Review

Nonaqueous Solvent Extraction for Enhanced Metal Separations: Concept, Systems, and Mechanisms

Zheng Li,*,[∇] Brecht Dewulf,[∇] and Koen Binnemans

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ABSTRACT: Efficient and sustainable separation of metals is gaining increasing attention, because of the essential roles of many metals in sustainable technologies for a climate-neutral society, such as rare earths in permanent magnets and cobalt, nickel, and manganese in the cathode materials of lithium-ion batteries. The separation and purification of metals by conventional solvent extraction (SX) systems, which consist of an organic phase and an aqueous phase, has limitations. By replacing the aqueous phase with other polar solvents, either polar molecular organic solvents or ionic solvents, nonaqueous solvent extraction (NASX) largely expands the scope of SX, since differences in solvation of metal ions lead to different distribution behaviors. This Review emphasizes enhanced metal extraction and remarkable metal separations observed in NASX systems and discusses the effects of polar solvents on the extraction mechanisms according to the type of polar solvents and the type of extractants. Furthermore, the considerable effects of the addition of water and complexing agents on metal separations in terms of metal ion solvation and speciation are highlighted. Efforts to integrate NASX into metallurgical flowsheets and to develop closed-loop solvometallurgical processes are also discussed. This Review aims to construct a framework of NASX on which many more studies on this topic, both fundamental and applied, can be built.
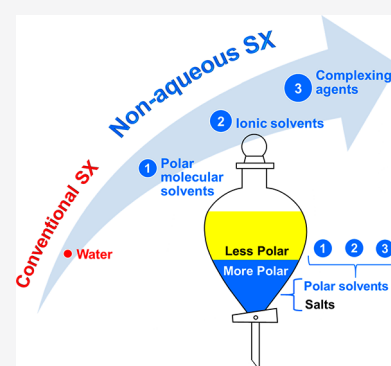
1. INTRODUCTION

Solvent extraction (SX) or liquid−liquid extraction is one of the most widely performed hydrometallurgical techniques for the separation and purification of precious metals,[1−3] base metals,[4,5] rare-earth elements (REEs),[6−9] actinides,[10−12] alkali and alkaline-earth metals,[13−20] and so on. This unit operation is based on differences in distributions of metal ions between two immiscible phases, typically an aqueous feed phase containing the metals to be separated and an organic extract phase containing an extractant diluted in a diluent.[21] Metal ions are often highly hydrated in the aqueous phase and, hence, are highly hydrophilic and insoluble in the organic phase. The transfer of metal ions from the aqueous phase to the organic phase is facilitated by the coordination of the metal ions to the extractant to form hydrophobic complexes.

The percentage extraction (%E), distribution ratio (D), and separation factor (α) are the most important parameters in solvent extraction. They are defined as follows:

$$D = \frac{c_{lp}}{c_{mp}} \tag{1}$$

$$\%E = \frac{c_{lp} \cdot V_{lp}}{c_{lp} \cdot V_{lp} + c_{mp} \cdot V_{mp}} \times 100 \tag{2}$$

$$\alpha = \frac{D_A}{D_B} \tag{3}$$

where c_{lp} and c_{mp}, V_{lp} and V_{mp} are, respectively, analytical concentrations and volumes in the organic (less polar) phase and the aqueous (more polar) phase, respectively; D_A and D_B are distribution ratios of metals A and B, respectively.

Both high extraction efficiency and high separation factors are desired in SX. There are multiple methods to optimize an SX system, and the focus has been mainly on the composition of the organic phase. Most common approaches include (1) modifying the structures of the extractants to improve selectivity;[22−25] (2) using a second extractant to enable synergism (synergistic solvent extraction);[4,13,26] (3) adding modifiers to prevent the third phase formation or enhance stripping;[27−29] and (4) changing diluents.[30,31]

Compared to the modifications of the organic phase, the number of studies investigating alterations to the aqueous phase is limited. Adjustment of pH is most effective for improving separations in SX systems involving acidic extractants. The change of salts concentration (ionic strength) is useful for neutral and basic extractants due to the salting-out effect. A less-common practice is the use of complexing agents,

e.g., lactic acid, EDTA, in the aqueous phase to selectively complex metal ions to enhance the separation. The most notable process using this approach is the TALSPEAK process used in the processing of spent nuclear fuel, where the separation of lanthanides and actinides is enhanced using aqueous complexing agents.[11,32] This approach was also used for REEs separations.[33,34]

Researchers have also observed that the addition of polar organic solvents to the aqueous solution modifies the extraction behavior.[35−41] Because of the addition of polar organic solvents, the aqueous−organic mixture could no longer be called aqueous phase, hence Alian et al. named it the "*polar phase*", and the organic phase is correspondingly called the "*nonpolar phase*", although the phase is also slightly polar.[42] Later, the two phases are renamed the "*more polar phase*" and the "*less polar phase*" by Batchu et al.[43] The addition of polar organic solvents influences the extraction performance from several dimensions:[44] (1) lowering water activity; (2) changing (lowering) the dielectric constants that affect the stability of complexes; (3) changing the mutual solubility of the two phases; and (4) altering the interfacial tensions. Also of importance is the solvation of the metal ion by the polar solvent. The Gutmann donor number, which is a measure for the basicity of a solvent, can be a reference for solvation strength. It is defined as the negative enthalpy value for the 1:1 adduct formation in dichloroethane between a Lewis base (the solvent) and $SbCl_5$, which is a standard Lewis acid.[45] These factors are not independent but are closely connected. Consequently, no simple correlations with a single factor can be made.

Water has been the default solvent for the more polar phase in solvent extraction of metals. However, it is not the only suitable solvent. Those solvents that can form two immiscible phases with the less polar phase can, in principle, substitute water. The use of *polar molecular organic solvents* (PMOSs) instead of water can be understood as the use of an aqueous−organic mixture that proceeds to the extreme of zero water. On the other hand, when the addition of salts to the aqueous phase goes to the extreme, the more polar phase becomes purely (molten) inorganic salts. Moreover, organic salts (ionic liquids) can form two immiscible phases with the less polar phase as well. SX of metals from pure nonaqueous solvents, or with a small quantity (<50 vol %) of water, is called *nonaqueous solvent extraction* (NASX).[46] Contrary to a conventional SX system, which contains an organic phase and an aqueous phase, a NASX system has two nonaqueous phases (Figure 1).
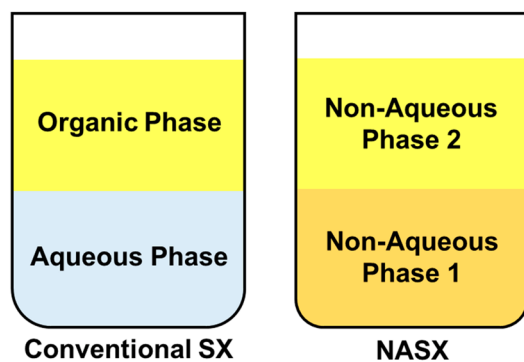

Figure 1. Comparison of (left) conventional solvent extraction and (right) nonaqueous solvent extraction (NASX) systems.

NASX is largely different from SX from aqueous solutions, and enhanced separations compared to conventional SX systems are often observed. However, strictly anhydrous conditions are not required to perform NASX, the presence of a small quantity of water in a NASX system is not only tolerable but can also be beneficial in some cases. It can reduce the viscosity of the more polar phase, reduce the miscibility of the two phases, increase the solubility of salts in the system, and even enhance metal separations by tuning metal ion solvation.

In this Review, we comprehensively summarize NASX of a wide range of metals from both PMOSs and ionic solvents [molten inorganic salts, molten hydrates, and ionic liquids (ILs)], encompassing publications from the earliest explorations in the 1950s to the latest research in 2021. Emphasis is given to enhanced extractions and improved separations, and the chemical mechanisms behind the unusual extraction performance are explained. Finally, the integration of NASX to metallurgical flowsheets is discussed.

2. EXTRACTANTS AND EXTRACTION MECHANISMS

There are four main types of extractants in SX systems, namely, acidic extractants (cation exchangers), neutral extractants (solvating extractants), basic extractants (anion exchangers), and binary extractants (acid−base extractants). Each type of extractant extracts metal ions via different mechanisms, and they have been overviewed by, for instance, Wilson et al.[47] and Eyal et al.[48] All four types of extractants have been applied in NASX systems.

The mechanism of metal extraction by an acidic extractant (denoted by HL) can be expressed in a simplified way as

$$M^{n+} + n\overline{HL} \leftrightarrows \overline{ML_n} + nH^+ \tag{4}$$
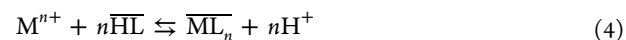
where M^{n+} is a metal cation, and the overbar indicates that the species reside in the organic phase. During the extraction, the proton of the extractant is replaced by the metal cations. This is why acidic extractants are also called *cation exchangers*. The extraction and stripping equilibria are controlled by pH, as shown by eq 4. Bis(2-ethylhexyl)phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), and Versatic Acid 10 (a mixture of C_{10} carboxylic acids; see Figure 2) are the most common acidic extractants.

The extraction of metal ions by a neutral extractant (denoted by S), in this example from nitrate media, proceeds as

$$M^{n+} + n(NO_3)^- + x\overline{S} \leftrightarrows \overline{M(NO_3)_n \cdot S_x} \tag{5}$$
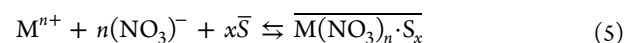
Neutral extractants solvate the metal ions; hence, they are also called *solvating extractants*. The extraction equilibrium is heavily dependent on the activity of the counteranion, e.g., nitrate in eq 5. On the other hand, the extracted metals can be stripped by acids, because neutral extractants have a tendency to interact with acids. Tri-*n*-butyl phosphate (TBP), tri-*n*-octyl phosphine oxide (TOPO), and Cyanex 923 (a mixture of trialkyl phosphine oxides) are the most common neutral extractants (Figure 2).

Amines (primary, secondary, tertiary, and quaternary) are classified as basic extractants, although quaternary amines are not Brønsted bases. Take Aliquat 336 (a mixture of methyltrialkylammonium chloride where the alkyls are *n*-hexyl and *n*-octyl, denoted by NR_4Cl, Figure 2) as an example. The extraction reaction from chloride media is
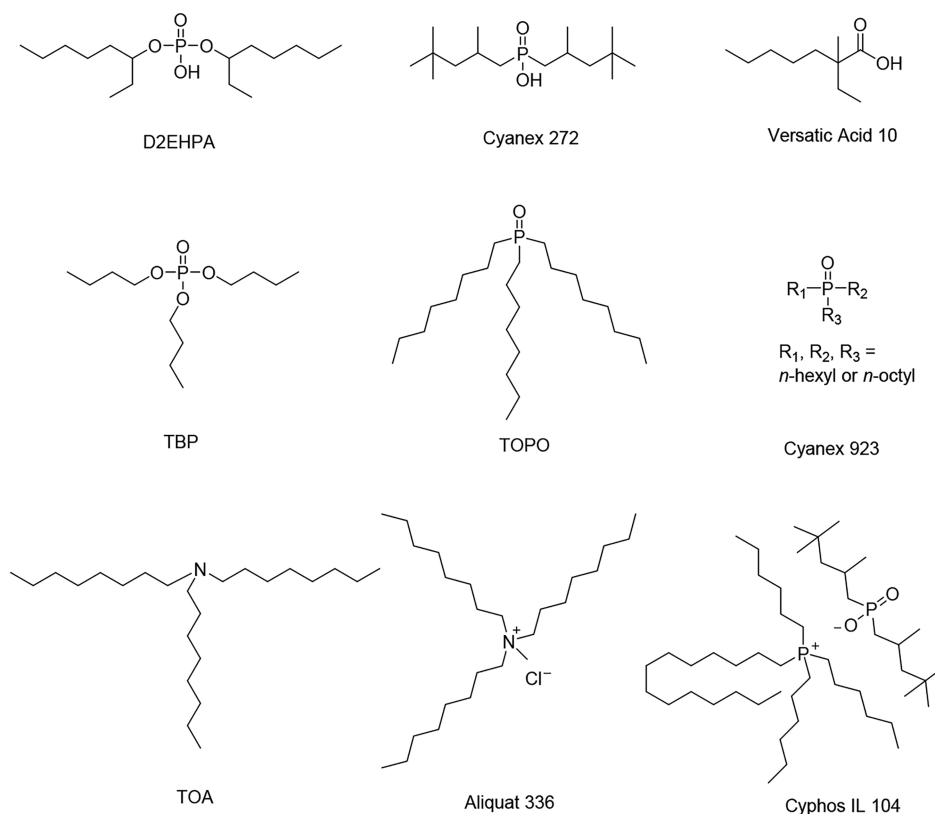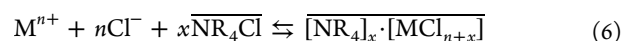
Figure 2. Structures of typical extractants.

$$M^{n+} + nCl^- + x\overline{NR_4Cl} \leftrightarrows \overline{[NR_4]_x \cdot [MCl_{n+x}]} \tag{6}$$

Although it is disputable whether the anionic complex is the most extractable species in the aqueous phase,[49] the observed complex in the organic phase is an ion-pair complex, as if the chloride anion of Aliquat 336 is exchanged with the chlorometallate anion (e.g., $[FeCl_4]^-$). Hence, quaternary amines are also called *anion exchangers*. Primary, secondary, and tertiary amines (e.g., tri-*n*-octyl amine, TOA, Figure 2) extract metal ions following a similar mechanism as quaternary amines except that the former amines have to first take up protons to transform into the ammonium form. Phosphonium extractants (e.g., Cyphos IL 101) are also regarded as basic extractants considering the similarity of phosphonium and ammonium ions.

Binary extractants are composed of the cation of a basic extractant and a deprotonated acidic extractant; hence, they are also called *acid−base extractants*.[48] A binary extractant works in a way similar to an acidic extractant, but it extracts salts instead of metal cations. The extraction of salts by an ammonium-based binary extractant (denoted by NR_4L) from chloride media can be written as

$$M^{n+} + nCl^- + n\overline{NR_4L} \leftrightarrows \overline{ML_n} + n\overline{NR_4Cl} \tag{7}$$

Cyphos IL 104 is an example of a binary extractant (Figure 2). However, the boundary between the different categories of extractants is not very sharp. For instance, acidic extractants can act as solvating extractants if the acidity of the feed solution is high.[50,51]

3. POLAR MOLECULAR ORGANIC SOLVENTS

3.1. Formation of Two Immiscible Liquid Phases. To perform NASX, first of all, a pair of two immiscible liquid phases should be selected. The miscibility of two solvents is governed by the rule of "like dissolves like". The Hansen solubility parameters are one of the most popular criteria to determine the likeness of solvents and solutes. Three parameters, δ_d, δ_p, and δ_h, which represent the energy from dispersion force, dipolar intermolecular force, and hydrogen bonds between molecules, respectively, are utilized. The total parameter of a compound, δ_T, can be calculated from the three parameters. The closer the parameters of a solute to that of a solvent, the higher solubility the solute has in the solvent.[52] The Hansen solubility parameters of the involved solvents in NASX systems are given in Table S1 in the Supporting Information. Based on these empirically regressed parameters, this methodology allows one to quantitatively estimate the mutual solubility of a wide range of solvents.

The miscibility of two solvents can be approximated more simply based on the polarity and hydrophobicity of the solvents. Polarity is reflected by the dipole moment of the solvent (Table S1), or δ_p of the Hansen solubility parameters. Generally, compounds with symmetric molecular structures have low polarity. For example, linear saturated hydrocarbons are nonpolar ($\delta_p = 0$). Hydrophobicity (lipophilicity) is most commonly expressed by the distribution (partition) of the solvent between octanol and water.[53] The higher the distribution ratio of the solvent, the more hydrophobic the solvent. For compounds with the same functional groups, longer carbon chains facilitate higher hydrophobicity. Hydrophobicity is also related to the dielectric constant (ε). Generally, a higher hydrophobicity corresponds to a lower

dielectric constant (Table S1). Therefore, the miscibility of two solvents can be easily estimated based on their chemical structures and their polarity and hydrophobicity parameters.

Hydrocarbon diluents in the less polar phase generally are hydrophobic solvents with low polarity. Therefore, the less polar phase can readily form immiscible phases with ionic solvents, such as molten inorganic salts and molten hydrates, because of the big difference in polarity and hydrophobicity between these two types of solvents. However, note that, when the cations of the salts are extractable (e.g., Ca(NO$_3$)$_2$), the change of volumes of the two immiscible phases can be non-negligible.[54] For this reason, alkali-metal salts, such as LiNO$_3$ or KNO$_3$, are preferred for molten inorganic salts, because of their low extractability.[55] Hydrophilic ILs are also polar and, hence, insoluble in the less polar phase, although they are organic salts. For example, tetraethylammonium chloride is insoluble in *p*-cymene. However, when the alkyl chains are longer, the hydrophobicity increases, resulting in a high solubility in the less polar phase, e.g., Aliquat 336 readily dissolves in *p*-cymene.

PMOSs are more likely to be miscible with the less polar phase, because of the relatively small difference in polarity. Many solvents, such as ethanol, are miscible with some hydrocarbon diluents, despite being miscible with water as well. Only those solvents with both low hydrophobicity and high polarity are immiscible with the less polar phase. The effect of the addition of extractants is also worth mentioning. For example, toluene and ethylene glycol have very low mutual solubilities. However, since Aliquat 336 is largely miscible with both solvents, the addition of Aliquat 336 to the SX system increases the mutual solubility of the two phases and even leads to the merging of the two phases. In this case, the amount of the extractant should be limited to minimize the mutual solubility of the two phases. Moreover, nonpolar diluents can sometimes be problematic, in combination with polar extractants. For example, *n*-dodecane is nonpolar and is immiscible with ethylene glycol. However, the addition of the extractant Aliquat 336 to *n*-dodecane induces the formation of a third phase. In this case, the replacement of the nonpolar *n*-dodecane with the slightly polar toluene would diminish the third phase. Finally, the addition of salts, especially lithium salts (e.g., LiCl, LiNO$_3$) could largely enhance the immiscibility due to the salting-out effect of salts. Lithium salts are often selected because of their high solubility in many PMOSs. The salt-induced phase separation in the methanol/*n*-dodecane system was described in detail by Macchieraldo et al.[56]

In short, the polarity and hydrophobicity of the nonaqueous solvents are the most important properties for forming immiscible phases with the less polar phase, and the effect of extractants and salts should also be taken into account. There are many empirical thermodynamic models to correlate the phase equilibria of ternary, quaternary, and even more-complicated systems with nonelectrolytes[57−61] and electrolytes,[62,63] and some predictive models for phase equilibria of nonelectrolytes.[64,65] However, quantitative studies on thermodynamic phase equilibria of NASX systems are lacking. It would be worthwhile to perform an in-depth study of the phase equilibria of NASX systems involving many extractants, nonaqueous solvents, and salts, to establish a thermodynamic equilibria library of NASX systems.

3.2. Systems without Extractants. A summary of NASX systems comprising PMOSs is given in Table S2 in the

Supporting Information. Larsen performed the first exploratory study on NASX for the separation of Zr(IV) and Hf(IV) using a system consisting of isoamyl ether and acetonitrile as two immiscible phases.[66] The utilization of NASX instead of a conventional organic/water SX system was driven by the fact that ZrCl$_4$ and HfCl$_4$ hydrolyze strongly in aqueous solutions, which can be avoided when less-reactive solvents than water are used. Both ZrCl$_4$ and HfCl$_4$ preferentially resided in the acetonitrile phase and a separation factor $\alpha_{\mathrm{Hf/Zr}}$ of 1.8 was obtained. Following the same route, distributions of several metals (Co(II), Fe(III), Mo(V), Mo(VI), Sn(II), Sn(IV)) as chlorides, bromides, nitrates, and thiocyanates were examined between a diethyl ether phase and a more polar phase containing either 2-aminoethanol, formamide, or hexanedinitrile.[67] All the salts distributed mainly in the more polar phase, except for SnCl$_4$, which showed some preference for the diethyl ether phase. The low distribution ratios of the metals are caused by the low polarity and high hydrophobicity of diethyl ether, as indicated by the low dipole moment and low dielectric constant (Table S1). However, SnCl$_4$, as a Lewis acid, can react readily with organic Lewis bases, such as diethyl ether,[68] leading to a higher distribution ratio of SnCl$_4$.

A two-phase system formed by methyl isobutyl ketone (MIBK) and formamide was used to separate Tl(III) from In(III), Ga(III), Fe(III), Sn(II), and Sn(IV).[69] These metals were first loaded to MIBK from an aqueous phase containing 2.0 mol L^{-1} HBr, presumably as ion pairs (i.e., [H(MIBK)$_2$]-[TlBr$_4$]), and subsequently stripped to a formamide phase with a lower HBr concentration. Tl(III) was largely maintained in the MIBK phase, while other metals were quantitatively stripped to the formamide phase, leading to efficient separation of Tl(III) from other metals. The retention of Tl(III) in the MIBK phase is most likely due to the stronger tendency of Tl(III) to form anionic bromo-complexes than other metal ions. However, no comparison of separation capabilities of the NASX system with aqueous SX systems was performed.

3.3. Systems with Neutral Extractants. Liquid ammonia was used as a polar solvent at −40 °C for the extraction of metals by undiluted TBP. The distribution ratios of all alkali-metal thiocyanates were very low (<0.1), and the extraction order was Li < Na < K < Rb.[70,71] The extraction was not directly compared with the extraction of alkali-metal thiocyanates from aqueous solutions, because of the lack of relevant literature data. However, the extraction of alkali-metal halides from aqueous solutions follows the opposite order, i.e., Li > Na > K > Cs.[72] The different anions (chloride and thiocyanate) might play a role in the opposite extraction order of the two systems. More importantly, although solvations of the alkali metals in ammonia and water follow the same order,[73,74] the solvation strength in the polar solvents relative to the solvation with TBP is an important factor affecting the extraction sequence. The extraction of Zn(II), Co(II), and Ca(II) thiocyanates to the TBP phase from ammonia was negligible, because of the strong solvation of these metals in ammonia.[71]

Matsui et al. studied the extraction of Zn(II) and Cd(II) by TOPO dissolved in toluene from ethylene glycol (EG) solutions containing either HCl, HBr, or alkali-metal chlorides or bromides. With the addition of acid or salt, the extraction efficiency of both Zn(II) and Cd(II) shows a maximum, but the maximum was reached at a lower acid (or salt) concentration than that in extraction from aqueous solutions.[75,76] The same trend was observed for the extraction of

Mn(II) by TOPO from EG solutions.[77] This observation shows that the metal halide complexes are more stable in EG solution than in water. The stability of $ZnCl^+$ and $ZnCl_2$ in propylene glycol (PG), EG, and an EG−water mixture (volume ratio = 9:1) was further estimated based on solvent extraction of Zn(II) by TOPO from these polar solvents.[78,79] The stability order was found to be PG > EG > EG−water mixture, which is consistent with the increasing dielectric constant. Zn(II) was extracted as $ZnX_2 \cdot (TOPO)_2$ (X = Cl, Br), which is the same as for extraction from aqueous solutions. The decrease of metal extraction at higher acid (or salt) concentrations was attributed to the formation of anionic complexes (i.e., $ZnCl_3^-$, $ZnCl_4^{2-}$) in the more polar phase.[75]

Batchu et al. developed a NASX system that showed superior separation of rare-earth elements (REEs).[43] Rare-earth nitrates, dissolved in EG with $LiNO_3$ as the salting-out agent, were extracted by Cyanex 923 dissolved in n-dodecane. Interestingly, heavy rare-earth elements (HREEs) were more efficiently extracted while light rare-earth elements (LREEs) were less efficiently extracted when compared with the extraction from aqueous solutions, leading to a better separation of the two groups of elements (Figure 3). Moreover,
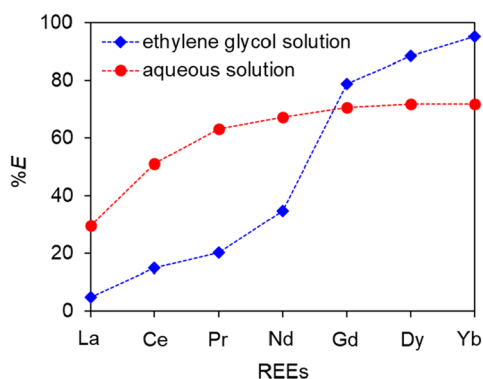

Figure 3. Separation of REEs by Cyanex 923 from aqueous and ethylene glycol solutions. [Adapted from Batchu et al.[43]]

the separation of neighboring REEs was also enhanced. The extracted complexes in the Cyanex 923 phase were found to be $[Ln(NO_3)_3L_3]$ (L represents Cyanex 923), which is the same as that in the extraction from aqueous solutions. Therefore, the enhanced separation is very likely caused by weaker solvation in the EG solution than in aqueous solutions, although further investigations are needed. The EG solution with $LiNO_3$ was further applied for the separation of Nd(III) and Dy(III) by a group of phosphine oxide, phosphinate, phosphonate, and phosphate with octyl chains. All four extractants showed better separation of the two elements, compared to extraction from the aqueous solutions.[80] Note that, combined with the EG solutions, the phosphinate and phosphonate extractants are more suitable for the separation of the two elements than the phosphine oxide and phosphate extractants, because the extraction by the phosphine oxide is too strong for both elements and the extraction by phosphates is too weak for both elements.

The EG solution could also enable the extraction of rare-earth chlorides by Cyanex 923 dissolved in n-dodecane (with 10 vol % decanol as a modifier to prevent third phase formation) with the assistance of LiCl as a chloride source, whereas the extraction of rare-earth chlorides is not feasible

from aqueous solutions.[81] EG, PG, and poly(ethylene glycol) 200 (PEG 200) were tested as the solvent of the more polar phase for the separation of Eu(III) and Y(III) in chloride media by Cyanex 923. The extraction efficiency followed this order: PEG 200 > PG > EG > water. Despite higher extraction efficiency from PEG 200 and PG solution, the separation factor for Y(III)/Eu(III) was low. As the EG system combined a satisfactory extraction efficiency with a high separation factor, a flowsheet was developed and tested on laboratory-scale mixer-settlers for the separation of the two elements.[82] While pure nonaqueous systems enhance extraction of most elements through weakening the solvation and increasing ion-pair formation with the anions, the addition of water to the polar organic solvent can enhance the separation between two metal ions. In the extraction of Nd(III) and Dy(III) by Cyanex 923, both elements were quantitatively extracted from PEG 200 solution (with 1.0 mol L^{-1} LiCl), while neither element could be extracted from aqueous solution (with 1.0 mol L^{-1} LiCl). However, with the addition of 30−40 vol % water in PEG 200 (with 1.0 mol L^{-1} LiCl), efficient extraction of Dy(III) and good separation of Dy(III)/Nd(III) could be concurrently obtained, with a separation factor of up to 69 (Figure 4).[83] The
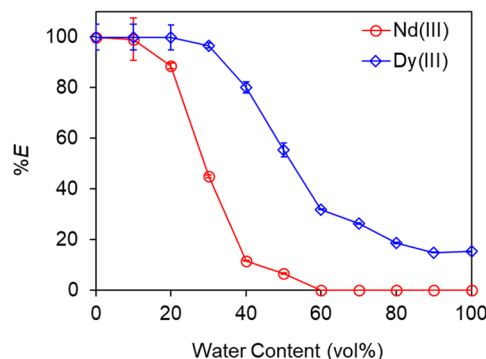

Figure 4. Extraction of Nd(III) and Dy(III) by Cyanex 923 from a mixture of PEG and water solutions. [Adapted from Dewulf et al.[83]]

extracted complex from the PEG 200 system was found to be $[LnCl_3 \cdot L_4]$ (L represents Cyanex 923),[83] which is the same as the complexes formed in the extraction from the EG system.[81] Based on the fact that the complexes formed in the LP phase are not influenced by MP phase composition, the differences in extraction efficiency can be ascribed, on the one hand, to the different solvation in the MP phase, and on the other hand, to the lower dielectric constants of the polar organic solvents, that increases the stability of inner-sphere chloride complexes.

3.4. Systems with Basic Extractants. Next to neutral extractants, basic extractants have also been applied to NASX. The extraction of Ni(II) from methanol halide solutions by trioctylamine (TOA) in cyclohexane was found to be enhanced significantly, compared to extraction from aqueous solutions (Figure 5). The extracted species is $[NiX_4]^{2-}$, the same as that extracted from an aqueous solution.[84] The higher extraction efficiency can be attributed to the stronger formation of $[NiX_4]^{2-}$, facilitated on the one hand by the weaker solvation with methanol compared to water, and on the other hand, by the lower dielectric constant of methanol, that enhances the inner-sphere complex formation. Although the Gutmann donor number of water is slightly smaller than that of methanol (Table S1), metal cations generally coordinate stronger to water than to alcohols.[44,85] Similar enhancement of
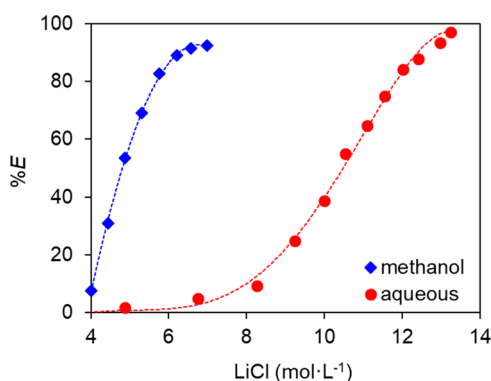
Figure 5. Extraction of Ni(II) from aqueous and methanolic solutions by Alamine 336. Data were taken from Florence and Farrar.[84]

the extraction by TOA was observed for Mn(II), Cr(III), and Th(IV) halides.[86] The extraction efficiency of Ni(II) and Cr(III) by addition of halide salts followed the order: LiCl < LiBr < LiI. However, the reverse order was observed for Mn(II) and Th(IV) extraction. Mn(II) and Cr(III) were extracted as $[MnX_4]^{2-}$ and $[CrX_5]^{2-}$, respectively, whereas Th(IV) was likely polymerized in the TOA phase. Extraction of $CuCl_2$ from methanol solutions by the secondary amine bis(3,5,5-trimethylhexyl)ammonium chloride also proceeded via the formation of the tetrachlorocuprate(II) anion $[CuCl_4]^{2-}$.[87] However, the extraction was very low ($D_{Cu} <$ 0.3), because of the high solubility of the secondary amine in methanol.

Primary, secondary, tertiary amines, and quaternary ammonium in toluene were tested for the extraction of Zn(II), Cd(II), and Co(II) chlorides from EG and PG solutions.[88] The Zn(II) extraction efficiency followed the order of primary

amine < secondary amine < tertiary amine < quaternary ammonium, which is similar to the extraction from aqueous solutions. The extraction of Zn(II) and Cd(II), as a function of the HCl concentration, showed a maximum, similar to the extraction from aqueous solutions, yet at a lower concentration of HCl, compared to aqueous systems. There are two explanations for the decreased extraction of metals at higher HCl concentrations. First, there is the competition for extractants by the coextraction of HCl in the form of $[HCl_2]^-$. Second, $[ZnCl_4]^{2-}$ is assumed to be stabilized in the MP phase at higher HCl concentrations, hence its extraction is lowered. This assumption is explained in detail by a new extraction model.[49] The extraction of Zn(II) and Cd(II) as a function of LiCl concentration also showed a maximum,[88] which is different from the extraction from aqueous solutions, where the extraction increases monotonously. It is plausible to attribute the decrease of extraction to the stabilization of $[ZnCl_4]^{2-}$ in the EG solution at higher LiCl concentrations, considering the enhanced formation of the chlorometallate anions in solutions having a lower dielectric constant. The extraction of Co(II) did not show a decrease because the LiCl concentration was not sufficient for stabilization of $[CoCl_4]^{2-}$. In another study, the extraction of Co(II) by Aliquat 336 from methanol and formamide solutions also showed a maximum at a higher LiCl concentration (6.0 mol L^{-1}).[89] In conclusion, the use of polar organic solvents instead of water enhances the formation of chlorometallate anions, which, on the one hand, can enhance the extraction of metals; and on the other hand, can stabilize the anions in the MP phase at higher chloride concentrations (or suppress the extraction).

Superior separation was observed for the extraction of Co(II) and Sm(III), making use of NASX combined with a basic extractant.[90] The LP phase of the system was Aliquat 336
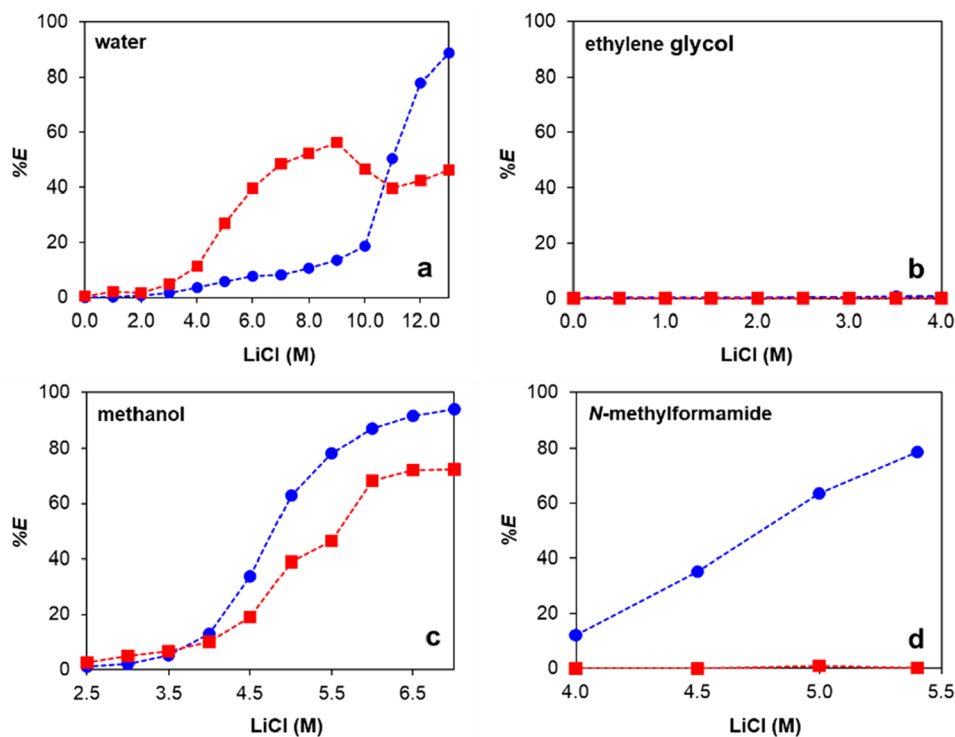

Figure 6. Extraction of La(III) and Ni(II) by Aliquat 336 from various polar molecular organic solvents. [Adapted from Li et al.[89]]

in toluene and the MP phase was EG with LiCl as the chloride source, which also reduced the mutual solubility of the two phases. Compared to the aqueous SX system, extraction of Co(II) was enhanced, while the extraction of Sm(III) was reduced to naught, leading to complete separation of Co(II) and Sm(III) in a single extraction step. The system was found to be generally suitable for the separation of transition metals (except for Ni(II)) from REEs, such as Zn(II)/Eu(III) and Fe(III)/Nd(III). The extracted species in the less polar phase were the same as those extracted from aqueous solutions; therefore, the enhanced extraction originates from the increased formation of chlorometallate complexes in the EG phase.

A similar NASX system, using Cyphos IL 101 instead of Aliquat 336, was applied to the separation of In(III) and Zn(II). The extraction of In(III) from EG solution was more efficient than from aqueous solution, whereas the extraction of Zn(II) was less efficient, leading to enhanced separation of these two elements.[91] The species of In(III) in EG was found to change from the bridging $(InCl_3)_2(EG)_3$ or mononuclear $(InCl_3)(EG)_2$ complex at low LiCl concentrations to [In-$(EG)Cl_4]^-$ at high LiCl concentrations.[91] In contrast, In(III) exists in aqueous HCl solution as mixed octahedral complexes, $[In(H_2O)_{6-n}Cl_n]^{3-n}$, in which n increases from 0 to 6 as the concentration of HCl increases in the range of 0−12 mol L^{-1}.[92] Given the presence of the same species of In(III) (i.e., $[InCl_4]^-$) in the LP phase in both SX systems, the different speciation of In(III) in aqueous and EG solutions is responsible for the different extraction behavior of In(III) in the two systems.

The NASX system with EG and Aliquat 336 was expanded to include other PMOSs, namely methanol, formamide, and N-methylformamide (NMF), to separate transition metals and REEs.[89] The change of polar solvents in the MP phase significantly affects the separation of metals. For example, in Figure 6, La(III) is overall more efficiently extracted than Ni(II) from aqueous solutions, but Ni(II) is more efficiently extracted than La(III) from methanol solution, neither of the two is extracted from EG solution, and only Ni(II) is extracted from NMF, leading to excellent separation of the two elements. The extraction of transition metals and REEs are affected by polar solvents in two different ways. Transition metals are extracted by Aliquat 336 as chlorometallate anions (e.g., $[CoCl_4]^{2-}$). The strength for the formation of $[CoCl_4]^{2-}$ in polar solvents follows the order NMF > methanol > formamide > EG > water, which is a result of different solvations and the physicochemical properties of the polar solvents (dielectric constants, molarity, etc.). For instance, consider the effect of the dielectric constant. Density functional theory (DFT) calculations show that chlorometallate anions (e.g., $[CoCl_4]^{2-}$) are more stable in solvents of lower dielectric constants.[89] This observation is consistent with the above discussions on the effect of the dielectric constant. In contrast, Ln(III) coordinates very weakly to Cl− ions; hence, it is extracted to the LP phase as solvated cationic or neutral complex (i.e., $[LnCl_x]^{3-x}$, in which $0 \leq x \leq 3$, solvating solvent molecules are omitted). As the extraction mechanism of transition metals and REEs differ, the two groups of metals are influenced differently by changing the polar solvents, creating the possibility of tuning metal separations.

4. IONIC SOLVENTS

Ionic solvents are essentially different from molecular solvents in that the former is composed of ionic bonds, while the latter is made entirely of covalent bonds. Molten inorganic salts, molten salt hydrates, ionic liquids, and deep-eutectic solvents are ionic solvents and they have been used as the solvent of the MP phase in NASX systems. These NASX systems have been summarized in Table S3 in the Supporting Information.

4.1. Low Melting Inorganic Salts. *4.1.1. KNO₃−LiNO₃ Eutectic. 4.1.1.1. Neutral Extractants.* Isaac et al. were the first to explore the use of a KNO_3-LiNO_3 eutectic mixture at a molar ratio of ~3:4, as the solvent of the MP phase in the extraction of lanthanides, actinides, and cobalt using TBP at 150 °C.[55] The use of molten salts was driven by the assumption that molten salts should have the maximum "salting-out" effect, based on the observation that the presence of salts considerably increases the distribution ratio of metal ions. Besides having a relatively low melting point (120 °C), the KNO_3-LiNO_3 eutectic is poorly extractable to the TBP phase, compared to alkaline-earth metal nitrates, making it a suitable candidate as the solvent of the MP phase. Polyphenyl hydrocarbons were used as diluents in the LP phase because they have high boiling points. Similarly, TBP was chosen as the extractant because of its thermal stability, and it had been proven efficient in the PUREX process as well. Distribution coefficients of Co(II), Eu(III), Nd(III), Am(III), Cm(III), Np(VI), and U(VI) between the nitrate eutectic and the TBP phase were found to be higher by a factor of 10^2-10^3, compared to concentrated aqueous nitrate solutions. However, the number of TBP molecules associated with the metal ions in the LP phase was found to be the same as those reported for the aqueous nitrate SX system. Consequently, the enhanced extraction of metals from the eutectic was attributed to the absence of water in the SX system.

From the same nitrate eutectic, Am(III), Cm(III), and Cf(III) was extracted by TOPO and several diphenyl diphosphine dioxides $((C_6H_5)_2PO(CH_2)_nPO(C_6H_5)_2, n = 2, 3, 4, 6,$ and denoted as n-DPO, respectively) at 160 °C.[93] The extraction of these elements by 2-DPO, 3-DPO, and 4-DPO was more efficient than the extraction by TOPO, but 6-DPO did not extract these elements. The same SX system was also applied to the extraction of Co(II), Pr(III), Eu(III), and Tm(III) from the nitrate eutectic.[94] However, the performance of these NASX systems was not compared with the corresponding aqueous SX systems.

Extraction of HgX_2 (X = Cl, Br, I, or a mixture of any two anions) from the KNO_3-LiNO_3 eutectic was investigated using a polyphenyl eutectic consisting of 48 mol % o-terphenyl, 15 mol % m-terphenyl, and 37 mol % biphenyl at 150−200 °C.[95−97] HgX_2 exists in the molten eutectic salt as $[HgX_2(NO_3)_2]^{2-}$, but was extracted as the covalent HgX_2 into the polyphenyl eutectic. The extraction of HgX_2 from the eutectic salt was considerably higher than that from dilute aqueous solutions. The higher extraction was also attributed to the "salting-out" effect, based on two observations: (1) addition of KNO_3 and $LiNO_3$ mixtures (in the same ratio as the KNO_3-LiNO_3 eutectic) to aqueous solutions linearly increased the D_{HgCl_2}; and (2) extrapolation of D_{HgCl_2} to 90 °C for the extraction from the KNO_3-LiNO_3 eutectic intersects with the extrapolation of D_{HgCl_2} at the same temperature from aqueous solution to full salt (same as the KNO_3-LiNO_3 eutectic). The linearity of "salting-out" of HgX_2 is due to the

covalent binding of HgX_2, whereas many other salts are hydrated in aqueous solutions. The extraction of HgX_2 by the polyphenyl eutectic as covalent molecules is similar to the extraction of solid $GaCl_3$ as covalent dimers by aliphatic hydrocarbons, although the latter extraction must be performed under anhydrous conditions, because of the water sensitivity of $GaCl_3$.[98]

4.1.1.2. Basic Extractants. Tetraheptylammonium nitrate (THAN) and tetraoctylphosphonium nitrate (TOPN) dissolved in a polyphenyl eutectic or 1-nitronaphthalene were used to extract $[ReO_4]^-$ and $[AgCl_2]^-$ from the KNO_3–$LiNO_3$ eutectic in the presence of KCl–$LiCl$ salts at 150 °C. The extraction was found to proceed as an anion exchange, i.e., $[ReO_4]^-$ and $[AgCl_2]^-$ exchange with $[NO_3]^-$ of THAN or TOPN, similar to extraction from aqueous solutions.[99,100]

4.1.1.3. Synergistic Solvent Extraction. Extraction of some REEs from KNO_3–$LiNO_3$ eutectic by a synergistic SX system consisting of 2-thenoyltrifluoroacetone (HTTA) and 2-DPO in polyphenyl eutectic was examined at 160 °C. The synergistic factors in the HTTA-2-DPO system were 2−10, which is smaller than extraction from aqueous solutions.[101] The low synergism is caused by the protons released by HTTA during the extraction, which are not neutralized in the molten salt phase. The difficulty of neutralizing protons and controlling pH is a general problem in NASX. A possible solution to this problem is to use saponified extractants, which have not been investigated in detail yet.

4.1.2. KSCN–NaSCN Eutectic. The extraction of Fe(III), Co(II), and Ni(II) from a molten KSCN–NaSCN eutectic mixture at 150−170 °C into TBP dissolved in biphenyl showed a marked enhancement when compared with extraction from aqueous systems, which could be explained by the salting-out effect.[102] The temperature was controlled below 170 °C to avoid decomposition of the eutectic. The species in the eutectic were elucidated by spectrophotometric measurements to be $[Fe(SCN)_6]^{3-}$, $[Co(SCN)_4]^{2-}$, and $[Ni(SCN)_4]^{2-}$, respectively. The extracted species were the same as in the eutectic phase but charge neutrality was achieved by solvated Na^+ or K^+ ions, e.g., $[Na(TBP)_x]_2[Co(SCN)_4]$. This is not the conventional solvation mechanism, but it is similar to the synergistic extraction of Li^+ by TBP and Fe(III) from aqueous chloride media in the form of $[Li(TBP)_x][FeCl_4]$.[103]

Zn(II) was extracted from KSCN at 195 °C by TOPO and several other uncommon neutral extractants dissolved in phenanthrene.[104] The extracted species was proposed to be $Zn(TOPO)_2(SCN)_2$. The different complexes of transition metals formed with TBP and TOPO might be caused by the different coordination capabilities of these extractants.

Basic extractants were also investigated for the extraction of metal ions from the KSCN–NaSCN eutectic at 150 °C. Co(II) in KSCN–NaSCN eutectic was extracted by di-*n*-dodecylammonium thiocyanate ($[NR_2H_2][SCN]$) dissolved in chloronaphthalene in the form of $[NR_2H_2]_2[Co(SCN)_4]$ via an anion exchange mechanism.[105]

4.1.3. KCl–CuCl Eutectic. Distribution ratios of U(IV), U(III), Pu(IV), Pu(III), and Am(III) between the KCl–CuCl eutectic at 180 °C and an LP phase containing TBP, trioctylamine (TOA), or di-*n*-butyl phosphoric acid (HDBP) dissolved in biphenyl were determined.[106] The amount of Cu(I) extracted into the TOA phase was comparable to the total amount of TOA, because of the formation of ion-pair complexes, e.g., $[(TOA)_2Cu][CuCl_2]$, hindering the extraction

of actinides. In contrast, the loading of Cu(I) into TBP and HDBP was lower, facilitating the extraction of actinide ions.

4.1.4. CsOAc–NaOAc–KOAc Eutectic. Extraction of Cr(III), Fe(II), Co(II), and Ni(II) from molten cesium acetate–sodium acetate–potassium acetate eutectic (50−25−25 mol %) at 140−180 °C into *n*-dodecane solutions containing Cyanex 272, D2EHPA, or TOPO was studied.[107] The metal cations in the eutectic melt were in the form of negatively charged complexes, whereas they are hydrated in aqueous solutions. TOPO did not extract any metals, D2EHPA formed a third phase, and Cyanex 272 extracted metals in this order: Co(II) > Fe(II) > Cr(III) > Ni(II). The extracted complexes were the same as the extraction from aqueous solutions, and acetate was not involved in the complexes. However, the distribution ratios were <0.1 for all metals, which might be due to the difficulty of controlling the acidity of the salt melt and the negatively charged complexes being too stable in the molten eutectic phase.

4.2. Molten Salt Hydrates. *4.2.1. Molten Nitrate Hydrates.* Molten inorganic salts or eutectics, especially the KNO_3–$LiNO_3$ eutectic, have been shown to enhance the extraction of a variety of metals, compared to extraction from aqueous solutions. However, the high melting points of the inorganic salts are associated with high energy consumption and extractant decomposition. Molten nitrate *salt hydrates*, also called *hydrate melts*, are considered to lie between anhydrous molten salts and concentrated aqueous electrolyte solutions. The low melting points of the molten hydrates (Table S3) make them interesting substitutes for molten inorganic salts, particularly in the extraction of lanthanides and actinides by TBP for the processing of nuclear waste.

Extraction of lanthanides and actinides by TBP from molten nitrate hydrates was more efficient than from typical aqueous solutions.[108−112] As the complexes in the LP phase extracted from molten nitrate hydrates or aqueous solutions are identical, the improved extraction was attributed to the increased chemical activity of the nitrate ions due to the water deficiency of the system.[108,110,112] TBP is poorly soluble in the molten hydrates. For example, the solubility of TBP in $Ca(NO_3)_2 \cdot 4H_2O$ is only 0.05 g L^{-1} at 45 °C.[118] However, the nitrate salts are well extractable to the TBP phase, e.g., up to 1.45 mol L^{-1} $Mn(NO_3)_2$ is extracted into pure TBP, leading to a 10% volume increase of the TBP phase.[54] The high extraction of molten nitrate hydrates hinders the extraction of target metal ions and makes the SX system complicated for fundamental studies. Yamana et al. suggested that the coextraction of Ca(II) from $Ca(NO_3)_2 \cdot 4H_2O$ can be neglected only when the concentration of TBP in the less polar phase is lower than 0.10 mol L^{-1}.[112]

As water is the dominating component in molten hydrates, in terms of mole fraction (e.g., x_{H_2O} is 0.8 in $Ca(NO_3)_2 \cdot 4H_2O$), the water activity in molten melts is not as low as one might expect (e.g., a_{H_2O} is ~0.30 in $Ca(NO_3)_2 \cdot 4H_2O$[113]). The water activity of $Ca(NO_3)_2 \cdot nH_2O$ (*n* is the number of water molecules), as a function of the water mole fraction at 70 °C, has been given in Figure 7.[114] The water activity decreases with decreasing water mole fraction, from 1.0 for pure water to ~0.30 for $Ca(NO_3)_2 \cdot 4H_2O$ and further decreases in a slower manner to <0.20. The relatively low water activity of $Ca(NO_3)_2 \cdot 4H_2O$, or water deficiency, explains the higher extraction of metals from molten nitrate hydrates than from aqueous solutions. However, metal ions in $Ca(NO_3)_2 \cdot 4H_2O$

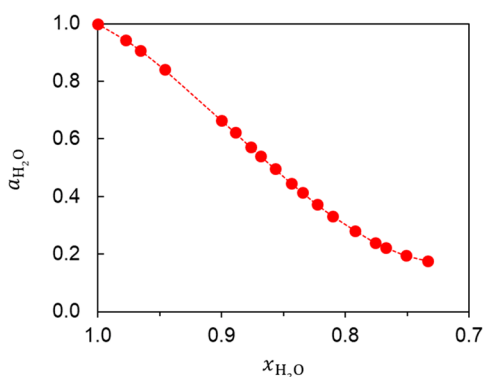**Figure 7.** Water activity in $Ca(NO_3)_2 \cdot nH_2O$, as a function of water mole fraction at 70 °C. [Data were taken from Yamana et al.[114]]
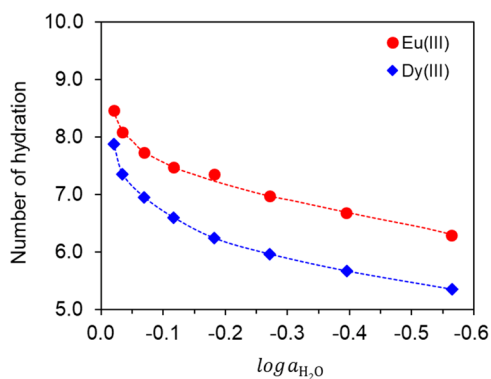

Figure 8. Hydration number of Eu(III) and Dy(III) in $Ca(NO_3)_2 \cdot nH_2O$ at 50 °C. [Adapted from Fujii et al.[115]]

are not free of hydration, since the water activity is still considerable. The hydration of Eu(III) and Dy(III), as a function of water activity, has been investigated by Fujii et al. (see Figure 8).[115] The number of hydrated water molecules in the first coordination sphere of Eu(III) and Dy(III) decreases from 8−9 in dilute aqueous solutions to 5−7 in $Ca(NO_3)_2 \cdot 4H_2O$, which is still significant. The extraction of lanthanides from $Ca(NO_3)_2 \cdot 4H_2O$ by TBP first increases with increasing atomic number, and then decreases, which is the same pattern as the extraction from dilute aqueous solutions. However, the extraction from molten KNO_3−$LiNO_3$ eutectic and highly concentrated nitric acid solutions (e.g., 18.5 mol L^{-1} HNO_3) increased monotonically.[54,112,116] The decrease of the extraction efficiency for heavier elements from the molten nitrate hydrates might be due to stronger hydration of these elements, as the hydration energy increases with increasing atomic numbers.[117,118] The water activity in highly concentrated nitric acid solution is lower than that of $Ca(NO_3)_2 \cdot 4H_2O$; for example, a_{H_2O} is 0.19 in 15 mol L^{-1} HNO_3 solution.[119] Hence, extraction of REEs from highly concentrated nitric acid is less affected by hydration, showing monotonically increasing extraction efficiency in the entire lanthanide series. Similarly, actinides are more sensitive to water activity in molten nitrate hydrates than lanthanides. A varying water activity helps to enhance the separation of the two groups of elements.[111] The water content in $Ca(NO_3)_2 \cdot nH_2O$ also affects the reaction rate. Equilibrium of REEs extraction by TBP from $Ca(NO_3)_2 \cdot nH_2O$ with $n = 4$ can be reached within 2 h, however, it takes more than 8 h to reach equilibrium when $n < 3$, mainly because of the higher viscosity of the drier molten nitrate hydrate.[114]

Extraction of REEs from $Ca(NO_3)_2 \cdot nH_2O$ by $[A336][NO_3]$ at 53 °C was investigated by Rout and Binnemans.[120] The extraction was highly efficient, although slightly lower than the extraction from molten inorganic nitrates. This extraction efficiency agrees well with the fact that molten nitrate hydrates lie between concentrated aqueous nitrate solutions and molten inorganic nitrates. The extraction efficiency of the REEs decreases as the atomic number increases, which is the same as the sequence of extraction from aqueous solutions.[121,122] The decrease of extraction efficiency might be explained by the hydration of REEs in the molten nitrate hydrates, as studies by Fujii et al.[115] indicate; these studies show that there are still 5−7 water molecules hydrated to REEs in molten $Ca(NO_3)_2 \cdot 4H_2O$. Furthermore, the addition of $Mg(NO_3)_2 \cdot 6H_2O$ or water to $Ca(NO_3)_2 \cdot 4H_2O$ both reduce the extraction efficiency, because of the increase in water activity. The loading of Ca(II) to the $[A336][NO_3]$ phase was not studied. However, it seems that coextraction of Ca(II) did not hinder the extraction of REEs, because more than 120 g L^{-1} Nd(III) could be loaded to the $[A336][NO_3]$ phase.

4.2.2. Molten Chloride Hydrates. Molten chloride hydrates, such as $CaCl_2 \cdot 4H_2O$ and $CaCl_2 \cdot 6H_2O$, were also used as the solvent of the MP phase in the extraction of lanthanides, actinides, and some fission products by TBP and [A336]-[Cl].[54,111,120] The extraction of actinides and lanthanides was much less efficient than from molten nitrate hydrates, because these elements are less able to coordinate to Cl^- ions than to nitrate ions.[85] The effect of water was similar to the case of molten nitrate hydrates, as discussed above. The loading of Ca(II) to the TBP phase was also significant; 1.03 mol L^{-1} was loaded to 75 vol % TBP.[54]

4.3. Ionic Liquids. *4.3.1. Immiscible Biphasic ILs or Inorganic Salt Systems.* Ionic liquids (ILs) are solvents composed entirely of ions. They are organic salts with lower melting points than inorganic salts, and many of them are liquids at room temperature or slightly elevated temperatures. Hydrophobic ILs are often used as extractants, such as Aliquat 336 and Cyphos IL 101. However, the use of hydrophilic ILs as the solvent of the MP (feed) phase is rare. Arce et al.[123] discovered three types of biphasic ILs mixtures: (1) a hydrophobic and a hydrophilic IL that share the same anion, e.g., $[P_{666,14}]Cl$ and $[C_n mim]Cl$, (where $n < 6$); (2) two hydrophobic ILs with a common anion, e.g., $[C_2 mim][NTf_2]$ and ($[P_{666,14}][NTf_2]$); and (3) two ILs with four different ions, e.g., $[C_2 mim][OSO_2 CH_3]$ and $[P_{666,14}][PO_2(C_8 H_{17})_2]$. Many more biphasic ILs were created afterward.[124−128] While both the anions and the cations affect the formation of biphasic IL systems,[128] only mixtures of two ILs with significantly structurally different IL cations or of highly different hydrogen-bond acidity can undergo liquid−liquid phase separation, highlighting the determining role of the IL cation.[127] Despite having two phases, all biphasic IL systems display significant ion exchange, and all display an *upper critical solution temperature* (UCST)-type behavior. Since both IL phases are polar and it is not straightforward to tell which phase is more polar, here, we can use the *feed phase* and the *extract phase* to distinguish the two phases.

Wellens et al.[129] performed a proof-of-concept study for the separation of Co(II) and Ni(II) using the biphasic IL system consisting of Cyphos IL 104 and $[C_2 mim]Cl$. Co(II) and Ni(II) formed $[CoCl_4]^{2-}$ and $[NiCl_4]^{2-}$, respectively, in the $[C_2 mim]Cl$ phase. Co(II) was efficiently extracted as $[Co(R_2 POO)_2]$, while the extraction of Ni(II) was low, leading to

a separation factor of >200. The high separation factor is not surprising, because phosphinic acids (e.g., Cyanex 272) are known to have a high $Co(II)/Ni(II)$ selectivity.[130] Increasing the temperature from 95 °C to 140 °C reduced the distribution of $Co(II)$, because of increased solubility of phosphinate anions in the $[C_2mim]Cl$ phase. The solubility increase with increasing temperature is consistent with the common UCST behavior of biphasic IL systems. The same biphasic IL system was further used for the extraction of REEs.[131] REEs in the $[C_2mim]Cl$ phase were expected to form anionic $[LnCl_6]^{3-}$ complexes, because of the absence of water, although the speciation was not comprehensively characterized. All tested REEs were efficiently extracted from the $[C_2mim]Cl$ phase to the Cyphos IL 104 phase, and could also be separated from $Ni(II)$.

Biphasic IL systems can further form three- or four-phase immiscible liquid systems with water and a nonpolar alkane, such as the pentane−$[P_{666,14}][NTf_2]$−water−$[C_2mim][NTf_2]$ system.[123] Vander Hoogerstraete et al.[132] made use of the triphasic $[Hbet][NTf_2]$−H_2O−$[P_{666,14}][NTf_2]$ system to separate $Sn(II)$, $Y(III)$, and $Sc(III)$, which were enriched in the $[Hbet][NTf_2]$ phase, the aqueous phase, and the $[P_{666,14}][NTf_2]$ phase, respectively. Strictly speaking, the IL−H_2O−IL system is not a NASX system, because of the involvement of an aqueous phase.

Similar to ILs, inorganic salts could also form two immiscible phases, although a higher temperature is needed. KBr and $AlBr_3$ form two immiscible phases, with one phase being mainly $AlBr_3$ (>99% mol %) and the other phase having ~20 mol % $AlBr_3$ and 80 mol % KBr. Ammon studied the distribution of 14 metal halides in this system at 200 °C and found that ionic compounds prefer the polar KBr-rich phase, while covalent-type compounds are enriched in the $AlBr_3$-rich phase, facilitating the separation of different types of metal halides.[133] The highest separation factor was found for $Cs(I)/Zr(IV)$, reaching 126. Smith investigated the distribution of $PdBr_2$, $RhBr_3$, and $RuBr_3$ between two phases of the same system at 110 °C. However, these halides exhibited similar distributions and, hence, the separation was poor. This poor separation might be explained by the similar property of these halides in that they are all ionic compounds, e.g., $[PdBr_4]^{2-}$ and $[RuBr_6]^{2-}$ were the main species in both phases, as determined by the spectroscopic study.[134] The ternary system $LiCl$−KCl−$AlCl_3$ could form two immiscible polar phases with the $KAlCl_4$ phase on the top and the $LiCl$ phase at the bottom. Distributions of some metal chlorides and oxychlorides (UO_2Cl_2) in this system were determined by Moore.[135] The distribution ratios range from 0.014 for $Sr(II)$ to 18.1 for $Cs(I)$, allowing possible separations of different metal chlorides. Because of the resistance of molten salts to radiation damage, immiscible salt systems might find applications in processing radioactive materials.

4.3.2. Ethylammonium Nitrate. Ethylammonium nitrate (EAN) is a hydrophilic IL with a low melting point (12 °C) and low viscosity (32 cP at 27 °C).[136] EAN is a suitable solvent for the feed phase of an SX system, because it does not need heating, in contrast to molten inorganic salts, and it does not contain water in contrast to molten nitrate hydrates. EAN was utilized as a polar solvent for the extraction of transition-metal nitrates by TBP.[137] The extraction from EAN is considerably stronger than that from a range of polar molecular solvents, which is consistent with the high extraction of $Co(II)$ from molten KNO_3−$LiNO_3$ eutectic by TBP. The main

species of $Co(II)$ and $Fe(III)$ in EAN were proposed as $[Co(NO_3)_4]^{2-}$ and $[Fe(NO_3)_4]^-$, respectively. The enhanced extraction is caused by the exclusion of other ligands (i.e., solvent molecules) to solvate the metal cations, besides nitrate ions. The addition of H_2O to EAN reduces the extraction because the metal cations coordinate more strongly to water than to nitrate ions. $Co(II)$ speciation converts from $[Co(NO_3)_4]^{2-}$ in EAN to $[Co(H_2O)_6]^{2+}$ with the addition of water to the EAN phase. Interestingly, different metals respond differently to the water content; therefore, the addition of water leads to enhanced separations for some metals pairs. For example, the extraction of $Ni(II)$ decreased from 84% to 21% with the addition of 5 vol % water, but the extraction of $Fe(III)$ remained almost the same at ~99%, leading to enhanced separation of $Fe(III)/Ni(II)$.

EAN was found to be a perfect solvent for studying the sequence of lanthanides extraction by quaternary ammonium nitrate ILs (e.g., $[A336][NO_3]$).[138] The extraction of lanthanides by $[A336][NO_3]$ from aqueous nitrate solutions shows a negative sequence (i.e., light lanthanides are more efficiently extracted than heavy lanthanides),[121,122] which has confused researchers in the field for decades, because it conflicts with the "lanthanide contraction". However, the extraction of lanthanides from EAN by $[A336][NO_3]$ shows a positive sequence, which is converted to a negative sequence with the addition of water (Figure 9). The transformation from
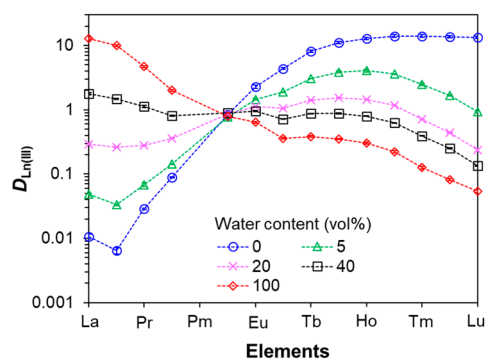

Figure 9. Transformation of lanthanides extraction sequence from positive to negative by addition of water. [Adapted from Li and Binnemans.[138]]

positive to negative sequences reveals that the negative sequence is caused by the hydration of lanthanide ions.[138] This observation is consistent with the effect of water on lanthanides extraction from molten nitrate hydrates.[120] The EAN−$[A336][NO_3]$ system contains only nitrate ions as ligands for metal cations and, hence, is a good simplified model system for many fundamental studies.

4.4. Deep-Eutectic Solvents. Deep-eutectic solvents (DESs) formed by a eutectic mixture of Lewis or Brønsted acids and bases can contain a variety of anionic and/or cationic species. DESs are a different type of solvent compared to ILs, which are formed from systems composed primarily of one type of discrete anion and cation.[139] Foreman investigated the extraction of metals from the lactic acid-choline chloride-based DES.[140] With the increase of the DES in the water−DES mixture, the extraction of $Zn(II)$ and $Cd(II)$ by Aliquat 336 dissolved in toluene decreased, while extraction of $Fe(III)$ and $Mn(II)$ increased, and the extraction of $Co(II)$ and $Cu(II)$ peaked at 80 vol % DES. It is known that these metals are

extracted by Aliquat 336 via the formation of chlorometallate anions that bind the ammonium cation of Aliquat 336. The different extraction efficiency of these metals reflects the different capabilities for the formation of their corresponding chlorometallate anions. One important factor affecting the formation of chlorometallate anions is the changing Cl^- ion concentration (and, hence, its activity) as the DES-to-water ratio changes in the DES-water mixture.[141,142] Besides, water molecules and lactate can coordinate to the metal cations as well. The detailed coordination of each metal ion in such a mixture remains unknown. The extraction of Co(II) by Aliquat 336 (dissolved in ethylbenzene) from loaded DES after leaching metallic cobalt would result in accumulation of lactate, which can inhibit the extraction of Co(II) due to the formation of CoL_2 (where L represents a lactate anion).[143] The accumulation of lactate can be avoided by using D2EHPA as an extractant. On the other hand, the extraction of these metals from the water−DES mixture by D2EHPA was less sensitive to the DES content,[140] because the extraction by D2EHPA is not dependent on the formation of chlorometallate anions, but on the acidity of the MP phase.

The lactic acid-choline chloride-based DES was also employed for the dissolution of NdFeB magnets, followed by two steps of SX for the recovery and separation of the metals.[144] The first step used [A336][SCN] to extract Fe(III), Co(II), and B(III), and the second step used Cyanex 923 to recover Nd(III) and Dy(III). Despite also efficiently extracting Nd(III) and Dy(III) from the DES, D2EHPA was not selected because of the difficulty of stripping. Compared with the extraction of these metals from aqueous solutions, higher extraction efficiency for all elements and enhanced separation for Nd(III) and Dy(III) were obtained for the extraction from the DES. More interestingly, while Fe(III) was extracted in the form of $[Fe(SCN)_6]^{3-}$ from aqueous solutions, it was extracted as $[FeCl_4]^-$ from the DES solutions. These observations indicate that the DES alters the speciation of metals in the MP phase, affecting the extraction mechanism and extraction efficiency.

5. COMPLEXING AGENTS IN THE FEED PHASE

Not only using alternative solvents in the MP phase affects the extraction efficiency, the addition of salts or complexing agents also does. The addition of Cl^- to the KNO_3-LiNO_3 eutectic[55] or EAN[137] significantly reduces the extraction of transition metals [Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)] by TBP. This is because of the formation of more stable chlorometallate complexes (e.g., $[CoCl_4]^{2-}$) in the MP phase. Extraction of Hg(II) from the KNO_3-LiNO_3 eutectic by polyphenyl is also subject to the formation of chlorometallate complexes (e.g., $[HgCl_3]^-$, $[HgCl_4]^{2-}$) upon the addition of LiCl.[95,97] However, the addition of Cl^- to the KSCN−NaSCN eutectic does not reduce the extraction of transition metals,[102] because transition metals preferentially coordinate to thiocyanate ions.[85] Nevertheless, the addition of a small amount of cyanide ions significantly lowers the extraction of transition metals by both neutral phosphorus extractants[104] and quaternary ammonium salts,[145] because cyanide ions coordinate stronger to transition metals than thiocyanate ions do. The effect of the anions in the MP phase on the extraction of transition metals follows the sequence of their coordination ability to transition metals: $CN^- > SCN^- > Cl^- > NO_3^-$.[85]

The use of salts or complexing agents in the MP phase could also enhance the metal separations. In the extraction of transition metals from EAN by TBP, the addition of LiCl significantly increased the separation factors of Fe(III)/Zn(II), Fe(III)/Cu(II), Fe(III)/Co(II), Fe(III)/Ni(II), and Mn(II)/Zn(II).[137] The separation factors of metal pairs with 0.50 mol L^{-1} LiCl in the MP phase are given in Table 1. Again, take

Table 1. Separation Factors ($\alpha_{M1/M2}$) of Six Transition Metals with 0.5 mol L^{-1} LiCl in EAN

	$\alpha_{M1/M2}$	M1					
		Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
M2	Mn(II)	1.0	38.5	–	–	–	–
	Fe(III)	–	1.0	–	–	–	–
	Co(II)	17.1	659.0	1.0	2.3	–	–
	Ni(II)	7.4	283.2	–	1.0	–	–
	Cu(II)	43.6	1680.7	2.6	5.9	1.0	–
	Zn(II)	104.2	4012.2	6.1	14.2	2.4	1.0

Co(II) as an example, the addition of LiCl converts $[Co(NO_3)_4]^{2-}$ in the feed phase to $[CoCl_4]^{2-}$. The latter is more stable, hence more difficult to be extracted by TBP as $[Co(NO_3)_2(TBP)_x]$ (x = 2, 3). These transition metals have different capabilities to coordinate to Cl^- ions, leading to the enlargement of separation factors by the addition of LiCl.

The same methodology applies to the separation of transition metals from REEs, since these two groups of elements have remarkably different coordination capabilities. Hydrophilic ILs were found to be suitable complexing agents in the MP phase to enhance the separation. For instance, both Co(II) and Sm(III) can be efficiently extracted by Cyanex 923 from EG solutions with LiCl as a chloride source. However, the addition of tetraethylammonium chloride (TEAC) to the MP phase holds back the extraction of Co(II) through the formation of $[N_{2222}]_2[CoCl_4]$ without affecting the extraction of Sm(III), leading to highly efficient separation of the two elements (Figure 10).[146] However, the role of the cations, i.e., why $[N_{2222}]^+$ is more efficient than Li^+ to stabilize $[CoCl_4]^{2-}$ in the more polar phase, has not been understood yet. Computational methods, such as molecular dynamics (MD) simulations, seem to be a powerful tool to gain deeper insights into the stability of complexes in solutions.[147] Therefore, it is recommended that more computational investigations should be conducted in future studies on NASX systems.

6. NASX IN METALLURGICAL FLOWSHEETS

A hydrometallurgical process from minerals to marketable salts or metals typically includes leaching, SX, and metal recovery by, for instance, precipitation or electrodeposition. NASX and other solvometallurgical unit processes can be used to enhance such existing metallurgical processes. As such, solvometallurgy is complementary to hydro- and pyro-metallurgy, and it can be applied whenever it provides economic and technical advantages. In terms of scaling up, it has been demonstrated that NASX systems can be operated smoothly in mixer-settlers, such as the Cyanex 923 and DES system for the separation of Dy(III) and Nd(III),[144] the Cyanex 923 and DES system for the separation of Fe(III) from Zn(II) and Pb(II),[148] and the Cyanex 923 and EG system for the separation of Y(III) and Eu(III).[82]

Complete solvometallurgical processes (Figure 11) have not been developed, yet efforts have been made toward this end.
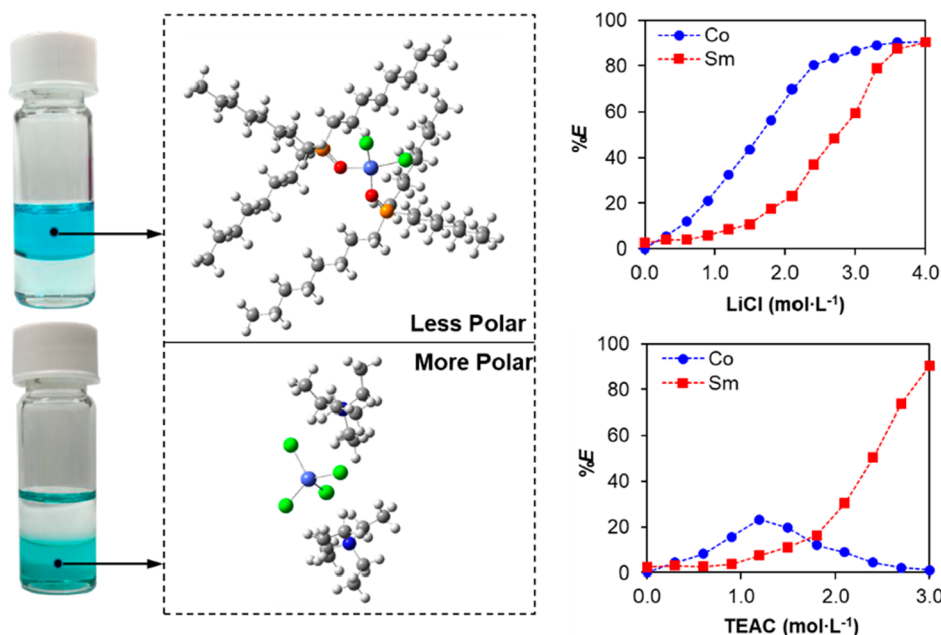
Figure 10. Addition of TEAC to EG solution enhances the separation of Co(II) and Sm(III). [Adapted from Li et al.[146]]
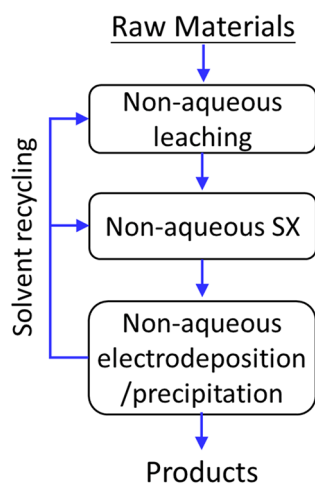

Figure 11. Flowsheet of a solvometallurgical process.

Orefice et al. used a mixture of aqueous HCl and EG to leach Co−Sm permanent magnets.[149] The resulting pregnant leachate was treated by SX using Aliquat 336 to recover Co(II), Cu(II), and Fe(III), which were then separated by selective stripping. The extraction from a mixture of water and EG was more efficient than from purely aqueous solutions, as discussed in Section 3.4. In another example, pyridine hydrochloride (PyHCl) was used to leach the production scrap of Nd−Fe−B permanent magnets at 165 °C for the recovery of REEs.[150] Dy(III) and Nd(III) in the pregnant leachate were recovered by NASX using PC 88A (2-ethylhexylphosphonic mono-2-ethylhexyl ester), and Fe(III)/Fe(II) was recovered using Cyphos IL 101. The loaded Dy(III) and Nd(III) were precipitated by aqueous oxalic acid solutions, and Fe(III)/Fe(II) was precipitated by aqueous NH$_3$ solutions. It is worth mentioning that REEs could not be precipitated as oxalates in PMOSs, e.g., ethylene glycol, because of the high solubility of rare-earth oxalates in PMOSs, although this is typically done in aqueous solutions.

In a similar study, Nd−Fe−B permanent magnets were leached by a DES composed of choline chloride and lactic acid (molar ratio of 1:2).[144] Fe(III), Co(II), and B(III) in the leachate were removed using the IL [A336][SCN], while Nd(III) and Dy(III) were further recovered by NASX using Cyanex 923. The loaded metals and B(III) in [A336][SCN] and Cyanex 923 were selectively stripped by aqueous solutions.

Besides the recovery of valuable metals from magnets, Peeters et al. studied solvometallurgical recovery of cobalt from lithium cobalt oxide (LiCoO$_2$).[151] A DES composed of choline chloride−citric acid (molar ratio of 2:1) diluted with 35 wt % water (to reduce viscosity) was used to leach LiCoO$_2$ with the assistance of metallic aluminum and copper as reducing agents. Cu(I/II) and Co(II) in the DES were recovered by LIX 984 and Aliquat 336, respectively, after which both were precipitated by aqueous oxalic acid solutions.

Recovery of platinum group metals (PGMs) from spent automotive catalysts by solvometallurgy was also investigated.[152] After two steps of solvoleaching of the automotive catalysts using acetonitrile and FeCl$_3$, and removal of acetonitrile by distillation, the solid residue was dissolved in EG. The EG solution containing Fe(III), Pt(IV), and Rh(III) was treated by NASX using [A336][Cl] to recover Fe(III) and Pt(IV), leaving behind Rh(III) in the raffinate. The loaded Fe(III) and Pt(IV) were scrubbed by water and stripped by thiourea solution, respectively.

All of the above processes consist of nonaqueous leaching and NASX, but the stripping used aqueous solutions, which may introduce water to the LP phase of NASX systems. The loaded metal ions in the LP phase could also be stripped to the nonaqueous MP phase, in which the ions could be recovered by nonaqueous electrodeposition. For example, Cu(I) and In(III) were directly electrodeposited from EG solution[153] and PEG 400 solution,[154] respectively.

7. CONCLUSIONS AND OUTLOOK

NASX systems can be developed starting with choosing the appropriate more polar and less polar phases to form

immiscible two-phase systems, based mainly on the polarity and hydrophobicity of the two phases. A variety of NASX systems involving polar molecular organic solvents and ionic solvents (molten inorganic salts, molten salt hydrates, ionic liquids, and deep eutectic solvents) as the solvent of the more polar phase have been investigated using four different types of extractants for the extraction of a wide range of metals.

The use of polar molecular organic solvents generally enhances the extraction of metals, mainly due to the higher stability of inner-sphere metal−ligand complexes in polar molecular organic solvents caused by the lower dielectric constants. This effect enables the extraction of REEs chlorides by Cyanex 923 and enhances extraction of transition metals, but also slightly suppresses extraction of transition metals (e.g., Zn(II)) at high chloride solutions, because of the anionic complexes (e.g., $[ZnCl_4]^{2-}$) being stable in the polar molecular organic solvents. Because different metals behave differently in terms of speciation at different anion and water concentrations in various solvents, NASX offers an extra dimension to improve metal separations. This effect leads to more efficient separations of REEs by NASX using polar molecular organic solvents and neutral extractants, and highly efficient separations of transition metals from REEs using polar molecular organic solvents and basic extractants.

Extraction of metals from inorganic salts, molten salt hydrates, and ionic liquids is much more efficient, compared to extraction from aqueous systems. The addition of water to these systems, on the one hand, reduces the extraction, but may also enhance the separation of metals. The NASX system consisting of $[A336][NO_3]$ and ethylammonium nitrate reveals that hydration of REEs counteracts the separation of REEs, which indicates that weaker solvation in the more polar phase is beneficial for separations. The $[A336][NO_3]$ and ethylammonium nitrate system can be a model for the study of ion transport, because it includes only one ligand. Furthermore, the introduction of complexing agents, either inorganic salts or ionic liquids, may enhance separations, because of the complexing of metal ions to the anions, but the role of the cations has not been understood yet.

Studies on NASX so far have covered a wide scope encompassing three aspects: (1) the use of molecular solvents, (2) the use of ionic solvents, and (3) the introduction of complexing agents. More work must be done to fully understand NASX and make better use of it for the separation of metals.

(1) The construction of correlation-based and even predictive thermodynamic models to describe the phase equilibria in NASX systems involving a range of polar solvents (molecular and ionic), including the effect of extractants and salts.

(2) Speciation of metals in the more polar phase and the solvation energy should be studied in more detail, by experimental and computational methods, to quantitatively understand the effect of the polar solvents on metal ion coordination.

(3) Neutral and basic extractants are mainly used, so far. The use of acidic extractants, either as such or in the saponified forms (or binary extractants), in NASX should be explored.

(4) So far, ethylammonium nitrate is the only ionic liquid (IL) that can be used at room temperature for NASX.

More low-melting hydrophilic ILs should be explored for use as the more polar phase, such as chloride ILs.

(5) More efforts should be made to develop either fully solvometallurgical processes or nonaqueous systems that can be integrated practically into existing metallurgical flowsheets. Those investigations should focus on attaining a high technology readiness level (TRL).

■ ASSOCIATED CONTENT

ⓈI Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org/. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c02287.

Physical and chemical properties of common polar molecular organic solvents (PMOSs) and some diluents; nonaqueous solvent extraction (NASX) systems with polar molecular organic solvents (PMOSs); NASX systems using ionic solvents in the more polar phase (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Zheng Li − *Department of Chemistry, KU Leuven, B-3001 Heverlee, Belgium;* ⓘ orcid.org/0000-0002-7882-5999; Email: zheng.li@kuleuven.be

Authors

Brecht Dewulf − *Department of Chemistry, KU Leuven, B-3001 Heverlee, Belgium;* ⓘ orcid.org/0000-0002-4325-273X

Koen Binnemans − *Department of Chemistry, KU Leuven, B-3001 Heverlee, Belgium;* ⓘ orcid.org/0000-0003-4768-3606

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.iecr.1c02287

Author Contributions

∇These authors contributed equally.

Notes

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■ ABBREVIATIONS

a = activity
Alamine 336 = *N,N*-dioctyl-1-octanamine, also known as tri-*n*-octyl amine (TOA)
Aliquat 336 = tricaprylmethylammonium chloride, where capryl is a mixture of *n*-octyl and *n*-decyl
Aliquat 4 = dodecyltrimethylammonium chloride
bipy = 2,2′-bipyridyl
Cyanex 272 = bis(2,4,4-trimethylpentyl)phosphinic acid
Cyanex 301 = bis(2,4,4-trimethylpentyl)dithiophosphinic acid

Cyanex 923 = mixture of trialkylphosphine oxides with the alkyl chains being *n*-hexyl and *n*-octyl

Cyphos IL 101 = trihexyl(tetradecyl)phosphonium chloride, $[P_{666,14}]Cl$

Cyphos IL 104 = trihexyl(tetradecyl)phosphonium bis-(2,4,4-trimethylpentyl)phosphinate

D = distribution ratio

D2EHPA = bis(2-ethylhexyl) phosphoric acid

DESs = deep eutectic solvents

DMF = *N,N*-dimethylformamide

DMSO = dimethyl sulfoxide

EAN = ethylammonium nitrate

EDTA = ethylenediaminetetraacetic acid

EG = ethylene glycol

GS190 = aliphatic diluent derived from gas-to-liquid technology having low levels of sulfur, olefins, and aromatics

HDBP = di-*n*-butyl phosphoric acid

HL = an acidic extractant molecule

HMPT = hexamethylphosphorotriamide

HREE = heavy rare-earth elements

HTTA = 2-thenoyltrifluoroacetone

ILs = ionic liquids

LIX 984 = 1:1 volume blend of LIX 860 (5-dodoecylsali-cylaldoxime) and LIX 84 (2-hydroxy-5-nonylacetophenone oxime)

Ln(III) = trivalent lanthanide ion

LP = less polar

LREE = light rare-earth elements

MIBK = methyl isobutyl ketone

mol % = mole percent

MP = more polar

NASX = nonaqueous solvent extraction

n-DPO = diphenyldiphosphine dioxides, $(C_6H_5)_2PO-(CH_2)_nPO(C_6H_5)_2$

NMF = *N*-methylformamide

NR_4Cl = quaternary ammonium chloride

NR_4L = a binary extractant with the cation being a quaternary ammonium

PC 88A = 2-ethylhexylphosphonic mono-2-ethylhexyl ester

PEG 200 = poly(ethylene) glycol with an average molecular weight of 200

PEG 400 = poly(ethylene) glycol with an average molecular weight of 400

PG = propylene glycol

PGMs = platinum-group metals

phen = 1,10-phenanthroline

PMOSs = polar molecular organic solvents

Progil pure = 2,4,5,7-tetramethyloctane

PyHCl = pyridine hydrochloride

REEs = rare-earth elements

S = neutral extractant molecule

SX = solvent extraction

TALSPEAK = trivalent actinide-lanthanide separation with phosphorus-reagent extraction from aqueous complexes

TBAI = tetra-*n*-butylammonium iodide

TBP = tri-*n*-butyl phosphate

TEAC = tetraethylammonium chloride, $[N_{2222}]Cl$

THAN = tetraheptylammonium nitrate

TOA = trioctyl amine, also known as Alamine 336

TOPN = tetraoctylphosphonium nitrate

TOPO = tri-*n*-octyl phosphine oxide

TPPO = triphenyl phosphine oxide

TRL = technology readiness level

ShellSol A150 = C9−C10 aromatic hydrocarbon solvent

UCST = upper critical solution temperature

Versatic Acid 10 = a mixture of carboxylic acids with the common structural formula $C_{10}H_{20}O_2$

vol % = volume percent

wt % = weight percent

x = mole fraction

α = separation factor

δ_d = Hansen solubility parameter representing dispersion forces

δ_p = Hansen solubility parameter representing intermolecular forces

δ_h = Hansen solubility parameter representing hydrogen bonding forces

δ_T = total Hansen solubility parameter

%*E* = percentage extraction

$[A336][NO_3]$ = Aliquat 336 nitrate

$[C_nmim]Cl$ = 1-alkyl-3-methylimidazolium chloride

$[Hbet][NTf_2]$ = betaine bis(trifluoromethylsulfonyl)imide

$[NR_2H_2][SCN]$ = di-*n*-dodecylammonium thiocyanate

■ REFERENCES

(1) Demopoulos, G. P. Solvent Extraction in Precious Metals Refining. *JOM* **1986**, *38* (6), 13−17.

(2) Saguru, C.; Ndlovu, S.; Moropeng, D. A Review of Recent Studies into Hydrometallurgical Methods for Recovering PGMs from Used Catalytic Converters. *Hydrometallurgy* **2018**, *182*, 44−56.

(3) Nguyen, V. T.; Riaño, S.; Binnemans, K. Separation of Precious Metals by Split-Anion Extraction Using Water-Saturated Ionic Liquids. *Green Chem.* **2020**, *22* (23), 8375−8388.

(4) Cheng, C. Y.; Barnard, K. R.; Zhang, W.; Robinson, D. J. Synergistic Solvent Extraction of Nickel and Cobalt: A Review of Recent Developments. *Solvent Extr. Ion Exch.* **2011**, *29* (5−6), 719−754.

(5) Banza, A. N.; Gock, E.; Kongolo, K. Base Metals Recovery from Copper Smelter Slag by Oxidising Leaching and Solvent Extraction. *Hydrometallurgy* **2002**, *67* (1), 63−69.

(6) Cheisson, T.; Schelter, E. J. Rare Earth Elements: Mendeleev's Bane, Modern Marvels. *Science* **2019**, *363* (6426), 489−493.

(7) Qi, D. Extractants Used in Solvent Extraction−Separation of Rare Earths: Extraction Mechanism, Properties, and Features. In *Hydrometallurgy of Rare Earths: Extraction and Separation*; Elsevier: Amsterdam, 2018; Chapter 2, pp 187−389.

(8) Doidge, E. D.; Carson, I.; Love, J. B.; Morrison, C. A.; Tasker, P. A. The Influence of the Hofmeister Bias and the Stability and Speciation of Chloridolanthanates on Their Extraction from Chloride Media. *Solvent Extr. Ion Exch.* **2016**, *34* (7), 579−593.

(9) Rout, A.; Binnemans, K. Influence of the Ionic Liquid Cation on the Solvent Extraction of Trivalent Rare-Earth Ions by Mixtures of Cyanex 923 and Ionic Liquids. *Dalt. Trans.* **2015**, *44* (3), 1379−1387.

(10) Ansari, S. A.; Pathak, P.; Mohapatra, P. K.; Manchanda, V. K. Chemistry of Diglycolamides: Promising Extractants for Actinide Partitioning. *Chem. Rev.* **2012**, *112* (3), 1751−1772.

(11) Nash, K. L. The Chemistry of TALSPEAK: A Review of the Science. *Solvent Extr. Ion Exch.* **2015**, *33* (1), 1−55.

(12) Mathur, J. N.; Murali, M. S.; Nash, K. L. Actinide Partitioning—A Review. *Solvent Extr. Ion Exch.* **2001**, *19* (3), 357−390.

(13) Su, H.; Li, Z.; Zhang, J.; Liu, W.; Zhu, Z.; Wang, L.; Qi, T. Combining Selective Extraction and Easy Stripping of Lithium Using a Ternary Synergistic Solvent Extraction System through Regulation of Fe^{3+} Coordination. *ACS Sustainable Chem. Eng.* **2020**, *8* (4), 1971−1979.

(14) Li, Z.; Binnemans, K. Selective Removal of Magnesium from Lithium-Rich Brine for Lithium Purification by Synergic Solvent Extraction Using *β*-Diketones and Cyanex 923. *AIChE J.* **2020**, *66* (7), e16246.

(15) Li, Z.; Mercken, J.; Li, X.; Riaño, S.; Binnemans, K. Efficient and Sustainable Removal of Magnesium from Brines for Lithium/Magnesium Separation Using Binary Extractants. *ACS Sustainable Chem. Eng.* **2019**, 7 (23), 19225−19234.

(16) Li, Z.; Binnemans, K. Opposite Selectivities of Tri-n-Butyl Phosphate (TBP) and Cyanex 923 in Solvent Extraction of Lithium and Magnesium. *AIChE J.* **2021**, 67, e17219.

(17) Wesselborg, T.; Virolainen, S.; Sainio, T. Recovery of Lithium from Leach Solutions of Battery Waste Using Direct Solvent Extraction with TBP and FeCl₃. *Hydrometallurgy* **2021**, 202, 105593.

(18) Masmoudi, A.; Zante, G.; Trébouet, D.; Barillon, R.; Boltoeva, M. Solvent Extraction of Lithium Ions Using Benzoyltrifluoroacetone in New Solvents. *Sep. Purif. Technol.* **2021**, 255, 117653.

(19) Torrejos, R. E. C.; Nisola, G. M.; Song, H. S.; Limjuco, L. A.; Lawagon, C. P.; Parohinog, K. J.; Koo, S.; Han, J. W.; Chung, W.-J. Design of Lithium Selective Crown Ethers: Synthesis, Extraction and Theoretical Binding Studies. *Chem. Eng. J.* **2017**, 326, 921−933.

(20) Li, Z.; Pranolo, Y.; Zhu, Z.; Cheng, C. Y. Solvent Extraction of Cesium and Rubidium from Brine Solutions Using 4-Tert-Butyl-2-(α-Methylbenzyl)-Phenol. *Hydrometallurgy* **2017**, 171, 1−7.

(21) Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G. R. *Solvent Extraction Principles and Practice*, 2nd Edition; Marcel Dekker: New York, 2004.

(22) Chandrasekar, A.; Rao, C. V. S. B; Sundararajan, M.; Ghanty, T. K.; Sivaraman, N. Remarkable Structural Effects on the Complexation of Actinides with H-Phosphonates: A Combined Experimental and Quantum Chemical Study. *Dalton Trans.* **2018**, 47 (11), 3841−3850.

(23) Omelchuk, K.; Szczepański, P.; Shrotre, A.; Haddad, M.; Chagnes, A. Effects of Structural Changes of New Organophosphorus Cationic Exchangers on a Solvent Extraction of Cobalt, Nickel and Manganese from Acidic Chloride Media. *RSC Adv.* **2017**, 7 (10), 5660−5668.

(24) Nifant'ev, I. E.; Minyaev, M. E.; Tavtorkin, A. N.; Vinogradov, A. A.; Ivchenko, P. V. Branched Alkylphosphinic and Disubstituted Phosphinic and Phosphonic Acids: Effective Synthesis Based on α-Olefin Dimers and Applications in Lanthanide Extraction and Separation. *RSC Adv.* **2017**, 7 (39), 24122−24128.

(25) Du, R.; Yu, D.; An, H.; Zhang, S.; Lu, R.; Zhao, G.; Xiao, J.-C. α,β-Substituent Effect of Dialkylphosphinic Acids on Lanthanide Extraction. *RSC Adv.* **2016**, 6 (61), 56004−56008.

(26) Petrova, M. A.; Kurteva, V. B.; Lubenov, L. A. Synergistic Effect in the Solvent Extraction and Separation of Lanthanoids by 4-(4-Fluorobenzoyl)-3-Methyl-1-Phenyl-Pyrazol-5-One in the Presence of Monofunctional Neutral Organophosphorus Extractants. *Ind. Eng. Chem. Res.* **2011**, 50 (21), 12170−12176.

(27) Perera, J. M.; Stevens, G. W. The Role of Additives in Metal Extraction in Oil/Water Systems. *Solvent Extr. Ion Exch.* **2011**, 29 (3), 363−383.

(28) Cheng, C. Y.; Boddy, G.; Zhang, W.; Godfrey, M.; Robinson, D. J.; Pranolo, Y.; Zhu, Z.; Wang, W. Recovery of Nickel and Cobalt from Laterite Leach Solutions Using Direct Solvent Extraction: Part 1 — Selection of a Synergistic SX System. *Hydrometallurgy* **2010**, 104 (1), 45−52.

(29) Swami, K. R.; Venkatesan, K. A.; Antony, M. P. Role of Phase Modifiers in Controlling the Third-Phase Formation During the Solvent Extraction of Trivalent Actinides. *Solvent Extr. Ion Exch.* **2019**, 37 (7), 500−517.

(30) Petrova, M. A.; Lachkova, V. I.; Vassilev, N. G.; Varbanov, S. G. Effect of Diluents on the Synergistic Solvent Extraction and Separation of Trivalent Lanthanoids with 4-Benzoyl-3-Phenyl-5-Isoxazolone and Tert-Butylcalix[4]Arene Tetrakis(N,N-Dimethyl Acetamide) and Structural Study of Gd(III) Solid Complex by IR and NMR. *Ind. Eng. Chem. Res.* **2010**, 49 (13), 6189−6195.

(31) Kuipa, P. K.; Hughes, M. A. Diluent Effect on the Solvent Extraction Rate of Copper. *Sep. Sci. Technol.* **2002**, 37 (5), 1135−1152.

(32) Weaver, B. Solvent Extraction in the Separation of Rare Earths and Trivalent Actinides. In *Ion Exchange and Solvent Extraction*;

Marinsky, J. A., Marcus, Y., Eds.; Marcel Dekker: New York, 1974; pp 189−277.

(33) Nishihama, S.; Hirai, T.; Komasawa, I. Selective Extraction of Y from a Ho/Y/Er Mixture by Liquid−Liquid Extraction in the Presence of a Water-Soluble Complexing Agent. *Ind. Eng. Chem. Res.* **2000**, 39 (10), 3907−3911.

(34) Kashi, E.; Habibpour, R.; Gorzin, H.; Maleki, A. Solvent Extraction and Separation of Light Rare Earth Elements (La, Pr and Nd) in the Presence of Lactic Acid as a Complexing Agent by Cyanex 272 in Kerosene and the Effect of Citric Acid, Acetic Acid and Titriplex III as Auxiliary Agents. *J. Rare Earths* **2018**, 36 (3), 317−323.

(35) Hala, J. Solvent Extraction of Europium from Aqueous-Organic Solutions by Solvating Extractants. *J. Radioanal. Nucl. Chem.* **1998**, 230 (2), 135−141.

(36) Mousa, S. B.; Altakrory, A.; Abdel Raouf, M. W.; Alian, A. Extraction and Separation of Zinc and Cadmium Chlorides by TOPO from Mixed Media. *J. Radioanal. Nucl. Chem.* **1998**, 227, 143−146.

(37) Shukla, J. P.; Kedari, C. S. Solvent Extraction of Plutonium(IV) into Dodecane by Bis(2-Ethylhexyl)Sulfoxide From Mixed Aqueous-Organic Solutions. *Radiochim. Acta* **1992**, 56 (1), 21−24.

(38) Kamitani, M.; Shibata, J.; Sano, M.; Nishimura, S. Extraction of Metal Ions with D2EHPA from Mixed Aqueous-Organic Media. *Solvent Extr. Ion Exch.* **1988**, 6 (4), 605−619.

(39) Alian, A.; Sanad, W.; Khaufa, H. Extraction of Certain Elements from Aqueous Methanol, Ethanol and Acetone by Tridodecylamine and Tributyl Phosphate. *Talanta* **1968**, 15 (2), 249−255.

(40) Hála, J.; Stodola, P. Solvent Extraction of Hafnium(IV) by TBP and TOPO from Acidic Organic-Aqueous Solutions. *J. Radioanal. Chem.* **1983**, 80, 31−41.

(41) Habana, R. S.; Ruf, H. Distribution from Mixed Solvents Analogy between Liquid-Liquid Extraction of Np-IV and Its Sorption on Solid Resins. *Radiochim. Acta* **1976**, 23, 123−126.

(42) Alian, A.; Sanad, W.; Shabaya, R. Extraction of Protactinium from Mineral Acid-Alcohol Media. *Talanta* **1968**, 15 (7), 639−651.

(43) Batchu, N. K.; Vander Hoogerstraete, T.; Banerjee, D.; Binnemans, K. Non-Aqueous Solvent Extraction of Rare-Earth Nitrates from Ethylene Glycol to n-Dodecane by Cyanex 923. *Sep. Purif. Technol.* **2017**, 174, 544−553.

(44) Hala, J. Solvent Extraction from Aqueous-Organic Media. In *Ion Exchange and Solvent Extraction: A Series of Advances*; Marinsky, J., Marcus, Y., Eds.; Marcel Dekker.: New York, 1981; pp 369−410.

(45) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

(46) Binnemans, K.; Jones, P. T. Solvometallurgy: An Emerging Branch of Extractive Metallurgy. *J. Sustain. Metall.* **2017**, 3 (3), 570−600.

(47) Wilson, A. M.; Bailey, P. J.; Tasker, P. A.; Turkington, J. R.; Grant, R. A.; Love, J. B. Solvent Extraction: The Coordination Chemistry behind Extractive Metallurgy. *Chem. Soc. Rev.* **2014**, 43 (1), 123−134.

(48) Eyal, A. M.; Bressler, E.; Bloch, R.; Hazan, B. Extraction of Metal Salts by Mixtures of Water-Immiscible Amines and Organic Acids (Acid-Base Couple Extractants). 1. A Review of Distribution and Spectroscopic Data and of Proposed Extraction Mechanisms. *Ind. Eng. Chem. Res.* **1994**, 33 (5), 1067−1075.

(49) Lommelen, R.; Vander Hoogerstraete, T.; Onghena, B.; Billard, I.; Binnemans, K. Model for Metal Extraction from Chloride Media with Basic Extractants: A Coordination Chemistry Approach. *Inorg. Chem.* **2019**, 58 (18), 12289−12301.

(50) Sato, T.; Nakamura, T. The Extraction of Titanium(IV) and Aluminium(III) from Sulphuric Acid Solutions by Di-(2-Ethylhexyl)-Phosphoric Acid. *Anal. Chim. Acta* **1975**, 76 (2), 401−408.

(51) Sato, T.; Nakamura, T.; Ikeno, M. The Extraction of Iron(III) from Aqueous Acid Solutions by Di(2-Ethylhexyl)Phosphoric Acid. *Hydrometallurgy* **1985**, 15 (2), 209−217.

(52) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*, 2nd Edition; CRC Press: Boca Raton, FL, 2007.

(53) Amézqueta, S.; Subirats, X.; Fuguet, E.; Rosés, M.; Ràfols, C. Octanol−Water Partition Constant. In *Liquid-Phase Extraction*; Poole, C. F., Ed.; Elsevier: Amsterdam, 2020; Chapter 6, pp 183−208.

(54) Akatsu, E.; Asano, M. Radiochemical Studies on the Solvent Extraction of Several Elements in Mn(NO$_3$)$_2$.6H$_2$O- and CaCl$_2$.6H$_2$O-Tri-*n*-Butyl Phosphate Systems. *Anal. Chim. Acta* 1971, 55 (2), 333−340.

(55) Isaac, N. M.; Fields, P. R.; Gruen, D. M. Solvent Extraction of Actinides and Lanthanides from Molten Salts. *J. Inorg. Nucl. Chem.* 1961, 21, 152−168.

(56) Macchieraldo, R.; Gehrke, S.; Batchu, N. K.; Kirchner, B.; Binnemans, K. Tuning Solvent Miscibility: A Fundamental Assessment on the Example of Induced Methanol/n-Dodecane Phase Separation. *J. Phys. Chem. B* 2019, 123 (20), 4400−4407.

(57) Sørensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection-Ternary and Quaternary Systems*; Behrens, D., Eckermann, R., Eds.; DECHEMA: Frankfurt, Germany, 1980.

(58) Sørensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection-Ternary Systems*; Behrens, D., Eckermann, R., Eds.; DECHEMA: Frankfurt, Germany, 1980.

(59) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* 1968, 14 (1), 135−144.

(60) Chen, J.; Mi, J.; Fei, W.; Li, Z. Liquid-Liquid Equilibria of Quaternary and Quinary Systems Including Sulfolane at 298.15 K. *J. Chem. Eng. Data* 2001, 46 (1), 169−171.

(61) Li, Z.; Mumford, K. A.; Smith, K. H.; Chen, J.; Wang, Y.; Stevens, G. W. Solution Structure of Isoactivity Equations for Liquid-Liquid Equilibrium Calculations Using the Nonrandom Two-Liquid Model. *Ind. Eng. Chem. Res.* 2016, 55 (10), 2852−2859.

(62) Song, Y.; Chen, C.-C. Symmetric Electrolyte Nonrandom Two-Liquid Activity Coefficient Model. *Ind. Eng. Chem. Res.* 2009, 48 (16), 7788−7797.

(63) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd Edition; CRC Press: Boca Raton, FL, 1991.

(64) Klamt, A. The COSMO and COSMO-RS Solvation Models. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2011, 1 (5), 699−709.

(65) Eckert, F.; Klamt, A. Fast Solvent Screening via Quantum Chemistry: COSMO-RS Approach. *AIChE J.* 2002, 48 (2), 369−385.

(66) Larsen, E. M.; Trevorrow, L. V. E. The Systems Formed by Zirconium and Hafnium Tetrachloride with Acetonitrile and Isoamyl Ether. *J. Inorg. Nucl. Chem.* 1956, 2 (4), 254−259.

(67) Latimer, G. W. Distribution of Ion Pairs between Immiscible Nonaqueous Solvents. *Anal. Chem.* 1963, 35 (12), 1983−1983.

(68) Fǎrcaşiu, D.; Leu, R.; Ream, P. J. The 1:1 and 2:1 Complexes of Diethyl Ether with Tin Tetrachloride and Their Stability, Studied by ^{119}Sn NMR Spectroscopy. *J. Chem. Soc., Perkin Trans. 2* 2001, 2, 427−432.

(69) Dean, J. A.; Eskew, J. B. Solvent Extraction with Two Immiscible Organic Solvents Separation of Thallium(III). *Anal. Lett.* 1971, 4 (11), 737−743.

(70) Hála, J.; Tuck, D. G. Solvent Extraction Studies. Part VIII. The Partition of Alkali-Metal and Ammonium Thiocyanates between Tri-*n*-Butyl Phosphate and Liquid Ammonia. *J. Chem. Soc. A* 1971, 0, 3437−3441.

(71) Hála, J.; Tuck, D. G. Extraction Equilibria and Solvation Effects in the System Liquid Ammonia−Tri-*n*-Butyl Phosphate. In *Solvent Extraction: Proceedings of the International Solvent Extraction Conference*, ISEC 71: The Hague, April 19−23, 1971; Society of Chemical Industry, 1971; Vol. 1, pp 197−203.

(72) Baldwin, W. H.; Higgins, C. E.; Soldano, B. A. The Distribution of Monovalent Electrolytes between Water and Tributyl Phosphate. *J. Phys. Chem.* 1959, 63 (1), 118−123.

(73) Fawcett, W. R. Thermodynamic Parameters for the Solvation of Monatomic Ions in Water. *J. Phys. Chem. B* 1999, 103 (50), 11181−11185.

(74) Orabi, E. A.; Lamoureux, G. Molecular Dynamics Investigation of Alkali Metal Ions in Liquid and Aqueous Ammonia. *J. Chem. Theory Comput.* 2013, 9 (5), 2324−2338.

(75) Matsui, M.; Aoki, T.; Enomoto, H.; Shigematsu, T. Non-aqueous Liquid-Liquid Extraction: Extraction of Zinc from Ethylene Glycol Solution of Chloride by Trioctylphosphine Oxide. *Anal. Lett.* 1975, 8 (4), 247−255.

(76) Matsui, M.; Aoki, T.; Inoue, O.; Shigematsu, T. Nonaqueous Liquid-Liquid Extraction. Extraction of Zinc and Cadmium from Ethylene Glycol Solution of Bromide by Trioctylphosphine Oxide. *Bull. Inst. Chem. Res., Kyoto Univ* 1974, 52, 5−6.

(77) Aoki, T. Nonaqueous Liquid-Liquid Extraction of Manganese from Ethylene Glycol Solution with Trioctylphosphine Oxide. *Bull. Inst. Chem. Res., Kyoto Univ* 1981, 59 (3), 191−195.

(78) Doe, H.; Matsui, M.; Shigematsu, T. Nonaqueous Liquid-Liquid Extraction: Solvent Extraction Studies of Zinc Chloride and Perchlorate Complexes in Glycols. *Bull. Inst. Chem. Res., Kyoto Univ* 1979, 57 (5−6), 343−348.

(79) Doe, H.; Matsui, M.; Shigematsu, T. Nonaqueous Extraction of Zinc from Ethylene Glycol Solution of Lithium Perchlorate and/or Chloride. *Bull. Inst. Chem. Res., Kyoto Univ* 1980, 58 (2), 133−139.

(80) Batchu, N. K.; Li, Z.; Verbelen, B.; Binnemans, K. Structural Effects of Neutral Organophosphorus Extractants on Solvent Extraction of Rare-Earth Elements from Aqueous and Non-Aqueous Nitrate Solutions. *Sep. Purif. Technol.* 2021, 255, 117711.

(81) Batchu, N. K.; Vander Hoogerstraete, T.; Banerjee, D.; Binnemans, K. Separation of Rare-Earth Ions from Ethylene Glycol (+LiCl) Solutions by Non-Aqueous Solvent Extraction with Cyanex 923. *RSC Adv.* 2017, 7 (72), 45351−45362.

(82) Batchu, N. K.; Dewulf, B.; Riaño, S.; Binnemans, K. Development of a Solvometallurgical Process for the Separation of Yttrium and Europium by Cyanex 923 from Ethylene Glycol Solutions. *Sep. Purif. Technol.* 2020, 235, 116193.

(83) Dewulf, B.; Batchu, N. K.; Binnemans, K. Enhanced Separation of Neodymium and Dysprosium by Nonaqueous Solvent Extraction from a Polyethylene Glycol 200 Phase Using the Neutral Extractant Cyanex 923. *ACS Sustainable Chem. Eng.* 2020, 8 (51), 19032−19039.

(84) Florence, T. M.; Farrar, Y. J. Liquid-Liquid Extraction of Nickel with Long-Chain Amines from Aqueous and Nonaqueous Halide Media. *Anal. Chem.* 1968, 40 (8), 1200−1206.

(85) Diaz-Torres, R.; Alvarez, S. Coordinating Ability of Anions and Solvents towards Transition Metals and Lanthanides. *Dalt. Trans.* 2011, 40 (40), 10742−10750.

(86) Florence, M.; Farrar, Y. J. Liquid-Liquid Extraction of Manganese, Chromium, and Thorium by Long-Chain Amines from Concentrated Halide Media. *Aust. J. Chem.* 1969, 22, 473−476.

(87) Burns, A. R.; Cattrall, R. W. The Distribution of Copper(II) Between Methanolic Lithium Chloride Solutions and Benzene Solutions of Bis(3,5,5-Trimethylhexyl)Ammonium Chloride. *J. Inorg. Nucl. Chem.* 1973, 35 (7), 2489−2496.

(88) Wada, Y.; Aoki, T.; Kumagai, T.; Matsui, M. Nonaqueous Liquid-Liquid Extraction of Zinc, Cadmium and Cobaltous Ions from Ethylene Glycol and Propylene Glycol Solutions of Chloride by Long Chain Alkyl Amine and Alkyl Ammonium Compound. *Bull. Inst. Chem. Res., Kyoto Univ* 1985, 62 (5−6), 348−355.

(89) Li, Z.; Zhang, Z.; Smolders, S.; Li, X.; Raiguel, S.; Nies, E.; De Vos, D.; Binnemans, K. Enhancing Metal Separations by Liquid-liquid Extraction Using Polar Solvents. *Chem. - Eur. J.* 2019, 25 (39), 9197−9201.

(90) Li, Z.; Li, X.; Raiguel, S.; Binnemans, K. Separation of Transition Metals from Rare Earths by Non-Aqueous Solvent Extraction from Ethylene Glycol Solutions Using Aliquat 336. *Sep. Purif. Technol.* 2018, 201, 318−326.

(91) Deferm, C.; Onghena, B.; Nguyen, V. T.; Banerjee, D.; Fransaer, J.; Binnemans, K. Non-Aqueous Solvent Extraction of Indium from an Ethylene Glycol Feed Solution by the Ionic Liquid Cyphos IL 101: Speciation Study and Continuous Counter-Current Process in Mixer-Settlers. *RSC Adv.* 2020, 10 (41), 24595−24612.

(92) Deferm, C.; Onghena, B.; Vander Hoogerstraete, T.; Banerjee, D.; Luyten, J.; Oosterhof, H.; Fransaer, J.; Binnemans, K. Speciation of Indium(III) Chloro Complexes in the Solvent Extraction Process

from Chloride Aqueous Solutions to Ionic Liquids. *Dalt. Trans.* **2017**, *46* (13), 4412−4421.

(93) Foos, J.; Mesplede, J. Solvent Extraction from Molten Eutectic LiNO₃-KNO₃ of Some "5f" Elements by Diphenyldiphosphine Dioxides and Tri-n-Octylphosphine Oxide. *J. Inorg. Nucl. Chem.* **1972**, *34* (6), 2051−2056.

(94) Mesplede, J.; Porthault, M. Extraction Liquide-Liquide a Partir de Nitrates Alcalins Fondus: Utilisation de Diphosphine Dioxyde Comme Agent d'extraction. *J. Inorg. Nucl. Chem.* **1971**, *33* (12), 4275−4282.

(95) Zangen, M.; Marcus, Y. Solvent Extraction from Molten Salts I. Mercury (II) Chloride, Bromide and Iodide. *Isr. J. Chem.* **1964**, *2* (2), 49−55.

(96) Zangen, M. Solvent Extraction from Molten Salts. II. Mixed Mercury (II) Halides. *Isr. J. Chem.* **1964**, *2* (3), 91−97.

(97) Zangen, M.; Marcus, Y. Solvent Extraction from Molten Salts. III [1, 2]. Formation of Anionic Mercury (II) Mixed-Halide Complexes. *Isr. J. Chem.* **1964**, *2* (4), 155−165.

(98) Li, Z.; Bruynseels, B.; Zhang, Z.; Binnemans, K. Separation of GaCl₃ from AlCl₃ by Solid−Liquid Extraction and Stripping Using Anhydrous n-Dodecane and NaCl. *Ind. Eng. Chem. Res.* **2019**, *58* (27), 12459−12464.

(99) Gal, I. J.; Mendez, J.; Irvine, J. W. Distribution of Some Simple and Complex Anions between Molten Lithium Nitrate-Potassium Nitrate and Tetraheptylammonium Nitrate in Polyphenyl. *Inorg. Chem.* **1968**, *7* (5), 985−991.

(100) Tan, Z. C. H.; Irvine, J. W. Extraction of Some Anions from Molten Lithium Nitrate-Potassium Nitrate by Tetraoctylphosphonium Nitrate in Polyphenyl or 1-Nitronaphthalene Solvent. *Inorg. Chem.* **1972**, *11* (7), 1701−1707.

(101) Targhetta, J.; Mesplede, J.; Porthault, M. Synergistic Solvent Extraction of Some "4f" Elements from Molten Alkali Nitrates at 160°C. *J. Inorg. Nucl. Chem.* **1974**, *36* (2), 445−450.

(102) de Haas, K. S.; Brink, P. A.; Crowther, P. Solvent Extraction of Iron, Cobalt and Nickel from Thiocyanate Melts. *J. Inorg. Nucl. Chem.* **1971**, *33* (12), 4301−4309.

(103) Zhou, Z.; Qin, W.; Chu, Y.; Fei, W. Elucidation of the Structures of Tributyl Phosphate/Li Complexes in the Presence of FeCl₃ via UV-Visible, Raman and IR Spectroscopy and the Method of Continuous Variation. *Chem. Eng. Sci.* **2013**, *101*, 577−585.

(104) Durand, G.; Billon, M.; Trémillon, B. Extraction Par Solvants Fondus: I - Équilibres de Distribution Du Zinc(II) Entre Le Thiocyanate de Potassium et Le Phénanthrène Fondus (à 195°C). *Anal. Chim. Acta* **1976**, *82* (2), 349−367.

(105) Zangen, M.; David-Auslaender, J.; Kertes, A. S. Solvent Extraction from Molten Salts-XI. Extraction of Cobalt(II) by Di-n-Dodecylammonium Thiocyanate. *J. Inorg. Nucl. Chem.* **1974**, *36* (1), 218−220.

(106) Borkowska, Z.; Mielcarski, M.; Taube, M. High Temperature Organic Extraction of Uranium, Plutonium and Americium Fused Chlorides. *J. Inorg. Nucl. Chem.* **1964**, *26* (2), 359−371.

(107) Maroni, V. A.; Philbin, C. E.; Yonco, R. M. Extraction of 3d Transition Metals from Molten Cesium-Sodium-Potassium/Acetate Eutectic Into Dodecane Using Organophosphorous Ligands. *Sep. Sci. Technol.* **1983**, *18* (14−15), 1699−1713.

(108) Mitsugashira, T.; Kamoshida, M.; Suzuki, Y.; Satoh, I. Extraction of Americium and Lanthanides with Tributylphosphate from Water-Deficient Nitrate Media. *J. Alloys Compd.* **1994**, *213-214* (C), 347−350.

(109) Akatsu, E.; Aratono, Y. Radiochemical Studies on the Liquid-Liquid Extraction of Several Elements in Fused Manganese Nitrate Hexahydrate-Tri-n-Butyl Phosphate in Various Diluents. *Anal. Chim. Acta* **1972**, *62* (2), 325−335.

(110) Aratono, Y.; Akatsu, E. Liquid-Liquid Extraction of Several Elements in the System of Fused Ca(NO₃)₂. 4H₂O and Tri-n-Butyl Phosphate. *J. Inorg. Nucl. Chem.* **1974**, *36* (5), 1141−1146.

(111) Fujii, T.; Okude, G.; Uehara, A.; Sekimoto, S.; Hayashi, H.; Akabori, M.; Minato, K.; Yamana, H. Coordination Characteristics of Trivalent Lanthanides and Actinides in Molten Hydrate Salts of

Ca(NO₃)₂ and CaCl₂. *J. Radioanal. Nucl. Chem.* **2011**, *288* (1), 181−187.

(112) Yamana, H.; Kaibuki, T.; Moriyama, H. Distribution Equilibrium of Lanthanides in the Liquid-Liquid Extraction System of TBP and Molten Ca(NO₃)₂·4H₂O. *Radiochim. Acta* **1999**, *84* (4), 191−200.

(113) Yamana, H.; Kaibuki, T.; Miyashita, Y.; Shibata, S.; Moriyama, H. Equilibrium Distributions of Trivalent Actinides and Lanthanides in the Liquid-Liquid Extraction System of TBP and Molten Ca(NO₃)₂·4H₂O. *J. Alloys Compd.* **1998**, *271−273*, 707−711.

(114) Yamana, H.; Asano, H.; Fujii, T.; Goto, R.; Moriyama, H. TBP Extraction of Lanthanides from Molten Calcium Nitrate Hydrate. *Radiochim. Acta* **2002**, *90* (2), 87−94.

(115) Fujii, T.; Asano, H.; Kimura, T.; Yamamoto, T.; Uehara, A.; Yamana, H. Spectroscopic Study of Trivalent Rare Earth Ions in Calcium Nitrate Hydrate Melt. *J. Alloys Compd.* **2006**, *408−412*, 989−994.

(116) Peppard, D. F.; Driscoll, W. J.; Sironen, R. J.; McCarty, S. Nonmonotonic Ordering of Lanthanides in Tributyl Phosphate-Nitric Acid Extraction Systems. *J. Inorg. Nucl. Chem.* **1957**, *4* (5−6), 326−333.

(117) Regueiro-Figueroa, M.; Esteban-Gómez, D.; de Blas, A.; Rodríguez-Blas, T.; Platas-Iglesias, C. Understanding Stability Trends along the Lanthanide Series. *Chem. - Eur. J.* **2014**, *20* (14), 3974−3981.

(118) Cosentino, U.; Villa, A.; Pitea, D.; Moro, G.; Barone, V. Extension of Computational Chemistry to the Study of Lanthanide-(III) Ions in Aqueous Solution: Implementation and Validation of a Continuum Solvent Approach. *J. Phys. Chem. B* **2000**, *104* (33), 8001−8007.

(119) Davis, W., Jr.; De Bruin, H. J. New Activity Coefficients of 0−100% Aqueous Nitric Acid. *J. Inorg. Nucl. Chem.* **1964**, *26* (6), 1069−1083.

(120) Rout, A.; Binnemans, K. Separation of Rare Earths from Transition Metals by Liquid-Liquid Extraction from a Molten Salt Hydrate to an Ionic Liquid Phase. *Dalton Trans.* **2014**, *43* (8), 3186−3195.

(121) Preston, J. S.; Du-Preez, A. C. Solvent Extraction Processes for the Separation of Rare Earth Metals. In *Solvent Extraction 1990*; Sekine, T., Ed.; Elsevier Science Publishers B.V.: Amsterdam, 1992; pp 883−894.

(122) Larsson, K.; Binnemans, K. Separation of Rare Earths by Split-Anion Extraction. *Hydrometallurgy* **2015**, *156*, 206−214.

(123) Arce, A.; Earle, M. J.; Katdare, S. P.; Rodríguez, H.; Seddon, K. R. Mutually Immiscible Ionic Liquids. *Chem. Commun.* **2006**, No. 24, 2548−2550.

(124) Arce, A.; Earle, M. J.; Katdare, S. P.; Rodríguez, H.; Seddon, K. R. Phase Equilibria of Mixtures of Mutually Immiscible Ionic Liquids. *Fluid Phase Equilib.* **2007**, *261* (1−2), 427−433.

(125) Annat, G.; Forsyth, M.; MacFarlane, D. R. Ionic Liquid Mixtures-Variations in Physical Properties and Their Origins in Molecular Structure. *J. Phys. Chem. B* **2012**, *116* (28), 8251−8258.

(126) Omar, S.; Lemus, J.; Ruiz, E.; Ferro, V. R.; Ortega, J.; Palomar, J. Ionic Liquid Mixtures - An Analysis of Their Mutual Miscibility. *J. Phys. Chem. B* **2014**, *118* (9), 2442−2450.

(127) Neves, C. M. S. S.; Silva, A. M. S.; Fernandes, A. M.; Coutinho, J. A. P.; Freire, M. G. Toward an Understanding of the Mechanisms behind the Formation of Liquid−Liquid Systems Formed by Two Ionic Liquids. *J. Phys. Chem. Lett.* **2017**, *8* (13), 3015−3019.

(128) Shimomura, T.; Sugiyama, M. Phase Behavior of Imidazolium-Based Ionic Liquid + Phosphonium-Based Ionic Liquid Mixtures with a Common Anion: Effects of the Alkyl-Chain Length of Cation. *J. Chem. Eng. Data* **2018**, *63* (2), 402−408.

(129) Wellens, S.; Thijs, B.; Moller, C.; Binnemans, K. Separation of Cobalt and Nickel by Solvent Extraction with Two Mutually Immiscible Ionic Liquids. *Phys. Chem. Chem. Phys.* **2013**, *15* (24), 9663−9669.

(130) Preston, J. S. Solvent Extraction of Cobalt and Nickel by Organophosphorus Acids I. Comparison of Phosphoric, Phosphonic and Phosphinic Acid Systems. *Hydrometallurgy* **1982**, *9* (2), 115−133.

(131) Rout, A.; Wellens, S.; Binnemans, K. Separation of Rare Earths and Nickel by Solvent Extraction with Two Mutually Immiscible Ionic Liquids. *RSC Adv.* **2014**, *4* (11), 5753−5758.

(132) Vander Hoogerstraete, T.; Blockx, J.; De Coster, H.; Binnemans, K. Selective Single-Step Separation of a Mixture of Three Metal Ions by a Triphasic Ionic-Liquid−Water−Ionic-Liquid Solvent Extraction System. *Chem. - Eur. J.* **2015**, *21* (33), 11757−11766.

(133) Ammon, R. V. Die Verteilung Einiger Kationen Zwischen Den Unmischbaren Flüssigen Phasen Im System AlBr₃−KBr. *J. Inorg. Nucl. Chem.* **1966**, *28* (11), 2569−2578.

(134) Smith, F. J. Distribution of PdBr₂, RhBr₃ and RuBr₃ between the Two Immiscible Liquid Phases in the AlBr₃-KBr System. *J. Less-Common Met.* **1984**, *97*, 21−26.

(135) Moore, R. H. Distribution Coefficients for Certain Actinide and Fission Product Chlorides in the Immiscible Salt System: LiCl−KAlCl₄. *J. Chem. Eng. Data* **1964**, *9* (4), 502−505.

(136) Greaves, T. L.; Drummond, C. J. Protic Ionic Liquids: Properties and Applications. *Chem. Rev.* **2008**, *108* (1), 206−237.

(137) Li, Z.; Binnemans, K. Ethylammonium Nitrate Enhances the Extraction of Transition Metal Nitrates by Tri-*n*-Butyl Phosphate. *AIChE J.* **2021**, *67*, e17213.

(138) Li, Z.; Binnemans, K. Hydration Counteracts the Separation of Lanthanides by Solvent Extraction. *AIChE J.* **2020**, *66* (9), e16545.

(139) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114* (21), 11060−11082.

(140) Foreman, M. R. S. Progress towards a Process for the Recycling of Nickel Metal Hydride Electric Cells Using a Deep Eutectic Solvent. *Cogent Chem.* **2016**, *2* (1), 1139289−1139299.

(141) Foreman, M. R. S. J.; Holgersson, S.; McPhee, C.; Tyumentsev, M. S. Activity Coefficients in Deep Eutectic Solvents: Implications for the Solvent Extraction of Metals. *New J. Chem.* **2018**, *42* (3), 2006−2012.

(142) Cen, P.; Spahiu, K.; Tyumentsev, M. S.; Foreman, M. R. S. J. Metal Extraction from a Deep Eutectic Solvent, an Insight into Activities. *Phys. Chem. Chem. Phys.* **2020**, *22* (19), 11012−11024.

(143) Albler, F.-J.; Bica, K.; Foreman, M. R. S.; Holgersson, S.; Tyumentsev, M. S. A Comparison of Two Methods of Recovering Cobalt from a Deep Eutectic Solvent: Implications for Battery Recycling. *J. Cleaner Prod.* **2017**, *167*, 806−814.

(144) Riano, S.; Petranikova, M.; Onghena, B.; Vander Hoogerstraete, T.; Banerjee, D.; Foreman, M. R. S.; Ekberg, C.; Binnemans, K. Separation of Rare Earths and Other Valuable Metals from Deep-Eutectic Solvents: A New Alternative for the Recycling of Used NdFeB Magnets. *RSC Adv.* **2017**, *7* (51), 32100−32113.

(145) Lessing, J. G. V.; Brink, P. A.; Fouché, K. F. Influence of Cyanide on the Extraction of Transition Elements from Molten and Aqueous Thiocyanate with Quaternary Amines. *J. Inorg. Nucl. Chem.* **1973**, *35* (6), 2009−2015.

(146) Li, Z.; Onghena, B.; Li, X.; Zhang, Z.; Binnemans, K. Enhancing Metal Separations Using Hydrophilic Ionic Liquids and Analogues as Complexing Agents in the More Polar Phase of Liquid-Liquid Extraction Systems. *Ind. Eng. Chem. Res.* **2019**, *58* (34), 15628−15636.

(147) Estes, S. L.; Qiao, B.; Jin, G. B. Ion Association with Tetra-*n*-Alkylammonium Cations Stabilizes Higher-Oxidation-State Neptunium Dioxocations. *Nat. Commun.* **2019**, *10* (1), 59.

(148) Spathariotis, S.; Peeters, N.; Ryder, K. S.; Abbott, A. P.; Binnemans, K.; Riaño, S. Separation of Iron(III), Zinc(II) and Lead(II) from a Choline Chloride−Ethylene Glycol Deep Eutectic Solvent by Solvent Extraction. *RSC Adv.* **2020**, *10* (55), 33161−33170.

(149) Orefice, M.; Audoor, H.; Li, Z.; Binnemans, K. Solvometallurgical Route for the Recovery of Sm, Co, Cu and Fe from SmCo Permanent Magnets. *Sep. Purif. Technol.* **2019**, *219*, 281−289.

(150) Orefice, M.; Binnemans, K. Solvometallurgical Process for the Recovery of Rare-Earth Elements from Nd−Fe−B Magnets. *Sep. Purif. Technol.* **2021**, *258*, 117800.

(151) Peeters, N.; Binnemans, K.; Riaño, S. Solvometallurgical Recovery of Cobalt from Lithium-Ion Battery Cathode Materials Using Deep-Eutectic Solvents. *Green Chem.* **2020**, *22* (13), 4210−4221.

(152) Nguyen, V. T.; Riaño, S.; Aktan, E.; Deferm, C.; Fransaer, J.; Binnemans, K. Solvometallurgical Recovery of Platinum Group Metals from Spent Automotive Catalysts. *ACS Sustainable Chem. Eng.* **2021**, *9* (1), 337−350.

(153) Li, X.; Monnens, W.; Li, Z.; Fransaer, J.; Binnemans, K. Solvometallurgical Process for Extraction of Copper from Chalcopyrite and Other Sulfidic Ore Minerals. *Green Chem.* **2020**, *22*, 417−426.

(154) Monnens, W.; Deferm, C.; Sniekers, J.; Fransaer, J.; Binnemans, K. Electrodeposition of Indium from Non-Aqueous Electrolytes. *Chem. Commun.* **2019**, *55* (33), 4789−4792.