

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

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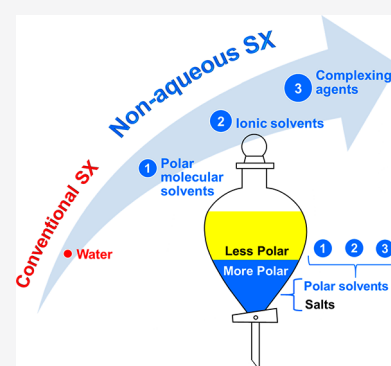
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**ABSTRACT:** Efficient and sustainable separation of metals is gaining increasing attention, because of the essential roles of many metals in sustainable technologies for a climate-neutral society, such as rare earths in permanent magnets and cobalt, 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,<sup>1–3</sup> base metals,<sup>4,5</sup> rare-earth elements (REEs),<sup>6–9</sup> actinides,<sup>10–12</sup> alkali and alkaline-earth metals,<sup>13–20</sup> 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.<sup>21</sup> 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 ( $\alpha$ ) are the most important parameters in solvent extraction. They are defined as follows:

$$D = \frac{c_{lp}}{c_{mp}} \quad (1)$$

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

$$\alpha = \frac{D_A}{D_B} \quad (3)$$

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;<sup>22–25</sup> (2) using a second extractant to enable synergism (synergistic solvent extraction);<sup>4,13,26</sup> (3) adding modifiers to prevent the third phase formation or enhance stripping;<sup>27–29</sup> and (4) changing diluents.<sup>30,31</sup>

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,

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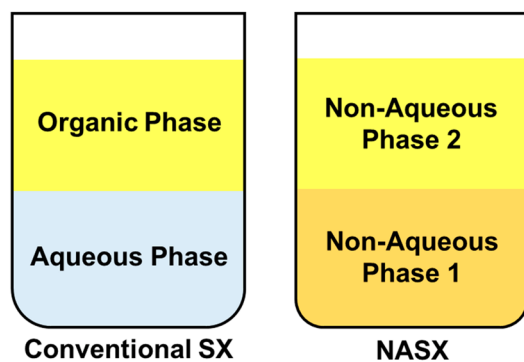
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e.g., lactic acid, EDTA, in the aqueous phase to selectively complex metal ions to enhance the separation. The most notable process using this approach is the TALSPEAK process used in the processing of spent nuclear fuel, where the separation of lanthanides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

Researchers have also observed that the addition of polar organic solvents to the aqueous solution modifies the extraction behavior.<sup>35–41</sup> 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.<sup>42</sup> Later, the two phases are renamed the “*more polar phase*” and the “*less polar phase*” by Batchu et al.<sup>43</sup> The addition of polar organic solvents influences the extraction performance from several dimensions:<sup>44</sup> (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  $\text{SbCl}_5$ , which is a standard Lewis acid.<sup>45</sup> 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).<sup>46</sup> 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.

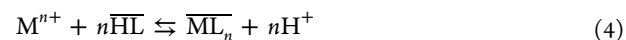
NASX is largely different from SX from aqueous solutions, and enhanced separations compared to conventional SX systems are often observed. However, strictly anhydrous conditions are not required to perform NASX, the presence of a small quantity of water in a NASX system is not only tolerable but can 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

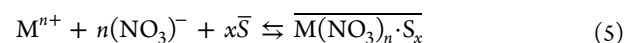
There are four main types of extractants in SX systems, namely, acidic extractants (cation exchangers), neutral extractants (solvating extractants), basic extractants (anion exchangers), and binary extractants (acid–base extractants). Each type of extractant extracts metal ions via different mechanisms,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



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



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  $\text{NR}_4\text{Cl}$ , Figure 2) as an example. The extraction reaction from chloride media is

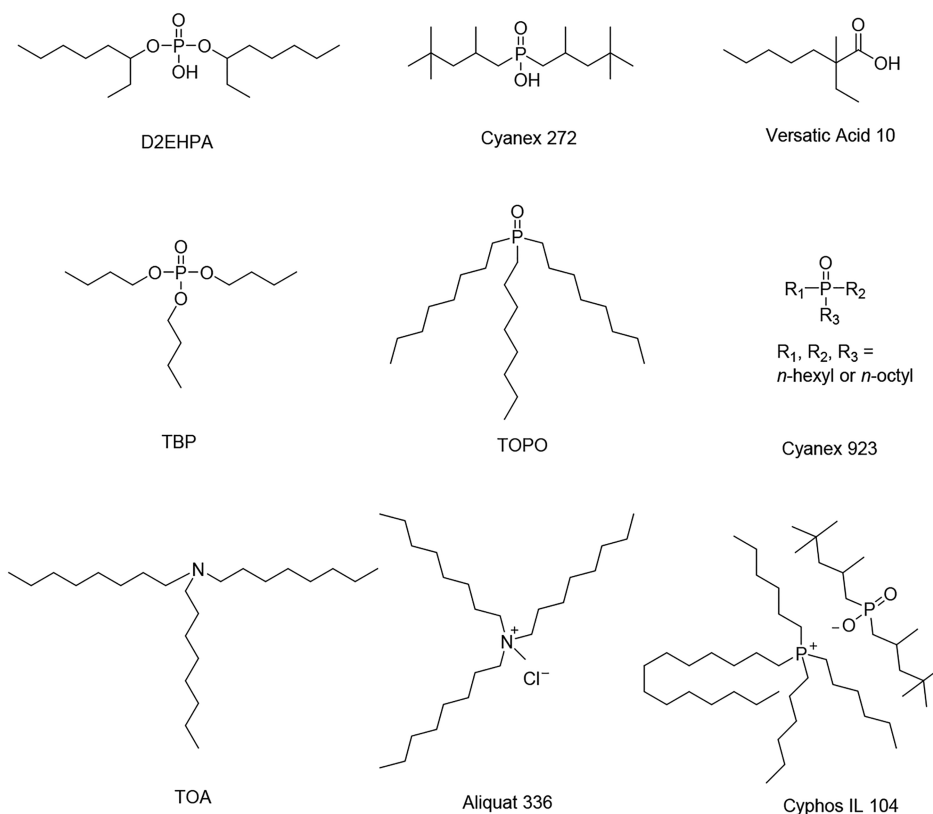
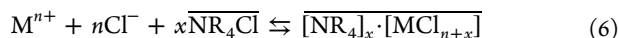
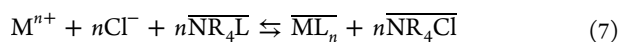


Figure 2. Structures of typical extractants.



Although it is disputable whether the anionic complex is the most extractable species in the aqueous phase,<sup>49</sup> 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*.<sup>48</sup> 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  $\overline{NR_4L}$ ) from chloride media can be written as



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.<sup>50,51</sup>

### 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,  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$ , which represent the energy from dispersion force, dipolar intermolecular force, and hydrogen bonds between molecules, respectively, are utilized. The total parameter of a compound,  $\delta_T$ , 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.<sup>52</sup> 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  $\delta_p$  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.<sup>53</sup> 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 ( $\epsilon$ ). 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.,  $\text{Ca}(\text{NO}_3)_2$ ), the change of volumes of the two immiscible phases can be non-negligible.<sup>54</sup> For this reason, alkali-metal salts, such as  $\text{LiNO}_3$  or  $\text{KNO}_3$ , are preferred for molten inorganic salts, because of their low extractability.<sup>55</sup> 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.,  $\text{LiCl}$ ,  $\text{LiNO}_3$ ) 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.<sup>56</sup>

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<sup>57–61</sup> and electrolytes,<sup>62,63</sup> and some predictive models for phase equilibria of nonelectrolytes.<sup>64,65</sup> 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.<sup>66</sup> The utilization of NASX instead of a conventional organic/water SX system was driven by the fact that  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  hydrolyze strongly in aqueous solutions, which can be avoided when less-reactive solvents than water are used. Both  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  preferentially resided in the acetonitrile phase and a separation factor  $\alpha_{\text{Hf/Zr}}$  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.<sup>67</sup> All the salts distributed mainly in the more polar phase, except for  $\text{SnCl}_4$ , 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,  $\text{SnCl}_4$ , as a Lewis acid, can react readily with organic Lewis bases, such as diethyl ether,<sup>68</sup> leading to a higher distribution ratio of  $\text{SnCl}_4$ .

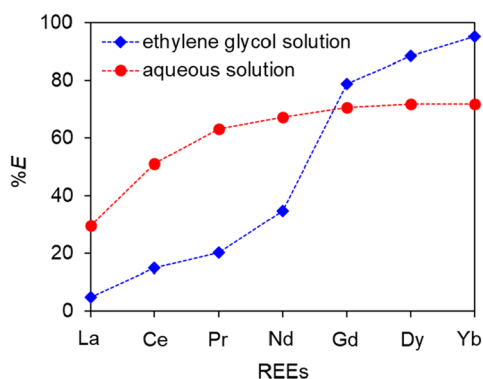
A two-phase system formed by methyl isobutyl ketone (MIBK) and formamide was used to separate Tl(III) from In(III), Ga(III), Fe(III), Sn(II), and Sn(IV).<sup>69</sup> These metals were first loaded to MIBK from an aqueous phase containing 2.0 mol L<sup>-1</sup> HBr, presumably as ion pairs (i.e.,  $[\text{H}(\text{MIBK})_2][\text{TlBr}_4]$ ), 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  $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ .<sup>70,71</sup> 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.,  $\text{Li} > \text{Na} > \text{K} > \text{Cs}$ .<sup>72</sup> 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,<sup>73,74</sup> 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.<sup>71</sup>

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.<sup>75,76</sup> The same trend was observed for the extraction of

Mn(II) by TOPO from EG solutions.<sup>77</sup> 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.<sup>78,79</sup> 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.<sup>75</sup>

Batchu et al. developed a NASX system that showed superior separation of rare-earth elements (REEs).<sup>43</sup> 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,

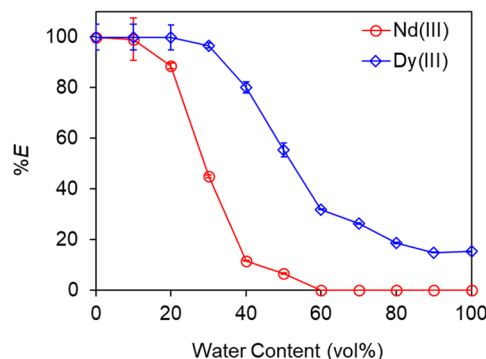


**Figure 3.** Separation of REEs by Cyanex 923 from aqueous and ethylene glycol solutions. [Adapted from Batchu et al.<sup>43</sup>]

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.<sup>80</sup> 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

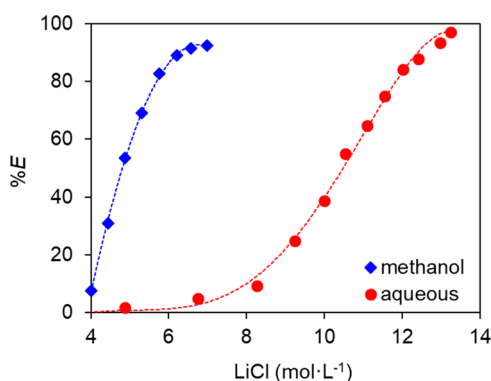
from aqueous solutions.<sup>81</sup> EG, PG, and poly(ethylene glycol) 200 (PEG 200) were tested as the solvent of the more polar phase for the separation of Eu(III) and Y(III) in chloride media by Cyanex 923. The extraction efficiency followed this order:  $PEG\ 200 > PG > EG > water$ . Despite higher 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.<sup>82</sup> 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).<sup>83</sup> 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.<sup>83</sup>]

extracted complex from the PEG 200 system was found to be  $[LnCl_3 \cdot L_4]$  ( $L$  represents Cyanex 923),<sup>83</sup> which is the same as the complexes formed in the extraction from the EG system.<sup>81</sup> 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.<sup>84</sup> 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.<sup>44,85</sup> Similar enhancement of



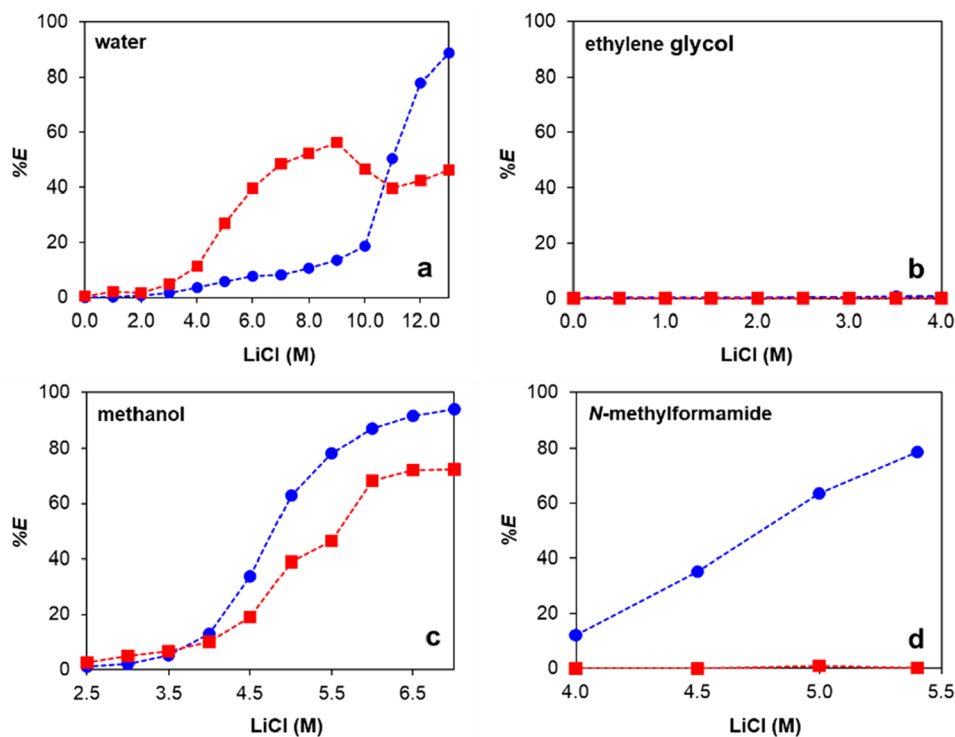
**Figure 5.** Extraction of Ni(II) from aqueous and methanolic solutions by Alamine 336. Data were taken from Florence and Farrar.<sup>84</sup>

the extraction by TOA was observed for Mn(II), Cr(III), and Th(IV) halides.<sup>86</sup> 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  $[\text{MnX}_4]^{2-}$  and  $[\text{CrX}_5]^{2-}$ , respectively, whereas Th(IV) was likely polymerized in the TOA phase. Extraction of  $\text{CuCl}_2$  from methanol solutions by the secondary amine bis(3,5,5-trimethylhexyl)ammonium chloride also proceeded via the formation of the tetrachlorocuprate(II) anion  $[\text{CuCl}_4]^{2-}$ .<sup>87</sup> However, the extraction was very low ( $D_{\text{Cu}} < 0.3$ ), 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.<sup>88</sup> 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  $[\text{HCl}_2]^-$ . Second,  $[\text{ZnCl}_4]^{2-}$  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.<sup>49</sup> The extraction of Zn(II) and Cd(II) as a function of LiCl concentration also showed a maximum,<sup>88</sup> 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  $[\text{ZnCl}_4]^{2-}$  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  $[\text{CoCl}_4]^{2-}$ . 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<sup>-1</sup>).<sup>89</sup> 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.<sup>90</sup> 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.<sup>89</sup>]

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.<sup>91</sup> The species of In(III) in EG was found to change from the bridging  $(\text{InCl}_3)_2(\text{EG})_3$  or mononuclear  $(\text{InCl}_3)(\text{EG})_2$  complex at low LiCl concentrations to  $[\text{In}(\text{EG})\text{Cl}_4]^-$  at high LiCl concentrations.<sup>91</sup> In contrast, In(III) exists in aqueous HCl solution as mixed octahedral complexes,  $[\text{In}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]^{3-n}$ , in which  $n$  increases from 0 to 6 as the concentration of HCl increases in the range of 0–12 mol L<sup>-1</sup>.<sup>92</sup> Given the presence of the same species of In(III) (i.e.,  $[\text{InCl}_4]^-$ ) 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.<sup>89</sup> 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.,  $[\text{CoCl}_4]^{2-}$ ). The strength for the formation of  $[\text{CoCl}_4]^{2-}$  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.,  $[\text{CoCl}_4]^{2-}$ ) are more stable in solvents of lower dielectric constants.<sup>89</sup> This observation is consistent with the above discussions on the effect of the dielectric constant. In contrast, Ln(III) coordinates very weakly to Cl<sup>-</sup> ions; hence, it is extracted to the LP phase as solvated cationic or neutral complex (i.e.,  $[\text{LnCl}_x]^{3-x}$ , 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.  $\text{KNO}_3$ – $\text{LiNO}_3$  Eutectic.** **4.1.1.1. Neutral Extractants.** Isaac et al. were the first to explore the use of a  $\text{KNO}_3$ – $\text{LiNO}_3$  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.<sup>55</sup> 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  $\text{KNO}_3$ – $\text{LiNO}_3$  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 ( $(\text{C}_6\text{H}_5)_2\text{PO}(\text{CH}_2)_n\text{PO}(\text{C}_6\text{H}_5)_2$ ,  $n = 2, 3, 4, 6$ , and denoted as *n*-DPO, respectively) at 160 °C.<sup>93</sup> 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.<sup>94</sup> However, the performance of these NASX systems was not compared with the corresponding aqueous SX systems.

Extraction of  $\text{HgX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ , or a mixture of any two anions) from the  $\text{KNO}_3$ – $\text{LiNO}_3$  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.<sup>95–97</sup>  $\text{HgX}_2$  exists in the molten eutectic salt as  $[\text{HgX}_2(\text{NO}_3)_2]^{2-}$ , but was extracted as the covalent  $\text{HgX}_2$  into the polyphenyl eutectic. The extraction of  $\text{HgX}_2$  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  $\text{KNO}_3$  and  $\text{LiNO}_3$  mixtures (in the same ratio as the  $\text{KNO}_3$ – $\text{LiNO}_3$  eutectic) to aqueous solutions linearly increased the  $D_{\text{HgCl}_2}$ ; and (2) extrapolation of  $D_{\text{HgCl}_2}$  to 90 °C for the extraction from the  $\text{KNO}_3$ – $\text{LiNO}_3$  eutectic intersects with the extrapolation of  $D_{\text{HgCl}_2}$  at the same temperature from aqueous solution to full salt (same as the  $\text{KNO}_3$ – $\text{LiNO}_3$  eutectic). The linearity of “salting-out” of  $\text{HgX}_2$  is due to the

covalent binding of  $\text{HgX}_2$ , whereas many other salts are hydrated in aqueous solutions. The extraction of  $\text{HgX}_2$  by the polyphenyl eutectic as covalent molecules is similar to the extraction of solid  $\text{GaCl}_3$  as covalent dimers by aliphatic hydrocarbons, although the latter extraction must be performed under anhydrous conditions, because of the water sensitivity of  $\text{GaCl}_3$ .<sup>98</sup>

**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  $[\text{ReO}_4]^-$  and  $[\text{AgCl}_2]^-$  from the  $\text{KNO}_3\text{--LiNO}_3$  eutectic in the presence of  $\text{KCl--LiCl}$  salts at 150 °C. The extraction was found to proceed as an anion exchange, i.e.,  $[\text{ReO}_4]^-$  and  $[\text{AgCl}_2]^-$  exchange with  $[\text{NO}_3]^-$  of THAN or TOPN, similar to extraction from aqueous solutions.<sup>99,100</sup>

**4.1.1.3. Synergistic Solvent Extraction.** Extraction of some REEs from  $\text{KNO}_3\text{--LiNO}_3$  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.<sup>101</sup> 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.<sup>102</sup> 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  $[\text{Fe}(\text{SCN})_6]^{3-}$ ,  $[\text{Co}(\text{SCN})_4]^{2-}$ , and  $[\text{Ni}(\text{SCN})_4]^{2-}$ , respectively. The extracted species were the same as in the eutectic phase but charge neutrality was achieved by solvated  $\text{Na}^+$  or  $\text{K}^+$  ions, e.g.,  $[\text{Na}(\text{TBP})_x]_2[\text{Co}(\text{SCN})_4]$ . This is not the conventional solvation mechanism, but it is similar to the synergistic extraction of  $\text{Li}^+$  by TBP and Fe(III) from aqueous chloride media in the form of  $[\text{Li}(\text{TBP})_x][\text{FeCl}_4]^{103}$

Zn(II) was extracted from KSCN at 195 °C by TOPO and several other uncommon neutral extractants dissolved in phenanthrene.<sup>104</sup> The extracted species was proposed to be  $\text{Zn}(\text{TOPO})_2(\text{SCN})_2$ . 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 ( $[\text{NR}_2\text{H}_2][\text{SCN}]$ ) dissolved in chloronaphthalene in the form of  $[\text{NR}_2\text{H}_2]_2[\text{Co}(\text{SCN})_4]$  via an anion exchange mechanism.<sup>105</sup>

**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.<sup>106</sup> 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.,  $[(\text{TOA})_2\text{Cu}][\text{CuCl}_2]$ , hindering the extraction

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

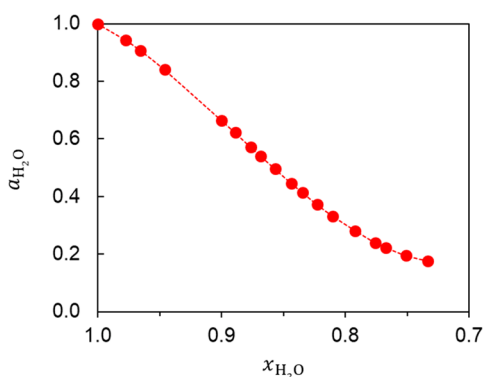
**4.1.4. CsOAc–NaOAc–KOAc Eutectic.** Extraction of Cr(III), Fe(II), Co(II), and Ni(II) from molten cesium acetate–sodium acetate–potassium acetate eutectic (50–25–25 mol %) at 140–180 °C into *n*-dodecane solutions containing Cyanex 272, D2EHPA, or TOPO was studied.<sup>107</sup> The metal cations in 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:  $\text{Co(II)} > \text{Fe(II)} > \text{Cr(III)} > \text{Ni(II)}$ . 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  $\text{KNO}_3\text{--LiNO}_3$  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.

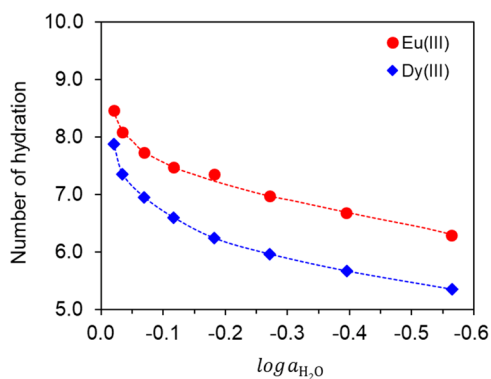
Extraction of lanthanides and actinides by TBP from molten nitrate hydrates was more efficient than from typical aqueous solutions.<sup>108–112</sup> As the complexes in the LP phase extracted from molten nitrate hydrates or aqueous solutions are identical, the improved extraction was attributed to the increased chemical activity of the nitrate ions due to the water deficiency of the system.<sup>108,110,112</sup> TBP is poorly soluble in the molten hydrates. For example, the solubility of TBP in  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is only 0.05 g L<sup>-1</sup> at 45 °C.<sup>118</sup> However, the nitrate salts are well extractable to the TBP phase, e.g., up to 1.45 mol L<sup>-1</sup>  $\text{Mn}(\text{NO}_3)_2$  is extracted into pure TBP, leading to a 10% volume increase of the TBP phase.<sup>54</sup> 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  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  can be neglected only when the concentration of TBP in the less polar phase is lower than 0.10 mol L<sup>-1</sup>.<sup>112</sup>

As water is the dominating component in molten hydrates, in terms of mole fraction (e.g.,  $x_{\text{H}_2\text{O}}$  is 0.8 in  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), the water activity in molten melts is not as low as one might expect (e.g.,  $a_{\text{H}_2\text{O}}$  is  $\sim 0.30$  in  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ <sup>113</sup>). The water activity of  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  ( $n$  is the number of water molecules), as a function of the water mole fraction at 70 °C, has been given in Figure 7.<sup>114</sup> The water activity decreases with decreasing water mole fraction, from 1.0 for pure water to  $\sim 0.30$  for  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and further decreases in a slower manner to  $<0.20$ . The relatively low water activity of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , or water deficiency, explains the higher extraction of metals from molten nitrate hydrates than from aqueous solutions. However, metal ions in  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$





**Figure 7.** Water activity in  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ , as a function of water mole fraction at 70 °C. [Data were taken from Yamana et al.<sup>114</sup>]



**Figure 8.** Hydration number of Eu(III) and Dy(III) in  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  at 50 °C. [Adapted from Fujii et al.<sup>115</sup>]

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).<sup>115</sup> 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  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , which is still significant. The extraction of lanthanides from  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  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  $\text{KNO}_3$ – $\text{LiNO}_3$  eutectic and highly concentrated nitric acid solutions (e.g., 18.5 mol L<sup>-1</sup>  $\text{HNO}_3$ ) increased monotonically.<sup>54,112,116</sup> 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.<sup>117,118</sup> The water activity in highly concentrated nitric acid solution is lower than that of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; for example,  $a_{\text{H}_2\text{O}}$  is 0.19 in 15 mol L<sup>-1</sup>  $\text{HNO}_3$  solution.<sup>119</sup> 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.<sup>111</sup> The water content in  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  also affects the reaction rate. Equilibrium of REEs extraction by TBP from  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  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.<sup>114</sup>

Extraction of REEs from  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  by  $[\text{A336}][\text{NO}_3]$  at 53 °C was investigated by Rout and Binnemans.<sup>120</sup> 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.<sup>121,122</sup> The decrease of extraction efficiency might be explained by the hydration of REEs in the molten nitrate hydrates, as studies by Fujii et al.<sup>115</sup> indicate; these studies show that there are still 5–7 water molecules hydrated to REEs in molten  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Furthermore, the addition of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or water to  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  both reduce the extraction efficiency, because of the increase in water activity. The loading of Ca(II) to the  $[\text{A336}][\text{NO}_3]$  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<sup>-1</sup> Nd(III) could be loaded to the  $[\text{A336}][\text{NO}_3]$  phase.

**4.2.2. Molten Chloride Hydrates.** Molten chloride hydrates, such as  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , were also used as the solvent of the MP phase in the extraction of lanthanides, actinides, and some fission products by TBP and  $[\text{A336}][\text{Cl}]$ .<sup>54,111,120</sup> The extraction of actinides and lanthanides was much less efficient than from molten nitrate hydrates, because these elements are less able to coordinate to  $\text{Cl}^-$  ions than to nitrate ions.<sup>85</sup> 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<sup>-1</sup> was loaded to 75 vol % TBP.<sup>54</sup>

**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.<sup>123</sup> discovered three types of biphasic ILs mixtures: (1) a hydrophobic and a hydrophilic IL that share the same anion, e.g.,  $[\text{P}_{666,14}]\text{Cl}$  and  $[\text{C}_n\text{mim}]\text{Cl}$  (where  $n < 6$ ); (2) two hydrophobic ILs with a common anion, e.g.,  $[\text{C}_2\text{mim}][\text{NTf}_2]$  and  $([\text{P}_{666,14}][\text{NTf}_2])$ ; and (3) two ILs with four different ions, e.g.,  $[\text{C}_2\text{mim}][\text{OSO}_2\text{CH}_3]$  and  $[\text{P}_{666,14}][\text{PO}_2(\text{C}_8\text{H}_{17})_2]$ . Many more biphasic ILs were created afterward.<sup>124–128</sup> While both the anions and the cations affect the formation of biphasic IL systems,<sup>128</sup> 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.<sup>127</sup> 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.<sup>129</sup> 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  $[\text{C}_2\text{mim}]\text{Cl}$ . Co(II) and Ni(II) formed  $[\text{CoCl}_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$ , respectively, in the  $[\text{C}_2\text{mim}]\text{Cl}$  phase. Co(II) was efficiently extracted as  $[\text{Co}(\text{R}_2\text{POO})_2]$ , 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.<sup>130</sup> 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<sub>2</sub>mim]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.<sup>131</sup> REEs in the [C<sub>2</sub>mim]Cl phase were expected to form anionic [LnCl<sub>6</sub>]<sup>3-</sup> complexes, because of the absence of water, although the speciation was not comprehensively characterized. All tested REEs were efficiently extracted from the [C<sub>2</sub>mim]Cl phase to the Cyphos IL 104 phase, and could also be separated from Ni(II).

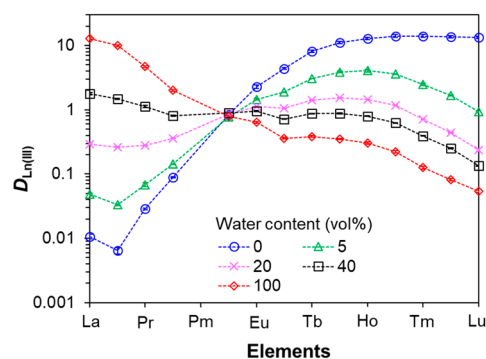
Biphasic IL systems can further form three- or four-phase immiscible liquid systems with water and a nonpolar alkane, such as the pentane–[P<sub>666,14</sub>][NTf<sub>2</sub>]<sup>-</sup>–water–[C<sub>2</sub>mim][NTf<sub>2</sub>] system.<sup>123</sup> Vander Hoogerstraete et al.<sup>132</sup> made use of the triphasic [Hbet][NTf<sub>2</sub>]<sup>-</sup>–H<sub>2</sub>O–[P<sub>666,14</sub>][NTf<sub>2</sub>] system to separate Sn(II), Y(III), and Sc(III), which were enriched in the [Hbet][NTf<sub>2</sub>] phase, the aqueous phase, and the [P<sub>666,14</sub>][NTf<sub>2</sub>] phase, respectively. Strictly speaking, the IL–H<sub>2</sub>O–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<sub>3</sub> form two immiscible phases, with one phase being mainly AlBr<sub>3</sub> (>99% mol %) and the other phase having ~20 mol % AlBr<sub>3</sub> 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<sub>3</sub>-rich phase, facilitating the separation of different types of metal halides.<sup>133</sup> The highest separation factor was found for Cs(I)/Zr(IV), reaching 126. Smith investigated the distribution of PdBr<sub>2</sub>, RhBr<sub>3</sub>, and RuBr<sub>3</sub> 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<sub>4</sub>]<sup>2-</sup> and [RuBr<sub>6</sub>]<sup>2-</sup> were the main species in both phases, as determined by the spectroscopic study.<sup>134</sup> The ternary system LiCl–KCl–AlCl<sub>3</sub> could form two immiscible polar phases with the KAlCl<sub>4</sub> phase on the top and the LiCl phase at the bottom. Distributions of some metal chlorides and oxychlorides (UO<sub>2</sub>Cl<sub>2</sub>) in this system were determined by Moore.<sup>135</sup> 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).<sup>136</sup> 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.<sup>137</sup> 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<sub>3</sub>–LiNO<sub>3</sub> eutectic by TBP. The main

species of Co(II) and Fe(III) in EAN were proposed as [Co(NO<sub>3</sub>)<sub>4</sub>]<sup>2-</sup> and [Fe(NO<sub>3</sub>)<sub>4</sub>]<sup>-</sup>, 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<sub>2</sub>O 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<sub>3</sub>)<sub>4</sub>]<sup>2-</sup> in EAN to [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> 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<sub>3</sub>]).<sup>138</sup> The extraction of lanthanides by [A336][NO<sub>3</sub>] from aqueous nitrate solutions shows a negative sequence (i.e., light lanthanides are more efficiently extracted than heavy lanthanides),<sup>121,122</sup> 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<sub>3</sub>] 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.<sup>138</sup>]

positive to negative sequences reveals that the negative sequence is caused by the hydration of lanthanide ions.<sup>138</sup>

This observation is consistent with the effect of water on lanthanides extraction from molten nitrate hydrates.<sup>120</sup> The EAN–[A336][NO<sub>3</sub>] 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.<sup>139</sup> Foreman investigated the extraction of metals from the lactic acid–choline chloride-based DES.<sup>140</sup> 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  $\text{Cl}^-$  ion concentration (and, hence, its activity) as the DES-to-water ratio changes in the DES-water mixture.<sup>141,142</sup> 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  $\text{CoL}_2$  (where L represents a lactate anion).<sup>143</sup> 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,<sup>140</sup> 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.<sup>144</sup> 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  $[\text{Fe}(\text{SCN})_6]^{3-}$  from aqueous solutions, it was extracted as  $[\text{FeCl}_4]^-$  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  $\text{Cl}^-$  to the  $\text{KNO}_3$ – $\text{LiNO}_3$  eutectic<sup>55</sup> or EAN<sup>137</sup> 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.,  $[\text{CoCl}_4]^{2-}$ ) in the MP phase. Extraction of Hg(II) from the  $\text{KNO}_3$ – $\text{LiNO}_3$  eutectic by polyphenyl is also subject to the formation of chlorometallate complexes (e.g.,  $[\text{HgCl}_3]^-$ ,  $[\text{HgCl}_4]^{2-}$ ) upon the addition of LiCl.<sup>95,97</sup> However, the addition of  $\text{Cl}^-$  to the KSCN–NaSCN eutectic does not reduce the extraction of transition metals,<sup>102</sup> because transition metals preferentially coordinate to thiocyanate ions.<sup>85</sup> Nevertheless, the addition of a small amount of cyanide ions significantly lowers the extraction of transition metals by both neutral phosphorus extractants<sup>104</sup> and quaternary ammonium salts,<sup>145</sup> 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:  $\text{CN}^- > \text{SCN}^- > \text{Cl}^- > \text{NO}_3^-$ .<sup>85</sup>

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).<sup>137</sup> The separation factors of metal pairs with 0.50 mol  $\text{L}^{-1}$  LiCl in the MP phase are given in Table 1. Again, take

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

	$\alpha_{\text{M1}/\text{M2}}$	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  $[\text{Co}(\text{NO}_3)_4]^{2-}$  in the feed phase to  $[\text{CoCl}_4]^{2-}$ . The latter is more stable, hence more difficult to be extracted by TBP as  $[\text{Co}(\text{NO}_3)_2(\text{TBP})_x]$  ( $x = 2, 3$ ). These transition metals have different capabilities to coordinate to  $\text{Cl}^-$  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  $[\text{N}_{2222}]_2[\text{CoCl}_4]$  without affecting the extraction of Sm(III), leading to highly efficient separation of the two elements (Figure 10).<sup>146</sup> However, the role of the cations, i.e., why  $[\text{N}_{2222}]^+$  is more efficient than  $\text{Li}^+$  to stabilize  $[\text{CoCl}_4]^{2-}$  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.<sup>147</sup> 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),<sup>144</sup> the Cyanex 923 and DES system for the separation of Fe(III) from Zn(II) and Pb(II),<sup>148</sup> and the Cyanex 923 and EG system for the separation of Y(III) and Eu(III).<sup>82</sup>

Complete solvometallurgical processes (Figure 11) have not been developed, yet efforts have been made toward this end.

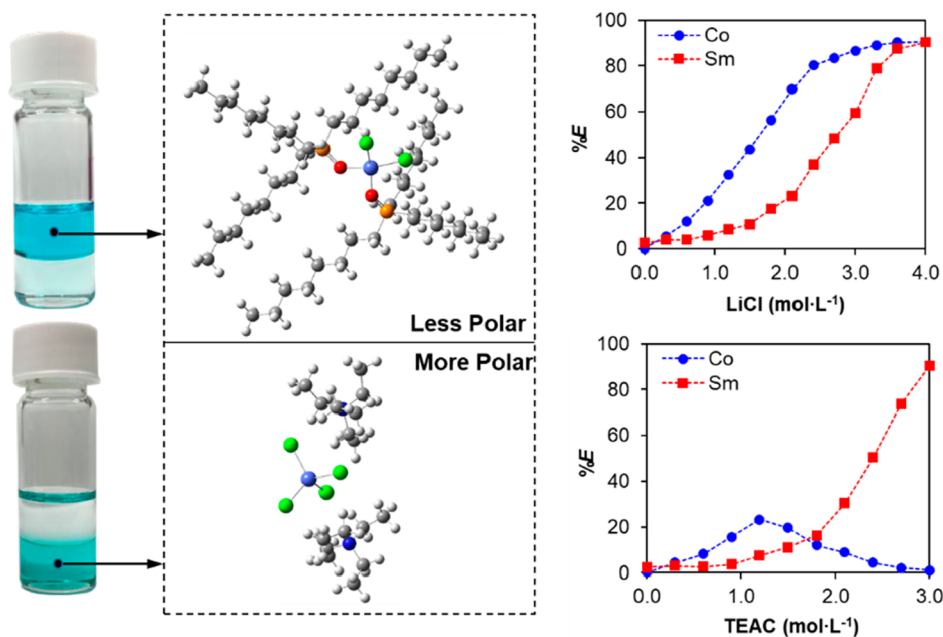


Figure 10. Addition of TEAC to EG solution enhances the separation of Co(II) and Sm(III). [Adapted from Li et al.<sup>146</sup>]

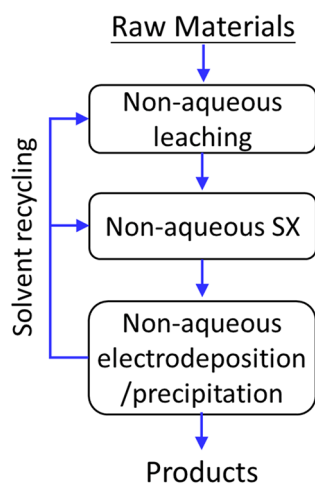


Figure 11. Flowsheet of a solvometallurgical process.

Orefice et al. used a mixture of aqueous HCl and EG to leach Co–Sm permanent magnets.<sup>149</sup> 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.<sup>150</sup> 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<sub>3</sub> 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).<sup>144</sup> 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<sub>2</sub>).<sup>151</sup> 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<sub>2</sub> 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.<sup>152</sup> After two steps of solvleaching of the automotive catalysts using acetonitrile and FeCl<sub>3</sub>, 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<sup>153</sup> and PEG 400 solution,<sup>154</sup> 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.,  $[\text{ZnCl}_4]^{2-}$ ) 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  $[\text{A336}][\text{NO}_3]$  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  $[\text{A336}][\text{NO}_3]$  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

### 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)

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

*a* = activity

Alamine 336 = *N,N*-dioctyl-1-octanamine, also known as tri-*n*-octyl amine (TOA)

Aliquat 336 = tricaprilmethylammonium 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<sub>666,14</sub>]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-dodecylsilylaldoxime) and LIX 84 (2-hydroxy-5-nonylaceto-phenone 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<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PO-(CH<sub>2</sub>)<sub>*n*</sub>PO(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
 NMF = *N*-methylformamide  
 NR<sub>4</sub>Cl = quaternary ammonium chloride  
 NR<sub>4</sub>L = 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<sub>2222</sub>]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 = C<sub>9</sub>–C<sub>10</sub> aromatic hydrocarbon solvent  
 UCST = upper critical solution temperature  
 Versatic Acid 10 = a mixture of carboxylic acids with the common structural formula C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>  
 vol % = volume percent  
 wt % = weight percent  
*x* = mole fraction  
 α = separation factor  
 δ<sub>d</sub> = Hansen solubility parameter representing dispersion forces  
 δ<sub>p</sub> = Hansen solubility parameter representing intermolecular forces  
 δ<sub>h</sub> = Hansen solubility parameter representing hydrogen bonding forces  
 δ<sub>T</sub> = total Hansen solubility parameter  
 %E = percentage extraction  
 [A336][NO<sub>3</sub>] = Aliquat 336 nitrate  
 [C<sub>*n*</sub>mim]Cl = 1-alkyl-3-methylimidazolium chloride  
 [Hbet][NTf<sub>2</sub>] = betaine bis(trifluoromethylsulfonyl)imide  
 [NR<sub>2</sub>H<sub>2</sub>][SCN] = di-*n*-dodecylammonium thiocyanate

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