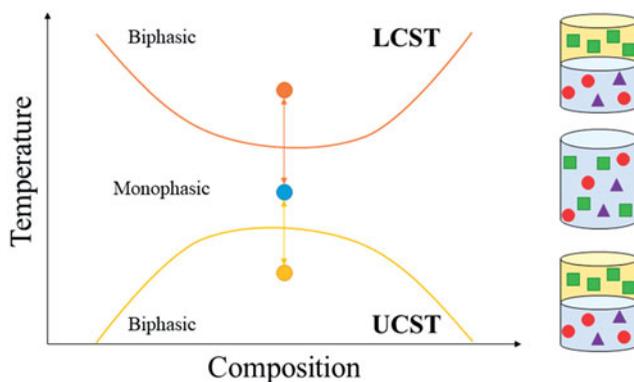
Figure 14. Schematic illustration of LCST or UCST behavior and its application to homogeneous liquid-liquid extraction.
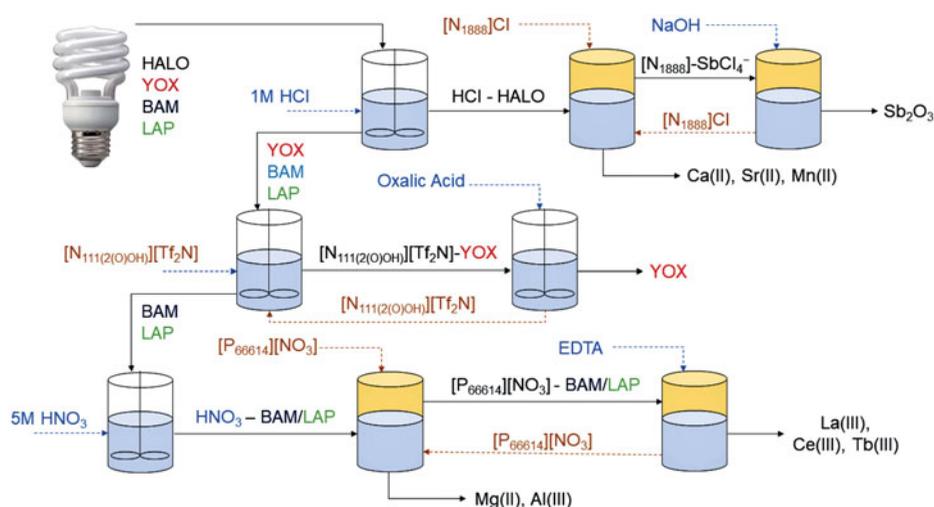
Figure 15. Suggested simplified process flow diagram for the recovery of antimony and REE from waste phosphor.

ILs incorporating polar functional groups in the alkyl side chain such as ether, hydroxyl and nitrile moieties displayed lower cytotoxicity compared to those with simple alkyl side chain. Regarding the anionic effects, fluorinated anions, particularly $[NTf_2]^-$, are generally more toxic than their halogenated counterparts (Viboud et al., 2012). In addition, some fluorinated anions have been shown to hydrolyze and can release the toxic product HF as a result of decomposition (Swatloski, Holbrey, & Rogers, 2003; Freire, Neves, Marrucho, Coutinho, & Fernandes, 2010). The authors show that $[C_4C_1im][PF_6]$ and $[C_4C_1im][BF_4]$, two of the most widely used ILs, decompose in contact with water. The decomposition reaction leads to the formation of toxic HF.

The "greenness" of molecular solvents is well documented according to multiple criteria. An established guide to green solvent selection is the
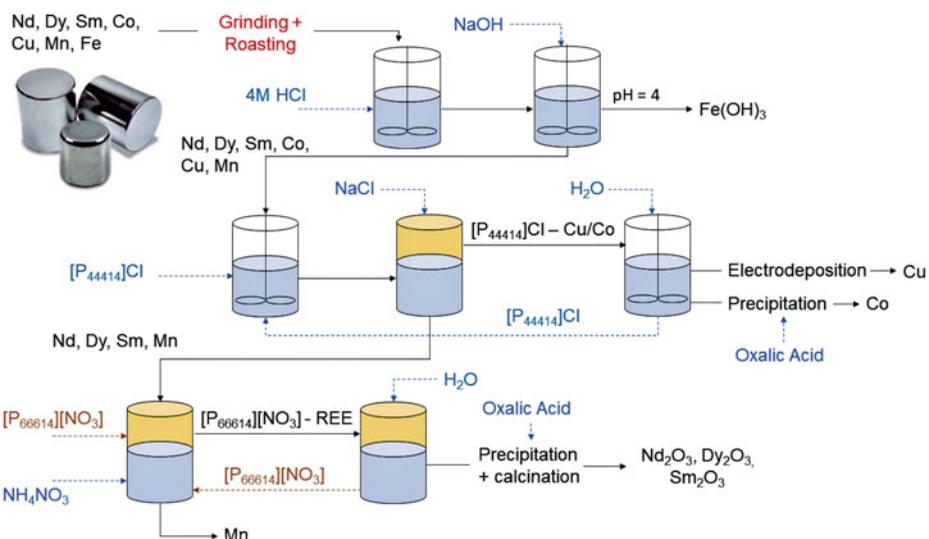
Figure 16. Suggested simplified process flow diagram for the recovery of cobalt, copper and REE from waste NdFeB magnets.

'Pfizer solvent selection guide' which classifies common organic diluents like hexane, benzene or petroleum spirits as undesirable (Byrne et al., 2016). In this context, it makes little sense to label the substitution of hexane in the organic phase by $[C_4C_1im][NTf_2]$ as environmentally friendly. 'Greener' alternatives include the substitution of imidazolium ILs to pyridinium-based ILs, the use of large fatty acid as anions over fluorinated anions to confer the IL hydrophobic properties and – if possible – the application of DES. Water-miscible ILs with shorter cationic alkyl chains can be salted-out to form a reversible biphasic system suitable for metal extraction. It is also worth considering that many ILs act both as the hydrophobic phase and extractant, thereby potentially reducing their over whole toxicological impact. Aliquat 336 ($[N_{1888}]Cl$) stands out as such an example. However, IL systems in which metal extraction proceeds via a cation-exchange mechanism should be avoided.

- Can ILs be designed to offer an improvement compared to existing industrial practices?

In other words, is there any advantage in using IL over existing solvents, either through increased selectivity, more favorable kinetics and thermodynamics or through process simplification? E-waste represents a variable and heterogeneous waste stream, with product composition changing between manufacturers and product iterations. Current industrial hydrometallurgical methods for the recovery of metals from e-waste borrow heavily from tried and tested processes established in the mining industry for the extraction

of metals from ores (Cui & Zhang, 2008). Any proposed IL-based approach needs to be robust and flexible to adapt to such variable conditions. Many of the studies reviewed here report distribution and separation factors superior to those obtained in conventional organic systems. Problematically, most of these IL studies only focused on simulated systems. Such an approach risks missing interactions that occur only in complex systems such as in leachates from WEEE from a waste treatment facility and ignores the role of trace contaminants. Physical separation processes, the preliminary step in all waste treatment facilities (Figure 1), are never 100% efficient due to the overlap between different physical properties, with impurities being entrained in the output stream. An example of a problematic trace contaminants is the extraction of Fe(III) from chloride solutions by phosphonium-based ILs. Fe(III) is strongly and efficiently extracted from even dilute chloride solutions and its stripping can prove problematic (Cui, Cheng, & Zhou, 2015). This in turn can complicate the regeneration of the IL and lower the extraction efficiency of target metals.

The high viscosity of ILs and especially DES is a well identified barrier to their application due to the increased cost of pumping and slow mixing processes and kinetics of mass transfer. Certain ILs, particularly those that operate by an anion-exchange mechanism, are known to significantly increase in viscosity after metal extraction due to strong intermolecular interactions. For example, the viscosity of water saturated $[P_{66614}]Cl$ at $60\,^{\circ}C$ increases from $95\,cP$ to approximately $800\,cP$ after contacting with a feed solution containing $40\,g.L^{-1}$ Co(II) (Vander Hoogerstraete et al., 2013). The problem of viscosity can be partially overcome by saturating the IL with water and operating at higher temperature and/or lower feed concentrations. ABS and thermomorphic ILs fully overcome the issues associated with viscosity by tuning their water miscibility through varying the salt concentration and temperature respectively.

This tunable and reversible water miscibility is extremely desirable in homogeneous liquid-liquid extraction. Performing the extraction in a monophasic solution prior to separation of the phases through a change in temperature reduces the viscosity of the solution and accelerates mass transfer, resulting in higher extraction efficiencies. This is schematically illustrated in Figure 14; ILs can either display LCST or an UCST.

The synthesis of ILs exhibiting thermomorphic behavior requires a balance between the hydrophilicity and hydrophobicity of the ions. The appearance of an LCST for $[P_{4444}]$- and $[N_{4444}]$-based ILs was shown to vary with anion selection (Khono & Ohno, 2012). Depuydt and coworkers (2017b) recently synthesized a range of phosphonium IL with dioctyl sulfosuccinate (DOSS) as anion. Whilst $[P_{4444}][DOSS]$ is hydrophobic, incorporation of three ethylene glycol moieties to the cation lowers the

hydrophobicity of [P$_{444(EG3)}$][DOSS]. [P$_{444(EG3)}$][DOSS] has an LCST of 19 °C in water and was shown to efficiently extract both divalent and trivalent metals. Furthermore, the presence of additional ions in solution can alter the LCST or UCST temperatures due to the strong polar/electrostatic interactions between the water, IL and the ions. The UCST and LCST of [N$_{111(2(O)OH)}$][NTf$_2$] and [P$_{44414}$]Cl significantly decrease after loading with REEs (Schaeffer, Grimes, & Cheeseman, 2016) and after addition of NaCl to the aqueous phase respectively (Onghena et al., 2015). The ability to separate an aqueous IL solution into two phases by varying the temperature or by addition of salting-out salts allows for the potential development of metal recycling processes combining leaching and extraction of metal ions.

- Are IL-based processes economically viable?

The most cited of all barriers to IL application is their high initial cost; ILs normally fall in the range of 5–20 times more expensive than molecular solvents (Plechkova & Seddon, 2008). Although prices for small quantities should not be used as a guide to commercial utility, at the time of writing the retail price on the Sigma-Aldrich website for [C$_4$C$_1$im][SCN], [C$_4$C$_1$im][NTf$_2$], [C$_4$C$_1$im][C$_1$COO] and [C$_4$C$_1$im]Cl is €2880 kg^{-1}, €1505 kg^{-1}, €776 kg^{-1} and €288 kg^{-1} (Sigma Aldrich, 2017). The economic sustainability of ILs is greatly improved if the IL is recycled. Due to their low vapor pressure and thermal and chemical stability, ILs are theoretically recyclable over numerous application cycles. It is estimated that 10 to 20 recycle and application cycles gives them the same cost per cycle as conventional organic solvents, and over 50 recycles makes them significantly cheaper (Plechkova & Seddon, 2008). As such, all research should aim to demonstrate the stability and recyclability of their ILs over multiple cycles. In addition, the solubility of well-known hydrophobic fluorinated ILs notably increases in the presence of inorganic acids such as HNO$_3$, HClO$_4$ and HCl (Fu et al., 2016; Mazan, Boltoeva, Tereshatov, & Folden Iii, 2016). This can lead to the irreversible loss of the IL to the aqueous phase during solvent extraction, lowering the environmental and financial sustainability of the process. A mass balance should be performed at each stage of the process to quantify overall IL losses and to determine which operation(s) primarily contribute.

However not all ILs are expensive, especially at an industrial scale. Chen and coworkers (2014) demonstrated through process modeling that the price of the Brønsted acidic IL triethylammonium hydrogen sulfate ([N$_{222}$][HSO$_4$]) and 1-methylimidazolium hydrogen sulfate ([HC$_1$im][HSO$_4$]) on an industrial scale was of $1.24 kg^{-1} and $2.96–5.88 kg^{-1}, making these significantly cheaper than fluorinated ILs. In

addition, DES along with tetraalkylammonium and tetralkylphosphonium salts are intrinsically cheaper than imidazolium-based ILs (Plechkova & Seddon, 2008). $[N_{1888}]Cl$ and $[N_{111(2OH)}]Cl$ (the starting component of most DES) currently retail at €92 kg^{-1} and €58 kg^{-1} respectively (Sigma Aldrich, 2017). As in all cases, a compromise must be made between the IL/DES selection (cation and anion selection, functionalisation, etc.), its intended application (leaching, extractant, hydrophobic diluent, medium for electrodeposition, etc.) and the price of the target metal. Whilst the use of more expensive IL can be economically justified for the recovery of In, Ag, Au, PGM and some rare earth elements, the application of fluorinated ILs for the leaching of La_2O_3 makes little economic sense.

The IL-based solvents covered in this review are for the most part limited to the recovery of value from PCBs, waste fluorescent phosphor, nickel metal hydride batteries and permanent magnets. To highlight the great strides made over the last years on the potential of IL-derived solvents for WEEE treatment, optimized process flowsheets are proposed for the extraction of value in fluorescent lamp phosphor waste (Figure 15) and nickel metal hydride battery waste (Figure 16). The versatility of quaternary phosphonium- and ammonium-based ILs for metal extraction based on the selective formation of anionic metal complexes in various leaching solution (chloride, nitrate, etc.) is fully exploited. When possible, solvent extraction processes were substituted for their ABS counterpart based on similar IL cations to further reduce the environmental impact and take advantage of the thermomorphic properties of phosphonium ILs. The substitution by ABS also simplifies the metal recovery process as electrodeposition of easily reduced metals or precipitation are possible directly from the IL-rich phase. The use of the more expensive $[N_{111(2(O)OH)}][NTf_2]$ is justified based on its great selectivity for YOX phosphor dissolution and the high price of the recovered Eu(III). Through careful analysis of the waste matrix, selective sequential leaching steps can be designed in order to solubilize elements of interest at each stage and simplify their purification. Furthermore, the addition of pretreatment steps such as mechanical activation, conversion of metals to oxides and/or the hydrolysis of Fe(III) greatly increases the recovery yields and simplifies the downstream purification of the other anionic chlorometallates. In all cases, closed-loop systems are suggested to recycle the IL, thereby improving the ecological and economic aspects of the proposed processes.

8. Conclusions

WEEE is a global problem issue but also a potentially opportunity due to its high content of valuable metals. The physico-chemical characteristics of

ILs mean they have potential applications in the recovery of metals from WEEE. Many experimental and theoretical studies have identified appropriate IL systems for the selective extraction and purification of metals from WEEE. The extraction performance of many IL systems has been characterized, allowing selection of a particular IL for a specific metal possible. Quaternary ammonium ILs, DESs and ILs-based ABS were highlighted as the most promising solutions due to their low environmental impact, competitive price, compositional flexibility and operational facility. However, significant barriers remain to commercial exploitation of ILs for metal recovery from WEEE. There is a lack of IL application to actual WEEE waste streams, as many researchers have worked on simulated systems and this risk missing interactions that occur with trace components present in WEEE. A further barrier is the high initial cost of many ILs and particularly fluorinated ILs. Despite high recyclability, the capital investment required has limited the use of ILs to extraction of high value metals from WEEE and use in systems were a high metal purity is achieved. Improved upstream collection and sorting to minimize the volume of commingled WEEE would allow more selective use of ILs.

Funding

ORCID

Nicolas Schaeffer http://orcid.org/0000-0002-0747-2532
Helena Passos http://orcid.org/0000-0002-0573-093X
João A.P. Coutinho http://orcid.org/0000-0002-3841-743X

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