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Efficient separation of transition metals from rare earths by an undiluted phosphonium thiocyanate ionic liquid

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Abstract

The ionic liquid trihexyl(tetradecyl)phosphonium thiocyanate has been used for the extraction of the transition metal ions Co(II), Ni(II), Zn(II), and the rare-earth ions La(III), Sm(III) and Eu(III) from aqueous solutions containing nitrate or chloride salts. The transition metal ions showed a high affinity for the ionic liquid phase and were efficiently extracted, while the extraction efficiency of the rare-earth ions was low. This difference in extraction behavior enabled separation of the pairs Co(II)/Sm(III), Ni(II)/La(III) and Zn(II)/Eu(III). These separations are relevant for the recycling of rare earths and transition metals from samarium cobalt permanent magnets, nickel metal hydride batteries and lamp phosphors, respectively. The extraction of metal ions from a chloride or nitrate solution with a thiocyanate ionic liquid is an example of "split-anion extraction", where different anions are present in the aqueous and ionic liquid phase. Close to 100% loading was possible for Co(II) and Zn(II) up to a concentration of 40 gL^{-1} of the transition metal salt in the initial aqueous feed solution, whereas the extraction efficiency for Ni(II) gradually decreased with increase in the initial feed concentration. Stripping of Co(II), Zn(II) and Ni(II) from the loaded ionic liquid phase was possible by a 15 wt% NH_3 solution. The ionic liquid could reused after extraction and stripping.

Introduction

Solvent extraction (SX) is the most important technique in hydrometallurgy for separation and purifications of metals.[1,2] This technique is based on the preferential distribution of metal ions between two immiscible phases, typically an aqueous phase and an organic phase that are in contact with each other.[3] The organic phase comprises several components: extractant, diluent and possibly a modifier. Replacement of volatile organic solvents by ionic liquids (ILs) in solvent extraction can lead to inherently safer and environmentally friendlier processes.[4] Earlier studies on the extraction of metal ions by ionic liquids made use of hydrophobic imidazolium ionic liquids with fluorinated anions as the solvent for a molecular extractant.[5-14] The extraction mechanism in ionic liquids can differ from those observed in molecular solvents.[15-17] This can be an advantage and allows designing more selective separation processes, but it could also be a disadvantage if the ionic liquid components are lost to the aqueous phase by an ion-exchange mechanism. More recent developments have led to the introduction of task-specific ionic liquids (TSILs) or functionalized ionic liquids (FILs), in which a metal-coordinating group is attached to the ionic liquid cation.[18-20] These ionic liquids can replace the molecular extractants dissolved in ionic liquids, leading to purely ionic extraction systems. Ionic liquids with coordinating anions can act both as extractant and diluent. A recent development is the use of these ionic liquids for homogeneous liquid-liquid extraction processes.[21]

Ionic liquids with fluorinated anions are not ideal for use in solvent extraction processes, both from an economical and environmental point of view. These ionic liquids typically contain a hydrophilic 1-alkyl-3-methylimidazolium cation. Replacement of the imidazolium cation by quaternary ammonium or phosphonium cations with long alkyl chains allows obtaining hydrophobic ionic liquids with non-fluorinated anions. Well-known examples are ionic liquids with the quaternary ammonium cation Aliquat 336 or with the trihexyl(tetradecyl)phosphonium cation.[22-34] These ionic liquids are structurally similar to anion-exchange extractants (basic extractants).[35-39] It is important that these ionic liquid cations do not exhibit surfactant properties, because otherwise emulsions will be formed and phase disengagement will become difficult. The advantage of trihexyl(tetradecyl)phosphonium ionic liquids over ionic liquids based on Aliquat 336 is the lower solubility of the former in water. It was thought for some time that these ionic liquids are too viscous to be used in undiluted form for solvent extraction.[40] However, several of the potential advantages of ionic liquids are lost by adding molecular diluents to the organic phase of the solvent extraction system. Recent research has shown that quaternary ammonium and phosphonium ionic liquids can be used without molecular diluents, provided that the ionic liquid phase is presaturated with water or that the extraction process is carried out at elevated temperatures to reduce the viscosity.[41-44] These non-fluorinated ionic liquids can also be used as diluents for functionalized ionic liquids or for molecular extractants.[20,45]

In this paper, the separation of the pairs Ni(II)/La(III), Co(II)/Sm(III) and Zn(II)/Eu(III) by solvent extraction with the ionic liquid trihexyl(tetradecyl)phosphonium thiocyanate, [P_{66614}][SCN], is described (Fig. 1). No molecular organic solvent is added as a diluent. Separation of Ni(II) from La(III) is relevant for the recovery of metals from nickel metal hydride batteries, whereas the separation of Co(II) from Sm(III) is of importance for the recycling of samarium cobalt magnets.[46] Separation of Zn(II) from Eu(III) is required when europium is separated from a mixture of rare earths by reduction of Eu(III) to Eu(II) by zinc powder or zinc amalgam, followed by reoxidation of Eu(II) to Eu(III), in an extraction process to separate europium from yttrium. This separation is found in recycling schemes for recovery of europium and yttrium from lamp phosphor waste.[46]

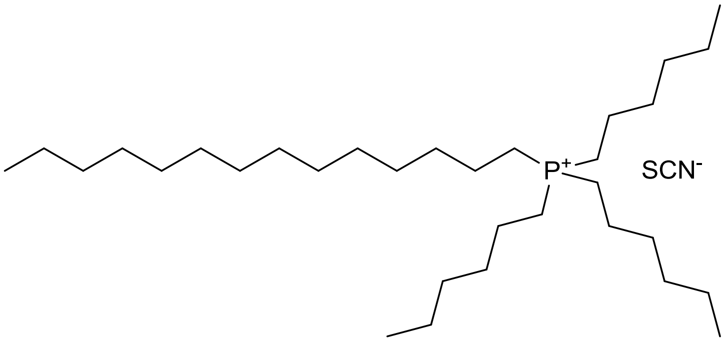

Fig. 1 Structure of the ionic liquid trihexyl(tetradecyl)phosphonium thiocyanate, $[P_{66614}][SCN]$.

Experimental

Chemicals and reagents

All chemical and reagents used in this study were used as received without further purification. Ammonium thiocyanate (99%), potassium thiocyanate (99%) and sodium nitrate (99%) were obtained from Sigma-Aldrich (Diegem. Belgium).

Trihexyl(tetradecyl)phosphonium chloride (98%, Cyphos® IL 101, Cytec Industries) was purchased from Iolitec (Heilbronn, Germany). The metal salts $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and the corresponding hydrated chloride salts had a purity of 99% or better and were purchased from Acros Organics (Geel, Belgium) or Sigma-Aldrich (Diegem, Belgium). A 1000 ppm gallium standard was purchased from Merck (Overijse, Belgium). Trihexyl(tetradecyl)phosphonium thiocyanate was synthesized by equilibrating trihexyl(tetradecyl)phosphonium chloride with an equal volume of an aqueous potassium or ammonium thiocyanate solution (3 to 4 M) for 1 h, with shaking. The organic phase was separated and the process was repeated four to five times to remove the chloride impurities as good as possible. Then, trihexyl(tetradecyl)phosphonium thiocyanate was washed with distilled water, followed by drying *in vacuo*. The chloride content of the thiocyanate ionic liquid was below the detection limit of the TXRF technique, which is for ionic liquids about 20 ppm.[47]

Instrumentation and analysis

The viscosity of the ionic liquid phase was measured by an automatic plate-cone viscometer (Brookfield Engineering Laboratories, USA, model LVDV-II+P CP). The water content of the ionic liquid phase before and after presaturation with water was determined with a coulometric Karl Fischer titrator (Mettler-Toledo DL 39). The metal content was quantified using a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker), with gallium as internal standard. The quartz glass sample carriers were first treated with 20 μL of a silicone solution in isopropanol (SERVA Electrophoresis GmbH, Heidelberg, Germany), followed by drying in a hot air oven at 60 °C for 5 min. The glass surface was siliconized for avoiding spreading of the sample droplet. Milli-Q water was used for dilution of the samples. An aliquot of 10 μL of sample solution was put on the glass carrier, dried in a hot-air-oven at 60 °C, and then measured with a measurement time of 200 s.

Extraction procedures

The initial feed concentration of all the metal ions was 5 g L^{-1}, unless otherwise specified. The volume ratio of the two phases was 1:1. All extraction experiments were performed by shaking (2000 rpm) the mixtures at 50 °C for 60 min with a Nemus Life Thermo Shaker TMS-200 (Nemus LIFE AB, Lund, Sweden). The effect of equilibration time was determined by varying the time from 2 to 60 min. A Heraeus Labofuge 200 centrifuge (Thermo Fisher Scientific, Asse, Belgium) was used to accelerate phase separation after extraction (3000 rpm, 5 min). The metal concentrations in the ionic liquid and aqueous phase were measured by TXRF (see previous section).

The *distribution ratio* (*D*) is the ratio of the concentration of the metal ion *M* in the ionic liquid phase (IL) and the aqueous phase (*aq*), at equilibrium:

$$D = \frac{[M]_{IL}}{[M]_{aq}} \qquad (1)$$

The distribution ratio is measured most conveniently by measuring the concentration of the metal ion in the aqueous phase after extraction and by comparing it to the initial concentration:

$$D = \frac{C_\mathrm{i} - C_\mathrm{f}}{C_\mathrm{f}} \qquad (2)$$

Here, C_i and C_f are the concentrations of the metal ions in the feed phase before (initial concentration) and after extraction (final concentration), respectively. The *percentage extraction* (*%E*) was determined by using the following equation:

$$\%E = \frac{D}{D+1} \times 100 \qquad (3)$$

This equation is valid for a phase volume ratio of 1:1. The *separation factor* $\alpha(M_1,M_2)$ was calculated as follows:

$$\alpha(M_1, M_2) = \frac{D_{M1}}{D_{M2}} \tag{4}$$

D_{M1} and D_{M2} are the distribution ratios of the metal ions M_1 and M_2, respectively.

Results and Discussion

The metal ions are extracted from an aqueous nitrate or chloride solution to the thiocyanate ionic liquid [P_{66614}][SCN]. This in an example of "*split-anion extraction*", a concept which has been introduced recently by our research group.[48] Because the thiocyanate ions have a much higher affinity for the ionic liquid phase than the chloride or nitrate ions, the thiocyanate ions are not released to the aqueous phase during the extraction experiment. This can be rationalized in terms of the position of the different anions in the Hofmeister series.[49] As shown further in this paper, the extraction efficiency can be modified by addition of extra thiocyanate ions to the aqueous phase.

The effect of the acid concentration of the aqueous feed solution on the extraction of metal ions by the ionic liquid [P_{66614}][SCN] was investigated because there can be competition between protons and metal ions for extraction by the ionic liquid and because thiocyanate ions might decompose in the presence of strong acids. In the presence of nitric acid, the formation of different species such as nitrosyl thiocyanate, ONSCN, has been observed.[50] To test the stability of [P_{66614}][SCN] towards strong acids, extractions were carried out using a 3 M HNO_3 aqueous feed solutions containing either Co(II), Zn(II) and

Ni(II) (each at a concentration of 5 g L^{-1}). As expected, the ionic liquid decomposed upon contact with this acidic aqueous solution, giving a yellow precipitate. Further tests revealed that the ionic liquid is stable in contact with a 1M HNO_3 aqueous solution. The influence of the pH on the extraction behaviour was investigated in the concentration range from 10^{-6} M (pH = 6) to 0.5 M HNO_3. The pH of the aqueous solution did not change upon extraction, so that the equilibrium pH values coincided with the initial pH values. This shows that no protons were co-extracted. The pH had a very minor influence on the distribution ratios of Co(II), Zn(II) and Ni(II) (Fig. 2). Most of the subsequent experiments were performed at a pH value of 0.1. It must be mentioned that the thiocyanate ionic liquid showed some sensitivity to light, so that the solutions were shielded from intense light.

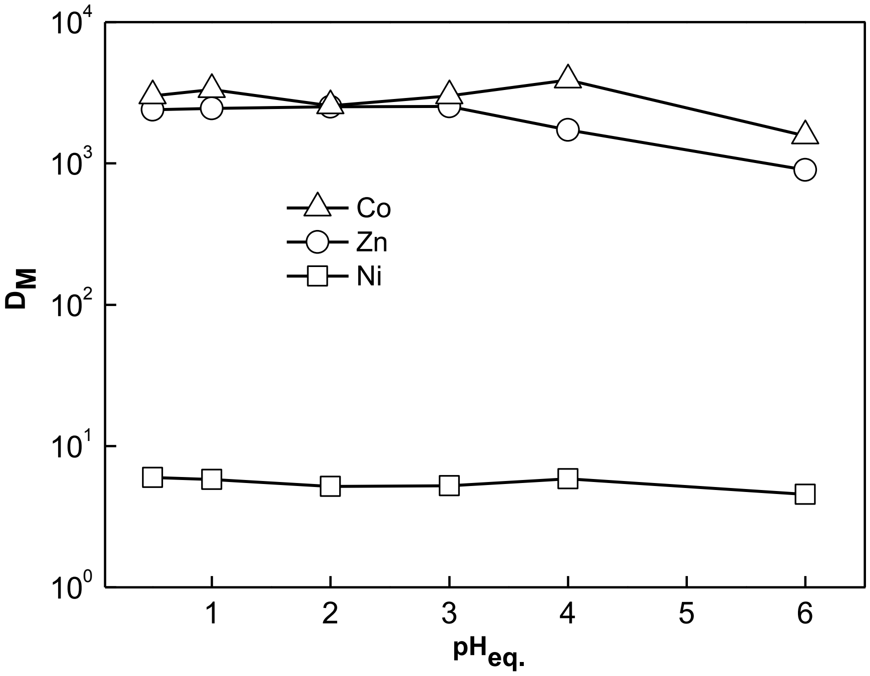

Fig. 2 Variation of the distribution ratio of the transition metal ions Co(II), Ni(II) and Zn(II) as a function of the acidity of the aqueous feed phase. Equilibrium pH values are given.

Organic phase: [P_{66614}][SCN]; aqueous phase: pH 0.5 – 6 (adjusted by HNO_3), transition metal ions (5 gL^{-1} each); temperature: 323 K; phase volume ratio = 1; equilibration time: 1 h.

The ionic liquid [P_{66614}][SCN] has a high viscosity at room temperature (720 cP). However, after pre-saturation with water, the viscosity decreased drastically to about 164 cP (at 30 °C) due to extraction of water (3.2 wt%) and this value further decreased to 46 cP at 50 °C, i.e. the temperature at which the extraction experiments were performed. A viscosity of 46 cP is sufficiently low for a convenient study of the extraction behavior of metal ions and to reach the equilibrium condition within a reasonably short period of time. Due to the strong affinity of thiocyanate ions for transition metal ions, equilibrium was achieved within 10 min, for extraction from aqueous solutions with an initial metal concentration of 5 gL^{-1} (Fig. 3). To determine the extraction kinetics at high feed concentrations, Ni(II) was selected as a representative transition metal ion and a feed concentration of 60 gL^{-1} was used. In this case, extraction was somewhat slower and the equilibrium condition was reached after 20 to 30 min. For all further extraction experiments described in this study, an equilibration time of 1 h was used, to ensure that equilibrium was reached in all conditions.

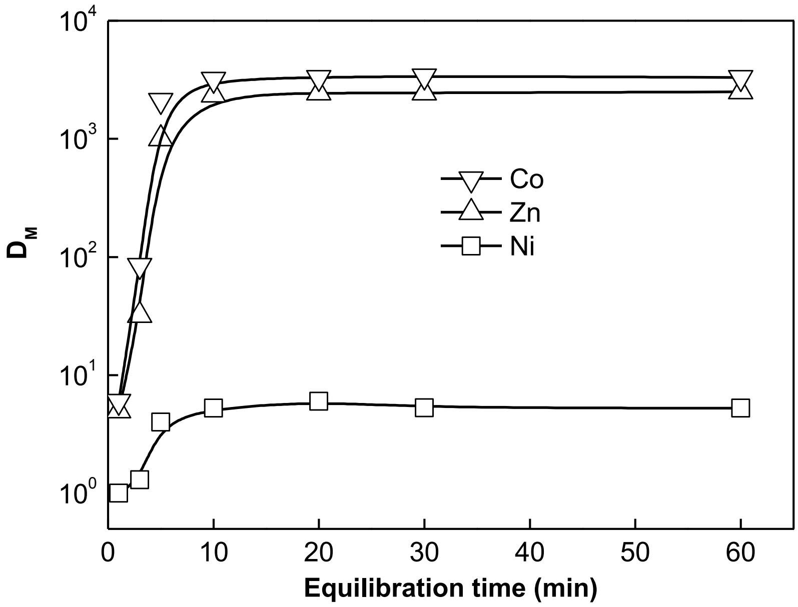

Fig. 3 Variation of the distribution ratio as a function of equilibration time for the extraction from the aqueous phase (pH 1, adjusted by HNO_3) to the ionic liquid phase [P_{66614}][SCN]. The concentration of each metal ion in the aqueous feed solution was 5 g L^{-1}.

A study of the extraction behavior of divalent transition metal ions and trivalent rare-earth ions by the ionic liquid [P_{66614}][SCN] from an aqueous nitrate solution showed that the distribution ratios of the 3d transition metal ions Ni(II), Zn(II) and Co(II) were high to very high (Fig. 2), whereas those of all the rare-earth ions are very small ($D \leq 0.2$). The strong extraction of transition metal ions can be attributed to the strong affinity of thiocyanate ions for coordination to 3d transition metal ions compared to coordination of thiocyanate ions to rare-earth ions.[51-56] This differences in coordination chemistry allows for an efficient separation of transition metals and rare-earth ions by extraction with [P_{66614}][SCN]. The following separation factors α were observed: $\alpha(\text{Co, Sm}) = 4.2 \times 10^5$, $\alpha(\text{Ni, La}) = 750$ and $\alpha(\text{Zn, Eu}) = 2 \times 10^5$. The reason for the relatively small separation factor α(Ni, La) is the low distribution ratio of Ni(II) compared to those of Co(II) and Zn(II). However, due to the very low distribution ratio of La(III) ($D = 0.008$), it is still possible to efficiently separate Ni(II) from La(III). Although the light rare-earth ions are poorly extracted, it must be noted the heavy rare-earth ions have a much stronger affinity for thiocyanate ions. It was recently shown by our research group that extraction with thiocyanate ionic liquids can be used for the separation of the heavy from the light rare earths.[48]

In solvent extraction, it is common practice to determine the extraction mechanism via slope analysis: the slope of the straight line obtained by plotting $\log D$ as a function of log[extractant] is an indication of the number of molecules of extractant involved per metal ion in the extraction process. However, in our case it was not possible to carry out such a slope analysis, because we are working with undiluted ionic liquids so that the concentration of the ionic liquid is constant and cannot be varied. On the basis of the facts that (1) Ni(II), Co(II) and Zn(II) can form tetrathiocyanate complexes $[M(SCN)_4]^{2-}$ (M = Ni, Co, Zn), (2) no thiocyanate ligands are present in the aqueous solution and (3) there needs to be a charge balance, the following equation can be proposed for the solvent extraction of the divalent transition metal ions:

$$\mathrm{M^{2+}} + 2\mathrm{NO_3^-} + 4\overline{[\mathrm{P_{66614}}][\mathrm{SCN}]} \Leftrightarrow \overline{[\mathrm{P_{66614}}]_2[\mathrm{M(SCN)_4}]} + 2\overline{[\mathrm{P_{66614}}][\mathrm{NO_3}]} \qquad (5)$$

Here the bar indicates molecules in the ionic liquid phase, and M = Ni, Co, Zn.

Loading experiments of the $[P_{66614}][SCN]$ phase by metal ions were carried out at different initial metal concentrations in the aqueous feed phase (0.1 M HNO_3), varying from 5 to 60 g L^{-1} for each metal (Fig. 4). Binary mixtures were used in the aqueous phase:

Co(II)/Sm(III), Ni(II)/La(III) and Zn(II)/Eu(III). It was observed that at all initial feed concentrations, the separation factors were extremely high, leaving all the rare-earth ions in the aqueous phase. The distribution ratios of the rare-earth ions were much smaller than 0.1. The percentage extraction of Co(II) and Zn(II) were almost constant as a function of the initial feed concentration, up to a concentration of 40 gL^{-1}, followed by a decrease up to a concentration of 60 gL^{-1}. The percentage extraction decreased from 99.9% to 72% for Co(II) and from 90% to 42% for Zn(II), when the initial feed concentration increased from 40gL^{-1} to 60 gL^{-1}. In contrast, the percentage extraction of Ni(II) decreased continuously from 84% to 38% when the Ni(II) concentration in the aqueous feed was increased from 5gL^{-1} to 60 gL^{-1}. All the rare-earth ions showed percentage extraction values of only 1 to 2%.

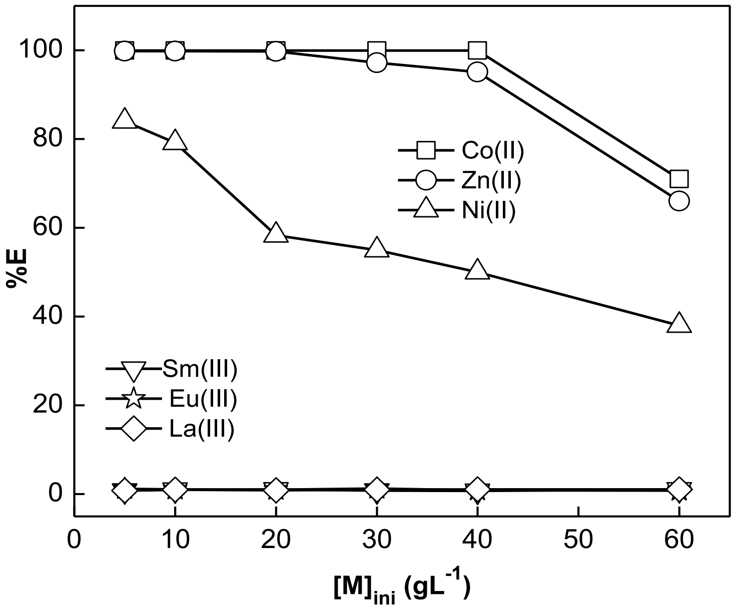

Fig. 4 Variation of the extraction efficiency (%*E*) of metal ions as a function of the initial concentration in the aqueous feed solution. Organic phase: [P_{66614}][SCN]; aqueous phase: pH = 1, metal ions (5 – 60 gL^{-1} each); temperature: 323 K; phase volume ratio = 1; equilibration time: 1 h.

The effect of the variation of the thiocyanate concentration on the extraction of the pairs Co(II)/Sm(III), Ni(II)/La(III) and Zn(II)/Eu(III) was investigated (Figs. 5-7). For the extraction of Co(II)/Sm(III) and Zn(II)/Eu(III) the initial metal concentration in the aqueous feed solution was 40 gL^{-1} for each of the metals in the binary mixture, as there was a decrease of the percentage extraction at concentrations of higher than 40 gL^{-1} for Co(II) and Zn(II) (*vide supra*). On the other hand, the concentration of Ni(II) and La(III) was fixed at 5 gL^{-1} for each of the two metals in the binary mixture, because the distribution ratio of Ni(II) is smaller than the distribution ratios of Co(II) and Zn(II) and because there was a sharp decrease on *D* values with increase in the initial Ni(II) concentration (*vide supra*). In the case of the Ni(II)/La(III) pair, the influence of an increase in thiocyanate concentration on the percentage extraction of Ni(II) was moderate: %*E* of Ni(II) increased from 86% to 99% when the thiocyanate concentration in the aqueous phase was increased from 0 M to 7 M. However, the effect of the thiocyanate concentration on the percentage extraction of La(III) was very pronounced: %*E* of La(III) increased from 0.9% to 88% when the thiocyanate concentration in the aqueous phase was increased from 0 to 7 M (Fig. 5). Similarly, for the Co(II)/Sm(III) and Zn(II)/Eu(III) pairs, the percentage extraction of Co(II) and Zn(II) was relatively insensitive to the thiocyanate concentration in the aqueous phase, whereas the percentage extraction of the rare-earth ions Sm(III) and Eu(III) did show a strong dependence on the thiocyanate concentration: for Sm(III), %*E* increased from 0.7% to 50%, whereas for Eu(III), %*E* increased from 0.8% to 64%.

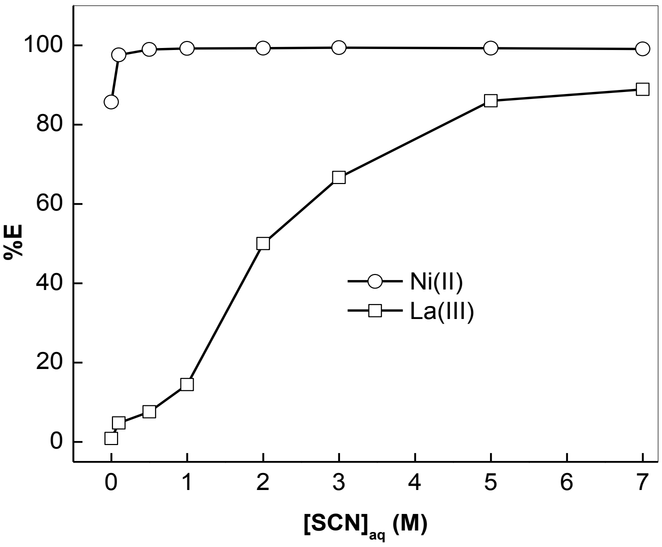

Fig. 5. Variation of the extraction efficiency of Ni(II) and La(III) as a function of the thiocyanate concentration in the aqueous phase. Organic phase: [P_{66614}][SCN]; aqueous phase: pH = 1, 0 – 7 M SCN^- ion (added as NH_4SCN) and metal ions (5 gL^{-1} each); temperature: 323 K; phase volume ratio = 1; equilibration time: 1 h.

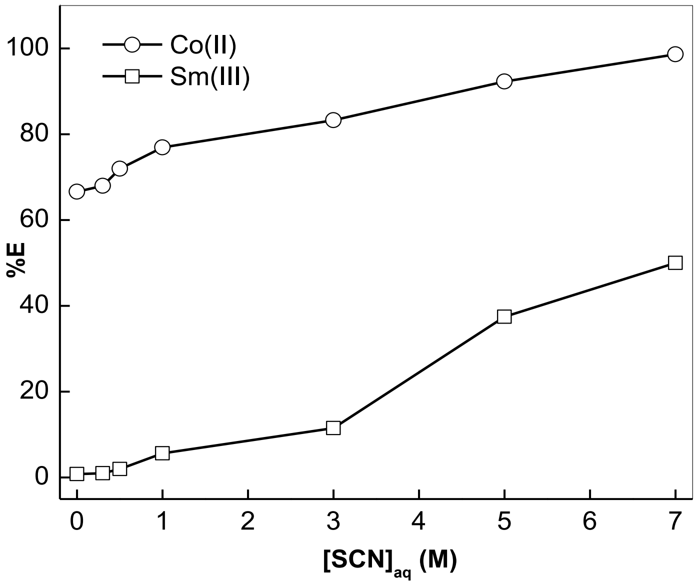

Fig. 6. Variation of the extraction efficiency of Co(II) and Sm(III) as a function of the thiocyanate concentration in the aqueous phase. Organic phase: [P_{66614}][SCN]; aqueous phase: pH = 1, 0 – 7 M SCN^- ion (added as NH_4SCN) and metal ions (5 gL^{-1} each); temperature: 323 K; phase volume ratio = 1; equilibration time: 1 h.

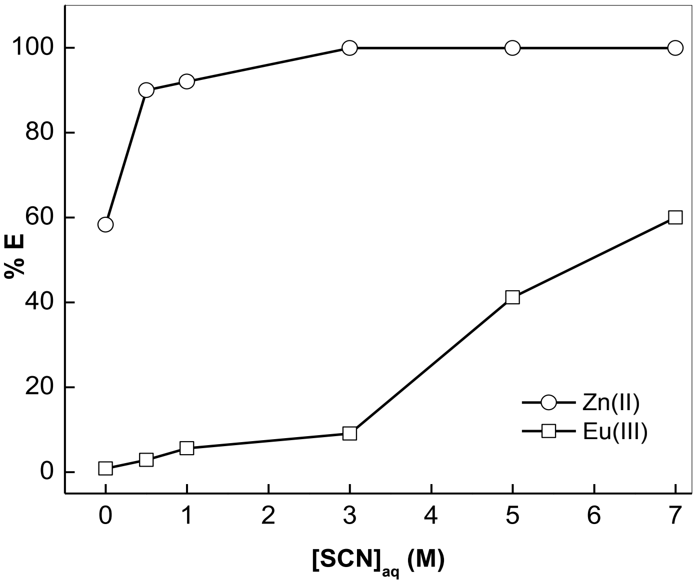

Fig. 7. Variation of the extraction efficiency of Zn(II) and Eu(III) as a function of the thiocyanate concentration in the aqueous phase. Organic phase: [P_{66614}][SCN]; aqueous phase: pH = 1, 0 – 7 M SCN^- ion (added as NH_4SCN) and metal ions (5 gL^{-1} each); temperature: 323 K; phase volume ratio = 1; equilibration time: 1 h.

In order to compare the effects of nitrate and chloride ions on the extraction of transition metal ions and rare-earth ions, the extraction was carried out with the ionic liquid [P_{66614}][SCN] from an aqueous phase containing the chloride salts of the metals, instead of the nitrate salts (Fig. 8). The concentration of the metal ion in the chloride solution (0.1 M HCl) was 5 gL^{-1}. The percentage extraction values of Co(II), Zn(II), La(III), Sm(III) and

Eu(III) for extraction from chloride medium to [P_{66614}][SCN] were very similar to those observed for extraction from nitrate medium. However, the percentage extraction for Ni(II) from chloride medium was much less (%*E* = 18%) compared to the value for extraction from nitrate medium (%*E* = 84%).

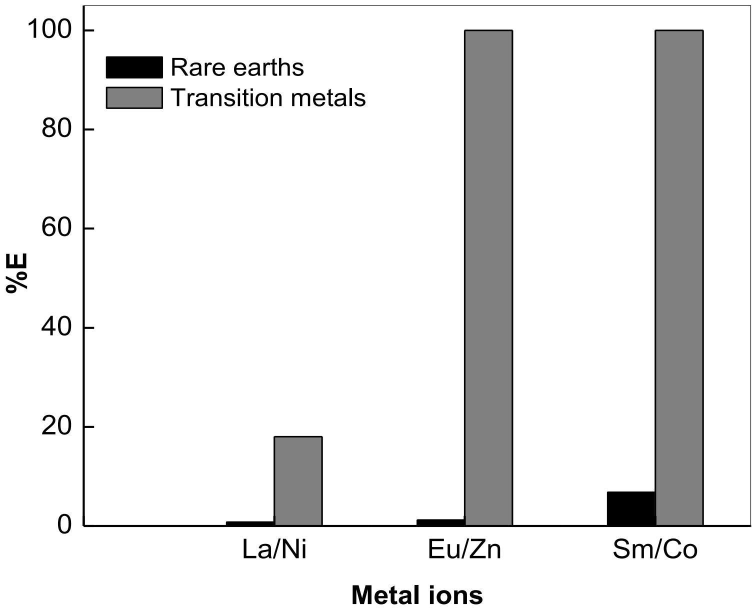

Fig. 8. Variation of the extraction efficiency of transition metals and rare earths by [P_{66614}][SCN] for extraction from aqueous chloride media (pH = 1). Temperature: 323 K; phase volume ratio = 1; equilibration time: 1 h.

The stripping of Co(II), Zn(II) and Ni(II) from the loaded ionic liquid phase was carried out with an aqueous ammonia solution. It was observed that complete stripping of Co((I), Ni(II) and Zn(II) was possible by a 10 wt% NH_3 solution after 3 to 4 stages. After stripping of the metal ions, the ionic liquid [P_{66614}][SCN] was washed thoroughly with water, followed by pre-equilibration with 0.1 M HNO_3 prior to its reuse for a next extraction experiment. The extraction efficiency for the second and third extraction step were almost identical to the values observed for the first extraction step with pristine [P_{66614}][SCN]. These experiments illustrate the recyclability of the ionic liquid.

Conclusions

The ionic liquid trihexyl(tetradecyl)phosphonium thiocyanate, [P_{66614}][SCN], efficiently extracts the transition metal ions Co(II), Ni(II) and Zn(II) from aqueous solutions containing nitrate or chloride salts. Under these conditions, the light rare-earth ions Sm(III), La(III) and Eu(III) are hardly extracted at all. This extraction behavior allows to separate the pairs Co(II)/Sm(III), Ni(II)/La(III) and Zn(II)/Eu(III). These separations are relevant for the recycling of rare earths and transition metals from SmCo permanent magnets, nickel metal hydride batteries and lamp phosphors, respectively. The extraction of metal ions from a chloride or nitrate solution with a thiocyanate ionic liquid is an example of “split-anion extraction”. While the ionic liquid is not suitable for extractions from highly acidic feed solutions (> 1M) and extractions at these conditions result in crud formation, the percentage extraction is largely independent of the pH up to pH = 6. Close to 100% loading is possible for Co(II) and Zn(II) up to a concentration of 40 gL^{-1} of the transition metal salt in the initial aqueous feed solution, whereas the extraction efficiency for Ni(II) decreases gradually with increase in the initial feed concentration. Stripping of Co(II), Zn(II) and Ni(II) from the loaded ionic liquid phase is possible by a 15 wt% NH_3 solution. The ionic liquid can reused after extraction and stripping.

Acknowledgments

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