SEPARATIONS: MATERIALS, DEVICES AND PROCESSES

Opposite selectivities of tri-*n*-butyl phosphate and Cyanex 923 in solvent extraction of lithium and magnesium

Zheng Li [ORCID] | Koen Binnemans [ORCID]

Department of Chemistry, KU Leuven, Heverlee, Belgium

Correspondence
Zheng Li, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, bus 2404, B-3001 Heverlee, Belgium.
Email: zheng.li@kuleuven.be

Abstract

The synergic solvent extraction system of tri-*n*-butyl phosphate (TBP) and $FeCl_3$ (or ionic liquids, ILs) has been extensively studied for selective extraction of Li from Mg-containing brines. However, Cyanex 923 (C923), which extracts many metals stronger than TBP, has not yet been examined for Li/Mg separation. Here, we report on the unexpected observation that the $C923/FeCl_3$ system has opposite Li/Mg selectivity compared to the $TBP/FeCl_3$ system. Detailed investigations show that the opposite selectivity of the $C923/FeCl_3$ (or IL) system is due to three factors: (1) the strong extraction of Fe by C923 leads to a low concentration of $[FeCl_4]^-$ in the system, which is essential for Li extraction; (2) C923 in combination with an IL extracts Mg strongly by an ion-pair mechanism; (3) most importantly, C923 extracts Mg by solvation, resulting in an insufficient concentration of C923 for Li extraction. The unexpected poor Li/Mg selectivity of C923 highlights the irreplaceable role of TBP in the selective recovery of Li.

KEYWORDS
Cyanex 923, lithium, magnesium, solvent extraction, tri-*n*-butyl phosphate

1 | INTRODUCTION

Lithium is an increasingly important element due to its essential role in lithium-ion batteries. In the past 10 years, the global consumption of Li_2CO_3 has been increasing rapidly,[1-3] and is expected to continue to increase in the following three decades, driven by the growing popularity of electric vehicles.[4-6] To meet the expanding global demand for Li_2CO_3, recovery of Li from salt lake brines, which contain about 70% of the Li resources, has attracted extensive attention and studies.[7-9] The biggest challenge of Li recovery from brines is the separation of Li from Mg, which always accompanies Li and is often more abundant than Li, in an efficient and cost-effective way.[10-12]

The synergic solvent extraction system containing tri-*n*-butyl phosphate (TBP, shown in Figure 1) in the organic phase and $FeCl_3$ in the aqueous phase was found to be able to selectively extract Li from Mg-containing brine solutions.[13] Because of the low cost of TBP and $FeCl_3$ and the good Li/Mg selectivity of this solvent extraction system, it has been studied extensively.[14-20] In the synergic solvent extraction of Li by the $TBP/FeCl_3$ system, the role of $FeCl_3$ is to form an anionic $[FeCl_4]^-$ complex that can further form an ion pair with the cation $[Li(TBP)_x]^+$ (x = 1, 2), as shown in Equation (1). In recent years it was found that anions of ionic liquids (ILs), such as $[PF_6]^-$, $[NTf_2]^-$, $[B(Phen)_4]^-$ and $[PW_{12}O_{40}]^{3-}$ can replace $[FeCl_4]^-$ as counter anions, provided that the cations of the ILs are hydrophilic.[21-25] Therefore TBP can also synergically extract Li from Mg-containing solutions in combination with ILs, although the use of ILs instead of $FeCl_3$ is not economic because of the high cost of ILs and the difficulty of recycling the ILs.
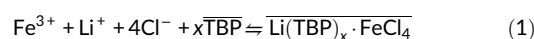
$$Fe^{3+} + Li^+ + 4Cl^- + x\overline{TBP} \rightleftharpoons \overline{Li(TBP)_x \cdot FeCl_4} \qquad (1)$$
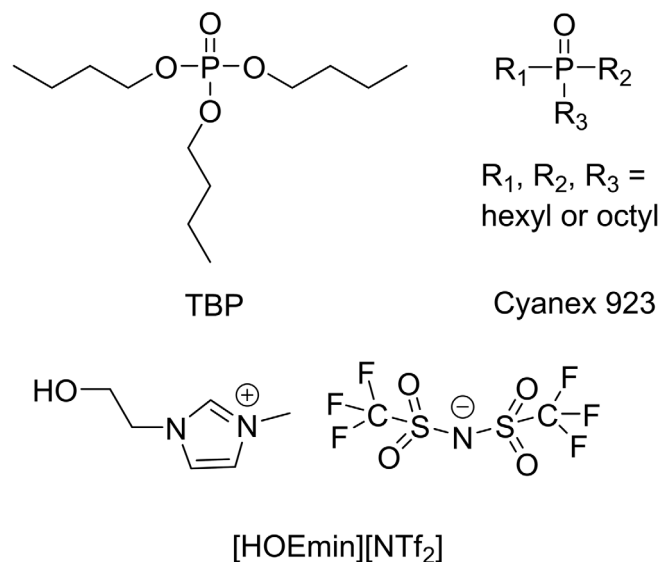
FIGURE 1 Chemical structures of TBP, C923, and [HOEmin][NTf$_2$]

where x = 1, 2, and the overbar means that the compound resides in the organic phase. The [FeCl$_4$]$^-$ anion in this equation can be replaced by an IL anion.

Cyanex 923 (C923, a commercial mixture of trialkyl phosphine oxides with mainly n-hexyl and n-octyl, shown in Figure 1) is a popular commercial neutral extractant that is similar to TBP. It has been used in the extraction of a wide range of metals, including rare earth elements (REEs), transition metals, and precious metals.[26-31] In general, extraction of metals by C923 is stronger than extraction by TBP, either for extraction by TBP or C923 alone,[26,32,33] or in combination with another extractant for synergic solvent extraction.[34,35] Recently, it was found that C923 and [NTf$_2$]$^-$-containing ILs, for example, 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HOEmin][NTf$_2$] (Figure 1), can synergically extract Li with high efficiency through the same ion-pair extraction mechanism as the TBP/FeCl$_3$ (or IL) systems.[36,37] Based on the Li-extracting capability of C923 and the fact that C923 is a stronger extractant than TBP in the extraction of many metals, we expect that the C923/FeCl$_3$ (or IL) system can perform as good as, if not better than, the TBP/FeCl$_3$ (or IL) system for selective extraction of Li from Mg-containing solutions.

In this study, we show that the Li/Mg selectivity of the C923/FeCl$_3$ (or IL) system is opposite to that of the TBP/FeCl$_3$ (or IL) system, that is, C923/FeCl$_3$ (or IL) extracts Mg stronger than Li. Detailed investigations have been performed to study how C923 alone and the C923/IL synergic solvent extraction system extract Fe and Mg. Besides, the mechanism of the opposite Li/Mg selectivity of the C923/FeCl$_3$ (or IL) system compared with that of the TBP/FeCl$_3$ (or IL) system has been demonstrated.

2 | EXPERIMENTAL SECTION

2.1 | Chemicals

Cyanex® 923 (90%) was obtained from Cytec Industries B.V. (Vlaardingen, Netherlands); HCl (37%), NaCl (>99.5%) and CsCl (>99%) were supplied by Fisher Scientific (Merelbeke, Belgium); LiCl (>99.5%) was obtained from Carl Roth (Karlsruhe, Germany); MgCl$_2$ (99%), FeCl$_3$ (98%), RbCl (>99.8) and p-cymene (>99%) were purchased from Acros Organics (Geel, Belgium); Li, Na, K, Rb, Cs, Mg, Ca and Fe standard solutions (1000 ± 10 mg·L^{-1}), KCl (>99.5%) and tributyl-n-phosphate (TBP, >99%) were purchased from Chem-Lab (Zedelgem, Belgium); CaCl$_2$·2H$_2$O (>99%) was purchased from VWR Chemicals (Leuven, Belgium); 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (99%) was purchased from IoLiTec (Heilbronn, Germany). Ultrapure water was used to prepare aqueous solutions. All chemicals were used as received, without any further purification.

2.2 | Experimental procedures

2.2.1 | Extraction experiments

Each extraction experiment was carried out in a 15 ml centrifuge tube with 5.0 ml of the aqueous solution and 5.0 ml of the organic solution containing either TBP or C923 dissolved in p-cymene. p-Cymene is a greener substitute of toluene for diluting extractants since it can be derived from biomass.[38] The use of p-cymene as the diluent in this study avoided the formation of the third phase in the whole concentration range of TBP and C923 due to the suitable polarity of p-cymene. p-Cymene can be regarded as a model of the commercial diluent SOLVESSO 150 Fluid (a mixture of C$_{10-12}$ alkylbenzenes), which is a common diluent in solvent extraction systems. Mixtures of the two phases were shaken for 30 min at 300 rpm using a Thermo Scientific 2000 shaker to attain extraction equilibrium. Afterward, the samples were centrifuged for 3 min at 4000 rpm in a Heraeus Megafuge 1.0 centrifuge to accelerate phase separation. Stripping of Li and Mg from both the loaded TBP and C923 phases was carried out following the same method as extraction using 2.0 ml of 6.0 mol·L^{-1} HCl and 1.0 ml of the loaded organic phase. Fe in the loaded TBP phase was stripped by water. The aqueous phases at equilibrium and the resultant aqueous solutions after stripping were analyzed for metals concentrations by inductively coupled plasma optical emission spectroscopy (ICP-OES), after appropriate dilutions. Fe in the loaded C923 was calculated based on Fe concentration in the aqueous raffinate according to mass balance, because it is difficult to strip Fe from the C923 phase. Aqueous-to-organic (A/O) phase ratios were varied by varying the organic and aqueous volumes, respectively. All experiments were conducted at room temperature (21 ± 1°C).

The *percentage extraction %E*, the *distribution ratio D*, and the *separation factor α* are defined as:

$$\%E = \frac{c_{org} \cdot V_{org}}{c_{org} \cdot V_{org} + c_{aq} \cdot V_{aq}} \times 100\% \qquad (2)$$

$$D = \frac{c_{org}}{c_{aq}} \qquad (3)$$

$$\alpha = \frac{D_A}{D_B} \qquad (4)$$

where c_{org} and c_{aq}, V_{org} and V_{aq} are concentrations and volumes of the organic and the aqueous phase at extraction equilibrium, respectively; D_A and D_B are the distribution ratios of metals A and B, respectively.

2.2.2 | Analytical instrumentation

Li, Na, K, Rb, Mg, Ca, and Fe concentrations were analyzed simultaneously by a PerkinElmer Optima 8300 ICP-OES equipped with a Scott Cross-Flow nebulizer. Cs was analyzed separately with the same setup using 1.0 g·L^{-1} Na as ionization buffer. UV–Vis absorption spectra were recorded by a Cary 6000i UV–Vis–NIR spectrophotometer using a pair of quartz cuvettes (10.0 mm path length). Raman spectra were measured on a Bruker Vertex 70 spectrometer with a RAM II FT-Raman module laser (λ = 1064 nm) at a power of 500 mW.

3 | RESULTS AND DISCUSSIONS

3.1 | Comparison of the TBP/FeCl$_3$ and C923/FeCl$_3$ systems

The TBP/FeCl$_3$ system has been intensively studied for the selective extraction of Li from high Mg-Li ratio brines by other researchers,[14-20] but the C923/FeCl$_3$ system has not been reported yet. The two systems are compared here for their extraction performance from a synthetic brine solution containing 0.10 mol·L^{-1} LiCl and 4.0 mol·L^{-1} MgCl$_2$ (Figure 2), which is a typical composition of concentrated brine.[11,16,19] The extraction of Li by the TBP/FeCl$_3$ system increased from 62% at 0.10 mol·L^{-1} FeCl$_3$ to 81% at 0.20 mol·L^{-1} FeCl$_3$. Although the extraction of Mg also increased with increasing FeCl$_3$ concentration, only 1.6% was extracted at 0.20 mol·L^{-1} FeCl$_3$. The separation factor ($\alpha_{Li/Mg}$) was in the range of 254–292, which means a very good separation was achieved. The results agree well with previous studies.[16,20] On the contrary, the C923/FeCl$_3$ system extracted Mg more efficiently than Li, resulting in an opposite Li/Mg selectivity compared with the TBP/FeCl$_3$ system. The Li extraction was significantly lower than in the TBP/FeCl$_3$ system. Only 2.7% Li was extracted at 0.10 mol·L^{-1} FeCl$_3$, which slightly increased to 4.2% at 0.20 mol·L^{-1} FeCl$_3$. By contrast, up to 8.1% Mg was extracted at 0.10 mol·L^{-1} FeCl$_3$, which slightly decreased to 7.0% at 0.20 mol·L^{-1} FeCl$_3$. It seems that competition exists between the extraction of Li and Mg. The surprisingly low Li extraction and high Mg extraction disables the C923/FeCl$_3$ system to selectively extract Li from Mg-containing brines. Considering the similarity of TBP and C923 molecules, this opposite Li/Mg selectivity of the two systems was not expected.
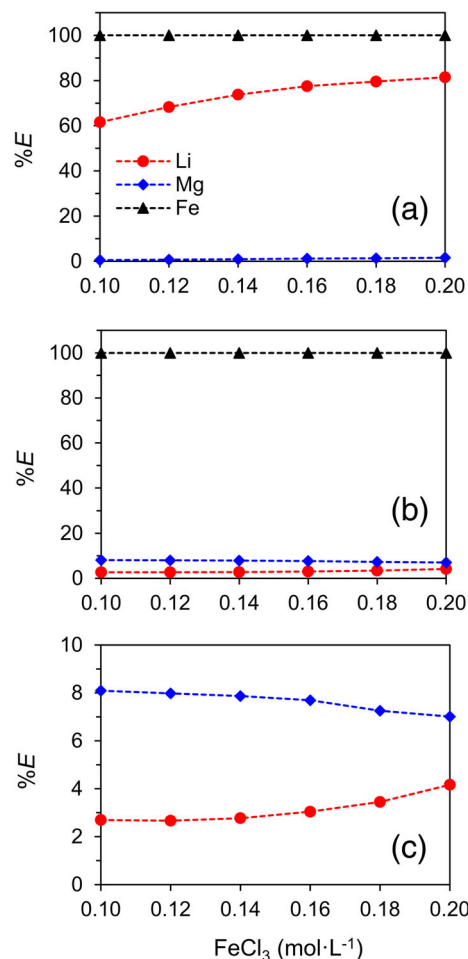

FIGURE 2 Extraction of Li by TBP/FeCl$_3$ (A) or C923/FeCl$_3$ (B, C) from chloride solutions. The aqueous phase was 0.10 mol·L^{-1} LiCl, 4.0 mol·L^{-1} MgCl$_2$ and 0.10–0.20 mol·L^{-1} FeCl$_3$; the organic phase was 60 vol% TBP or C923 in p-cymene. Part (C) is an enlargement of part (B) [Color figure can be viewed at wileyonlinelibrary.com]

3.2 | Role of Fe in the TBP/FeCl$_3$ and C923/FeCl$_3$ systems

The role of Fe was investigated first. Fe was completely loaded into the organic phase in both the TBP/FeCl$_3$ and C923/FeCl$_3$ systems. The extraction of Fe by TBP and C923 from acidic chloride media has been well-documented. Fe is extracted in the form of [HL$_2$][FeCl$_4$] (L represents TBP or C923).[33,39,40] In fact, the extraction of Li (and Mg) by the TBP/FeCl$_3$ system follows the same principle, but Li$^+$ replaces H$^+$ in the complex forming [LiL$_2$][FeCl$_4$]. At low acidity, extraction of Fe occurs via the neutral form of [FeCl$_3$·(TBP)$_3$],[39,41] [FeCl$_3$·TOPO],[41] and [FeCl$_3$·(Ph$_3$PO)$_3$][42] (TOPO and Ph$_3$PO represent trioctylphosphine oxide and triphenylphosphine oxide, respectively). Besides, the extraction of Fe in the form of [FeCl$_2$L$_4$·FeCl$_4$] has been reported for both phosphates and phosphine oxides.[43,44] Although Fe can be extracted by TBP and C923 in many forms, they can be categorized into three classes: (1) anionic [FeCl$_4$]$^-$, (2) cationic [FeCl$_2$L$_4$]$^+$ and (3) neutral FeCl$_3$L$_x$ species. Only the anionic [FeCl$_4$]$^-$ can assist the extraction of Li.
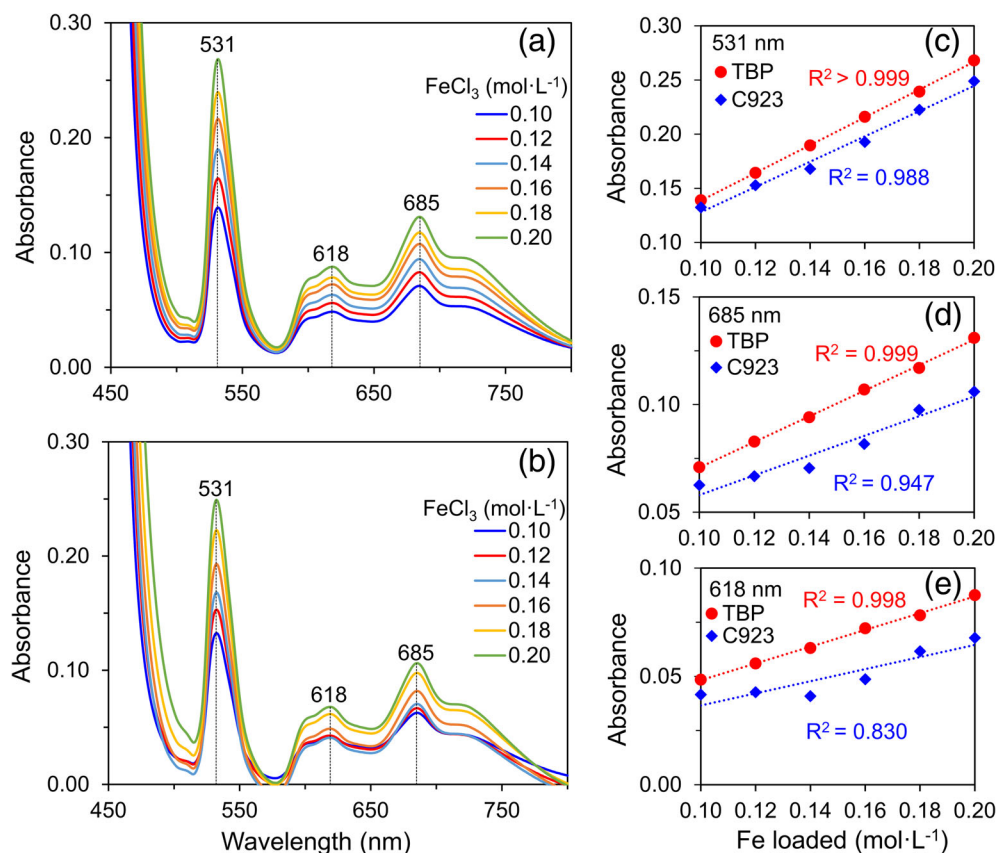
FIGURE 3 UV–Vis absorption spectra of the loaded organic phase: loaded TBP phase with varying Fe concentration (A); loaded C923 phase with varying Fe concentration (B), and linear fitting of absorption as a function of the Fe concentration at 531 nm (C), 685 nm (D) and 618 nm (E) [Color figure can be viewed at wileyonlinelibrary.com]

UV–Vis absorption spectra of the loaded TBP and C923 phases were recorded (Figure 3A,B). Three characteristic peaks of $[FeCl_4]^-$ at 531, 618, and 685 nm are observed for both the two systems. Because Fe in the aqueous feed solution was fully extracted in both the TBP/FeCl$_3$ and the C923/FeCl$_3$ systems (Figure 2), absorption of the organic phases should be proportional to the concentration of Fe in the feed. Absorption spectra of the TBP system as a function of Fe concentration show excellent linearity at all three wavelengths (Figure 3C–E), indicating that all the Fe extracted into the TBP phase is in the form of $[FeCl_4]^-$. By contrast, the absorption spectra of the C923 system has good linearity only at 531 nm (Figure 3C), the linearity is much poorer at 685 and 618 nm (Figure 3D,E). More importantly, the absorbance of the C923 system is always lower than the TBP system at the same Fe concentration. This lower absorbance of the C923 system and poorer linearity is an indication that other species besides $[FeCl_4]^-$ are present in the C923/FeCl$_3$ system.

Raman spectra of the loaded phases were also measured and the characteristic vibration of $[FeCl_4]^-$ at 333 cm^{-1} was observed for both systems (Figure 4). Again, spectra of the TBP/FeCl$_3$ system exhibit excellent linearity with increasing Fe concentration, while the linearity of the C923/FeCl$_3$ system is poorer. This observation further supports the conclusion that other species besides $[FeCl_4]^-$ have formed in the C923/FeCl$_3$ system.

Furthermore, extraction of FeCl$_3$ by TBP and C923, respectively, was conducted at low acidity (Figure 5). CsCl was used as the chloride source because the extraction of Cs by the TBP/IL and the C923/IL systems is the lowest among the alkali and alkaline earth metals (Figure 13). The extraction of Fe by C923 is much stronger than by

TBP. Because of the lack of acids to form $[HL_2][FeCl_4]$ (L represents TBP or C923), part of Fe has to be extracted either in the neutral form of $FeCl_3L_x$ or in the cationic form of $[FeCl_2L_2]^+$ ($[FeCl_2L_2][FeCl_4]$). The stronger extraction of Fe by C923 means that Fe in the C923/FeCl$_3$ system is more likely to be present as species other than anionic $[FeCl_4]^-$, which is disadvantageous for the extraction of Li. This is probably one of the reasons why the extraction of Li by the C923/FeCl$_3$ system is lower than the TBP/FeCl$_3$ system.

3.3 | Extraction of Mg by TBP and C923

The strong extraction of Mg in the C923/FeCl$_3$ system (Figure 2B,C) indicates that C923 alone may extract Mg, although this has not been reported in the literature yet. The extraction of Mg by TBP or C923 was investigated (Figure 6). The loading of Mg to TBP was negligible below 2.0 mol·L^{-1} MgCl$_2$ in the feed, only 0.004 g·L^{-1} Mg was loaded at 2.0 mol·L^{-1} MgCl$_2$, and it slightly increased to 0.16 g·L^{-1} at 4.4 mol·L^{-1} MgCl$_2$. However, the loading of Mg to the C923 phase was much stronger: 0.007 g·L^{-1} was loaded at 0.5 mol·L^{-1} MgCl$_2$, and it increased rapidly with the increasing MgCl$_2$ in the feed, reaching 9.2 g·L^{-1} at 4.4 mol·L^{-1} MgCl$_2$.

To understand how Mg was extracted by C923, a series of C923 concentrations were used to extract Mg from 4.4 mol·L^{-1} MgCl$_2$ (Figure 7A). Interestingly, the loading of Mg was largely proportional to the C923 concentration and the C923/Mg ratio was in the range of 3.5–4.0. This ratio points to an assumption that the C923 phase was fully loaded and the C923/Mg ratio was about 4.
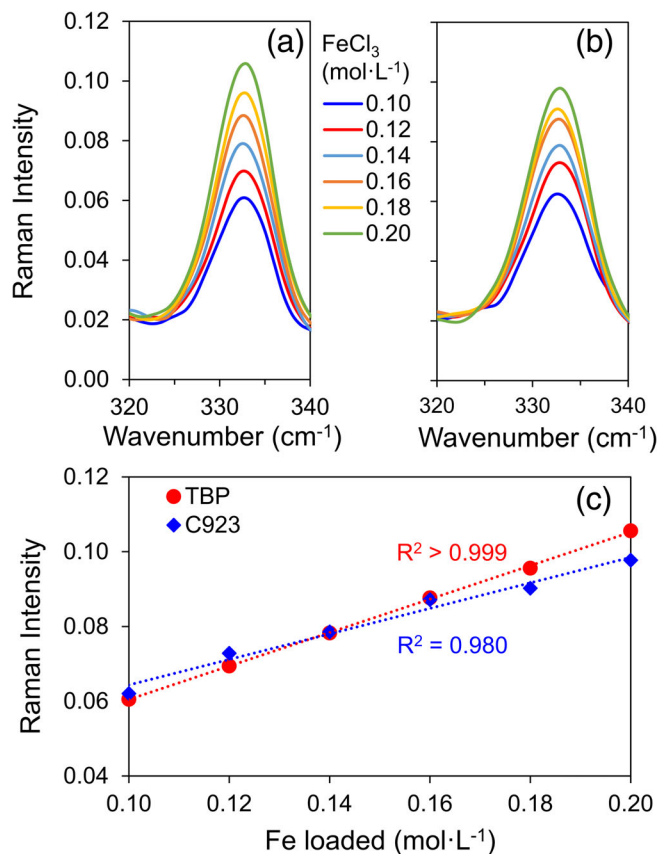
FIGURE 4 Raman spectra (λ = 1064 nm) of the loaded organic phase: loaded TBP phase with varying Fe concentration (A); loaded C923 phase with varying Fe concentration (B), and linear fitting of intensity as a function of the Fe concentration at 333 cm^{-1} (C) [Color figure can be viewed at wileyonlinelibrary.com]
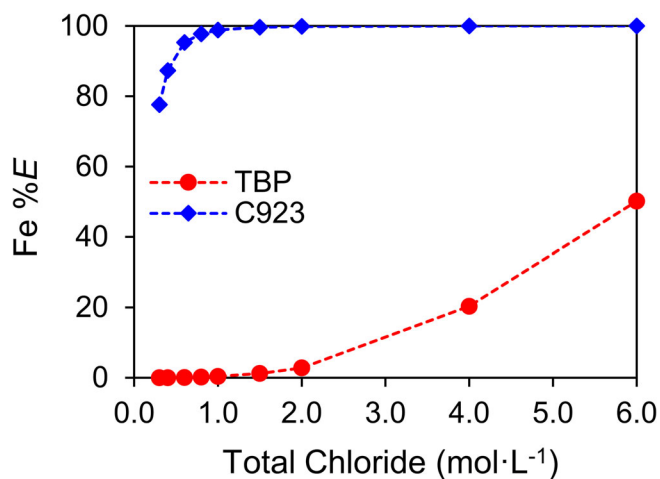

FIGURE 5 Extraction of Fe by TBP and C923 from low-acidity chloride media. The aqueous phase was 0.10 mol·L^{-1} FeCl$_3$, varying CsCl concentrations, and 0.04 mol·L^{-1} HCl to prevent hydrolysis. The organic phase was 60 vol% TBP or C923 in p-cymene [Color figure can be viewed at wileyonlinelibrary.com]
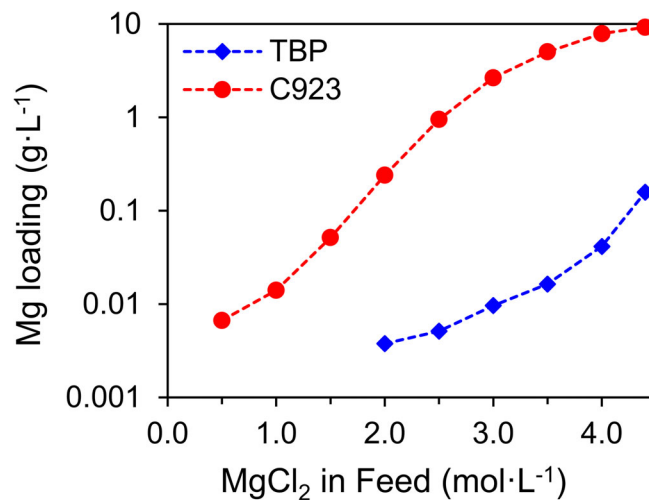

FIGURE 6 Loading of Mg to TBP and C923 with varying MgCl$_2$ concentrations in the aqueous feed solution. The organic phase was 60 vol% TBP or C923 in p-cymene [Color figure can be viewed at wileyonlinelibrary.com]
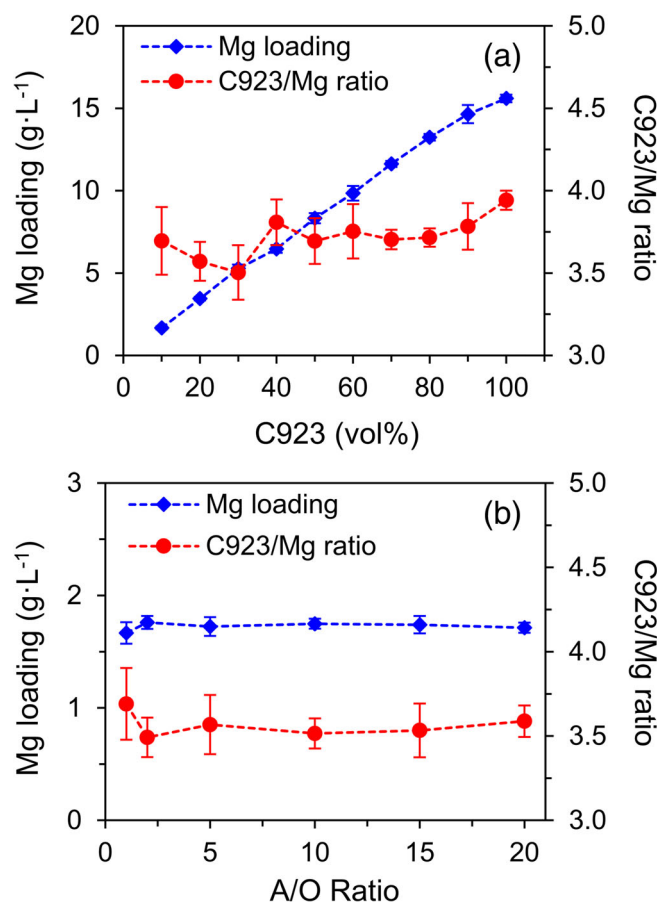

FIGURE 7 Loading of Mg to the C923 phase with varying C923 concentrations (A) and A/O phase ratios (B). The aqueous solution was 4.4 mol·L^{-1} MgCl$_2$; the organic phase was 10 vol% C923 in p-cymene for the phase ratio study [Color figure can be viewed at wileyonlinelibrary.com]
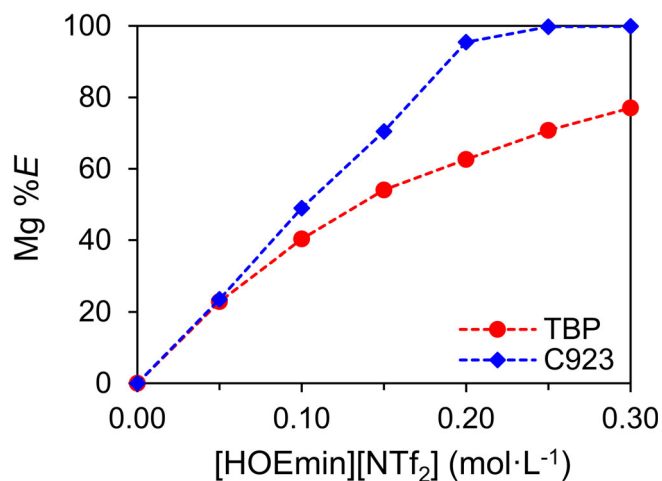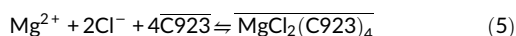
FIGURE 8 Extraction of Mg to the TBP/IL and C923/IL systems with varying IL concentrations. The aqueous phase contained 0.10 mol·L^{-1} MgCl$_2$ and the organic phase was 60 vol% TBP or C923 in *p*-cymene [Color figure can be viewed at wileyonlinelibrary.com]
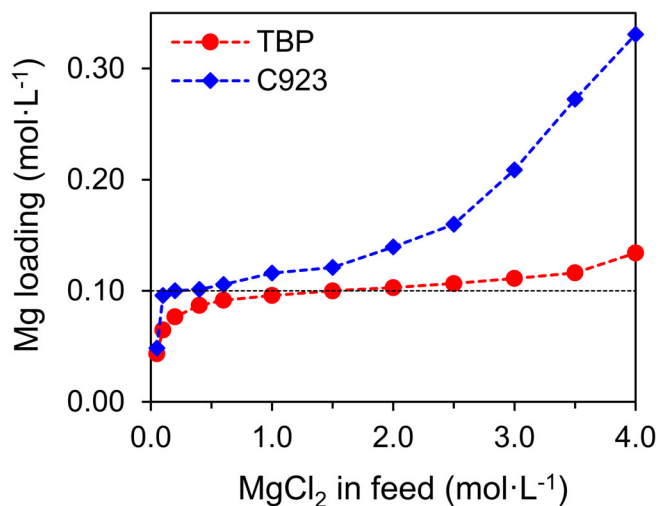

FIGURE 9 Loading of Mg to the TBP/IL and C923/IL systems with varying MgCl$_2$ concentrations in the feed. The organic phase contained 0.20 mol·L^{-1} IL and 60 vol% TBP (or C923) in *p*-cymene [Color figure can be viewed at wileyonlinelibrary.com]

To confirm the above assumption, maximum loading was conducted by varying the A/O ratios (Figure 7B). The loading of Mg was in the range of 1.66–1.75 g·L^{-1}, corresponding to a C923/Mg ratio of 3.5–3.7. This result supports the assumption that Mg is extracted by solvation as [MgCl$_2$·(C923)$_4$] at high MgCl$_2$ concentration, taking into account the charge neutrality. The reaction is given in Equation (5), where the overbar means that the compound resides in the organic phase. In retrospect to Figure 2, the loading of 8.1 g·L^{-1} Mg to 60 vol % C923 (~1.52 mol·L^{-1}) corresponds to a C923/Mg ratio of 4.0, indicating that C923 in the organic phase was about fully loaded with Mg, which is perhaps the main reason for the low extraction of Li.

$$Mg^{2+} + 2Cl^- + 4\overline{C923} \rightleftharpoons \overline{MgCl_2(C923)_4} \tag{5}$$

3.4 | Extraction of Mg by the TBP/IL and C923/IL systems

Besides the extraction of Mg by TBP or C923 alone, TBP and C923 may extract Mg in combination with FeCl$_3$ or ILs. To avoid the interference of Fe extraction by TBP or C923, the extraction of Mg by the TBP/IL and C923/IL systems was studied using the IL of [HOEmin][NTf$_2$] (Figure 8). [HOEmin][NTf$_2$] was selected because it showed the highest Li extraction efficiency in combination with C923 among many tested ILs.[36] At a concentration as low as 0.10 mol·L^{-1}, MgCl$_2$ was used in the aqueous solution to avoid the extraction of Mg by TBP or C923 by a solvation mechanism. The extraction of Mg by the C923/IL system increased linearly with the increasing IL concentration until 0.20 mol·L^{-1} IL. The ratio of the added IL and the extracted Mg (n_{IL}/n_{Mg}) was 2.1–2.2, that is, close to 2. This ratio indicates that two [NTf$_2$]$^-$ anions are needed in one Mg-complex and this ratio agrees well with the charge neutrality principle. As the IL concentration

further increased, the extraction of Mg was quantitative. The extraction of Mg by the TBP/IL system also increased with increasing IL concentrations, but was lower than that of the C923/IL system and no linear relationship could be observed.

Maximum loading studies were performed for the TBP/IL and C923/IL systems containing 0.20 mol·L^{-1} IL to further investigate the n_{IL}/n_{Mg} ratios (Figure 9). The loading of Mg to the C923/IL system was constant at about 0.10 mol·L^{-1} in the range of 0.20–0.40 mol·L^{-1} MgCl$_2$, corresponding to an n_{IL}/n_{Mg} ratio of 2.0. The extracted complex can be proposed as [Mg(C923)$_x$][NTf$_2$]$_2$ (*x* is to be determined). As the MgCl$_2$ in the feed increased, the Mg loading in the C923 phase further increased, which is due to the extraction of Mg by C923 in the form of [MgCl$_2$·(C923)$_4$], as shown in Equation (5). With respect to the TBP/IL system, the loading of Mg gradually approached 0.10 mol·L^{-1} at 1.0 mol·L^{-1} MgCl$_2$, where the n_{IL}/n_{Mg} ratio is 2.0, implying the formation of the complex [Mg(TBP)$_x$][NTf$_2$]$_2$. However, with further MgCl$_2$ concentration increase, the loading of Mg further increased slowly, reaching 0.134 mol·L^{-1} at 4.0 mol·L^{-1} MgCl$_2$. The amount of Mg that can be loaded in the form of [Mg(TBP)$_x$][NTf$_2$]$_2$ is 0.10 mol·L^{-1} and the amount by solvation is only about 0.006 mol·L^{-1} at 4.0 mol·L^{-1} MgCl$_2$ according to Figure 6. The sum of the two contributions is obviously smaller than the actual amount of 0.134 mol·L^{-1}. Therefore, above 1.0 mol·L^{-1} MgCl$_2$ in the feed, a complex between the ion-pair mechanism and the solvation mechanism, that is, [MgCl(TBP)$_x$][NTf$_2$], might have formed. [MgCl(TBP)$_x$][NTf$_2$] requires only one [NTf$_2$]$^-$ anion for extraction of one Mg^{2+}, hence allowing higher loading of Mg. Many studies have shown that [MgCl]$^+$ is a stable and even dominating (>50%) species in aqueous solution in the whole range of MgCl$_2$ concentrations.[45-48] At 0.20 mol·L^{-1} MgCl$_2$ and room temperature, the percentage of free Mg^{2+} is about 50%, which drops quickly as the MgCl$_2$ concentration increases and approaches 0 at 1.0 mol·L^{-1} MgCl$_2$, and the MgCl$^+$ species dominates onwards.[45] The high

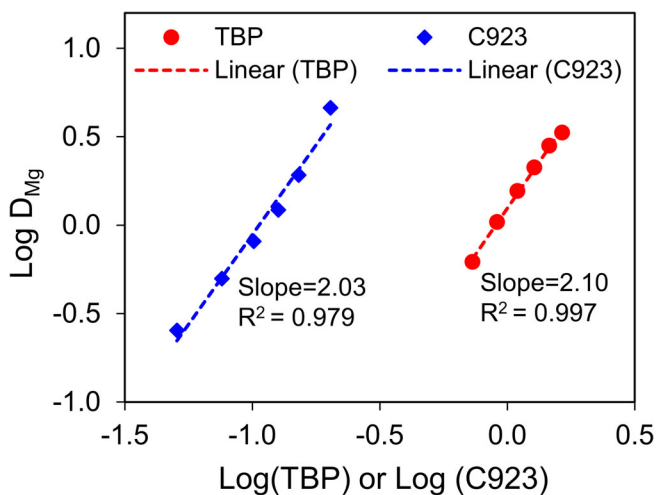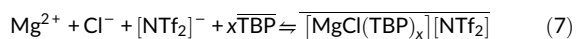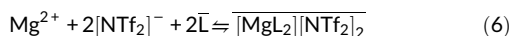**FIGURE 10** Slope analysis for the TBP/IL and the C923/IL systems. The aqueous phase contained 0.035 mol·L^{-1} MgCl$_2$. The organic phase was composed of varying TBP or C923 concentrations in *p*-cymene [Color figure can be viewed at wileyonlinelibrary.com]

stability of MgCl$^+$ supports the hypothesis of [MgCl(TBP)$_x$][NTf$_2$] formation. In short, [Mg(C923)$_x$][NTf$_2$]$_2$ is the main species for Mg extraction by the C923/IL system at MgCl$_2$ concentrations lower than 0.40 mol·L^{-1}; a mixture of [Mg(TBP)$_x$][NTf$_2$]$_2$ and [MgCl(TBP)$_x$][NTf$_2$] co-exists in the TBP/IL system.

Slope analysis was conducted at low MgCl$_2$ concentrations to study the stoichiometric ratios of TBP (or C923) to Mg in the extraction of Mg in combination with ILs (Figure 10). Low concentrations were used to avoid the formation of multiple complexes and the change of activity coefficients.[49] Both the TBP/IL and the C923/IL systems showed slopes of about 2.0, indicating that two TBP or C923 molecules are involved in the extraction of one Mg^{2+} cation. Combining the slope analysis and the above n_{IL}/n_{Mg} ratios, it can be concluded that Mg is extracted by the TBP/IL and the C923/IL systems in the form of [MgL$_2$][NTf$_2$]$_2$ (L represents TBP or C923) at low MgCl$_2$ concentrations, and that the formation of [MgCl(TBP)$_x$][NTf$_2$] is also possible at higher MgCl$_2$ concentrations. The extraction is expressed in Equations (6) and (7), where L represents TBP or C923 and the overbar means that the compound resides in the organic phase. This extraction mechanism is similar to the extraction of Li by the ion-pair mechanism.

$$Mg^{2+} + 2[NTf_2]^- + 2\overline{L} \rightleftharpoons \overline{[MgL_2][NTf_2]_2} \tag{6}$$

$$Mg^{2+} + Cl^- + [NTf_2]^- + x\overline{TBP} \rightleftharpoons \overline{[MgCl(TBP)_x][NTf_2]} \tag{7}$$

3.5 | Effect of Mg on Li extraction

The above discussions have shown that Mg can be extracted by TBP and C923 via both the solvation mechanism and the ion-pair mechanism.
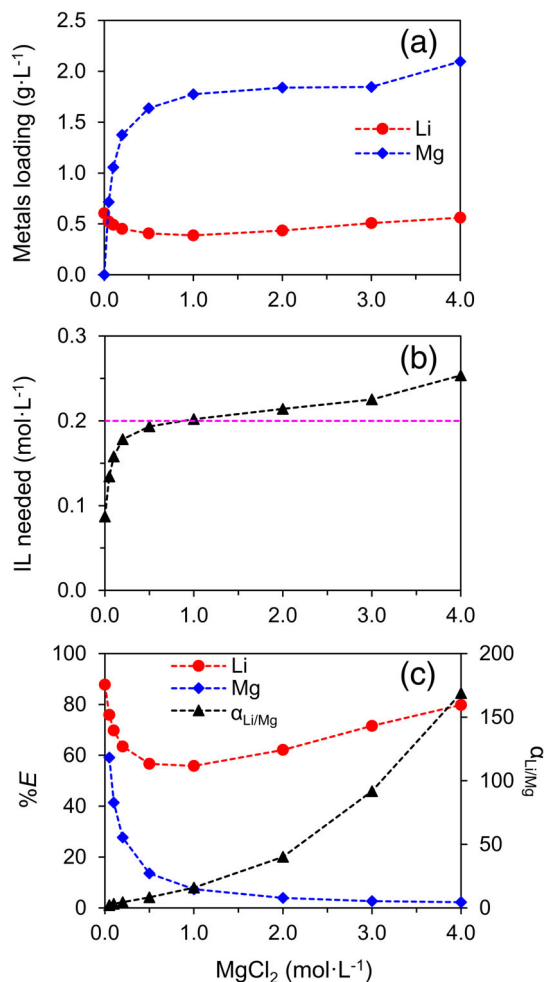

FIGURE 11 Effect of Mg concentration on the extraction of Li by the TBP/IL system. (A) loading of Li and Mg to the organic phase; (B) amount of IL theoretically needed for the Li and Mg loading assuming the ion-pair extraction mechanism; (C) percentage extraction of Li and Mg and $\alpha_{Li/Mg}$. The aqueous phase was 0.10 mol·L^{-1} LiCl and varying MgCl$_2$; the organic phase was 60 vol% TBP in *p*-cymene [Color figure can be viewed at wileyonlinelibrary.com]

Following these results, the effect of Mg on the extraction of Li in the TBP/IL (Figure 11) and the C923/IL (Figure 12) systems has been studied.

We first discuss the TBP/IL system (Figure 11). Loading of Mg to the TBP phase increased with increasing Mg concentration in the feed until reaching a plateau at 1.0 mol·L^{-1} MgCl$_2$. Below 1.0 mol·L^{-1} MgCl$_2$, the loading of Li decreased due to competition with Mg for IL. Li and Mg were extracted both by ion-pair mechanism, that is, forming [Li(TBP)$_x$][NTf$_2$] (x = 1, 2) or [Mg(TBP)$_2$][NTf$_2$]$_2$. At 1.0 mol·L^{-1} MgCl$_2$, the loading of Li and Mg was 0.39 g·L^{-1} and 1.78 g·L^{-1}, respectively. The amount of IL theoretically needed to load these amounts of Li and Mg through the ion-pair mechanism (Equation 6) is about 0.20 mol·L^{-1} (Figure 11B), which is the same amount of IL that was initially added. Therefore, all the added IL had been consumed for Li and Mg extraction through ion-pair extraction under this condition. The loading of Mg slightly increased between 1.0 and 3.0 mol·L^{-1} MgCl$_2$ in the feed, and it increased to about 2.1 g·L^{-1} at 4.0 mol·L^{-1}
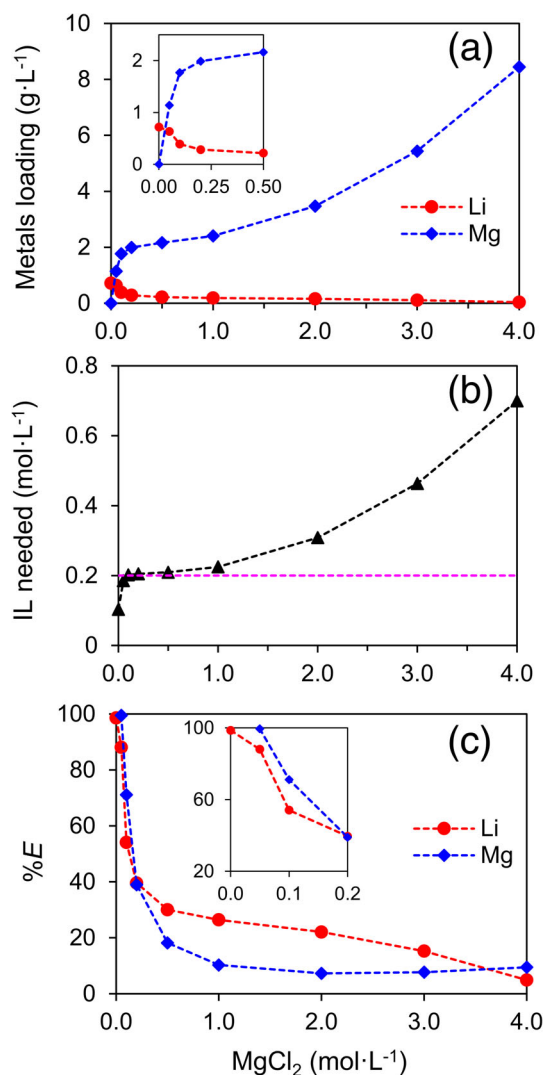
FIGURE 12 Effect of Mg concentration on the extraction of Li by the C923/IL system. (A) loading of Li and Mg to the organic phase; (B) amount of IL theoretically needed for the Li and Mg loading assuming the ion-pair extraction mechanism; (C) percentage extraction of Li and Mg. The aqueous phase was 0.10 mol·L^{-1} LiCl and varying MgCl$_2$ concentrations. The organic phase was 60 vol% C923 in *p*-cymene [Color figure can be viewed at wileyonlinelibrary.com]

MgCl$_2$. In addition, the loading of Li further increased when the MgCl$_2$ in the feed was above 1.0 mol·L^{-1}, but there was no more IL available for Li extraction by the ion-pair mechanism. Here we propose two hypotheses to explain the additional Li and Mg extraction. First, Li might be extracted by a solvation mechanism, similar to the extraction of Mg at high MgCl$_2$ concentration (shown in Equation 5). A control experiment of Li extraction with varying MgCl$_2$ but without IL was conducted. It was found that Li extraction was negligible. Therefore, Li was not solvated. Second, as the MgCl$_2$ concentration increases, the MgCl$^+$ species starts to dominate in the aqueous solutions,[45,47] hence more [MgCl(TBP)$_x$][NTf$_2$] instead of [Mg(TBP)$_2$][NTf$_2$]$_2$ would be formed. The [MgCl(TBP)$_x$][NTf$_2$] complex consumes less IL for the

same amount of Mg extraction compared with [Mg(TBP)$_2$][NTf$_2$]$_2$, hence IL is released for further Li and Mg extraction. Although Mg could also be solvated by TBP as shown in Figure 6, the amount of solvated Mg is negligible compared to the extraction in combination with the IL. In summary, below 1.0 mol·L^{-1} MgCl$_2$ in the feed, both Mg and Li were extracted by the ion-pair mechanism and they compete for the IL. Above 1.0 mol·L^{-1} MgCl$_2$, Li was further extracted, which is probably due to available IL molecules released by conversion of [Mg(TBP)$_2$][NTf$_2$]$_2$ to [MgCl(TBP)$_x$][NTf$_2$].

The percentage extraction of Mg decreased with increasing MgCl$_2$ concentration, although the loading increased. The percentage extraction of Li first decreased from 88% at 0 MgCl$_2$ to 56% at 1.0 mol·L^{-1} MgCl$_2$ due to competition with Mg extraction, then increased because of available IL molecules released from conversion of [Mg(TBP)$_2$][NTf$_2$]$_2$ to [MgCl(TBP)$_x$][NTf$_2$]. At 4.0 mol·L^{-1} MgCl$_2$, 80% Li was extracted, while only 2.3% Mg was extracted, $\alpha_{Li/Mg}$ was 168, which is a good separation. This performance is comparable to the results in Figure 2B at 4.0 mol·L^{-1} MgCl$_2$ and 0.20 mol·L^{-1} FeCl$_3$, where 81% Li was extracted with 1.6% Mg extraction and the separation factor was 254. In fact, the $\alpha_{Li/Mg}$ value increased significantly with the increasing MgCl$_2$ in the feed because the percentage extraction of Mg decreased. In other words, in terms of $\alpha_{Li/Mg}$, the increasing MgCl$_2$ concentration enhances the Li/Mg separation.

The C923/IL system performed differently from the TBP/IL system (Figure 12). Below 0.50 mol·L^{-1} MgCl$_2$, loading of Mg increased with the increasing MgCl$_2$ concentration, while the loading of Li decreased due to competition with Mg for IL through the ion-pair extraction mechanism. It should be noted that the extraction of Mg by C923 through the solvation mechanism is negligible below 0.50 mol·L^{-1} MgCl$_2$. At 0.50 mol·L^{-1} MgCl$_2$, the loaded Li and Mg were 0.22 g·L^{-1} and 2.17 g·L^{-1}, respectively. The amount of IL needed for Li and Mg extraction through the ion-pair mechanism is 0.209 mol·L^{-1}, matching the added amount of 0.20 mol·L^{-1} IL, indicating that all the IL had been consumed for Li and Mg extraction.

Above 0.50 mol·L^{-1} MgCl$_2$, the loading of Mg further increased, which is due to the extraction by a solvation mechanism, as discussed above in Figures 6 and 7. As C923 was gradually consumed by the loaded Mg, less C923 was available for Li extraction, hence the Li extraction decreased further. The high loading of Mg to C923 by solvation is an important reason for the reduction of Li extraction. At 4.0 mol·L^{-1} MgCl$_2$ in the feed, 8.4 g·L^{-1} Mg was loaded, which requires 1.38 mol·L^{-1} C923 according to a C923/Mg ratio of 4:1. On the other hand, 60 vol% C923 is about 1.52 mol·L^{-1}. This comparison indicates that the majority of the C923 molecules in the organic phase have been consumed by solvation with Mg, leading to an insufficient C923 concentration for Li extraction.

Without Mg, 98.6% of Li was extracted by C923 (Figure 12C), which is much higher than the extraction by TBP, which was 88% (Figure 11C). With 0.05 mol·L^{-1} and 0.10 mol·L^{-1} MgCl$_2$, the extraction of Mg was 99.5% and 71%, higher than the extraction of Li, which was 88% and 54%. This comparison clearly shows that the extraction of Mg is stronger than Li even by the ion-pair extraction at low MgCl$_2$ concentrations. The percentage extraction of Mg decreased as the MgCl$_2$ concentration further increased, although the loading raised. The
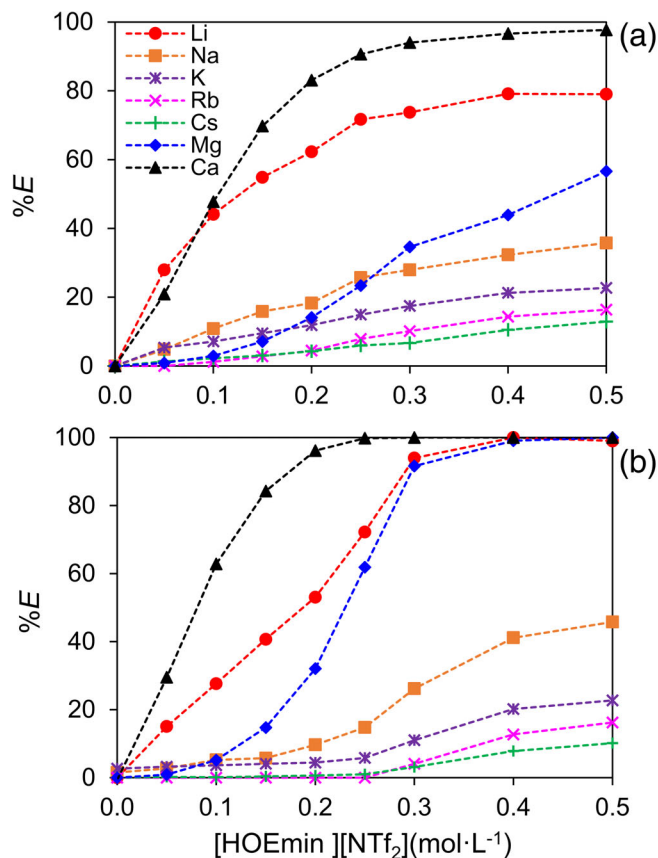
FIGURE 13 Sequence of metals extraction by the TBP/IL (A) and the C923/IL (B) systems. The aqueous phase contained 0.05 mol·L^{-1} of each metal. The organic phase was 60 vol% TBP or C923 in *p*-cymene and various IL concentrations [Color figure can be viewed at wileyonlinelibrary.com]

percentage extraction of Li also decreased, but the reduction is due to the decreased loading of Li. At 4.0 mol·L^{-1} MgCl$_2$, the extraction of Mg was again higher than Li, being 9.5% and 4.9%, respectively. This is comparable to the C923/FeCl$_3$ system as shown in Figure 2B at 4.0 mol·L^{-1} MgCl$_2$ and 0.20 mol·L^{-1} FeCl$_3$, in which the percentage extraction of Mg and Li was 7.0% and 4.2%, respectively.

In summary, the C923/IL system does not have Li selectivity over Mg, neither through the ion-pair extraction mechanism nor the solvation mechanism. C923 extracts all three metals (Li, Mg, and Fe) stronger than TBP, but the extraction of Mg by C923 is far stronger than by TBP both via the ion-pair mechanism and the solvation mechanism. The stronger Mg extraction by C923 than by TBP is the main reason for the opposite Li/Mg selectivities of the C923/FeCl$_3$ (or IL) and the TBP/FeCl$_3$ (or IL) systems.

3.6 | Extraction sequence of alkali and alkaline earth metals

Besides Li and Mg, other alkali and alkaline earth metals, including Na, K, Rb, Cs, and Ca, may present in brines. The extraction of a

mixture of these metals by the TBP/IL and the C923/IL systems was studied (Figure 13). It should be noted that these metals were extracted by the ion-pair mechanism due to the low metal concentrations. The extraction sequence of the metals by the TBP/IL system is: Ca^{2+} > Li$^+$ > Mg^{2+} > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$. The sequence is largely the same as for the TBP/FeCl$_3$ system, except that the extraction of Ca by the TBP/FeCl$_3$ is slightly weaker than the extraction of Li.[15,16] The extraction sequence of metals by the C923/IL system is: Ca^{2+} > Li$^+$ ≈ Mg^{2+} > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$. The main difference between the TBP/IL system and the C923/IL system is that the C923/IL system has a much stronger capability to extract Mg.

4 | CONCLUSIONS

The C923/FeCl$_3$ (or IL) system has opposite Li/Mg selectivity compared with the TBP/FeCl$_3$ (or IL) system when extracting the metals from concentrated brine solution, despite the similarity in the molecular structure of TBP and C923. The two synergic solvent extraction systems were studied in detail to investigate the origin of this opposite selectivity. C923 extracts Mg by solvation in the form of [MgCl$_2$(C923)$_4$]. On the contrary, the solvation of Mg by TBP is negligible. The high loading of Mg to the C923 phase largely consumes the C923 molecules, leading to an insufficient concentration of C923 for the extraction of Li. In addition, both the TBP/IL system and the C923/IL system can extract Mg by the ion-pair mechanism in the form of [MgL$_2$][NTf$_2$]$_2$ (L represents TBP or C923), which competes with the extraction of Li. Moreover, C923 extracts Fe much stronger than TBP, resulting in a lack of [FeCl$_4$]$^-$ anions, which are essential for the extraction of Li in the C923/FeCl$_3$ system. Among the three reasons, the consumption of C923 by solvation with Mg is the main reason for the very low extraction efficiency of Li by the C923/FeCl$_3$ (or IL) system. The incapability of the C923/FeCl$_3$ (or IL) system to selectively extract Li underlines the irreplaceable role of TBP in the recovery of Li from Mg-containing brines.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
Data available on request from the authors

ORCID
Zheng Li https://orcid.org/0000-0002-7882-5999
Koen Binnemans https://orcid.org/0000-0003-4768-3606

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