

Enhancing Metal Separations Using Hydrophilic Ionic Liquids and Analogues as Complexing Agents in the More Polar Phase of Liquid–Liquid Extraction Systems

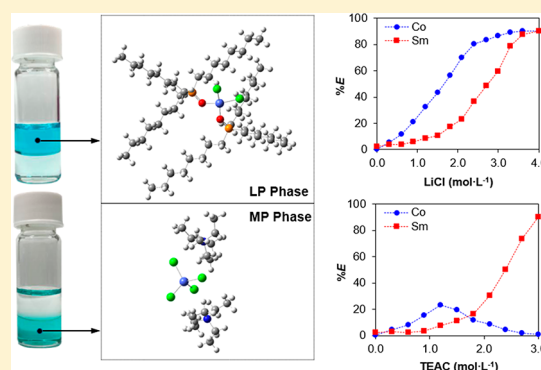
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Supporting Information

ABSTRACT: The separation of metals by liquid–liquid extraction largely relies on the affinity of metals to the extractants, which normally reside in the organic (less polar) phase because of their high hydrophobicity. Following a different route, using aminopoly(carboxylic acid)s (e.g., EDTA) as complexing agents in the aqueous (more polar) phase was found to enhance metal separations by selectively complexing metal cations. In this study, we demonstrate that, hydrophilic ionic liquids and analogues in the more polar phase could also selectively complex with metal cations and hence enhance metal separations. As an example, Cyanex 923 (a mixture of trialkyl phosphine oxides) dissolved in *p*-cymene extracts CoCl_2 more efficiently than SmCl_3 from a chloride ethylene glycol (EG) solution. However, when tetraethylammonium chloride is added into the EG solution, CoCl_2 is selectively held back (only 1.2% extraction at 3.0 M tetraethylammonium chloride), whereas the extraction of SmCl_3 is unaffected (89.9% extraction), leading to reversed metal separation with a separation factor of $\text{Sm(III)/Co(II)} > 700$. The same principle is applicable to a range of hydrophilic ionic liquids, which can be used as complexing agents in the more polar phase to enhance the separations of various metal mixtures by liquid–liquid extraction.



1. INTRODUCTION

Liquid–liquid extraction (solvent extraction) is one of the most widely used techniques for separation and purification of metals. Conventionally, a liquid–liquid extraction system consists of an aqueous (more polar, MP) phase with the metals to be separated and an organic (less polar, LP) phase that comprises extractants and a diluent.¹ The extractants always reside in the LP phase because of their high hydrophobicity, which minimizes the loss of extractants to the aqueous solution and enables extraction of metals in the form of hydrophobic metal complexes. The optimization of metal separations largely depends on the composition of the LP phase, such as the type and concentration of the extractant and the type of diluent,² and sometimes a second extractant can be used as a synergist to enhance separation.^{3–6} To a lesser extent, adjustment of the aqueous pH for acidic extractants and addition of salts for solvating extractants can also optimize separations. However, the affinity of metals to an extractant has a specific sequence that is independent of the extractant concentration in the LP phase and the pH and salt concentration of the MP phase.

Recently, several studies observed enhanced metal separations through replacement of water by polar organic solvents.^{7–12} The use of polar organic solvents in liquid–liquid extraction is called “nonaqueous solvent extraction”.¹³

The substitution of water by polar organic solvents modifies the solvation of metals in the MP phase, which may alter the metal extraction sequence. Nevertheless, extractants in these liquid–liquid extraction systems still reside in the LP phase. Studies on the use of modifiers residing in the MP phase of liquid–liquid extraction systems are relatively few.

A famous example of enhancing metal separations by modification of the aqueous phase is the trivalent actinide–lanthanide separation with phosphorus-reagent extraction from aqueous complexes (TALSPEAK) process, which was originally developed by the Oak Ridge National Laboratory of the United States for the selective extraction of lanthanides from actinides.^{14,15} In the TALSPEAK process, bis-2-ethylhexyl phosphoric acid (HDEHP) in the LP phase was used for lanthanide extraction, whereas diethylenetriamine-*N,N,N',N'',N'''*-pentaacetic acid (DTPA) in the buffered aqueous solution was used as a complexing agent to hold back the actinides, leading to enhanced separation of lanthanides and actinides. Following the same principle, the actinide–lanthanide separation (ALSEP) process uses a

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mixture of a neutral diglycolamide extractant and the acidic extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) for coextraction of lanthanides and actinides and uses an aminopoly(carboxylic acid)/citrate buffered aqueous solution to selectively strip actinides.¹⁶ The methodology of selectively complexing metals in the aqueous phase using aminopolycarboxylic acids has also been applied to separation of rare earth elements; heavier rare earth elements are held back, whereas extraction of lighter rare earth elements are enhanced.^{17,18} Despite the enhancement of metal separations, the use of these aminopolycarboxylic acids as complexing agents requires strict control of pH to optimize selectivity. To overcome this drawback, the i-SANEX process, a process for separating actinides(III) from used nuclear fuels by solvent extraction, uses a hydrophilic sulfonated bistriazinylpyridine (SO₃-Ph-BTP) as a complexing agent in the aqueous solution to selectively hold back actinides. The i-SANEX process does not need buffering agents to control pH because SO₃-Ph-BTP is not an acid.¹⁹ All the complexing agents used in the TALSPEAK, i-SANEX, and related processes are directly involved in the complexation with the metals via the active functional groups (either the carboxylic group or the pyridine group).

In this study, we demonstrate the use of hydrophilic ionic liquids (ILs) and analogues as complexing agents in the MP phase of liquid–liquid extraction systems to enhance metal separations. These hydrophilic ILs and analogues are homologues of hydrophobic ILs that have been utilized as extractants in the LP phase for metal extractions via anion exchanges.^{20–22} In principle, hydrophilic ILs and analogues containing the same functional groups (anions) as those of the hydrophobic ILs that can extract metals should also be able to complex with metals and hence tune metal separations.

2. MATERIALS AND METHODS

2.1. Chemicals. CoCl₂·6H₂O (analytical grade), Co(NO₃)₂·6H₂O (99%), ethylene glycol (99.9%), *p*-cymene (99%), nitric acid (70%), tetraethylammonium chloride (98%), tetraethylammonium nitrate (99%), and tetraethylammonium hydrogen sulfate (99%) were purchased from Acros Organics (Geel, Belgium). Co, Sm, and Ga standard solutions (1000 ± 10 mg L⁻¹) were purchased from Chem-Lab (Zedelgem, Belgium). Acetonitrile-*d*₃ (99.9%), Triton X-100 (for molecular biology), and 1-ethyl-3-methylimidazolium chloride (>95%) were obtained from Sigma-Aldrich (Diegem, Belgium). Cyanex 923 was purchased from Solvay (Vlaardingen, Netherlands). Isopropanol (analytical reagent) and LiCl (analytical reagent grade) were supplied by Fisher Scientific (Merelbeke, Belgium). SmCl₃·6H₂O (99.9%) was ordered from Strem Chemicals (Newburyport, MA). A silicone solution in isopropanol for the treatment of the TXRF quartz glass carriers was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). Choline chloride (98%) was purchased from J&K Scientific (Pforzheim, Germany). 1-Butyl-1-methylpyrrolidinium chloride (99%) was obtained from IoLiTec (Heilbronn, Germany). Tetraethylammonium bromide (99%) was ordered from J. T. Baker Chemicals (Deventer, Netherlands).

2.2. Experimental Procedures. Mutual Solubility. In 4 mL glass vials, 1.0 mL of the MP phase solution (1.0 mol·L⁻¹ tetraethylammonium chloride (TEAC) or trimethyl phosphate (TMP) or 10 vol % H₂O in ethylene glycol (EG)) was put in contact with 1.0 mL of the LP phase solution (0–60 vol %

Cyanex 923 (C923) in *p*-cymene). The other six hydrophilic ILs were only determined for 20 vol % C923. The two-phase mixtures were shaken on a benchtop shaker at 260 rpm for 60 min at room temperature (22 °C); this was followed by centrifugation at 3000 rpm for 5 min. The ¹H NMR spectra of the LP phases were recorded directly by a Bruker Avance 400 spectrometer operating at 400 MHz with acetonitrile-*d*₃ as solvent. The MP phases were diluted by *N,N*-dimethylformamide (as reference) before their ¹H NMR spectra were recorded. The compositions of the two phases were calculated by the quantitative ¹H NMR spectra, on the basis of which the mutual solubility was calculated. The water contents in both the LP phase and the MP phase were determined by a Karl Fischer Coulometer (Mettler-Toledo C30s).

Liquid–Liquid Extraction. In 4 mL glass vials, 1.0 mL of the MP phase solution (0.30 g·L⁻¹ Co(II) as CoCl₂, 0.30 g·L⁻¹ Sm(III) as SmCl₃, and various concentrations of LiCl or hydrophilic ILs in EG) was put in contact with the LP phase solution (0–60 vol % C923 in *p*-cymene). The two-phase mixtures were shaken in a table shaker at 260 rpm for 60 min at room temperature (22 °C); this was followed by centrifugation at 3000 rpm for 5 min. The slope analysis tests followed the same procedures as the normal liquid–liquid extraction tests. The MP phase contained 0.30 g·L⁻¹ Co(II) (as CoCl₂) and 3.0 mol·L⁻¹ LiCl. C923 in the LP phase varied from 5 to 30 vol %.

The metal concentrations in the LP phase were measured by a total reflection X-ray fluorescence (TXRF) spectrometer (Bruker S2 Picofox). Samples from the LP phase were diluted with a mixture of aqueous Triton X-100 solution and 2-propanol with Ga standard solution as reference to an appropriate concentration. The quartz glass sample carriers for TXRF measurements were pretreated with 30 μL of a silicone solution in isopropanol and dried in an oven for 5 min at 60 °C. Then, a diluted sample of 5 μL was added to a carrier and dried at 60 °C for 30 min. Each sample was measured for 1000 s in the TXRF spectrometer. The MP phase was measured by ICP-OES (PerkinElmer OPTIMA 8300) after being diluted with 2 wt % HNO₃.

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

$$\%E = \frac{c_{lp} \times V_{lp}}{c_{lp} \times V_{lp} + c_{mp} \times V_{mp}} \times 100\% \quad (1)$$

$$D = \frac{c_{lp}}{c_{mp}} \quad (2)$$

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

where *c*_{lp}, *c*_{mp}, *V*_{lp}, and *V*_{mp} are concentrations and volumes in the LP phase and the MP phase, respectively; *D*_A and *D*_B are the distribution ratios of metals A and B, respectively.

UV–Vis Spectra. UV–vis absorption spectra were measured by a Varian Cary 5000 spectrophotometer with a resolution of 1.0 nm using a pair of quartz cuvettes (10.0 mm path length). The EG solutions contained 0.30 g·L⁻¹ Co(II) (as CoCl₂) and various concentrations of LiCl or TEAC. Pure EG solvent was used as a reference. The LP phase obtained from the slope analysis containing only Co(II) was also measured, using pure *p*-cymene as a reference solvent.

EXAFS. Extended X-ray absorption fine structure (EXAFS) spectra of the Co(II) K-edge (7709 eV) were collected at the Dutch–Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.²³ The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The measurements were conducted in transmission mode using Ar/He gas filled ionization chambers at ambient pressure. Both the LP phase solution after loading Co(II) and the reference solution were measured in duplicate. A brass sample holder with Kapton windows and a flexible polymeric spacer (VITON) with a thickness of 0.8 mm was used as a sample holder. Visual Processing in EXAFS Researches (VIPER) software was used for averaging the two scans and isolating the EXAFS function (χ), using standard procedures for pre-edge subtraction, data normalization, and subtraction of the atomic background with a smoothing spline.²⁴ The EXAFS function of the unknown sample was k^3 -weighed and Fourier transformed over the k -range from 3.3 to 13 Å⁻¹. The data were fitted with a model consisting of one Co–Cl interaction at 2.2 Å and one Co–O interaction at 2.0 Å. The ab initio code FEFF 7.0 was used to calculate the theoretical phase and amplitude functions that were subsequently used in the nonlinear least-squares refinement of the experimental data.²⁵ The EXAFS spectrum was fitted in the $R + \Delta$ (Å) space between 0 and 2.25 Å without a window function, with the Co–Cl and Co–O single scattering paths used as input. Estimated standard deviations as calculated by VIPER are reported in parentheses. The amplitude reduction factor, S_0 , was fixed to 0.8, which was deduced by fitting of the coordination number of the Co(H₂O)₆²⁺ reference. The reference was prepared by dissolving 0.10 mol·L⁻¹ Co(NO₃)₂·6H₂O (>99%) in ultrapure water. The data of the reference were fitted in the $R + \Delta$ (Å) space between 0 and 2.06 Å without a window function with a model consisting of one Co–O single scattering path.

Estimation of Errors. The metal concentrations in both the LP phase and the MP phase were measured. The mass balances of all extraction tests were in the range of 85–115%, and most of them were within 90–110%. To estimate the errors for percentage extraction, the extraction of Co(II) and Sm(III) with varying concentrations of tetraethylammonium chloride was conducted in triplicate, and the standard deviations were calculated, with the results shown Table S1. In terms of percentage extraction (%E), the largest error for Co(II) extraction occurred at 1.8 M TEAC (3.3% standard deviation); the largest error for Sm(III) extraction occurred at 2.4 M TEAC (1.4% standard deviation). In terms of relative error (standard deviation relative to the corresponding percentage extraction), the largest error for Co(II) extraction also occurred at 1.8 M TEAC (21%); the largest error for Sm(III) extraction occurred at 0.6 M TEAC (26%). All the extraction tests in this study are of the same type and in the same concentration range; therefore, the errors in terms of percentage extraction are estimated to be <3.5%, and the relative errors are <30%.

2.3. Computational Details. A molecular simulation method was utilized to further study the coordination complex structure to provide a better understanding of the extraction process on the molecular level. The geometries of possible coordination complexes in the MP phase ([CoCl₄]²⁻·2[N(C₂H₅)₄]⁺) and LP phase (CoCl₂(C923)₂) were investigated in the gas phase by density functional theory (DFT).²⁶ The

structures were optimized at the B3LYP/6-31g(d) level of theory.^{27–29} The frequency calculations were also performed to confirm that the obtained structures were stationary points (energy minimums) on the potential energy surfaces. All calculations were performed by the quantum chemistry package Gaussian 09.³⁰

3. RESULTS AND DISCUSSION

3.1. Liquid–Liquid Extraction System with Hydrophilic ILs in the More Polar Phase. We developed a liquid–liquid extraction system with a conventional extractant in the LP phase and a hydrophilic IL or analogue as a complexing agent in the MP phase. 1-Methyl-4-(propan-2-yl)benzene (*p*-cymene) and ethylene glycol (EG) were selected as solvents for the LP phase and the MP phase, respectively. EG has been proven to be a suitable solvent for the MP phase because of its good solubility for salts and low solubility for many hydrophobic extractants.^{7–9,31} *p*-Cymene has suitable polarity to dissolve hydrophobic extractants and to avoid formation of a third phase. Moreover, both *p*-cymene and EG are recommended green solvents for solvent extraction applications,³² and they have limited mutual solubility.

The commercial extractant Cyanex 923 (C923, a mixture of trialkyl phosphine oxides, Figure 1),³³ was used as the

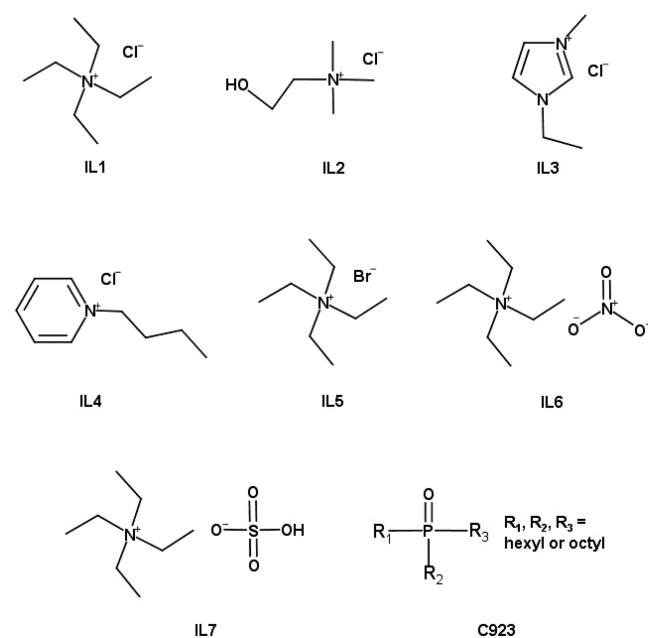


Figure 1. Structures of C923 and of the hydrophilic ILs and analogues: tetraethylammonium chloride (IL1), choline chloride (IL2), 1-ethyl-3-methylimidazolium chloride (IL3), 1-butylpyridinium chloride (IL4), tetraethylammonium bromide (IL5), tetraethylammonium nitrate (IL6), and tetraethylammonium hydrogen sulfate (IL7).

extractant in the LP phase because it has limited solubility in EG, and C923 extracts metals more efficiently from EG solutions than from aqueous solutions.^{7,8} Tetraethylammonium chloride (TEAC, MW = 165.7 g·mol⁻¹) is a hydrophilic organic salt, and it was chosen as the complexing agent in the MP phase. The melting point of TEAC (364 °C³⁴) is higher than 100 °C, which is sometimes regarded as a criterion for the melting points of ILs. However, the choice of 100 °C is arbitrary, and there is no agreement on the definition of IL.³⁵

TEAC and other hydrophilic organic salts with relatively higher melting points are analogues of ILs, although they are not classified as ILs.

The assumption that TEAC can complex with metals is based on the fact that Aliquat 336 (a commercial mixture of trioctylmethylammonium chloride and tridecylmethylammonium chloride) is a well-known extractant for many metal chloride salts,³⁶ and it is a long-chain homologue of TEAC. This assumption was validated by recording the UV-vis absorption spectra of $[\text{CoCl}_4]^{2-}$. Aliquat 336 extracts CoCl_2 by forming an ionic complex: $2[\text{NR}_3\text{R}'^+] \cdot [\text{CoCl}_4]^{2-}$ (R = octyl or decyl, R' = methyl).³⁷ The octahedral complex $[\text{CoCl}_x(\text{EG})_y(\text{H}_2\text{O})_{6-x-2y}]^{2-x}$ (EG is usually a bidentate ligand when solvating with Co(II) or Ni(II)^{38–40}) and the tetrahedral complex $[\text{CoCl}_4]^{2-}$ have distinct absorption spectra, the former showing one absorption band at around 530 nm and the latter showing three absorption bands between 600–700 nm.^{41–43} UV-vis absorption spectra of EG solutions containing 0.30 g·L⁻¹ Co(II) (as CoCl_2) and various concentrations of LiCl or TEAC were recorded (Figure 2).

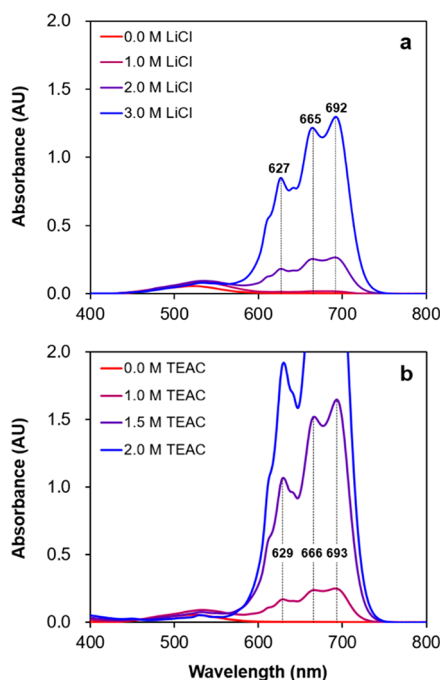


Figure 2. UV-vis absorption spectra of CoCl_2 in EG solutions (0.30 g·L⁻¹ Co(II)) (a) with varying LiCl concentrations and (b) with varying TEAC concentrations.

Evidently, the formation of $[\text{CoCl}_4]^{2-}$ was much stronger when TEAC was added than when LiCl was added. For instance, the absorbance at 693 nm was 1.65 for 1.5 mol·L⁻¹ TEAC, whereas the corresponding absorbance with 3.0 mol·L⁻¹ LiCl was only 1.30. The strong formation of $[\text{CoCl}_4]^{2-}$ in the presence of TEAC indicates that TEAC can readily complex with Co(II). The stronger formation of $[\text{CoCl}_4]^{2-}$ with TEAC than with LiCl might be because tetraalkylammonium cation can enhance coordination of chloride to the metal cation. For instance, compared with Li⁺, tetramethylammonium cation was found to drive coordination of chloride to neptunium dioxocation.⁴⁴

3.2. Mutual Solubility Property of the New System.

The mutual solubility of the LP phase containing *p*-cymene

and various C923 concentrations and the MP phase containing EG and 1.0 mol·L⁻¹ TEAC was determined at room temperature (Figure 3). TEAC could not be detected in the

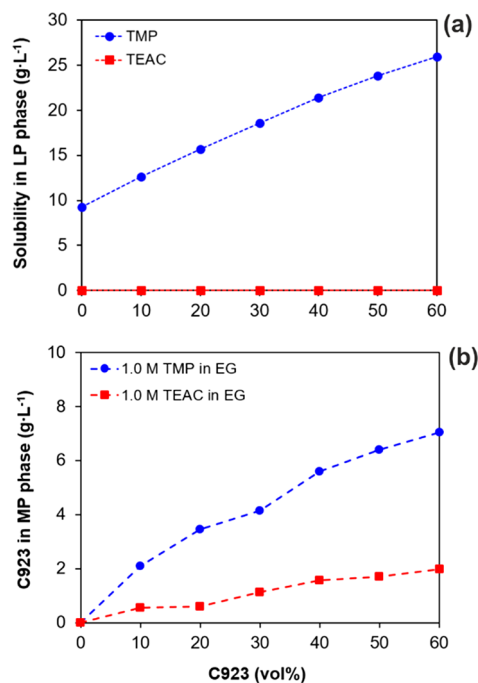


Figure 3. Mutual solubility of the two phases: (a) solubility of trimethyl phosphate (TMP) and tetraethylammonium chloride (TEAC) in the LP phase and (b) solubility of C923 in the MP phase. The LP phase contained various C923 concentrations in *p*-cymene; the MP phase contained 1.0 mol·L⁻¹ TMP or 1.0 mol·L⁻¹ TEAC in EG.

LP phase. The solubility of C923 in the MP phase was less than 2.0 g·L⁻¹ (~0.4% of the total C923) under all the tested conditions. Therefore, C923 and TEAC were very well confined to their own phases.

As a comparison, the mutual solubility of the MP phase containing EG and 1.0 mol·L⁻¹ trimethyl phosphate (TMP, MW = 140.1 g·mol⁻¹) and the same LP phase was measured. TMP is a hydrophilic molecular compound with a molecular weight comparable to TEAC, and its hydrophobic homologue is the well-known extractant tributyl phosphate (TBP). The solubility of TMP in the less polar phase was 25.9 g·L⁻¹ (18.5% of the total TMP) at 60 vol % C923. The solubility of C923 in the MP phase was also much higher compared with that of the TEAC system. Consequently, the C923/*p*-cymene and TMP/EG system cannot be used for metal separations because of the high mutual solubility.

EG is also highly soluble in the LP phase (Figure S1). In fact, even water, which is very polar and is the smallest liquid molecular compound at room temperature, was dissolved in the LP phase for up to 8% of the total amount when equilibrating 10 vol % water in EG with the LP phase (Figure S2). By contrast, many other hydrophilic ILs with various cations and anions (Figure 1) were further tested for mutual solubility, and none of them were detected in the LP phase. These comparisons clearly demonstrate that the high polarity of the hydrophilic ILs resulting from the ionic bonds is indispensable for completely confining the hydrophilic ILs in the MP phase.

3.3. Separation of Co(II) and Sm(III) by the New System. The liquid–liquid extraction system with C923 as an extractant in *p*-cymene and TEAC as a complexing agent in EG was developed and used to separate Co(II) and Sm(III). This separation is relevant to the recycling of valuable metals from SmCo magnets, and both Sm and Co are critical metals.⁴⁵ When LiCl was used as the chloride source (Figure 4a),

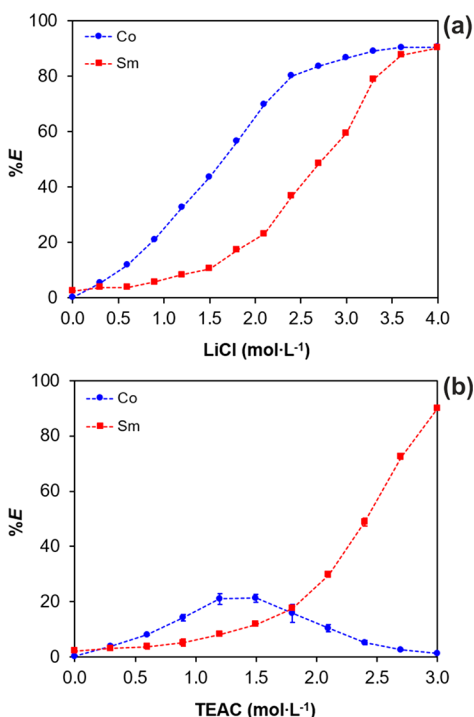


Figure 4. Percentage extraction of Sm(III) (0.30 g·L⁻¹) and Co(II) (0.30 g·L⁻¹) by 20 vol % Cyanex 923 dissolved in *p*-cymene from EG solutions LiCl (a) or TEAC (b, with error bars).

extractions of both Co(II) and Sm(III) increased with increasing LiCl concentration, and Co(II) was more efficiently extracted than Sm(III). It is worth mentioning that the extraction of Sm(III) by C923 from aqueous chloride solutions is negligible, but the use of EG as solvent enables the extraction of Sm(III) by C923.⁸ With TEAC as the chloride source (Figure 4b), the extraction of Sm(III) increased monotonically with increasing TEAC concentrations. By contrast, the extraction of Co(II) increased with increasing TEAC concentrations up to 1.2 mol·L⁻¹ and then decreased. For 3.0 mol·L⁻¹ TEAC, the percentage extraction of Sm(III) was 89.9%, whereas only 1.2% Co(II) was coextracted, leading to a separation factor (α) of Sm(III)/Co(II) of up to 736. This preferential extraction of Sm(III) over Co(II) is unusual, because both C923 and Aliquat 336 preferentially extract Co(II) over Sm(III), and it is not possible to selectively extract Sm(III) by using either C923 or Aliquat 336 alone.

3.4. Speciation in the New System. To explain the extraction isotherms in Figure 4, a number of characterization methods have been applied to determine the structure of the Co(II) complex in the LP phase. A slope analysis of Co(II) extraction by C923 from the EG solution gave a slope of 1.78 (Figure 5a), very close to 2.0. This slope indicates that the stoichiometric ratio of C923 to Co(II) is 2:1.

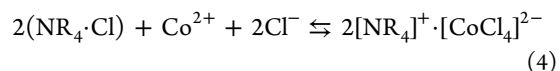
Additionally, two chloride anions are needed in the complex to keep charge neutrality. As a result, a complex of CoCl₂·L₂ (L

= C923) can be hypothesized, which might be tetrahedral. The UV–vis absorption spectrum of this species (Figure 5b) is similar to that of [CoCl₄]²⁻ but with a blueshift of about 30 nm (Figure 2). [CoCl₄]²⁻ is tetrahedral; hence, CoCl₂·L₂ is likely to have a distorted tetrahedral structure.

Furthermore, an X-ray absorption spectrum of the complex was recorded, from which the EXAFS function and Fourier transform were deduced, which were fitted using a theoretical model based on the expected Co(II) complex. The model consisted of two interactions: a Co–Cl interaction at 2.2 Å and a Co–O interaction at 2.0 Å, both in the first coordination sphere around the central Co(II) atom. Only the two single scattering paths were used as input for fitting. The fitting results are presented in Figure 5 and summarized in Table S2. The *r*-values of both Co–Cl and Co–O corresponded well to the expected distances of a tetrahedral Co(II) complex with two chloride ligands and two Cyanex 923 ligands (with oxygen as the coordinating atom) directly coordinated to the metal center. The expected degeneracy of 2 for both Co–Cl and Co–O paths fitted well within the error range of the results. Therefore, the hypothesized complex structure, CoCl₂·L₂ (L = C923), in the LP phase is experimentally confirmed.

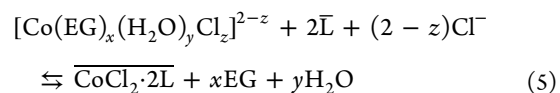
On the basis of speciation studies, the mechanism of this liquid–liquid extraction system with a hydrophilic IL or analogue as complexing agent is evident:

- (a) TEAC exhibits complexing capabilities toward Co(II) and Sm(III) similar to those of Aliquat 336;⁹ it does not complex with Sm(III), but it does complex with Co(II) following eq 4:

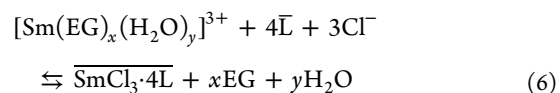


where [NR₄]Cl represents TEAC.

- (b) The extraction of Co(II) by C923 follows eq 5, which is the same as the extraction of Co(II) from aqueous solutions by C923.⁴⁶



- (c) The extraction of Sm(III) by C923 can be expressed by eq 6 according to Batchu et al.⁷



where L represents C923, and the overbar represents species in the LP phase.

Although LiCl only acts as a chloride source to promote extraction of Co(II) and Sm(III) (according to eqs 5 and 6, respectively), TEAC plays different roles for the extraction of Sm(III) and Co(II): (1) It acts only as a chloride source for Sm(III) extraction (according to eq 6), but the ammonium cation does not bind with Sm(III) because Sm(III) cannot form an anionic chlorometallate complex in ethylene glycol as a result of the low stability of the Sm–Cl complex.^{47,48} (2) It functions both as a chloride source (when TEAC < 1.2 mol·L⁻¹, according to eq 5) and as a complexing agent in the case of Co(II) extraction (when TEAC > 1.2 mol·L⁻¹, according to eq 4).

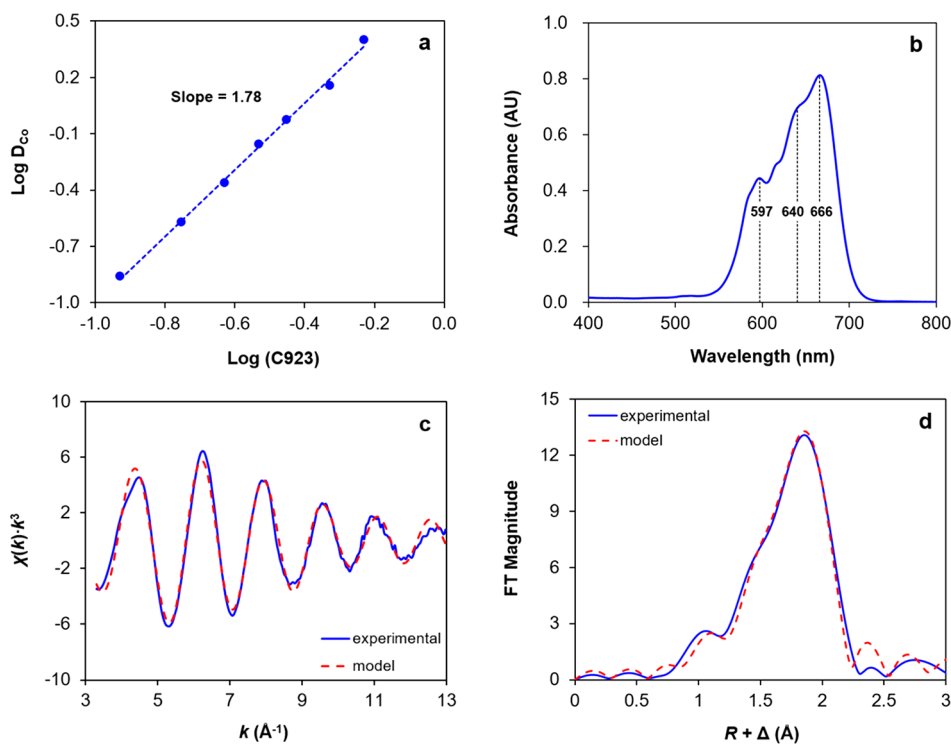


Figure 5. Characterization of the Co(II) complex in the LP phase: (a) slope analysis of Co(II) extraction by C923, (b) UV-vis absorption spectrum of the loaded LP phase, (c) k^3 -weighted EXAFS function, and (d) Fourier transform of the EXAFS function of the Co(II) complex.

In this liquid–liquid extraction system, C923 extracts both Co(II) and Sm(III) to the LP phase, whereas TEAC selectively holds back Co(II) in the MP phase. A schematic illustration of Co(II) extraction based on density functional theory (DFT) calculations is given in Figure 6. Compared with conventional liquid–liquid extraction systems, this liquid–liquid extraction system with hydrophilic ILs or analogues as complexing agents in the MP phase has an additional adjustable parameter, which

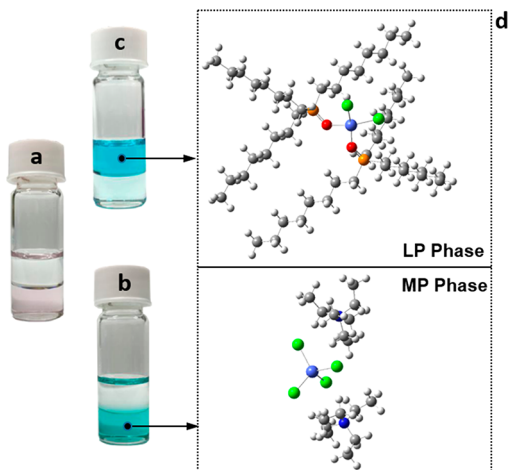


Figure 6. Mechanism of Co(II) extraction in the liquid–liquid extraction system with TEAC in the MP phase: (a) pink octahedral $[\text{Co}(\text{EG})_x(\text{H}_2\text{O})_y]^{2+}$ in EG; (b) blue tetrahedral $[\text{CoCl}_4]^{2-}$ in EG with $3.0 \text{ mol}\cdot\text{L}^{-1}$ TEAC; (c) blue distorted tetrahedral $\text{CoCl}_2\cdot\text{L}_2$ ($\text{L} = \text{C923}$) in the loaded LP phase; and (d) Co(II) complexes in the two phases optimized by DFT on the basis of experimental characterizations: cyan is Co(II), green is chloride, red is oxygen, yellow is phosphorus, blue is nitrogen, gray is carbon, and white is hydrogen.

led to the reversed separations of Co(II) and Sm(III). The complexing mechanism in this liquid–liquid extraction system is via coordination with anions of the ILs or analogues, which is different from TALSPEAK and related systems, in which the complexation is achieved by coordination with the active functional groups, such as carboxyl or pyridine groups.

3.5. Performance of Other Hydrophilic ILs and Analogues. In addition to TEAC (IL1), choline chloride (IL2) and 1-ethyl-3-methylimidazolium chloride (IL3) were tested as complexing agents in the EG solution, with the results shown in Figure 7. 1-Ethyl-3-methylimidazolium chloride performed similar to TEAC, as can be seen from the extraction isotherms. However, extraction of Sm(III) is always higher than that of Co(II) in the presence of 1-ethyl-3-methylimidazolium chloride (IL3), but extraction of Co(II) is higher than that of Sm(III) when TEAC is $<1.5 \text{ M}$. From the speciation study, cations of the hydrophilic ILs are not involved the first coordination sphere and only neutralize the anionic complex as a counteranion. How the cations affect the metal extraction warrants further investigation in a separate study. By contrast, the extraction of Sm(III) from the MP phase containing choline chloride (IL2) was much lower, which might be caused by the interaction of Sm(III) with the hydroxyl group of choline chloride.

Furthermore, 1-butylpyridinium chloride (IL4), tetraethylammonium bromide (IL5), tetraethylammonium nitrate (IL6), and tetraethylammonium hydrogen sulfate (IL7) were tested as complexing agents in the EG solution, and the results are given in Figure 8. IL1 to IL4 and LiCl have the same anion (Cl^-) with varying cations. The extractions of Co(II) in the presence of IL1 to IL4 are similar overall, but the extraction of Co(II) in the presence of LiCl is much higher. The higher extraction of Co(II) in the presence of LiCl is because LiCl is less able to hold back Co(II) as a result of its lower capability

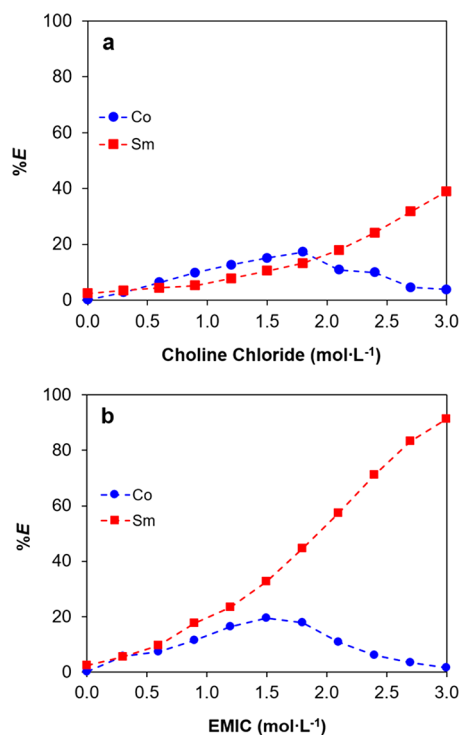


Figure 7. Percentage extraction (%E) of SmCl₃ (0.30 g·L⁻¹ Sm) and CoCl₂ (0.30 g·L⁻¹ Co) by 20 vol % Cyanex 923 dissolved in *p*-cymene from EG solutions with (a) choline chloride or (b) 1-ethyl-3-methylimidazolium chloride (EMIC).

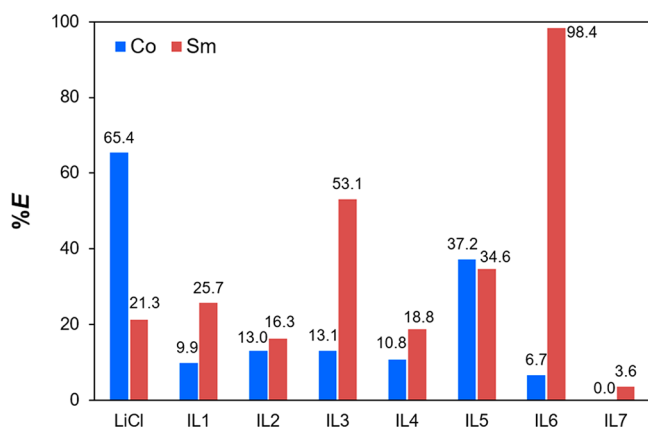


Figure 8. Extraction of Sm(III) (0.30 g·L⁻¹) and Co(II) (0.30 g·L⁻¹) by 20 vol % Cyanex 923 dissolved in *p*-cymene from EG solutions with 2.0 mol·L⁻¹ LiCl or hydrophilic ILs and analogues. The ILs and analogues are shown in Figure 1.

of complexing with Co(II). Extraction of Sm(III) also varies in the presence of different hydrophilic ILs and analogues, especially in that the extraction is higher in the presence of IL3. As discussed above, the cations are not involved in the first coordination sphere; how they affect the formation of chlorometallate anions needs further study. IL4 to IL7 have the same cation ($[N(C_2H_5)_4]^+$) with varying anions. Extraction of both Co(II) and Sm(III) is more efficient in the presence of bromide than in the presence of chloride. Extraction of Sm(III) is almost quantitative with nitrate anion (IL6), whereas extraction of Co(II) is very low. By contrast, extraction of both Co(II) and Sm(III) is low in the presence of hydrogen sulfate anion (IL7). The significant effect of

anions on the extraction is because metal cations have different tendencies to coordinate with these anions. The coordinating abilities of anions toward transition metals and lanthanides have been given by Diaz-Torres and Alvarez,⁴⁹ whose observations are consistent overall with those in this study. These results clearly show that both cations and anions affect the extraction of metals significantly, which could be a basis for regulating the separation of many metals using different kinds of hydrophilic ILs and analogues as complexing agents in the MP phase.

3.6. Recyclability of the New System. To make a liquid–liquid extraction system economically feasible, it is important to reuse the extractants and diluents. Despite the high separation factor of Sm(III)/Co(II) with a 3.0 mol·L⁻¹ TEAC solution, it is difficult to recover Co(II) from the MP phase after extraction of Sm(III) because the Co(II) extraction is too low. Using a combination of LiCl and TEAC, the extraction of Co(II) can be enhanced, while keeping efficient extraction of Sm(III), at the expense of slightly decreased selectivity. For example, with 1.8 mol·L⁻¹ TEAC and 1.2 mol·L⁻¹ LiCl, the extractions of Sm(III) and Co(II) were 82.6 and 9.2%, respectively, and the separation factor was 47 (Figure 9).

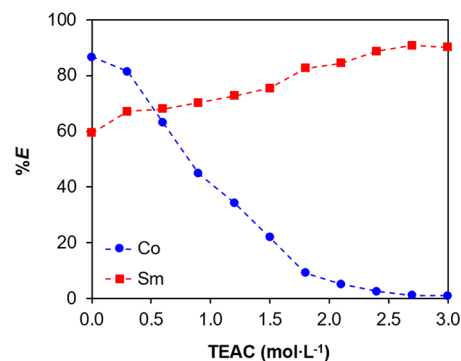


Figure 9. Separation of Co(II) and Sm(III) with varying tetraethylammonium chloride (TEAC) concentrations. The total concentration of TEAC and LiCl was kept at 3.0 mol·L⁻¹.

Under these conditions, Sm(III) and Co(II) can be separated efficiently, and Co(II) in the raffinate can be recovered with a higher C923 concentration and a higher phase ratio (Figure 10). With 60% C923 in *p*-cymene and a phase ratio of 5:1 (LP phase/MP phase), 86.8% Co(II) was recovered from the raffinate of the MP phase in a single stage. After removal of Co(II), the MP phase can be reused. The loaded LP phase was efficiently stripped by either EG or water. The regenerated LP phase can also be reused.

4. CONCLUSIONS

A liquid–liquid extraction system with Cyanex 923 in *p*-cymene as the less polar phase and tetraethylammonium chloride (a hydrophilic ionic liquid analogue) in EG as the more polar phase has been developed for the separation of Sm(III) and Co(II). Cyanex 923 and tetraethylammonium chloride in this extraction system are respectively well confined in the two immiscible phases because of the high polarity of the tetraethylammonium chloride. Cyanex 923 extracts both Sm(III) and Co(II) to the less polar phase, but tetraethylammonium chloride selectively holds back Co(II) in the more polar phase by formation of a chlorometallate complex, leading to enhanced metal separation. Following the same principle, a

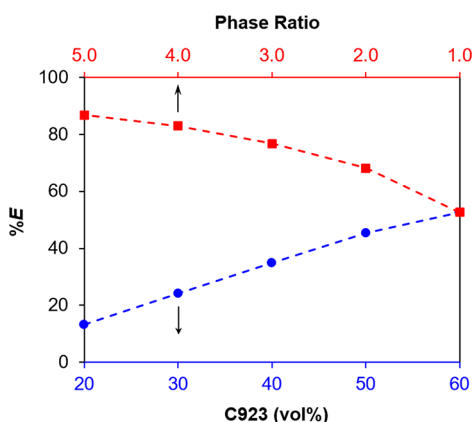


Figure 10. Recovery of Co(II) from MP raffinate: effect of C923 concentration with phase ratio at 1:1 (blue circles) and effect of phase ratio (LP phase/MP phase) with C923 concentration at 60 vol % (red squares).

range of hydrophilic ionic liquids and analogues can be used as complexing agents in the more polar phase to enhance metal separations, and both cations and anions of the ionic liquids and analogues affect metal extraction.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b03472.

More discussions on the mutual solubility of the two immiscible phases and explanations about fitting of EXAFS spectra for the reference solution (PDF)

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Notes

The authors declare no competing financial interest.

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