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Deep eutectic solvents for separation and purification applications in critical metal metallurgy: Recent advances and perspectives

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Abstract: Solvent extraction, a separation and purification technology, is crucial in critical metal metallurgy. Organic solvents commonly used in solvent extraction exhibit disadvantages, such as high volatility, high toxicity, and flammability, causing a spectrum of hazards to human health and environmental safety. Neoteric solvents have been recognized as potential alternatives to these harmful organic solvents. In the past two decades, several neoteric solvents have been proposed, including ionic liquids (ILs) and deep eutectic solvents (DESs). DESs have gradually become the focus of green solvents owing to several advantages, namely, low toxicity, degradability, and low cost. In this critical review, their classification, formation mechanisms, preparation methods, characterization technologies, and special physicochemical properties based on the most recent advancements in research have been systematically described. Subsequently, the major separation and purification applications of DESs in critical metal metallurgy were comprehensively summarized. Finally, future opportunities and challenges of DESs were explored in the current research area. In conclusion, this review provides valuable insights for improving our overall understanding of DESs, and it holds important potential for expanding separation and purification applications in critical metal metallurgy.

Keywords: deep eutectic solvents; preparations; properties; separation and purification; critical metal metallurgy

1. Introduction

Solvent extraction, an effective separation and purification technology, is crucial in critical metal metallurgy [1]. Organic solvents, which are primarily utilized for solvent extraction, are generally carbon-based molecules with high volatility, high toxicity, and flammability, causing a spectrum of hazards for human health and environmental safety. In the two previous decades, several neoteric solvents, particularly ionic liquids (ILs) and deep eutectic solvents (DESs), have been proposed. While this review does not focus on traditional ILs, a brief introduction to ILs and a comparison between ILs and DESs are crucial. At present, ILs have emerged as a highly researched area in the field of science [2].

ILs consist of organic cations and organic/inorganic anions that remain in liquid form even at temperatures below 10°C [3]. The most commonly used ILs can be divided into two categories. The first type is formed by combining eutectic mixtures of metal halides with organic salts. In this type of ILs, the mixture's eutectic composition creates bulky chloroaluminate or chlorozincate ions, which effectively reduce the lattice energy and freezing point of the mixture [4]. Another type of ILs contains discrete anions, such as PF_6 or $(CF_3SO_2)_2N^-$. This class of ILs has the advantage of possessing large electrochemical windows, which enables electrodeposit of some noble metals [5]. ILs exhibit some unique physiochemical properties, including high polarity, non-flammability, excellent chemical stability, non-volatility, high thermal stability, and recyclability. Furthermore, these characteristics can be adjusted according to requirements by selecting different anions and/or cations; thus, they are also called "Task-specific ILs" [6]. Currently, ILs have completely changed some extraction processes, and they are extensively applied to solid-phase extraction, pressurized liquid extraction, liquid–liquid extraction, and novel liquid phase microextraction due to their high separation coefficients. However, the potential toxicities and non-biodegradability of ILs pose a risk to their broader applications as neoteric solvents with environmentally friendly features. The development of neoteric green reagents is essential to compensate for the shortcomings of ILs, serving as a viable alternative.

DESs, as neoteric green reagents, have gradually become the focus of green solvents due to a series of advantages. Fig. 1 displays the similarities and differences between DESs

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and ILs. DESs are generally composed of “hydrogen bond donor compounds” and “hydrogen bond acceptor compounds.” They can lead to the formation of a new eutectic phase through some intermolecular interactions. In addition, they have a significantly lower melting point than the individual components. The primary focus in the eutectic system is the melting point reduction. Fig. 2(a) depicts a phase diagram that represents the relationship between the melting temperature and composition of the eutectic system [7–8]. In the case of a eutectic mixture containing A and B, the eutectic point marks the lowest melting temperature. During the cooling process of a liquid system, eutectic mixtures do not undergo isothermal reactions between different components. Therefore, the melting point of eutectic mixtures is lower than that of individual components. In particular, DESs are known for their ability to depress melting point significantly, often reaching temperatures as low as 150°C or even lower. This characteristic provides a broad spectrum of liquid phases for DESs [9]; many DESs remain liquid between 70°C and room temperature.

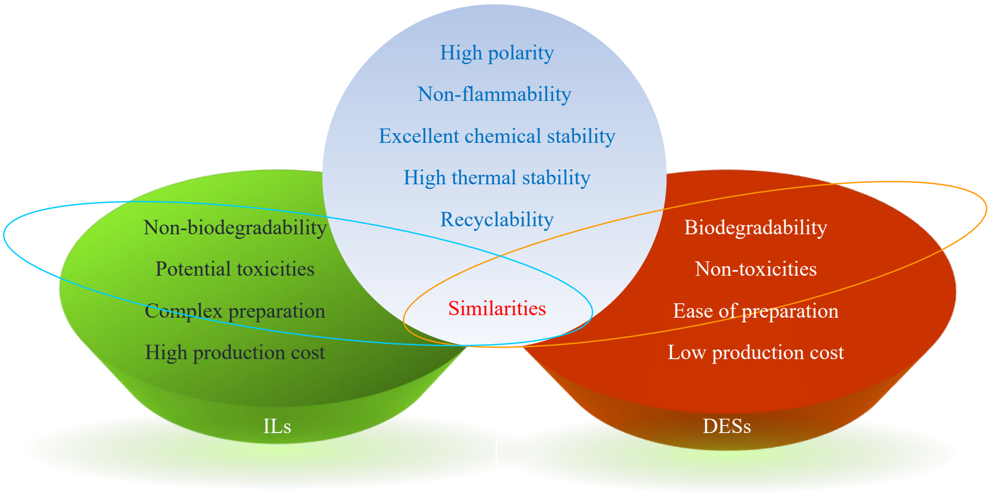

Fig. 1. Similarities and differences between DESs and ILs.

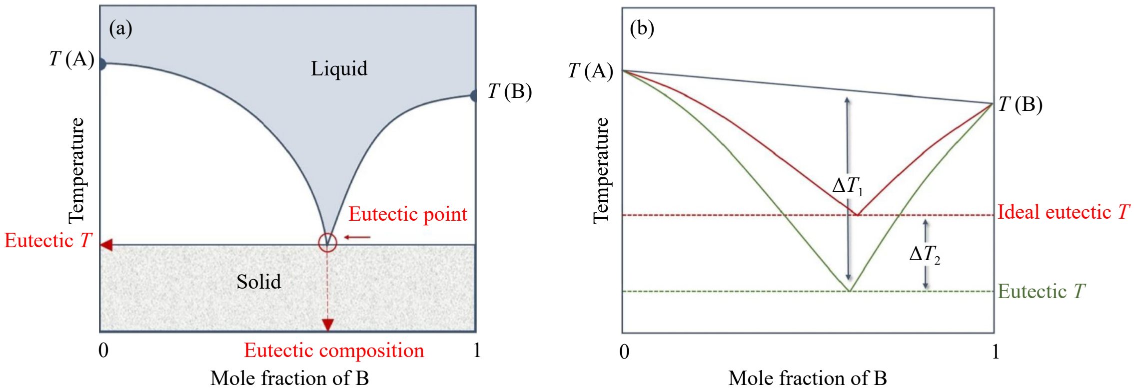

Fig. 2. (a) Solid–liquid phase diagram of a binary mixture [7]. (b) Two different definitions to explain the temperature drop concerning DESs [8]. (a) Reprinted by permission from Springer Nature: *Environ. Chem. Lett.*, Basics and properties of deep eutectic solvents: A review, T. El Achkar, H. Greige-Gerges, and S. Fourmentin, Copyright 2021 [7]. (b) Reprinted by permission from Springer Nature: *J. Solution Chem.*, Insights into the nature of eutectic and deep eutectic mixtures, M.A.R. Martins, S.P. Pinho, and J.A.P. Coutinho, Copyright 2019 [8].

Moreover, Martins *et al.* [8] suggested that a DES should possess a liquid state at operating temperature, even if this condition requires a composition different from the eutectic mixture. Therefore, developing a phase diagram and understanding the melting characteristics of the individual compounds are crucial to ascertaining the optimal solubility curve. The presence of a distinct eutectic point and a decrease in the melting point on the phase diagram indicates the formation of DES. Abbot *et al.* [10] explained the low melting point of DESs by the hydrogen bond interactions in these mixtures and defined the temperature drop as the difference between the melting point of the pure components and the ideal eutectic point (ΔT_1). However, Martins *et al.* [8] had a contrasting viewpoint and argued determining the temperature drop as the difference between the ideal eutectic point and the actual eutectic point (ΔT_2) is more suitable (Fig. 2(b)).

The initial publication reporting DES was released in 2001 [11], and the term “deep eutectic solvents” was defined in 2003 by Abbott *et al.* [12], who coupled choline chloride (ChCl) and urea (Fig. 3(a)) [13]. The hydrogen bond acceptors (HBAs) for synthesizing DESs generally include quaternary ammonium salts, tetraalkylammonium, metal salts, and phosphorus salts, and the hydrogen bond donors (HBDs) are generally amides, alcohols, organic acids, and carbo-

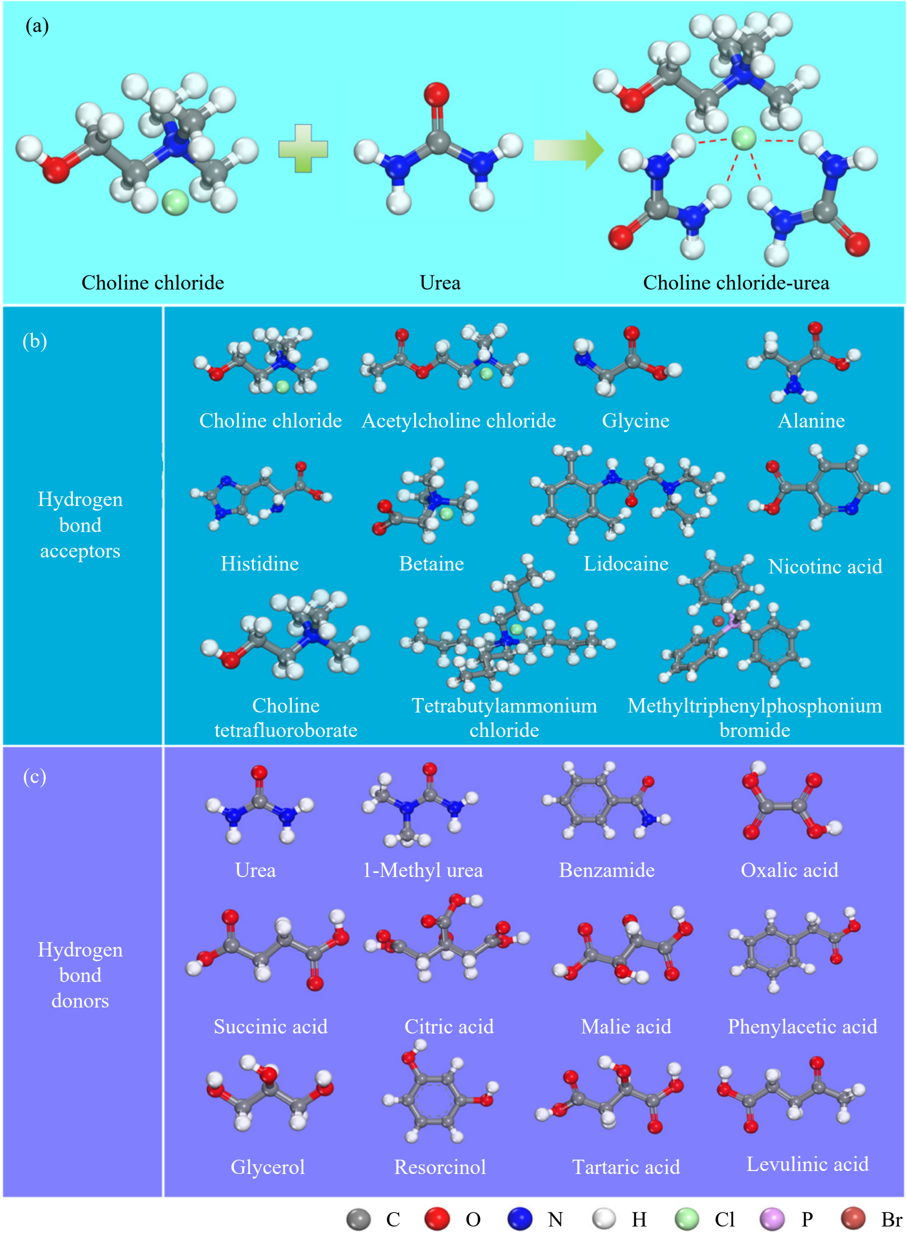

Fig. 3. (a) Schematic of using choline chloride and urea to form DES. Reprinted (adapted) with permission from reference [13]. (b) Some common hydrogen bond acceptors (HBAs) [14]. (c) Some common hydrogen bond donors (HBDs) [14]. (a) Reprinted with permission from K. Rong, H. Zhang, H. Zhang, Y.Y. Hu, Y.X. Fang, and S.J. Dong, *ACS Appl. Electron. Mater.*, 1, 1038-1045 (2019) [13]. Copyright 2019 American Chemical Society. (b, c) Reprinted from *J. Indian Chem. Soc.*, 11, M.B. Singh, V.S. Kumar, M. Chaudhary, and P. Singh, A mini review on synthesis, properties and applications of deep eutectic solvents, art. No. 100210, Copyright 2021, with permission from Elsevier.

hydrates. Fig. 3(b) and (c) depicts some common HBAs and HBDs [14]. DESs offer more benefits than traditional organic solvents and ILs, including low toxicity, adaptability, recyclability, renewability, low cost, and environmental friendliness [15–20]. Therefore, they are referred to as “the neoteric green solvent of the 21st century” [21].

Over the past 20 years, DES applications have become increasingly extensive, and they have been widely applied to metallurgy, CO_2 absorption [22], biocatalysis [23], preparation of nanomaterials [24], extraction of active components from natural products [25], organic synthesis [26], electrochemistry [23], analytical chemistry [27], electrodeposition [28], and other fields. In the field of metallurgy, DES exhibits its varying coordination abilities between components and metals, excellent repeatability, and low price, rendering it a low-cost green strategy to selectively separate critical metals from complex minerals and secondary resources on a large scale.

Critical metals refer to a group of metal elements with irreplaceable and significant applications in various emerging industries, such as new materials, new energy, information technology, aerospace, national defense, and military industry [29]. They are vital resources that support strategic industries. Some examples of critical metals include rare earth elements, cobalt, gallium, indium, niobium, platinum group metals, lithium, and tin. The global dependence on critical metals increases with the development of technology, and ensuring the stable supply of these materials is a strategic consideration for many countries. Fig. 4 illustrates the significant milestones in the advancement of DESs in the field of critical metal metallurgy. In 2005, a DES prepared with 1 $mol\cdot L^{-1}$ choline chloride and 2 $mol\cdot L^{-1}$ urea selectively dissolved transition metal oxides. When tested at a temperature of 60°C, the solubility of zinc oxide, lead oxide, and ferric oxide was 8466, 9157, and 49 $mg\cdot L^{-1}$, respectively [30]. Subsequently, in 2009, non-aqueous DESs were successfully integrated into the field of metallurgy, providing a solution to the issue of wastewater discharge in traditional metallurgical processes [31]. Consequently, the focus was directed toward developing new DESs and improving the ability to effectively extract critical metals from complex minerals and secondary sources utilizing mild conditions. These concepts have become key areas of research in the field of critical metal metallurgy [28].

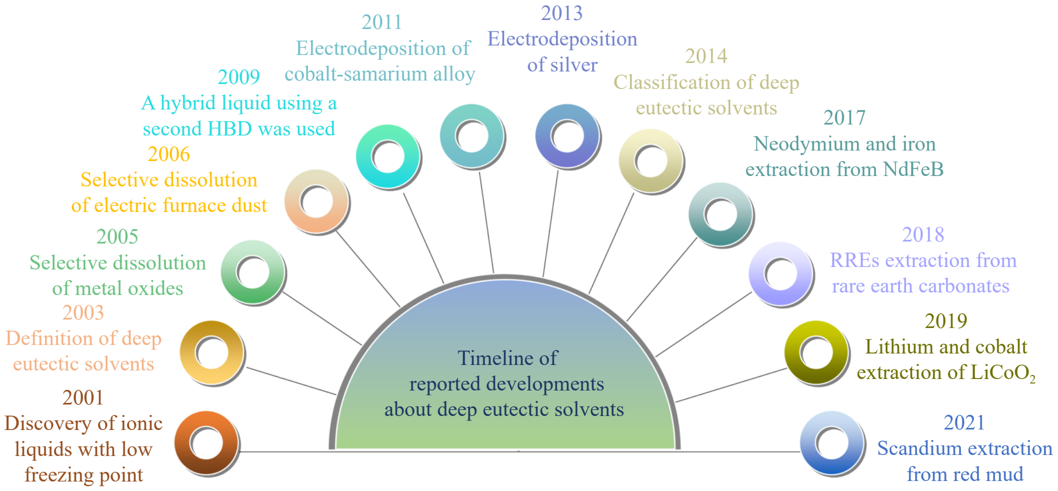

Fig. 4. Historical milestone of DESs in the field of critical metal metallurgy.

Despite the significant progress and discoveries in the field of DESs over the past two decades, research in this area is still in its early stages. Thus far, attempts to gather and compile a comprehensive report on DES applications in critical metal metallurgy are limited. This comprehensive review introduces the classification, formation mechanisms, preparation methods, characterization technologies, and special physicochemical properties of DESs. It focuses on the separation and purification applications of critical metal metallurgy related to DES publications in the past two decades. DESs are expected to be widely employed in critical metal metallurgy industries instead of organic solvents due to their high separation coefficients and potential as environmentally benign substitutes.

2. Classification of DESs

DESs are formed by combining Lewis or Brønsted acids and bases, resulting in a eutectic mixture that can incorporate different anionic and/or cationic species. In comparison, ILs are mainly created by a system of discrete anions and cations. Smith *et al.* [32] outlined a general formula for DESs as follows:

$$\mathrm{Cat}^{+}\mathrm{X}^{-}z\mathrm{Y} \tag{1}$$

where Cat^{+} involves ammonium, phosphine, or sulfonamide cation in principle, X^{-} refers to a Lewis base, and Y is a Lewis or Brønsted acid. These compounds form complex anion species through the interaction of X with Y (where z represents the number of Y molecules that are involved in the interaction).

At present, DESs can be categorized into three types according to their aqueous solubility: hydrophilic DESs, quasi-hydrophobic DESs, and hydrophobic DESs. According to the nature of the complexing agents used, they can be divided into four types: non-hydrated metal halides and quaternary ammonium salts, hydrated metal halides and choline chloride, choline chloride and HBDs, and metal halides and urea, as shown in Fig. 5.

Among them, type III is widely used in the field of critical metal metallurgy because of its ability to dissolve and solvate various transition metal species. The HBDs used in type III are generally composed of amides, carboxylic acids, and alcohols, which are simple to obtain and have no reaction with water. DESs are highly diverse in their composition, given the abundance of HBDs. Moreover, the physicochemical properties of DESs could be customized by selecting HBDs that are suitable for specific applications. Various application requirements can be satisfied by altering the components of DESs. This versatility has rendered DESs widely popular for several purposes, such as separating and purifying critical metals, eliminating glycerol from biodiesel, and synthesizing cellulose derivatives.

3. Preparation methods, characterization, and properties of DESs

3.1. Formation mechanisms

DESs can only be created when the combined interactions between different components are more powerful than the individual impacts of each component. Fig. 6 illustrates that three main types of interactions greatly influence the forma-

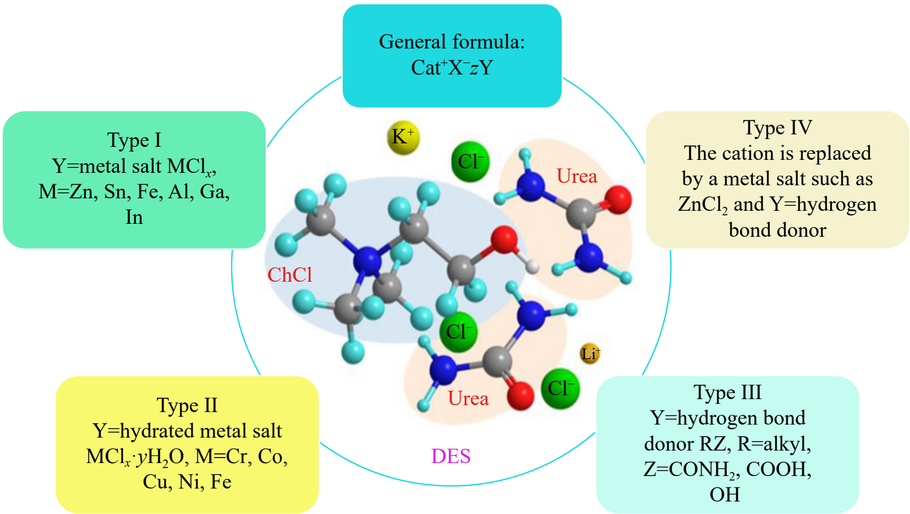

Fig. 5. Four types of DESs based on their general formula. Reprinted (adapted) with permission from reference [8]. Reprinted by permission from Springer Nature: *Environ. Chem. Lett.*, Basics and properties of deep eutectic solvents: A review, T. El Achkar, H. Greige-Gerges, and S. Fourmentin, Copyright 2021 [8].

tion of DESs [33]. Moreover, the physicochemical properties of DESs, including their melting point, viscosity, conductivity, and surface tension, are directly influenced by intermolecular interactions. On this basis, the three intermolecular interactions can be manipulated to enhance the properties of DESs.

Hydrogen bond interactions form mostly DESs containing at least one HBD and one HBA, and the relatively strong hydrogen bonds formed between the HBDs and HBAs reduce their intermolecular interactions, decreasing the melting point of DES. The interactions between Lewis acids and bases in DESs are not anticipated to be sufficiently robust to facilitate Lewis chemical reactions involving the covalent bond formation. However, these interactions can only change the coordination environment, thereby reducing the melting point of DES. Van der Waals interactions have low strength, but they are still important given their ability to exist between any two molecules. Van der Waals interactions become dominant in DES when they are stronger than the original intermolecular interactions in each component. The formation and properties of DESs are influenced by the combination of the three main interactions.

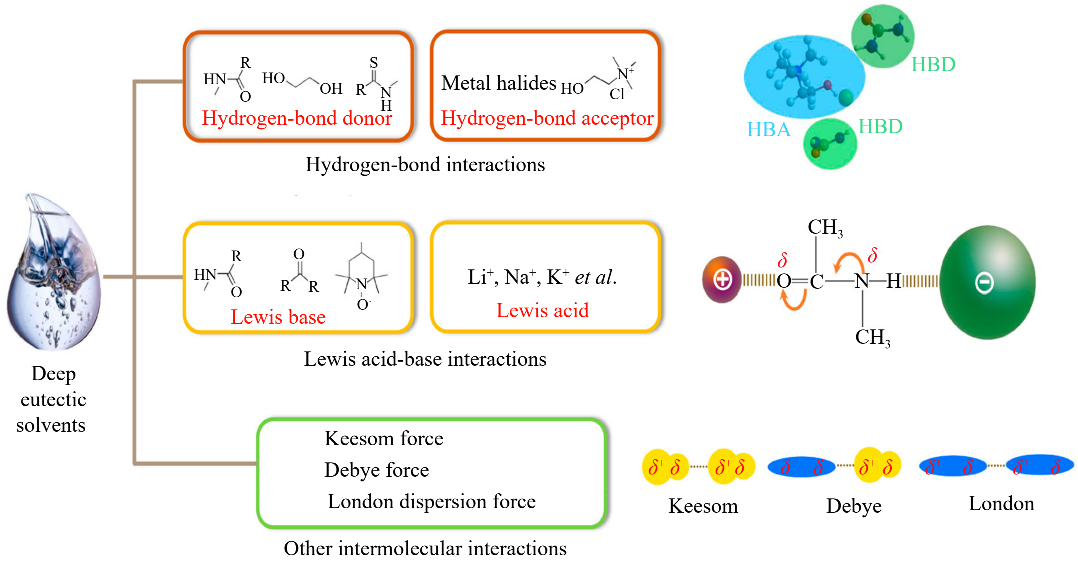

Fig. 6. Formation mechanisms of DESs [33]. Reprinted with permission from C.K. Zhang, L.Y. Zhang, and G.H. Yu, *Acc. Chem. Res.*, 53, 1648-1659 (2020) [33]. Copyright 2020 American Chemical Society.

3.2. Preparation methods

The methods for preparing DESs are simple. Currently, three main preparation methods, namely mixed heating, freeze-drying, and grinding, are available, as shown in Fig. 7. Among them, the mixed heating method is the most widely used [10,34]; the freeze-drying method and the grinding method are more cumbersome than the mixed heating method [35–37]. Hanada *et al.* [38] successfully prepared DES using thenoyltrifluoroacetone (HTTA) and trioctylphosphine oxide (TOPO) as raw materials through a simple heating process. The preparation process of DESs does not require addi-

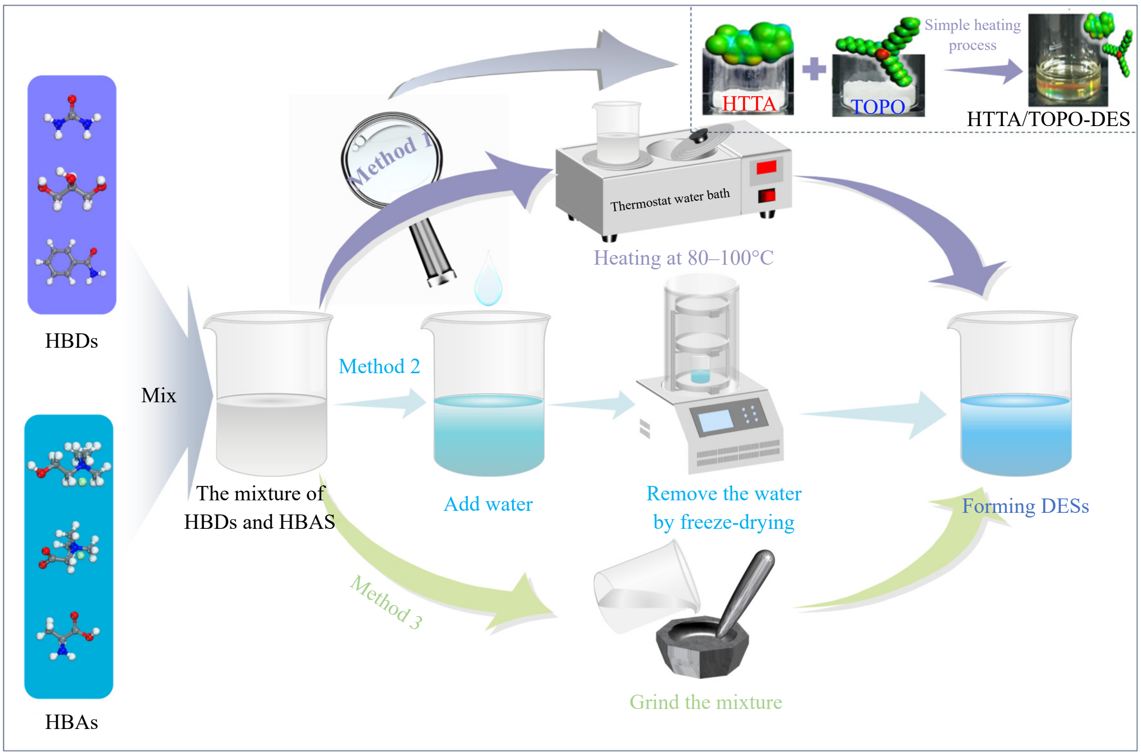

Fig. 7. Schematic of the formation of DESs.

tional solvents, and no additional reactions occur; thus, in theory, no purification process is required. Consequently, its potential as a low-cost alternative to conventional organic solvents and ILs is improved [21].

3.3. Characterization technologies

DESs are created through hydrogen bond interactions between HBDs and HBAs. This characteristic can be applied to determine whether DESs have been successfully prepared. At present, the characterization methods of DESs include Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance (^{1}H NMR). Zhu *et al.* [39] prepared a new DES by mixing decanol (DEO) and *N*, *N*-diisooctylacetamide (DOA). Zhu *et al.* [39] conducted FTIR characterization, and the results are presented in Fig. 8(a). The figure illustrates that the hydroxyl peak(−OH) of DEO and the carbonyl peak(−C=O) of DOA were significantly shifted. This finding indicates the formation of hydrogen bonds within the DES molecules. Generally, the structural changes can be observed through the widening, narrowing, and shifting of the hydroxyl peaks, which confirm the formation of DESs [40]. Moreover, the ^{1}H NMR spectrum was exemplified, as shown in Fig. 8(b). The spectra analysis of the DEO/DOA-DES showed no new peaks when compared with DEO and DOA. This finding demonstrates that no chemical reaction occurred in this process. However, the hydroxyl peak(−OH) of DEO was clearly shifted, thereby suggesting the occurrence of hydrogen bond interactions within the DES molecules.

3.4. Physicochemical properties

Most physicochemical properties of DESs are consistent

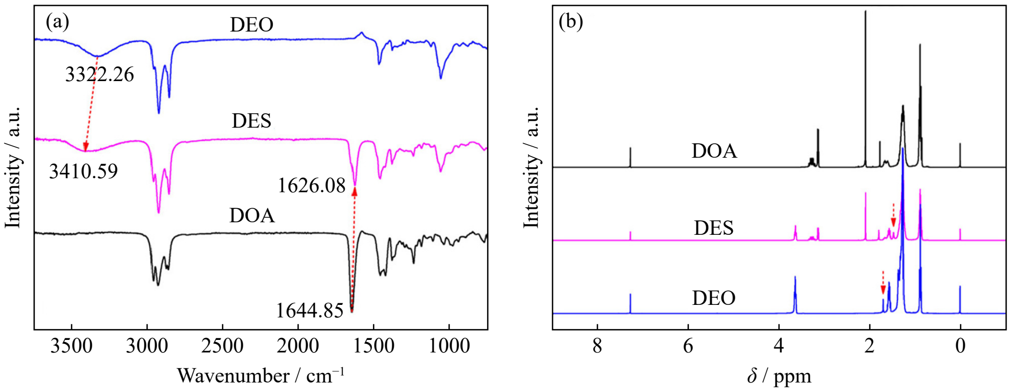

Fig. 8. Characterization methods of DES (molar ratio DEO : DOA = 1:1): (a) FTIR spectroscopy change during the formation of DEO/DOA-DES; (b) ^{1}H NMR spectroscopy change during the formation of DEO/DOA-DES [39] (δ represents chemical shift). Reprinted with permission from K.Y. Zhu, Q.F. Wei, H.Q. Li, and X.L. Ren, *ACS Sustainable Chem. Eng.*, 10, 2125-2135 (2022) [39]. Copyright 2022 American Chemical Society.

with those of the traditional ILs. In addition, DESs have some special properties that distinguish them from ILs, including low vapor pressure, a wide range of liquid phases, and non-flammability. Hence, the main properties of DESs, namely melting point, viscosity, conductivity, density, solubility, and polarity, are presented and discussed. These properties determine whether DESs can be used as extractants in solvent extraction [41].

3.4.1. Melting point

The melting point generally refers to the temperature at which a substance changes from solid to liquid. It is determined by some factors, such as the symmetry of the molecular structure, the existence of hydrogen bonds, and van der Waals interactions. The DESs are eutectic mixtures that can contain various anionic and/or cationic species. Among them, the ions obtained from the complexation of quaternary ammonium salts with metal salts or HBDs have larger asymmetric characteristics and lower lattice energy. This mixture undergoes a charge delocalization, thereby reducing the melting point of DESs [42]. The melting points (T_f) of some common DESs derived from choline chloride are presented in Table 1. Pavoković *et al.* [44] and Durand *et al.* [45] believe that the melting point is closely related to the structure, charge distribution, and interaction strength of HBAs and HBDs. Generally speaking, the higher the hydrogen bond energy within the DES molecules, the easier the crystal structure to be destroyed and the greater the melting point reduction [46].

Table 1. Melting point of some common DESs derived from choline chloride

HBAs (melting point / °C)	HBD (melting point / °C)	Molar ratio of HBA/HBD	T_f / °C	Reference
Choline chloride (302)	Glycol (−13)	1:2	−66	[12]
	Glycerol (18)	1:2	−40	[12]
	Phenol (41)	1:3	−20	[43]
	2,3-xylenol (75)	1:3	−12	[43]
	Malonic acid (134)	1:1	10	[10]
	Urea (132)	1:2	12	[12]
	Oxalic acid (101)	1:1	34	[10]
	Citric acid (149)	1:1	69	[10]
	Succinic acid (185)	1:1	71	[10]
	Benzoic acid (122)	1:1	95	[10]

3.4.2. Viscosity, conductivity and density

The important physical parameters of DESs, namely the viscosity, ionic conductivity, and density, determine their suitability as extractants and influence their diffusion and solubility within the target matrix during extraction. In general, DESs have a high viscosity (>0.1 Pa·s) [10,43], low ionic conductivity (<2 $mS\cdot cm^{-1}$) [8], and high density (>1 $g\cdot mL^{-1}$), which can be elucidated utilizing the hole theory. The solvent molecules achieve a certain mobility through the movement of holes in the opposite direction. However, DESs are a special type of solvents with smaller holes compared with regular solvents, such as HBDs and HBAs. The composition of the DESs is difficult to move, thereby reducing their mobility. Thus, they exhibit high viscosity and low ionic conductivity. In addition, the reduction in the hole radius leads to a denser DES, producing higher density. In general, the viscosity, ionic conductivity, and density of DESs are closely related to some factors described in Table 2. These influencing factors can be modified to change the properties of DESs.

3.4.3. Solubility

DESs are environmentally friendly solvents with excellent solubility properties. The solubility of DESs is determined by the structural properties of HBDs and HBAs and the ionic forces between them. Morrison *et al.* [52] found that DESs have great value in increasing the solubility of insoluble drugs. Abbott *et al.* [53] found that DESs can not only dissolve biological macromolecules, such as amino acids and proteins, but also exhibit excellent solubility for oxides that are difficult to dissolve in water, such as ZnO, CuO, and Fe_3O_4. Complexants, such as malonic acid, urea, and ethylene glycol, are widely used as DES components, which can be attributed to their ability to form complexes with different metals [54].

The dissolution process of metal oxides in DESs is a complex issue that depends largely on the Lewis acidity of the metal and the Lewis basicity of possible ligands available in the DES. During this process, metal oxide is either protonated or substituted by the anionic component of the solvent [55]. Abbott *et al.* [54] predicted the kinetics of reactions in DESs where hydrogen bonding interactions dominate. This condition improves the metal oxide solubility. Recent studies

Table 2. Some factors that influence the properties of DESs

Property	Influencing factors	Reference
Viscosity	HBDs, HBAs, and their molar composition	[41]
	Temperature and water content	[47]
	Addition of surfactant	[32]
Conductivity	HBDs, HBAs, and their molar composition	[10]
	Temperature	[48]
	Water content	[49]
Density	HBDs, HBAs, and their molar composition	[50]
	Temperature	[51]

have highlighted the remarkable ability of these specific DESs to effectively dissolve various metal oxides and then separate pure metals from complex dissolved solutions through the use of electrochemical principles. Fig. 9 visually illustrates the solubility of 10 metal oxides in three DESs derived from choline chloride. The flexible selection of HBDs enables the targeted extraction critical metals from complex minerals and secondary resources. This condition also indicates that the DESs are greatly influential in the field of critical metal metallurgy.

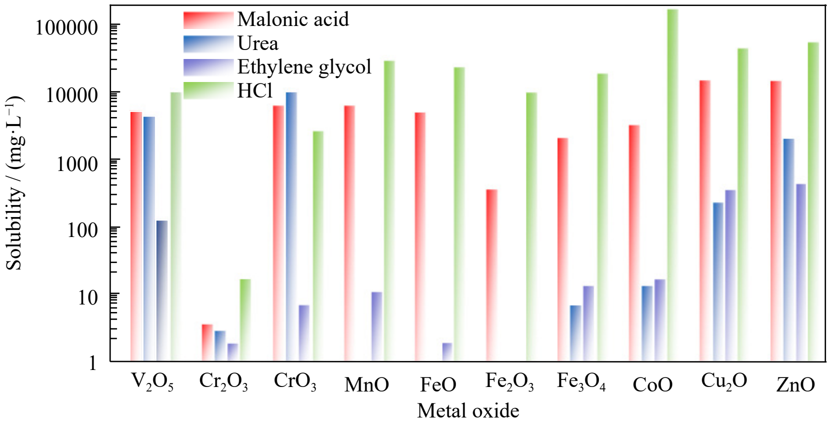

Fig. 9. Solubility of 10 metal oxides in three DESs derived from choline chloride and HCl [54]. Reproduced from Ref. [54] with permission from the Royal Society of Chemistry.

3.4.4. Polarity

In general, the strength of intermolecular attractions determines the polarity of a substance, indicating a solubilization property. This characteristic is commonly estimated using solvatochromic parameters, employing Reichardt's organic dyes or Nile red. The widely used scales for measuring polarity are Dimroth's and Reichardt's scales ($E_T^{(30)}$ and E_T^N, respectively) [56]. The electronic transition energy (E_T) of a probe dye in a solvent can be determined using UV-vis technology and calculated using Eqs. (2) and (3), as follows:

$$E_T^{(30)} = hc\nu_{\max,30}N_A = 119625/\lambda_{\max,30} \tag{2}$$

$$E_T^{(NR)} = hc\nu_{\max,NR}N_A = 119625/\lambda_{\max,NR} \tag{3}$$

where 30 refers to Reichardt's organic dyes, and NR refers to Nile red. In addition, h, c, N_A, $\nu_{\max}$, and $\lambda_{\max}$ represent Planck's constant, light speed, Avogadro constant, wavenumber (cm^{-1}), and wavelength of a maximum UV absorbance (nm), respectively.

While solvatochromism in organic solvents spans the entire range of visible light, the solvatochromic effects of PRIM-based DES species are only observed in certain parts of the visual spectrum [8]. To assess the polarity, the parameter E_T^N can be utilized in a quantitative manner and can be calculated using Eq. (4) as follows:

$$E_T^N = \frac{E_T(\text{Solvent}) - E_T(\text{TMS})}{E_T(\text{Water}) - E_T(\text{TMS})} \tag{4}$$

where E_T^N is a normalized parameter. Both water and tetramethylsilane (TMS) are reference solvents. E_T(Water) = 1. E_T(TMS) = 0.

Table 3 presents the polarity data for different ChCl–glycerol DESs using Reichardt's organic dyes method [41]. Evidently, as the molar ratio of ChCl to glycerol increases, the $E_T^{(30)}$ of the DES also increases. However, the polarity scales are not universally applicable and depend on the solvatochromic probe used. Therefore, the polarity parameters obtained from different solvatochromic probes cannot be compared.

3.4.5. Surface tension

Surface tension is an essential property that highly depends on the intensity of the intermolecular forces occurring between HBDs and the corresponding salts. Therefore, liquids with high viscosity, such as DESs, generally have high surface tensions, which can be continuously estimated by ionic conductivity, consistency, and thickness. Zhang *et al.* [41] reported some data about the surface tension of DESs, as shown in Table 4. These values were observed to be higher than the surface tensions of the majority of conventional molecular solvents. Some studies [57–58] have indicated that the surface tension of DESs is affected by the HBDs, the HBAs, and their molar composition. In addition, temperature is a crucial factor that affects the surface tension; that is, as the temperature rises, it tends to decrease. By selecting different HBAs and HBDs, the surface tension of DESs can be adjusted to make them suitable for specific applications.

4. Separation and purification applications of DESs in critical metal metallurgy

At present, the main applications of DESs in critical metal metallurgy involve the separation and purification of critical metals. Fig. 10 depicts the separation and purification pro-

Table 3. Solvent polarity parameters of different ChCl–glycerol DESs

Solvent (molar ratio)	$E_T^{(30)}$ / (kJ·mol^{-1})
Glycerol	239.20
ChCl:glycerol (1:3)	242.50
ChCl:glycerol (1:2)	243.84
ChCl:glycerol (1:1.5)	243.55
ChCl:glycerol (1:1)	244.72

Table 4. Surface tension of some common DESs

HBA	HBD	Molar ratio of HBA/HBD	Surface tension / (mN·m^{-1})
Choline chloride	Phenylacetic acid	1:2	41.86
Choline chloride	Ethylene glycol	1:3	45.40
Choline chloride	1,4-Butanediol	1:3	47.60
$ZnCl_2$	1,6-Hexanediol	1:3	49.00
Choline chloride	Glycerol	1:3	50.80
$ZnCl_2$	Acetamide	1:4	53.00
$ZnCl_2$	Ethylene glycol	1:4	56.90
Choline chloride	Malonic acid	1:1	65.68
$ZnCl_2$	Urea	1:3.5	72.00

cesses of DESs in critical metal metallurgy. DESs exhibit a low-cost green strategy of selectively separating critical metals from complex minerals and secondary resources (such as rare earth minerals, electric furnace dust, and spent lithium batteries) on a large scale as leaching agents and extractants owing to those high solubilities of metal oxides and the different coordination abilities between components and metals. Furthermore, DESs have been used as electrolytes for electrodeposition purification owing to their sufficient conductivity and wide electrochemical window. Therefore, the separation and purification processes using DESs have been expanded in critical metal metallurgy industries.

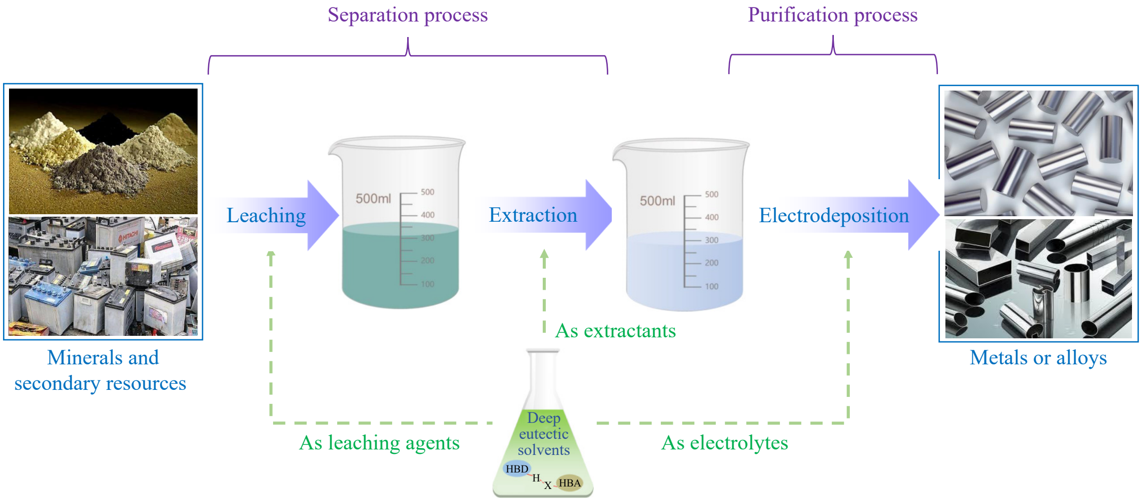

Fig. 10. Schematic representation of separation and purification processes of DESs in critical metal metallurgy.

4.1. Rare earth elements (REEs) separation from rare earth minerals

REEs are extensively utilized in advanced technology applications due to their exceptional magnetic, electronic, and optical properties [59]. REEs are primarily found in mineral form within the Earth's crust. However, rare earth minerals, such as bastnasite, monazite, and ion adsorption deposits, have a very complex composition. High-purity REEs are difficult to prepare because they have similar physicochemical properties [60]. Solvent extraction is a widely used industrial method for producing REEs because of its high production capacity, efficient separation capabilities, and ability to facilitate rapid mass transfer [61]. However, large quantities of industrial wastes are generated in the separation processes, posing a significant hazard to the environment. [62]. Over the past several years, DESs have been used to separate REEs from rare earth minerals, overcoming the disadvantages of solvent extraction and representing a green separation technology.

Numerous studies on the applications of DESs in separating REEs have been conducted. However, these studies mostly focus on rare earth carbonates orrare earth oxides (REOs). In 2018, Entezari-Zarandi *et al.* [63] investigated the leaching process of REEs from various pure carbonate salts using DESs derived from choline chloride within multicomponent mineral mixtures. As exemplified in Fig. 11(a), with the addition of dolomite, the dissolution ratio of Nd, Y, and Sm was 60%–80%, whereas La and Ce reached a dissolution ratio of 20%–40%. Compared with conventional leaching methods using mineral acids, DES leaching can be used to dissolve higher-atomic-number REEs selectively, as well as certain lower-atomic-number REEs and elements that are associated with the gangue minerals [64–65].

In addition to rare earth carbonates, rare earth oxides are significant in the extraction of REEs [66]. However, they are not easily soluble in regular solvents. In 2019, Chen *et al.* [67] initially used maleic acid–ethylene glycol DES to selectively dissolve rare earth oxides. They indicated that this DES had been successfully used to separate REOs, such as La–Ce, Y–Eu, and Sm–Eu. Notably, the obtained REO exhibited a

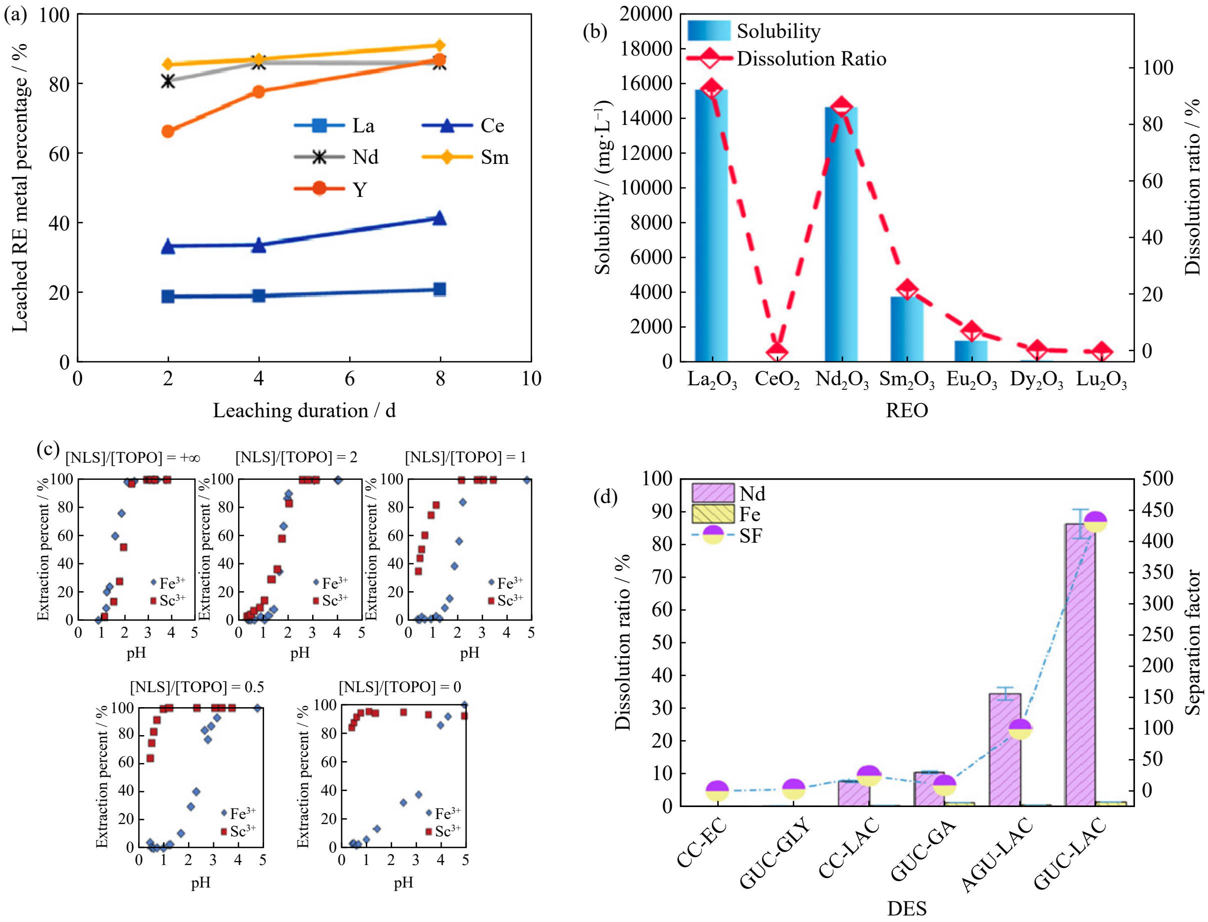

Fig. 11. (a) Solubility of rare earth carbonate mixtures in DESs based on choline chloride [63]. (b) Solubility and dissolution ratios of different REOs in GUC–LAC [68]. (c) Effect of the molar ratio of [NLS]/[TOPO] on the selective separation of Fe^{3+} and Sc^{3+}(NLS: *N*-lauroylsarcosine) [75]. (d) Dissolution ratio and separation factor of Fe and Nd in several DESs (SF: separation factor, CC–EG: choline chloride–ethylene glycol, GUC–GLY: guanidine hydrochloride–glycerol, CC–LAC: choline chloride–L-lactic acid, GUC–GA: guanidine hydrochloride–glycolic acid, AGU–LAC: 1-aminoguanidine hydrochloride–L-lactic acid, GUC–LAC: guanidine hydrochloride–L-lactic acid [78]. (a) Reprinted from *J. Rare Earths*, 37, A. Entezari-Zarandi and F. Larachi, Selective dissolution of rare-earth element carbonates in deep eutectic solvents, 528, Copyright 2019, with permission from Elsevier. (b) Reprinted with permission from Q.B. Yan, C.Y. Liu, X.W. Zhang, L.C. Lei, and C.L. Xiao, *ACS Sustainable Chem. Eng.*, 9, 8507-8514 (2021) [68]. Copyright 2021 American Chemical Society. (c) Copyright 2021 from Selective extraction of Sc(III) over Y(III) and Fe(III) with a deep eutectic solvent composed of *N*-lauroylsarcosine and tri-*n*-octylphosphine oxide by M. Matsumoto, T. Ito, S. Kanemaru, Y. Baba, and K. Sugamoto. Reproduced by permission of Taylor and Francis Group, LLC, a division of Informapic. (d) Reprinted with permission from C.Y. Liu, Q.B. Yan, X.W. Zhang, L.C. Lei, and C.L. Xiao, *Environ. Sci. Technol.*, 54, 10370-10379 (2020) [78]. Copyright 2020 American Chemical Society.

remarkably high purity level of 99.9wt% [67]. However, the separation factors of this DES for most rare earth combinations are insignificantly high. Subsequently, Yan *et al.* [68] introduced a new DES that consisted of guanidine hydrochloride and lactic acid (GUC–LAC DES), which is applied to the separation of rare earth minerals. Fig. 11(b) displays a significant difference in solubilities and dissolution ratios between La_2O_3 and Dy_2O_3 in the GUC–LAC DES, leading to the enormous superiority of GUC–LAC DES in effectively separating La_2O_3 and Dy_2O_3. The results displayed that GUC–LAC DES is more suitable for separating REEs from most rare earth combinations than the maleic acid–ethylene glycol DES [69]. Söldner *et al.* [70] conducted a study on the solubility of Ln_2O_3 for various DESs. DESs that included ChCl and carboxylic acids were found to be effective for dissolving light lanthanide oxides. In addition, Xiao *et al.* [71] have managed to create covalent organic frameworks (COFs) utilizing DESs as the reaction medium. The results suggested that these COFs can effectively and rapidly separate various REEs.

In addition, the recovery of REEs from waste rare earth materials, such as red mud and NdFeB permanent magnets, offers a potential solution for the sustainable production of these valuable elements [72–73]. Red mud, a bauxite waste from an alumina production process, is rich in rare earth elements, such as scandium [74]. The separation of scandium from red mud leachates becomes very difficult when using traditional extractants given the difficulty in addressing phase separation. Matsumoto *et al.* [75] successfully separated Sc^{3+} and Fe^{3+} from red mud leachates using the features of high selectivity and easy recovery of DESs. Fig. 11(c) illustrates that the molar ratio of [NLS]/[TOPO] significantly affects the extraction of scandium. When [NLS]/[TOPO] = 0.5, Sc^{3+} and Fe^{3+} can achieve the most efficient separation at pH = 1. However, when this ratio continues to decrease, the baseline extraction of Sc^{3+} decreases slightly. Overall, the combination of NLS and TOPO has been identified as a promising extraction system for selectively separating and recovering Sc^{3+} and Fe^{3+} from red mud leachates.

NdFeB permanent magnets are widely used in electronic devices with high demands in various industries. These magnets are particularly known for their abundance of neodymium metal [76]. Riaño *et al.* [77] used ChCl–lactic acid to separate Nd and Fe from NdFeB successfully. Notably, the obtained Nd exhibited a remarkably high purity level of 99wt%. However, this DES type has high viscosity (0.156 Pa·s), and the dissolution ratio of Nd and Fe is relatively low. Subsequently, Liu *et al.* [78] prepared a new GUC–LAC DES to separate Nd from NdFeB. Fig. 11(d) reveals that GUC–LAC is more suitable for separating Nd from NdFeB than other DESs. In addition, GUC–LAC has a lower viscosity, measuring below 0.04 Pa·s at 50°C, facilitating the extraction reaction process. Recently, Yu *et al.* [79] have managed to create a ternary DES using trioctylphosphine oxide for the recovery of REEs from NdFeB. This DES exhibits low viscosity and low water content, delivering superior extraction and separation capabilities. The recovery of REEs can reach 99% under optimized conditions by using this DES in the extraction process. Moreover, Yang *et al.* [80] utilized a DES that consisted of ethylene glycol and maleic acid and successfully applied it to the separation of Nd from NdFeB. This DES exhibited high selectivity for Nd and showed no reactivity toward Fe, facilitating efficient separation. The separation coefficient of Nd/Fe can reach 3000 under optimal conditions [80].

4.2. Critical metal separation from electric furnace dust

In electric furnace steelmaking, molten steel production generates a large amount of dust. An average of 10–20 kg of dust is generated for every ton of molten steel produced [81]. The dust from electric furnaces consists of various heavy metal elements, such as iron, zinc, chromium, nickel, lead, indium, and tin. These metal elements must be recycled and utilized efficiently [82]. At present, treatment methods of electric furnace dust mainly include the landfill method, solidification method, reflux sintering method, wet extraction method, fire extraction method, and physical method [83–85]. However, these treatment methods are limited by high energy consumption and serious environmental pollution. In recent years, a method of treating electric furnace dust with DESs has been suggested, exhibiting the advantages of low energy usage, recyclability, and less environmental pollution.

In 2006, Abbott *et al.* [86] initially used choline chloride–urea DES to extract Zn and Pb from electric furnace dust, with leaching efficiencies of 31% (Zn) and 23% (Pb), respectively. Fig. 12(a) displays that this DES can selectively extract zinc and lead oxides that are presented in electric furnace dust, whereas iron and aluminum oxides are insoluble. Xu *et al.* [87] successfully used this DES to leach and extract ZnO with a purity of up to 99.76wt% from Zn-containing dust. However, the DES is characterized by a relatively high viscosity, approximately 0.8 Pa·s at 298 K, posing challenges when pumping the fluid and filtering out any undissolved particles. A hybrid liquid is created by incorporating a second HBD into the solvent to overcome this issue, effectively reducing its viscosity. Abbott *et al.* [31] prepared a new hybrid DES, which can be expressed as follows:

$$1\ \text{choline chloride} : x\ \text{ethylene glycol} : (2-x)\ \text{urea} \tag{5}$$

Among them, choline chloride is HBA, ethylene glycol (EG) and urea are HBDs, and x represents the number of ethylene glycol molecules involved in the DESs.

As shown in Fig. 12(b), the extraction efficiency of this hybrid DES for Zn and Pb remains relatively unchanged except for $x = 2$ [88]. When $x = 1.5$, this hybrid DES is characterized by a relatively reduced viscosity, approximately 0.056 Pa·s at 298 K [54]. Moreover, 1 ChCl : 0.5 EG : 1.5 urea (represented by the hybrid DES when $x = 0.5$) [89] and 1 ChCl : 1 EG : 1 urea (represented by the hybrid DES when $x = 1$) [90] have been successfully used in the recycling of electric furnace dust.

In addition to extracting zinc and lead from the electric furnace dust, Zürner *et al.* [91] have successfully separated In and Sn from the same dust using a DES formulated with oxalic acid. The presence of In and Sn in the franklinite phase of electric furnace dust hinders the effective extraction of these metals using ChCl–EG DES and ChCl–urea DES. However, DES formulated with oxalic acid has shown excellent performance in this regard. The findings revealed that the leaching rates of In and Sn were 92% and 88%, respectively, after 48 h. While the leaching rate of this DES for target metals is high, the selectivity is often limited. Fig. 12(c) summarizes the streamlined method of extraction after leaching; it can be divided into two steps [88]. First, mixing the flue dust leachates with water quickly forms a white precipitate, which contains various metal elements such as Zn, Pb, and Cu. Second, yellow precipitates of Fe can be formed by photoinduced reduction reaction [92]. In and Sn were not detected as constituents in any of the precipitates, indicating that they were still present in the leachates [93]. Fig. 12(d) shows that over time, other impurity metal elements, such as Zn, Pb, Cu, and Fe, are present at very low levels, whereas In and Sn remain in the solution at high levels, Subsequently, they are further separated by conventional extraction techniques. The DES systems can reduce the losses of In in the Fe precipitation step while maintaining a higher recovery rate of Sn than the aqueous system. This finding can be attributed to the significant effect of the high concentration of chloride in the DES system, preventing the simultaneous precipitation of Fe with In.

4.3. Critical metal separation from spent lithium batteries

The increasing use of different mobile devices, electric vehicles, and other applications has produced numerous lithi-

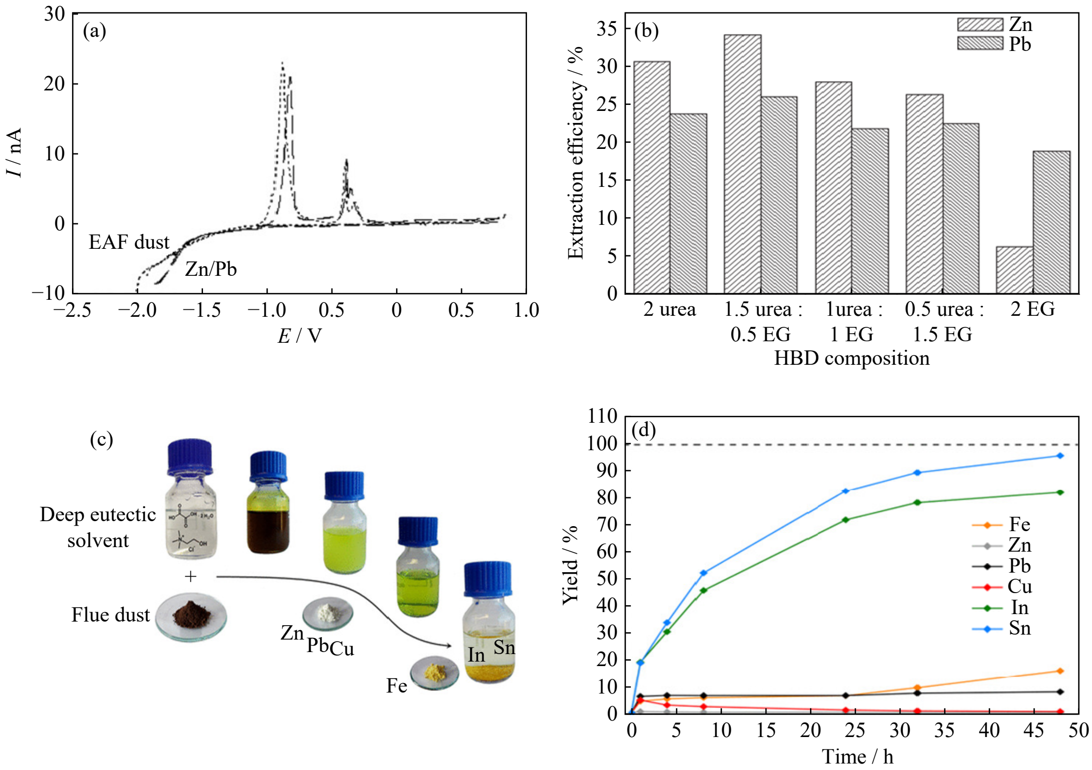

Fig. 12. (a) Cyclic voltammograms of electric furnace dust dissolved in a DES (molar ratio ChCl : urea = 1:2), *I* and *E* represent current and voltage) [86]. (b) Extraction efficiency of various hybrid DESs for Zn and Pb. Reprinted and adapted from reference [31]. (c) Streamlined method for extracting In and Sn from dust using DES based on oxalic acid, (d) Compositional analysis of furnace dust leachates. Reprinted (adapted) with permission from reference [91]. (a) Copyright 2006 from Processing metal oxides using ionic liquids by A.P. Abbott, G. Capper, D.L. Davies, and P. Shikotra. Reproduced by permission of Taylor and Francis Group, LLC, a division of Informapic. (b) Used with permission of *Aust. J. Chem*., from Processing of electric arc furnace dust using deep eutectic solvents, A.P. Abbott, J. Collins, I. Dalrymple, *et al.*, 62, 2009, permission conveyedthrough Copyright Clearance Center, Inc. (c, d) Reprinted with permission from P. Zürner and G. Frisch, *ACS Sustainable Chem. Eng.*, 7, 5300-5308 (2019) [91]. Copyright 2019 American Chemical Society.

um batteries. Among them, $LiCoO_2$ batteries make up approximately 20% of the total. Current batteries typically contain harmful organic electrolytes and critical metals [94]. However, thus far, a staggering 55% of batteries have not been recycled, leading to serious pollution and resource waste. Currently, lithium batteries are recovered using two main methods. Although pyrometallurgy is simple and effective, it suffers from drawbacks, namely, high energy consumption and significant gas emissions. Hydrometallurgy addresses the limitations of pyrometallurgy [95], but its challenges include the production of significant amounts of wastewater and high cost attributed to the use of leaching and reducing agents. Hence, the development of a sustainable and economical leaching process is crucial for extracting Li and Co from lithium batteries [96]. At present, DESs have emerged as a preferred option for extracting Li and Co from batteries. They not only prevent the release of wastewater but also offer the potential for repeated extraction, rendering them a popular research prospect in recent years [97–98].

In 2019, Tran *et al.* [99] used a DES (molar ratio ChCl : EG = 1:1) to leach $LiCoO_2$ for the first time and soaked it for 24 h at a hydrothermal temperature of 25–220°C. The results of the experiment in Fig. 13(a) display that the extraction rate of cobalt is determined by the extraction temperature, and it reaches the highest value of 94.1% at 220°C. However, the extraction temperature and time determine that its economy is unsatisfactory, and it is difficult to apply to large-scale industrial applications. Subsequently, Wang *et al.* [97] used a DES (molar ratio ChCl : urea = 1:2) to recover cobalt from discarded lithium-ion batteries. As shown in Fig. 13(b), 97.9% of the cobalt extraction rate could be obtained after treatment at 180°C for 12 h. The electrochemical study revealed that urea-based DESs have a more negative reduction potential than EG-based DES. This finding indicates that urea possesses stronger coordination and reduction abilities, which can enhance the efficiency of leaching processes [28,100].

Peeters *et al.* [98] designed a DES (molar ratio ChCl/citric acids = 1:2), which can obtain a 90% cobalt leaching rate and 93% lithium leaching rate after treatment at 40°C for 1 h. Although the DES leaching conditions of this ChCl–organic acid system are relatively mild, the method has not gained widespread usage owing to the high viscosity and low efficiency of the solution in leaching metals [98]. Subsequently, Roldán-Ruiz *et al.* [101] designed a DES (molar ratio ChCl : p-toluenesulfonic acid : H_2O = 1:1:2) that exhibits excellent extraction capabilities for $LiCoO_2$. Moreover, it is effective even at low temperatures of 90°C and requires only a short

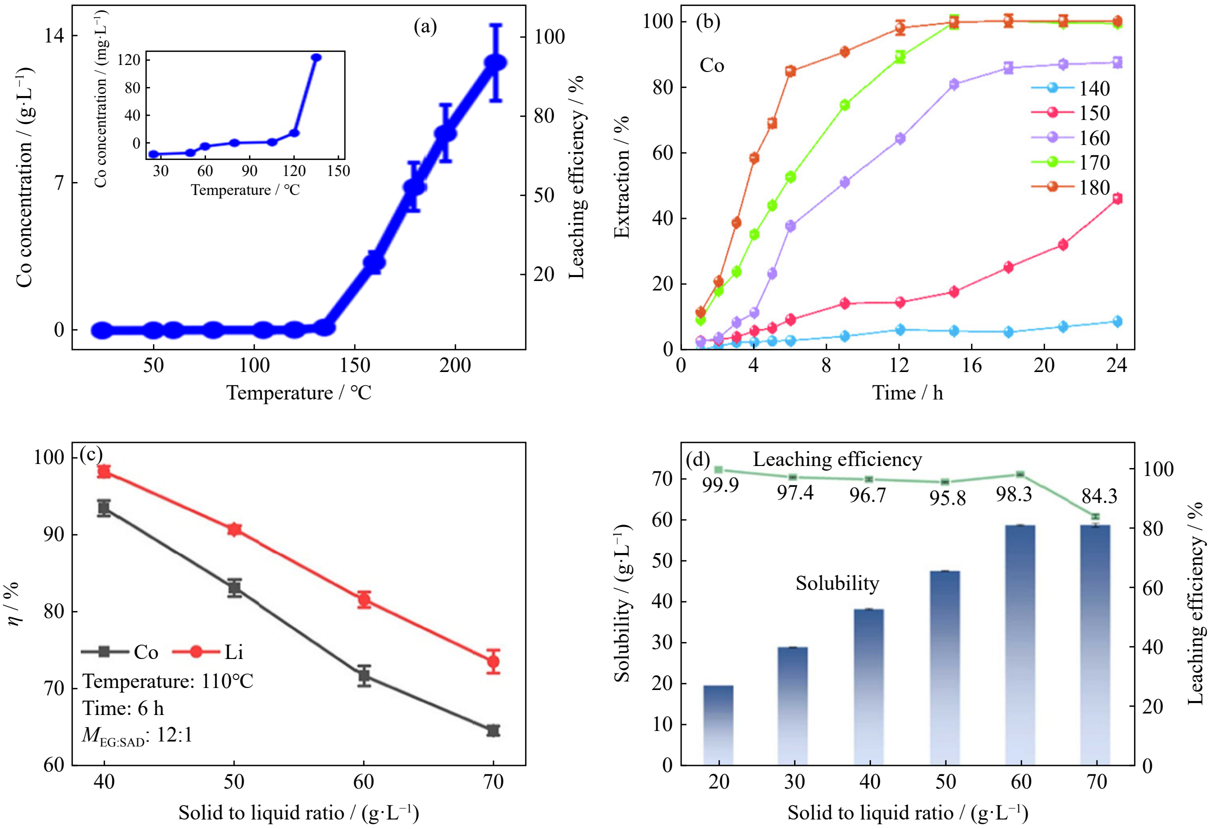

Fig. 13. (a) Leaching efficiency of Co from $LiCoO_2$ using DES (molar ratio ChCl : EG = 1:1) [99]. (b) Efficiency of Co leaching from discarded lithium-ion batteries using DES (molar ratio ChCl:urea 1:2) [97]. (c) Leaching efficiency of Co and Li from $LiCoO_2$ using DES (molar ratio of EG/SAD, $M_{EG:SAD}$ = 12:1) [94]. (d) Leaching efficiency of Co from $LiCoO_2$ using DES (EG-MA) [103]. (a) Reprinted by permission from Springer Nature: *Nat. Energy*, Deep eutectic solvents for cathode recycling of Li-ion batteries, M.K. Tran, M.T F. Rodrigues, K. Kato, G. Babu, and P.M. Ajayan, Copyright 2019. (b) Reproduced from Ref. [97] with permission from the Royal Society of Chemistry. (c) Reprinted with permission from S.J. Tang, M. Zhang, and M. Guo, *ACS Sustainable Chem. Eng.*, 10, 975–985 (2022) [94]. Copyright 2022 American Chemical Society. (d) Reprinted from *J. Alloys Compd.*, 966, H.H. Li, N.Y. Chen, W.F. Liu, et al., A reusable deep eutectic solvent for the regeneration of Li and Co metals from spent lithium-ion batteries, art. No. 171517, Copyright 2023, with permission from Elsevier.

period of 15 min for the extraction process [99]. Compared with organic acids, this DES significantly reduces the amount of solute required to fully dissolve in the solvent, exhibiting economic and sustainability advantages [102]. However, this DES type has high corrosion performance, which is not conducive to industrial production.

However, the strong intermolecular force of ChCl results in a high viscosity for ChCl-based DES, causing challenges in the extraction and separation [103]. Therefore, Chen *et al.* [67] developed the organic acid–EG DES to extract Li and Co from $LiCoO_2$. Organic acids and EG interact through hydrogen bonding. This interaction reduces the viscosity of the organic acid–EG system. Moreover, organic acids offer acidity and coordination, enhancing the solubility of metal oxides. EG possesses a reduction capacity and low viscosity. Therefore, the organic acid–EG DES is more suitable for treating spent lithium batteries than ChCl-based DES.

Tang *et al.* [94] designed a new EG–sulfosalicylic acid dihydrate (SAD) DES in 2022. This DES possesses a remarkable coordination ability and exhibits low viscosity, rendering it suitable for extracting metals [101]. Fig. 13(c) illustrates that when $LiCoO_2$ is extracted at 110°C for 6 h, the extraction rate of Co reaches the maximum (93.5%) and that of Li reaches the maximum (98.3%). Li *et al.* [103] designed a new EG–maleic acid (MA) DES in 2023 to further improve the leaching efficiency. Fig. 13(d) shows that this DES has a high loading capacity of 59 g·L^{-1}, and the leaching efficiency of Co can reach 98.3% under optimal conditions. Even after four cycles, the leaching efficiency of Co remains at 90%.

The dissolution of $LiCoO_2$ in the organic acid−EG DES is a complex liquid−solid reaction process that typically involves three steps. (1) The diffusion of reactants, where some molecules and ions (organic acids, EG, and hydrogen ions) are diffused and adsorbed to the $LiCoO_2$ surface. (2) Interfacial chemical reaction, where Li^+ in $LiCoO_2$ is replaced by H^+ and dissolved into the solution. At the same time, the Co^{3+} in the structure is reduced and bonded with organic acids and EG to create soluble complexes. (3) The diffusion of products, where the generated soluble complexes and Li^+ diffused into the organic acid–EG DES.

The leaching kinetics of $LiCoO_2$ in DES can be understood through diffusion and interfacial chemical reaction processes. These processes are commonly analyzed using a shrinking core model [104]. The experimental results indicated that the leaching reactions of Li and Co are regulated by interfacial chemical reactions. In the leaching process of Li and Co from $LiCoO_2$ using DES, the relationship between the apparent reaction rate constant (k) and leaching efficiency (η) can be described by the following equation:

$$1-\left(\frac{2}{3}\right)\eta-(1-\eta)^{\frac{2}{3}}=kt \tag{6}$$

where η represents the leaching efficiency of Co and Li, k is the apparent reaction rate constant, and t is the leaching time.

4.4. Electrodeposition purification of metals and alloys

As a relatively low-cost purification technology, electrochemical deposition can achieve the preparation of metal coatings at relatively low temperatures. The basic principle is that the metal ions in the electroplating solution obtain electrons and undergo a reduction reaction on the cathode surface, and the corresponding metal or alloy is precipitated on the cathode surface [105]. The traditional aqueous-based electroplating solutions have some disadvantages: poor electrochemical stability, limited potential windows, and passivation of deposits. ILs possess a broad electrochemical range of 3–5 V and demonstrate satisfactory conductivity. However, they exhibit low solubility for metal ions and high cost. As substitutes for ILs, DESs have been used for electrodeposition purification because of their adequate conductivity, wide electrochemical window, similar mass transport properties, and high solubility for metal salts [106].

Currently, DESs provide the appropriate media for achieving numerous technical objectives in various industries [107]. New coating methods for the deposition of metals, new alloys, and composite coatings can be accomplished within a suitable DES system [32]. The reduction processes of various metals, such as Cr, Ni, Ti, and Sm in DESs, have been investigated. Moreover, DES can contain multiple alloy components. Consequently, the deposition of alloys is easier than that of aqueous electrolytes. The redox potentials of the alloying elements in aqueous electrolytes have significant differences owing to the presence of hydrated metal ions. In DES, the formation of metal chloride ions may change the redox potential of the alloys, thereby simplifying the deposition process. Table 5 summarizes some metal electrodeposition processes using DESs. Fig. 14 demonstrates the simplified process flow of metal electrodeposition using DESs, mainly including four steps. (1) Step I: DES preparation, where selecting the appropriate combination of DESs based on deposited metals or alloys is crucial. The composition of DESs can impact the shape of the metal deposits. In addition, DES must be preheated to a specific temperature prior to electrodeposition to ensure complete fusion of components while removing potential moisture and other impurities. The shape of metal deposits can also be adjusted using additives [118]. (2) Step II: electrode preparation, where selecting suitable anode and cathode materials is

Table 5. Electrodeposition purification of metals and alloys using DESs

Deposited metals or alloy	DESs (molar ratio)	Main conclusions	Reference
Ni	1 ChCl : 2 urea	The shape of the Ni deposits was influenced by the substrates employed; round Ni nanoparticles were formed on Pt at a low deposited charge.	[106]
Zn	1 [EMIm]TFSI : 3 GBL	The electrolyte mixture is capable of reversible Zn electrodeposition at temperatures down to −60°C.	[108]
Ag	1 ChCl : 2 EG, 1 ChCl : 2urea	The nucleation and growth of Ag deposits are quite pronounced and strongly influenced by the HBDs of DESs.	[109]
Bi	1 ChCl : 1 MA	The shape of the Bi film is significantly influenced by the deposition potential.	[110]
Cr	1 ChCl : 1 EG, 1 ChCl : 2 EG, 1 ChCl : 3 EG, 1 ChCl : 4 EG	Compared to the aqueous system, ChCl–EG DES has a wider electrochemical window (EW). As the EG content increases, the EW of DES increases from 2.1 to 2.3 V.	[111]
Co	1 ChCl : 2 urea	Co deposits through a typical nucleation and three-dimensional process.	[112]
Sm	1 ChCl : 2 urea	The conductivity of the substrates will be limited by the deposits at low overpotentials. The normal behavior can be observed at high overpotentials.	[112]
Ru	1 ChCl : 2 EG	The addition of sulfamic acid to a DES containing Ru^{3+} can facilitate the deposition process. Optimized plating conditions can produce coatings that are uniform and free of cracks.	[113]
Co–Sm	1 ChCl : 2 urea	Constant current deposition allows for homogeneous deposits on metal substrates whose composition varies with the current density.	[114]
Sn–Ni	1 ChCl : 2 urea	The Sn–Ni coating that was prepared had a consistent and porous structure. Additionally, it demonstrated a remarkable ability to effectively adsorb black dyes.	[115]
Zn–Ni	1 ChCl : 2 EG	From an electrochemical perspective, both Zn and Ni displayed varying levels of complexation depending on the molar ratio of ChCl and EG.	[116]
Zn–Sn	1 ChCl : 2 EG, 1 ChCl : 2 PG, 1 ChCl : 2 urea	The presence of additives, specifically Idranal VII, significantly influenced the structure and composition of the Zn–Sn deposit.	[117]

Note: [EMIm]TFSI—1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide; GBL—γ-butyrolactone; MA—malonic acid; PG—1,2-prpylene glycol.

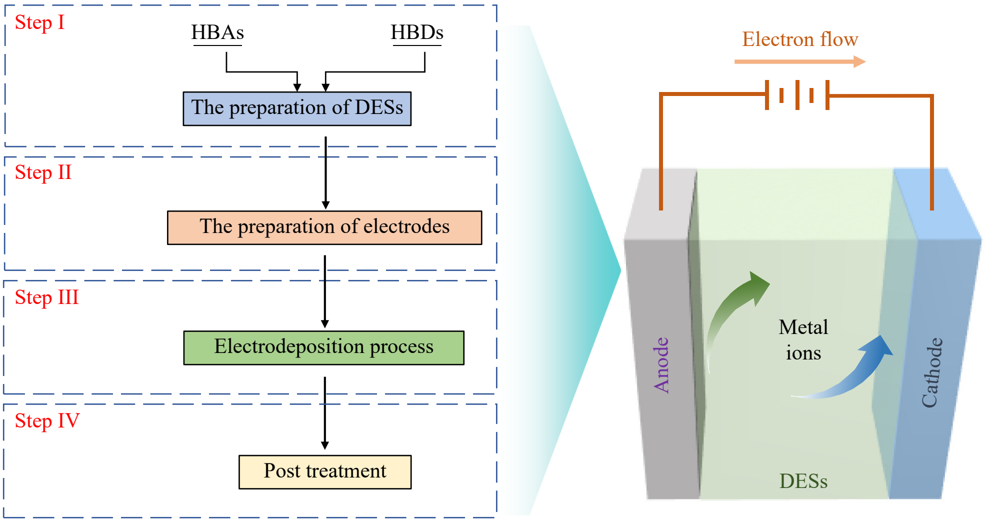

Fig. 14. Simplified process flow of metal electrodeposition using DESs.

essential. Anode materials are generally selected from metals or alloys that require purification. On the contrary, cathode materials are generally high-purity metal plates or wires. These electrodes must be cleaned to remove surface oxides and other pollutants prior to electrodeposition. (3) Step III: electrodeposition process, where metal ions are reduced on the cathode, forming a deposition layer of metals or alloys. Accurate regulation of parameters, such as current, voltage, and current density, is crucial. Metal deposits can be acquired through either constant current or constant voltage conditions. The current density plays a significant role in determining the shape and attachment of these deposits. (4) Step IV: post-treatment, where the deposition layer is removed from DESs and thoroughly cleaned upon the completion of electrodeposition. Furthermore, characterization tests and purity assessments on the obtained metals or alloys must be conducted. To achieve a more sustainable process, DESs used for electrodeposition can be recovered and reused through evaporation or filtration methods. At present, DESs have become increasingly popular as an appropriate method for synthesizing nanoparticles with controlled shapes. This capability holds potential for the applications of electrocatalysts, sensors, batteries, and fuel cells [32].

5. Conclusions and outlook

DESs have become superior alternatives to organic solvents and ILs in the field of critical metal metallurgy. The use of DESs for the separation and purification of metals offers several advantages. (1) Many DESs can effectively dissolve various metal ions, given their high solubility, which is particularly important for the separation and purification of metals. (2) The composition of DESs can be customized to optimize the dissolution and electrodeposition performance of specific metal ions owing to their excellent adjustability. (3) DESs often have excellent thermal stability, which is conducive to continuous operation at higher temperatures. (4) Only the components are required to be blended in a molar ratio because of the simple preparation of DESs, thereby reducing the cost to some extent. (5) The potential range for electrochemical dissolution or deposition of metals is relatively large, which provides more possibilities for metal separation and purification.

However, DESs still have some drawbacks when applied to the separation and purification of metals. (1) The viscosity of DESs is generally high, affecting the fluidity and mixing of solvents, as well as the extraction efficiency. (2) Although most DESs are relatively low in corrosivity, some types of DESs may still be corrosive to certain materials. Selecting appropriate DESs and materials for use is necessary. (3) Although the adjustability of DESs is a major advantage, selecting or designing a DES with excellent selectivity to separate and purify specific metals may be challenging.

Only a small fraction of DESs have been explored and utilized thus far, exhibiting great potential for future expansion of the HBA and HBD types employed. In addition, their physicochemical properties demonstrate that they can be used in other applications that are yet to be explored, and a considerable amount of work is required to expand the usage of DESs. The future research prospects of DESs include the following directions: (1) optimization of composition and structure, (2) assessment of environmental impact, (3) energy consumption and cost analysis, (4) industrial applications and scaling, (5) theoretical and modeling research, (8) research on corrosiveness and stability, and (9) recycling and reuse technology. These research directions are not only aimed at addressing existing technological challenges but also contribute to introducing new application areas. We firmly believe that their environmentally friendly nature and cost-effectiveness play a significant role in driving the industrial development of this new medium in the coming years.

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Conflict of Interest

All authors do not have competing interests to declare.

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