

Selective Extraction of Metals from Chloride Solutions with the Tetraoctylphosphonium Oleate Ionic Liquid

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Supporting Information

ABSTRACT: The solvent extraction behavior of a series of metal ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , In^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+}) from an aqueous chloride feed solution by the nonfluorinated fatty acid-based ionic liquid (IL) tetraoctylphosphonium oleate $[\text{P}_{888}][\text{oleate}]$ has been investigated as a function of the pH. The possibility to extract metal chlorides from an aqueous stream via the anion or cation of the hydrophobic, low-viscous water-saturated $[\text{P}_{888}][\text{oleate}]$ IL has been exploited. $[\text{P}_{888}][\text{oleate}]$ can be considered as a bifunctional or binary IL. At high pH values ($\text{pH} > 5$), all metals are extracted via the oleate anion, whereas some transition metals are extracted at high HCl concentrations and thus low pH values as anionic chloro complexes in combination with $[\text{P}_{888}]$ cations. A difference of one pH unit is observed between the extraction curves (%*E* as a function of the pH) of the transition metals and those of the rare earth metals. Rare earths are not extracted at low pH values, whereas some transition metals (Fe, Mn, Co, Zn, Cu, In) are extracted. This makes $[\text{P}_{888}][\text{oleate}]$ a promising extractant for the separation of transition metals from rare earths. It is also shown that this bulky and long-chained IL has a very low viscosity due to the uptake of water.

INTRODUCTION

Although metals are essential for our economy, their supply is often at risk. Therefore, the metallurgical industry is more and more focusing on the recycling of metals.¹ Separation and purification of metal ions is often performed by liquid–liquid extraction (solvent extraction).² In this process, the metal is extracted from an aqueous phase by a hydrophobic organic extractant. However, conventional liquid–liquid extraction systems make use of organic solvents, which are often toxic and flammable. Ionic liquids (ILs) are proposed as a substituent for volatile organic solvents.³ ILs are composed of organic cations and organic or inorganic anions and are generally liquid below 100 °C. Strong electrostatic forces between the ions ensure a negligible volatility.⁴ Nevertheless, their low volatility does not imply that they are nontoxic.⁵ A proper selection of the cation and anion is necessary to develop environmentally acceptable ILs with desired properties.^{3,6}

Metal extraction with ILs can be performed by adding molecular extractants to a common commercially available IL.⁷ These extractants interact with the metal ions to form a hydrophobic complex that dissolves in the hydrophobic IL phase. However, ion exchange is often involved in the extraction mechanism, causing the IL cations or anions to be transferred to the aqueous phase. Hereby, the water phase gets contaminated with organic ions from the IL.⁸ Cation exchange can be avoided by choosing bulky and hydrophobic cations, such as tetraalkylphosphonium or tetraalkylammonium ions. However, for ILs where the mechanism of metal extraction is based on ion exchange, increasing the length of the cation can

diminish the extraction efficiency.⁹ Other hydrophobic and low-viscous ILs are often prepared by using fluorinated anions such as hexafluorophosphate (PF_6^-) or bis(trifluoromethylsulfonyl)-imide (Tf_2N^-). Besides the instability of the PF_6^- anion toward hydrolysis,^{5a} fluorinated anions also have a high persistency in nature. All these properties make fluorine-based ILs not as “green” as first assumed.

Functionalized ionic liquids (FILs) are ILs that have a specific functionality built into their structure. This is a metal-binding functional group in metal extraction systems.¹⁰ In the search for biocompatible, nontoxic FILs, we recently synthesized several nonfluorinated fatty acid-based ILs. Long-chained tetraalkylphosphonium or tetraalkylammonium entities were selected as cations. These hydrophobic ILs have been applied for the extraction of several transition metals and showed excellent extraction efficiencies.¹¹ The bulky and hydrophobic cations prevent loss of the IL to the water phase. Another advantage of the fatty acid-based ILs is that the anion of the IL is not lost during acidic stripping and regeneration, because protonation of the oleate anion to oleic acid does not alter the immiscibility with water. The conjugated acids of some IL anions, such as in phthalate¹² and β -diketonates,^{10c,13} are (partly) water miscible or volatile which limits the reuse of these ILs.

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Tetraoctylammonium oleate $[P_{8888}][\text{oleate}]$ is a bifunctional extractant (Figure 1). It has the possibility to extract metals via

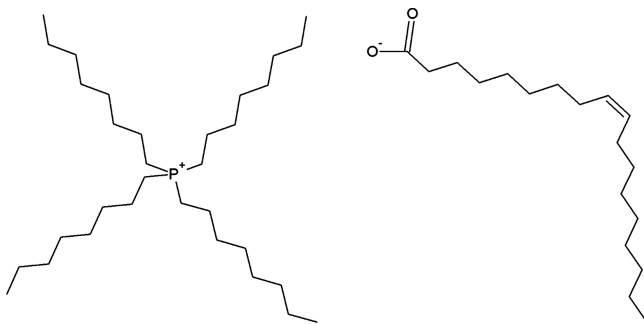


Figure 1. Structure of the tetraoctylphosphonium oleate IL.

its cation as anionic chloro complexes or via its anion by the formation of carboxylate complexes and a chloride IL ($[P_{8888}][\text{Cl}]$). This bifunctionality, useful for the extraction of metals, has also been observed for other ILs.^{10a,14} In this research, we exploited this bifunctional extraction behavior for selective metal separation. The formation of the metal fatty acid complex is pH dependent.¹⁵ The formation of an anionic chloro complex with transition metals such as zinc, copper, cobalt, manganese, and indium depends on the chloride concentration in the system.¹⁶ Metal extraction via the cation or via the anion has to compete with HCl extraction in both cases. Therefore, changing the pH with hydrochloric acid (HCl) has a significant influence on the extraction behavior. The aim of this paper was to investigate the effect of the HCl concentration and, thus, the pH on the extraction of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , In^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Dy^{3+} , Er^{3+} , and Yb^{3+} with a new IL derived from oleic acid, i.e., tetraoctylphosphonium oleate.

EXPERIMENTAL SECTION

Materials. The salts used for preparing the salt solutions for the extraction experiments all had a purity of at least 98%. Copper(II) chloride dihydrate, manganese(II) chloride dihydrate, nickel(II) chloride hexahydrate, iron(III) chloride tetrahydrate, lithium chloride, and sodium chloride were supplied by Boom BV. Dysprosium(III) chloride, zinc(II) chloride, cobalt chloride hexahydrate, indium(III) chloride, and magnesium chloride were supplied by Sigma-Aldrich as well as oleic acid ($\geq 99\%$). Strem Chemicals supplied erbium(III) chloride, samarium(III) chloride, and ytterbium(III) chloride. Lanthanum(III) chloride heptahydrate and neodymium(III) chloride were supplied by Alfa-Aeser, and praseodymium(III) chloride was obtained from GFS Chemicals. Calcium(II) chloride dihydrate and potassium chloride were purchased from VWR Chemicals as well as the sodium hydroxide pellets (99%), hydrogen chloride (37%), and absolute ethanol. The copper and gallium standards (1000 ppm) were obtained from Chemlab. Ammonium hydroxide (35%) and oxalic acid dihydrate ($>99.5\%$) were supplied by J.T. Baker, and tetraoctylphosphonium bromide ($>95\%$) was from IoLiTec. In addition, Milli-Q water ($>18 \text{ M}\Omega\cdot\text{cm}$) used for all the experiments was obtained from a Millipore Milli-Q Biocel, which used a Q-grade column or a Synergy UV water purification system. All chemicals were used as received, without any additional purification steps.

Synthesis of the IL $[P_{8888}][\text{Oleate}]$. The tetraoctylphosphonium oleate IL $[P_{8888}][\text{oleate}]$ was synthesized via a one-pot synthesis procedure. Sodium oleate was formed by stirring oleic acid (21 mL, 66.52 mmol) and sodium hydroxide (3.55 g, 88.69 mmol) for 5 h in 250 mL of water at room temperature. Afterward, $[P_{8888}][\text{Br}]$ (25 g, 44.34 mmol) was added to the reaction mixture. The mixture was stirred for an additional 3 h at 55 °C. The organic phase was vigorously washed with water ($6 \times 200 \text{ mL}$) to remove NaBr and the excess of sodium oleate and NaOH. Concentrating the IL under vacuum resulted in a dark yellow liquid in a yield of 70% (23.76 g). Bromide content: 5 ppm. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): $\delta = 0.86$ (m, 15H), 1.27 (m, 54H), 1.47 (m, 14H), 1.59 (m, 2H), 1.98 (m, 4H), 2.17 (t, 2H), 2.32 (m, 8H), 5.32 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , δ/ppm): 179.3 (C=O), 77.3, 77.0 ($2 \times \text{C}=\text{C}$), 75.6, 38.4, 31.9, 31.7, 30.9, 30.7, 30.0, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.3, 29.0, 29.9, 27.3, 27.2, 26.8, 22.7, 22.6, 21.9, 21.8, 19.1, 18.6, 14.1, 14.0. MS (ESI): Calcd for $[P_{8888}(\text{C}_{32}\text{H}_{68}\text{P})]^+$ $m/z = 483.9$; found $m/z = 483.6$ and calculated for $[\text{Oleate} (\text{C}_{18}\text{H}_{33}\text{O}_2)]^-$ $m/z = 281.5$; found $m/z = 281.3$. Additional peaks were observed in the negative mode: 573.5 ($[P_{8888}]^+ + 2 \times [\text{formate}]^-$), 809.7 ($[P_{8888}]^+ + [\text{oleate}]^- + [\text{formate}]^-$), 1046.0 ($[P_{8888}]^+ + 2 \times [\text{oleate}]^-$), formic acid is for 1% present in the eluent of the LC-MS.

Characterization of the IL. The purity of the IL was determined using ^1H and ^{13}C NMR on a 400 MHz Bruker nuclear magnetic resonance (NMR) spectrometer. Density and viscosity measurements of the pure IL were carried out on an Anton Paar SVM 3000/G2 type Stabinger, with an uncertainty of $\pm 0.0005 \text{ g}\cdot\text{cm}^{-3}$ for the density, $\pm 0.005 \text{ mPa}\cdot\text{s}$ for the viscosity, and $\pm 0.01 \text{ K}$ for the temperature. The viscosity of the dried IL (0.49 wt % water) was measured on a Brookfield plate-cone viscometer, Model CAP 2000+ (Brookfield Engineering Laboratories, USA) with an uncertainty of $\pm 0.01 \text{ Pa}\cdot\text{s}$. Viscosities as a function of the metal loading and temperature were measured with an automatic Brookfield plate-cone viscometer, Model LVDV-II+P CP (Brookfield Engineering Laboratories, USA), with an accuracy of $\pm 0.01 \text{ mPa}\cdot\text{s}$. The decomposition temperature was determined with a thermogravimetric analysis (TGA) Q 500 apparatus (TA Instruments, USA) at a scan rate of $10 \text{ K}\cdot\text{min}^{-1}$ under a nitrogen flow (see the Supporting Information SI 3 and SI 4). The spectra were analyzed with TG instruments software. Determination of bromide impurities was done via total reflection X-ray fluorescence (TXRF) on a Bruker S2 Picofox TXRF spectrometer.¹⁷ About 0.03 g of IL was dissolved in 0.8 mL of ethanol, 0.1 mL of a 25% NH_4OH solution, and 0.1 mL of a 1000 ppm copper standard. Afterward, about 2 μL of this mixture was mounted on a TXRF sample carrier and dried for 10 min at 333 K. The water content of the IL was determined by a coulometric Karl Fischer titrator (Mettler-Toledo, model DL39). Electrospray-ionization combined with mass spectrometry (ESI-MS) was used to analyze the IL after synthesis with acetonitrile as eluent. An Agilent Technologies 1200 series ESI-MS was used with acetonitrile/water 90:10 as eluent working with an Agilent mass hunter workstation data acquisition.

Experimental Salt Extraction Procedure. Different salt solutions have been prepared. A transition metal solution, containing 2000 ppm of each metal (MnCl_2 , CoCl_2 , NiCl_2 , CuCl_2 , ZnCl_2), a rare earth metal solution, containing 2000 ppm of each rare earth (LaCl_3 , NdCl_3 , SmCl_3 , DyCl_3 , ErCl_3 , YbCl_3), a 2000 ppm FeCl_3 solution, a 2000 ppm InCl_3 solution, and an alkali and alkaline earth metal solution, containing 2000

ppm of each metal (LiCl, NaCl, KCl, MgCl₂, CaCl₂) were prepared by dissolving the metal salts in 50 mL of water. Then, 0.5 mL of this salt solution was added to 1 mL of the IL, presaturated with water. An aqueous solution containing HCl or NaOH (0.5 mL) was then added to this solution to obtain the desired pH and final metal concentrations of 1000 ppm. Metal loading of the organic phase was studied by presaturating the IL with water of the same pH as the metal solution. Afterward, a specific volume of a 60 000 ppm Yb, 45 000 ppm La, or 58 000 ppm Nd solution was added and further diluted with water of the same pH until a volume of 1 mL was obtained. The kinetics of the extraction were studied by contacting 1 mL of a 4800 ppm Ni solution and a 5000 ppm Nd solution with 1 mL of the IL phase without adjustment of the pH. Therefore, five different mixtures were shaken at 2000 rpm and 40 °C between 1 and 10 min. The viscosity of the IL as a function of the metal loading was studied with the IL obtained from the loading experiments performed with Nd. It was decided, after investigating the kinetics of the extraction, to perform all further extractions by intensive shaking at 2000 rpm for 10 min at 40 °C on a thermo shaker TMS-200 (Nemus). Later, the mixture was centrifuged on a Heraeus Labofuge 200 (Thermo Scientific) for 5 min at 5300 rpm to accelerate the separation of the two layers prior to analysis. Stripping of Nd by precipitation with oxalic acid was performed after the extraction of 11 000 ppm Nd to the IL phase. Oxalic acid was added to the IL after removal of the water phase. The IL was shaken and centrifuged in identical conditions as described for the extraction experiments.

Analysis of the Water Phase and IL Phase after Metal Extraction. The metal content of the aqueous phase and the IL phase after the extraction experiments of MnCl₂, CoCl₂, NiCl₂, CuCl₂, ZnCl₂, LaCl₃, NdCl₃, SmCl₃, DyCl₃, ErCl₃, and YbCl₃ was analyzed using a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Bruker S2 Picofox). In general, 100 μL of a gallium standard solution (1000 ppm) was added to 100 μL of the aqueous phase and diluted until 1 mL with Milli-Q water. Twenty to 35 mg of the IL was diluted in ethanol prior to analysis of the IL phase. Then, 5 μL of each solution was dried in a hot air oven at 60 °C on quartz glass carriers and analyzed with TXRF. After the extraction experiments of FeCl₃, InCl₃, LiCl, NaCl, KCl, CaCl₂, and MgCl₂, the metal content of the aqueous phase was analyzed with a PerkinElmer, precisely induced coupled plasma (ICP), which used an optical atomic emission spectrometer (AES) Optima 5300DV. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-AES has a detection limit of 25–250 μg L⁻¹, with an uncertainty of 1.4–2%.

The extraction percentage (%E) in the case of equal volumes of the aqueous and organic phase can be calculated by

$$\%E = \left[\left(\frac{C_{\text{org}}}{C_{\text{aq}} + C_{\text{org}}} \right) \right] \times 100 \quad (1)$$

or

$$\%E = \left(\frac{C_{\text{aq},0} - C_{\text{aq}}}{C_{\text{aq},0}} \right) \times 100 \quad (2)$$

where C_{aq} and C_{org} are the metal concentrations in the aqueous phase and organic phase after extraction and $C_{\text{aq},0}$ is the metal concentration of the initial aqueous phase. Distribution factors

can be found for all the metals studied in the Supporting Information.

After the extraction experiments with NdCl₃, the IL was regenerated by acidic stripping with an aqueous oxalic acid solution. The percentage stripped (%S) from the organic phase was calculated by

$$\%S = \left(\frac{C_{\text{org},0} - C_{\text{aq},s}}{C_{\text{org},0}} \right) \times 100 \quad (3)$$

where $C_{\text{org},0}$ is the metal concentration in the IL before stripping and $C_{\text{aq},s}$ is the metal concentration in the aqueous phase after the stripping process. The separation factors between two lanthanides are calculated as

$$\alpha_{\text{Ln1,Ln2}} = \frac{\frac{C_{\text{Ln1,org}}}{C_{\text{Ln1,aq}}}}{\frac{C_{\text{Ln2,org}}}{C_{\text{Ln2,aq}}}} \quad (4)$$

The pH of the water phase was measured after the metal extraction experiment with a pH/ion meter S220 (SevenCompact) and a Slimtrode electrode (Hamilton) or with a Metrohm 827 pH lab. The solubility of the IL in the water phase was measured by Total Organic Carbon analysis (Shimadzu TOC-L_{CPH}) with a detection limit of 1.00 mg L⁻¹. 35 mL of a 0.05 M NaCl solution was mixed for 1 h at 600 rpm with 1 mL of IL and tested on its total organic carbon content. From this solution, a mole fraction x_i of the IL into the aqueous phase was calculated via:

$$x_i = \frac{n_i}{n_{\text{tot}}} \quad (5)$$

in which n_i stands for the amount of a constituent in mole and n_{tot} is the total molar amount of all constituents.

Samples were always measured directly after the experiments to avoid disturbance of the equilibrium media due to degradation of the oleate anion of the IL. One should be careful with fatty acids because they can undergo a polymeric decomposition reaction.¹⁸ These reactions are very slow at room temperature, in air-closed vials, and in the absence of UV light or a catalyst. However, at higher pH values (e.g., [H⁺] concentration of 10⁻⁶ M), small amounts of decomposition products can influence the measured pH values in time.

RESULTS AND DISCUSSION

The influence of the pH on the metal salt extraction efficiencies of five different solutions by using the IL [P₈₈₈][oleate] was investigated: (1) a transition metal solution consisting of MnCl₂, CoCl₂, NiCl₂, CuCl₂, and ZnCl₂, (2) a rare earth metal solution consisting of LaCl₃, NdCl₃, SmCl₃, DyCl₃, ErCl₃, and YbCl₃, (3) an alkali and alkaline earth metal solution consisting of LiCl, NaCl, KCl, MgCl₂, and CaCl₂, (4) a FeCl₃ solution, and (5) an InCl₃ solution. In addition, the metal loading studies were carried out with rare earth chlorides. Important physical parameters such as the viscosity and density were also determined before and after extraction and compared to those measured for the dried IL.

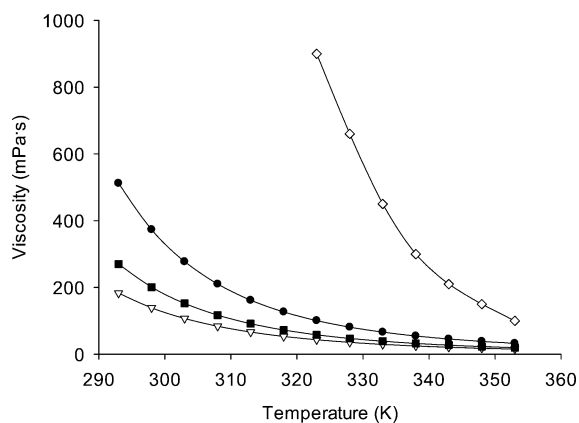
IL Synthesis and Characterization. In this study, the IL [P₈₈₈][oleate] was selected, because the phosphonium cation is more chemically and thermally stable compared to tetraoctylammonium oleate, used in previous work.^{19,20} In general, this is beneficial for metal extractions with ILs, where higher temperatures are often used in order to decrease the

Table 1. Physical Properties (Density, ρ ; Dynamic Viscosity, η ; Kinematic Viscosity, ν ; Melting Point, T_m ; Decomposition Temperature, T_d ; Bromide Content, $[\text{Br}^-]$; Water Content, $[\text{H}_2\text{O}]$) of the IL, $[\text{P}_{8888}][\text{oleate}]$ with Different Water Contents (wt %)

temperature (K)	water content (wt %)	ρ (g/cm ³)	η (mPa·s)	ν (mm ² /s)	T_m (K)	T_d (K)	$[\text{Br}^-]$ (ppm)	$[\text{H}_2\text{O}]$ (ppm)
293	10.8	0.897	183.1	204.3	245.3	421.5	5	108 310
	2.3	0.886	512.2	577.9	255.1	425.2	5	23 000
323	10.8	0.877	43.4	49.5	245.3	421.5	5	108 310
	0.49		900				5	4900

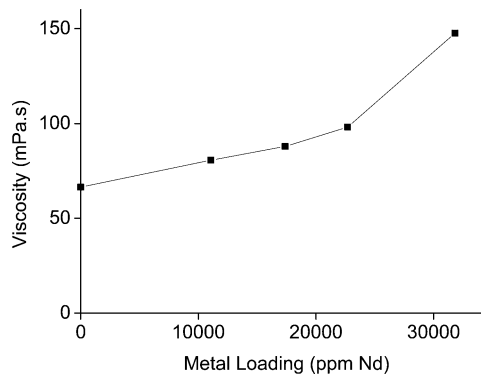
viscosity of the IL and to increase the speed of mass transfer between the water and IL phase. Because ILs are proposed as replacements for volatile organic compounds (VOCs), it was decided to synthesize the IL $[\text{P}_{8888}][\text{oleate}]$ without the use of VOCs. First, synthesis of the IL was performed according to a VOCs-free synthesis reported in the literature,³⁵ in which the precursors were mixed with a 0.5 M NaHCO_3 solution. However, bromine determination by TXRF showed that the IL still contained a large concentration of bromide anions (>25 000 ppm). To solve the issue of bromide contamination, an alternative synthesis was applied. To that end, 2 equiv of NaOH and 1.5 equiv of oleic acid were applied. After synthesis, thoroughly washing with water was necessary to remove the excess of NaOH and sodium oleate. One should keep in mind that the separation of the two phases was slow and the water phase was turbid due to emulsion formation in the aqueous phase by the excess of sodium oleate.

The physical properties (melting point, decomposition temperature, density, kinematic and dynamic viscosity, water content, bromide content) of the synthesized IL $[\text{P}_{8888}][\text{oleate}]$ were measured and are summarized in Table 1. The water-saturated fatty acid-based and long-chained IL has a very low viscosity in comparison with the dried IL. This is due to the larger water uptake of the IL (10.8 wt %) in comparison with the dried IL (0.49 wt %). The viscosity decreases by a factor of 9 at 323 K (Figure 2).

**Figure 2.** Influence of the temperature on the viscosity of the IL $[\text{P}_{8888}][\text{oleate}]$ with different water contents: (∇) 10.8 wt %, (\blacksquare) 7.39 wt %, (\bullet) 2.30 wt %, and (\diamond) 0.49 wt %.

The viscosity of ILs in solvent extraction experiments is very important, because it has a significant effect on the extraction kinetics and the energy necessary to obtain extraction equilibrium. In the past, fluorinated ILs were mainly chosen as diluents for extractants in solvent extraction studies. Fluorinated ILs are known to have a low viscosity, so that extraction kinetics are fast. Bulky and long-chained ILs were

avoided, because it was generally assumed that these kinds of ILs have higher viscosities, which makes it more difficult to obtain extraction equilibrium. Nevertheless, the viscosity of an IL used in solvent extraction systems does depend not only on the cation and anion but also on the amount of water dissolved in the IL, which is related to the structure of the IL.²⁰ The influence of the temperature on the viscosity of dried and water-saturated $[\text{P}_{8888}][\text{oleate}]$ is presented in Figure 2. Water-saturated $[\text{P}_{8888}][\text{oleate}]$ contains 10.8 wt % of water, which results in a low viscosity (30 mPa·s at 333 K and 43 mPa·s at the extraction temperature of 323 K). Reducing the water content to 0.49 wt % makes the IL extremely viscous (900 mPa·s at 323 K). Higher viscosity was observed in previous research for the same IL, but this is probably because the IL was then not completely water saturated and/or because halide impurities were remaining in the IL.¹¹ Comparing these values with the viscosity of water saturated trihexyl(tetradecyl)-phosphonium chloride (water content 15.47 wt %, 110 mPa·s at 323 K)^{14d} and trihexyl(tetradecyl)phosphonium nitrate (water content 3.92 wt %, 560 mPa·s at 323 K),²¹ having comparable cations as $[\text{P}_{8888}][\text{oleate}]$, shows that $[\text{P}_{8888}][\text{oleate}]$ has a remarkable lower viscosity. The low viscosity of the ionic liquid is due to the large, unsymmetrical oleate anion and the large water uptake. The viscosity of water-saturated $[\text{P}_{8888}][\text{oleate}]$ is comparable with the viscosity for water-saturated $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ (water content 1.99 wt %, 13.3 mPa·s at 323 K) and $[\text{C}_4\text{mim}][\text{PF}_6]$ (water content 2.68 wt %, 30.8 mPa·s at 323 K).²² Influence of the metal loading on the viscosity was studied as well. Figure 3 shows that the viscosity

**Figure 3.** Influence of the Nd loading on the viscosity of the IL $[\text{P}_{8888}][\text{oleate}]$ at the extraction temperature of 313 K.

increased by a factor of 2 when it was loaded with 32 000 ppm Nd (148 mPa·s at 313 K), which is still significantly lower than that observed for other similar bulky metal-loaded IL extraction systems.²¹ Moreover, TOC analysis showed that the solubility of $[\text{P}_{8888}][\text{oleate}]$ in a 0.05 M NaCl solution was only 31.5 mg·L⁻¹; this corresponds to a mole fraction of 7.4×10^{-7} , which is very low compared to fluorinated ILs.²³ The combination of

low viscosity, very low water solubility, and cheap starting materials make this IL an excellent candidate for replacing organic solvents in solvent extraction studies, even on an industrial scale where these kinds of properties are beneficial.

It has to be reported that, in this study, an ionic liquid with a nontoxic anion was chosen in order to avoid pollution of the water phase. Therefore, the biological and biodegradable oleate ion was selected. However, an anion with a double bond has the drawback of having a low long-term stability. Especially, highly acidic conditions and/or metals can catalyze the degradation of the anion.^{18,19}

Extraction Time. Prior to the extraction experiments, the kinetics of the extraction and the rate of extraction were studied in order to determine the conditions necessary to reach equilibrium. To that end, 1 mL of a 4800 ppm Ni solution and a 5000 ppm Nd solution were extracted toward 1 mL of the IL phase without adjustment of the pH. Five different mixtures were shaken at 2000 rpm and 313 K between 1 and 10 min. Figure 4 shows that the Nd extraction equilibrium is already

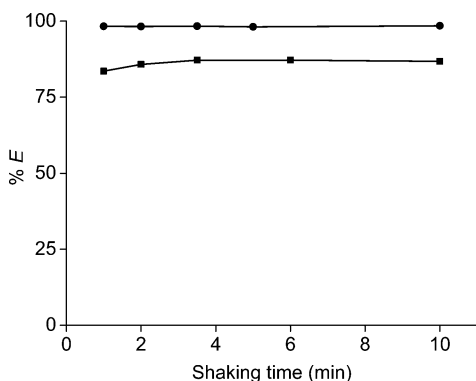


Figure 4. Extraction percentage (%E) of 5000 ppm neodymium (●) and 4800 ppm nickel (■) as a function of the shaking time.

reached after 1 min with an %E of 98%. The equilibrium for the extraction of Ni was reached somewhat slower (4 min) compared to Nd. The fast kinetics of this extraction system is most likely due to the low viscosity (66 mPa·s at 313 K) of the water-saturated IL, even when the latter is loaded with metals. As shown in Figure 4, it could be concluded that 10 min of shaking at 313 K is sufficient to reach equilibrium during metal extraction via the anion of the IL. This result is most probably due to the large water uptake of the IL (10.5 wt %). A comparison shows that the water content in $[P_{888}][\text{oleate}]$ is high compared to the ILs containing the trihexyl(tetradecyl)phosphonium cation and the bis(trifluoromethylsulfonyl)imide (0.22 wt %), nitrate (3.92 wt %), and bromide (6.72 wt %) anion, but it is lower than trihexyl(tetradecyl)phosphonium chloride (15.47 wt %), trihexyl(tetradecyl)phosphonium decanoate (17.46 wt %), and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (19.03 wt %).^{14c,21,24} The latter ones, containing a higher water content than the $[P_{888}][\text{oleate}]$ IL, still have a much higher viscosity.²⁵ The main difference between the oleate IL and the decanoate IL, apart from the smaller alkyl chain length, is the double bond in the anion, which has a large influence on the alignment of the molecules and is expected to contribute to the low viscosity of the IL.²⁶

Extraction of Transition Metals ($MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$). Next, extractions of a transition metal

solution consisting of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ using $[P_{888}][\text{oleate}]$ was carried out at different equilibrium pH values. Figure 5 shows the effect of pH on the color of the



Figure 5. Color switch observed for the IL phase because of the extraction from the transition metal solution at different pH values. pH of the aqueous phase is mentioned on each bottle.

IL after extraction as a result of the different extraction behaviors. A plot showing the %E as a function of the pH is given in Figure 6. The uptake of protons by the anion of the IL

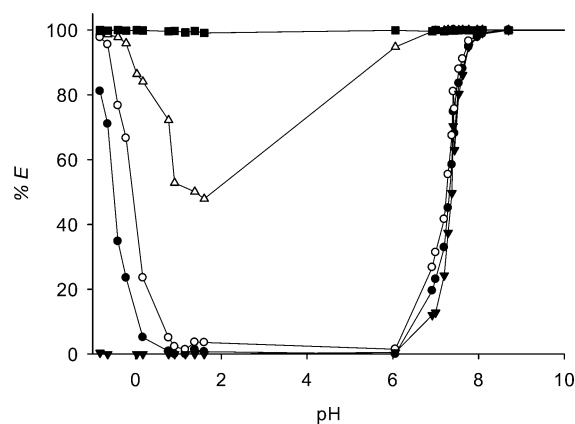


Figure 6. Extraction percentage (%E) using the IL $[P_{888}][\text{oleate}]$ as a function of the pH for the transition metals. Zinc (■), copper (Δ), cobalt (○), manganese (●), and nickel (▼).

resulted in an increase of the pH in the aqueous phase in comparison with the initial pH of the metal solution. For example, the pH of the transition metal solution was 4.19 before extraction and increased to 7.41 after metal extraction. This is due to the buffer capacity of the IL as it can extract protons from the aqueous phase in which oleic acid and $[P_{888}]Cl$ are formed. For consistency reasons, only pH values after extraction (equilibrium pH) are reported throughout this Article.

Extraction at a pH of 7 resulted in a dark green color of the IL because of the formation of the colored manganese(II), cobalt(II), and nickel(II) oleate complex. In this pH region, Mn, Co, and Ni are extracted via the oleate anion. The IL is yellow (its intrinsic color) between pH = 1 and pH = 6 and is not extracting metals that color the IL in this pH range due to protonation of the IL anions and competitive HCl extraction.²⁷ However, at very low pH (<1), the IL turns bright green due to the formation and extraction of tetrachlorocobaltate(II) and tetrachloromanganate(II) complexes. Thus, extraction of Mn and Co occurs in this region via the cation. At these low pH values, Ni is not extracted because this metal cannot form an anionic chloro complex in the applied media.²⁸ Zn and Cu show a different extraction pattern as a function of pH (Figure

6). Zn and Cu are extracted via a combined mechanism in the IL, both via the anion and via the cation as a chloro complex between pH = 1 and pH = 6,^{14d} so that the %E does not completely drop. The copper and zinc chloro complexes are not coloring the IL.

From Figure 6, it can be concluded that it is possible to extract all transition metals between a pH of 7 and 8. Trials to extract at higher pH values caused hydrolysis of the metals and the formation of an emulsion due to the dissolution of sodium oleate in the aqueous phase. It is also possible to selectively strip the metals by lowering the pH. Efficient separation of Mn and Co is difficult, because their extraction curves as a function of the pH are similar.

Extraction of Rare Earths (LaCl₃, NdCl₃, SmCl₃, DyCl₃, ErCl₃, and YbCl₃). Figure 7 shows a plot of the extraction

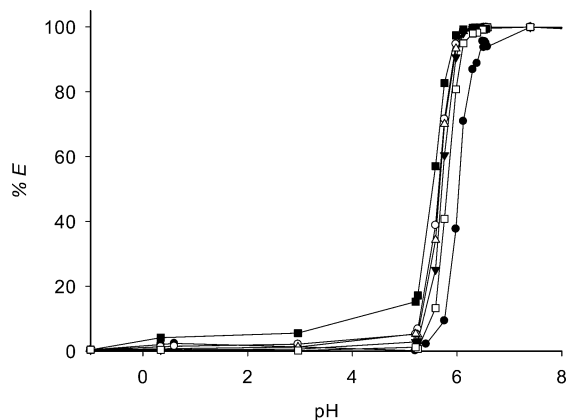


Figure 7. Extraction percentage (%E) with the IL [P₈₈₈][oleate] as a function of the pH for the rare earth metals. Lanthanum (●), neodymium (□), samarium (▼), dysprosium (△), erbium (○), and ytterbium (■).

efficiencies as a function of the pH for a rare earth solution consisting of LaCl₃, NdCl₃, SmCl₃, DyCl₃, ErCl₃, and YbCl₃. Due to low extinction coefficients for the lanthanide salts used here, no color change of the IL was observed during extraction. The extraction pattern of all rare earths follows the same trend: extraction starts at pH = 5 and extraction efficiencies are almost 100% around pH = 6.5. All rare earths are extracted via the anion of the IL.²⁸ Rare earth ions cannot form chloro complexes at low pH values and high chloride concentrations.²⁹ Because of competitive HCl extraction at low pH values, no extraction of rare earths is observed at a low pH.²⁷

It can be concluded from Figure 7 that separation of the individual rare earths will be difficult. The separation factors between adjacent lanthanides are very low due to their similar ionic radii and chemical properties. It is commonly known that carboxylic acids can be used for the separation of light rare earths but are often not useful for the separation of heavy rare earths due to the similar extraction curves. Still, there is a correlation between the molecular mass of the rare earth and the pH at which extraction occurs. The heaviest rare earths form stronger complexes than the light rare earths (Yb > Er > Dy > Sm > Nd > La) with the oleate anion and are therefore extracted at lower pH. This is in agreement with the results for extraction of rare earths with different carboxylic acids.³⁰ The curved line with the extraction percentage for La is situated at a higher pH than those of the other lanthanides. The separation factors between La and the other rare earths (Nd, Sm, Dy, Er,

and Yb) are rather low and not interesting for any industrial application. (Table SI 5 in the Supporting Information).

Extraction of Alkali and Alkaline Earth Metals (LiCl, KCl, MgCl₂, and CaCl₂). The extraction of an alkali and alkaline earth metals solution consisting of LiCl, KCl, MgCl₂, and CaCl₂ using [P₈₈₈][oleate] as a function of pH is shown in Figure 8. No extraction was observed for these metals at pH <

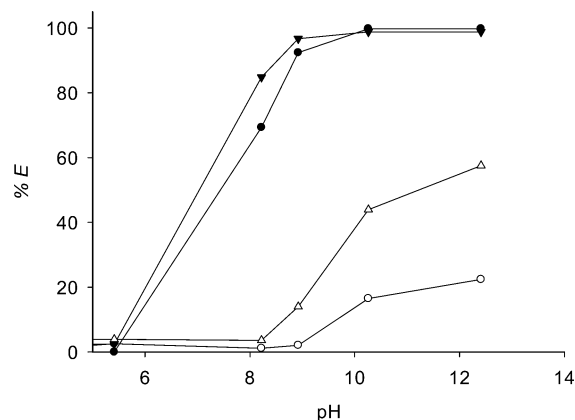


Figure 8. Extraction percentage (%E) with the IL [P₈₈₈][oleate] as a function of the pH for the light metals. Calcium (●), potassium (○), magnesium (▼), and lithium (△).

6. Ca and Mg are extracted similarly at a pH ranging from 6 to 8. This extraction might interfere with the extraction curve of Mn, Co, and Ni. From pH = 9, extraction of Li and K is observed with Li being extracted more efficiently. Extraction of Li, K, and Na results in the formation of a monovalent metal salt with oleate, which acts as an emulsifier and induces the formation of a microheterogeneous phase. Therefore, it is advised to avoid extraction above a pH of 9.

Extraction of Single Metal Solutions (FeCl₃ and InCl₃).

The extraction of Fe(III) with [P₈₈₈][oleate] is carried out separately from other metals, because it coprecipitates other metals and hydrolyses with release of HCl above a pH of 2. The effect of pH on the extraction of a single metal solution containing FeCl₃ is shown in Figure 9. At very low pH (pH < 0.3), excellent extraction efficiencies were observed for Fe, because it is extracted via the cation of the IL in the form of a chloro complex.³¹ At higher pH values, the water phase starts to

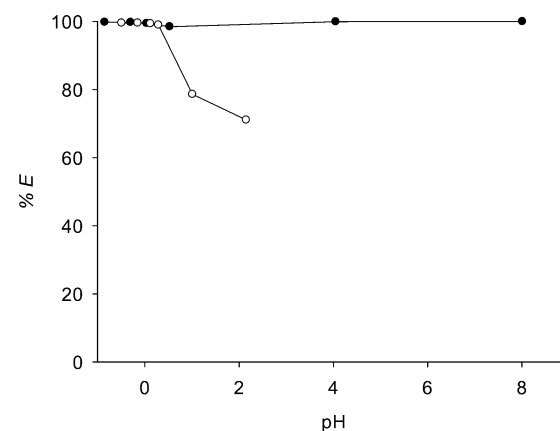


Figure 9. Extraction percentage (%E) with the IL [P₈₈₈][oleate] as a function of the pH for FeCl₃ (○) and InCl₃ (●).

become red due to the formation of water-soluble iron hydroxide ($\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$) complexes.³² Further increase of the pH ($\text{pH} > 2$) results in the formation of an iron(III) hydroxide precipitate. Therefore, no results of the extraction at $\text{pH} > 2$ were presented. The red iron precipitate can clearly be seen at the bottom of the bottle and on the interphase at $\text{pH} = 7.03$ in Figure 10.

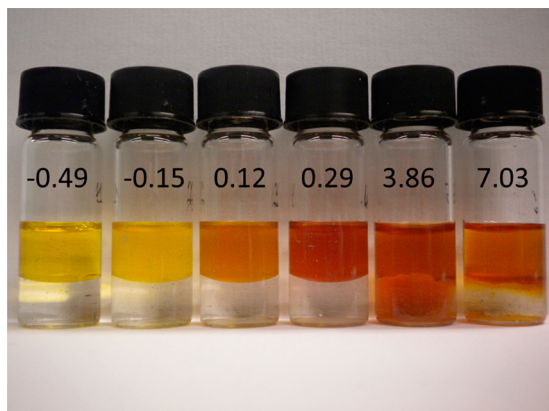


Figure 10. Color of the IL phase after extraction of FeCl_3 at different pH values. pH values of the aqueous phases are mentioned on each bottle.

Finally, because indium according to the European Commission is a critical metal, the extraction efficiencies as a function of the pH for a single metal solution containing InCl_3 were measured.^{1c} The extraction pattern of In is plotted in Figure 9 and shows that at each pH the %E was 100%, which is similar to the extraction behavior of ZnCl_2 . Such a result is in agreement with the fact that In can easily form chloro complexes and is extracted together with the tetraalkyl ammonium or phosphonium cation.³³

Metal Loading of the IL. The metal loading of the IL $[\text{P}_{888}][\text{oleate}]$ was studied with the rare earths La, Nd, and Yb by measuring the extraction efficiency at different concentrations of rare earths in the aqueous phase. Figure 11 shows that the extraction efficiencies decrease when the metal loading increases. A significant decrease in pH was observed when higher metal loadings were used. The aqueous phase had a pH of 7.5 when the initial aqueous Nd concentration was 11 000 ppm. The pH stepwise decreased down to 5.5 when the initial aqueous metal concentration was increased to 58 000 ppm.

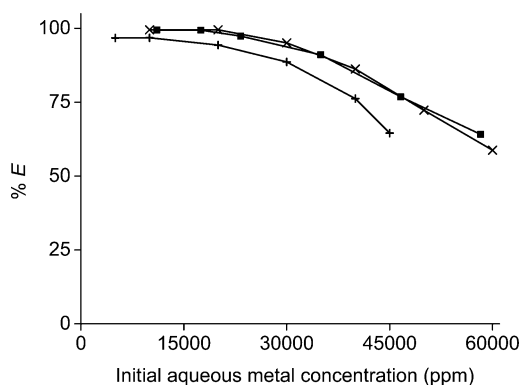


Figure 11. Extraction percentage (%E) as a function of the initial aqueous La (+), Nd (■), and Yb (×) concentration.

This resulted in a decrease in extraction efficiency (Figure 7). Therefore, small amounts of NaOH were added to the aqueous phase in order to increase the pH and to obtain 100% Nd extraction at higher initial NdCl_3 concentrations in the aqueous phase. However, the pH did not increase upon NaOH addition. Instead, the formation of a $\text{Ln}(\text{OH})_3$ precipitate was observed. This means that $[\text{P}_{888}][\text{oleate}]$ is not suitable for the extraction of higher rare earth metal concentrations. The extraction efficiency of La decreased much faster than that of Nd and Yb with increasing metal concentration in the aqueous phase (Figure 7). This is probably due to the higher number of moles of lanthanum at equal ppm values, because the extraction of La is more sensitive to decreasing pH values than the two other metals and because of the higher basicity of this element leading to a lower solubility product for $\text{La}(\text{OH})_3$.

Regeneration of the IL. Because the extraction is strongly pH dependent, as shown in Figure 7, stripping was first carried out using aqueous HCl solutions. For instance, about 0.45 mL of a 37 wt % HCl is necessary to strip all rare earths from 1 mL of the IL phase (12 000 ppm Ln). The concentration of the metal in the aqueous phase can be increased by a factor of 2.2 in comparison with the concentration in the IL phase by stripping 1 mL of organic phase with 0.45 mL of 37 wt % HCl, which can be interesting if one wants to concentrate a metal. Large amounts of acids are necessary to fully protonate the anion of the IL and to break the buffer system. The use of large amounts of acid to strip the metals is not interesting from an economical and environmental point of view. Therefore, it was decided to use oxalic acid as stripping agent, to combine stripping and precipitation (precipitation stripping). It is known that oxalic acid can form sparingly soluble oxalate complexes with rare earth ions. Different amounts of oxalic acid dihydrate were added to 1 mL of IL containing 11 000 ppm Nd. (Figure 12). The stripping process in the case of an excess of oxalic acid can be written as

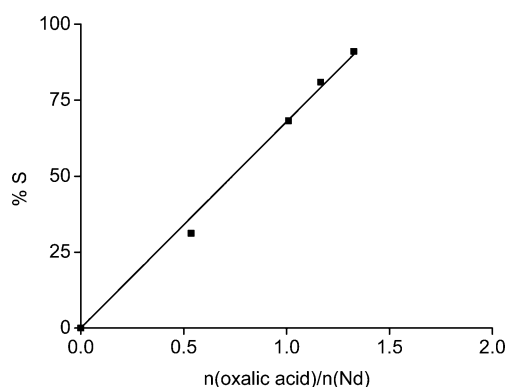
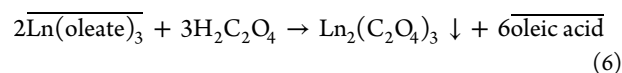
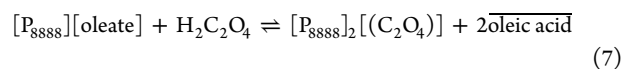


Figure 12. Percentage stripped (%S) of 11 000 ppm Nd from 1 mL IL as a function of the equivalents of oxalic acid ($n(\text{oxalic acid})/n(\text{Nd})$).

It was observed that the %S increased linearly until a ratio of 1.5 mol of oxalic acid per mole of Nd (Figure 12). After this point, a decrease in %S was observed, probably because of the exchange of oleate anions by oxalate anions as oxalic acid is more acidic than oleic acid. The anion exchange process is



Stripping the metals via precipitation has several advantages over stripping with HCl. First, stripping with oxalic acid avoids the use of large amounts of acidic stripping agent. Second, not all anions from the IL are protonated during the stripping process. In this case, stripping of two Nd atoms will regenerate six oleic acid molecules. For an extraction and stripping step of 1 mL of 11 000 ppm (0.075 mmol) Nd, only 0.450 mmol of the starting products oleic acid and $[P_{888}][Cl]$ are formed. One mL of IL contains 1.29 mmol of IL, meaning that about 35% of the IL has been converted into the starting products. This is important for the regeneration of the IL and it means that less NaOH is necessary for the regeneration of the IL in comparison with a stripping process with HCl, where 100% of the IL is converted to the starting products. Third, the precipitation stripping process avoids one extra HCl stripping step if the aim is to obtain a highly concentrated rare earth precipitate as final product. Fourthly, the rare earth oxalates can also easily be converted into the corresponding oxides by calcination at relatively low temperature.³⁴ The “contamination” of a solvent extraction system with solid particles is nowadays not an issue anymore. Instead of filtration or static settling, solid bowl decanters or continuous centrifuges can be used for efficient removal of solid particles from liquid streams.³⁵ Finally, oxalic acid is currently produced and used in large amounts during the Bayer process for the production of alumina from bauxite and is therefore a cheap chemical.³⁶

CONCLUSIONS

The IL tetraoctylphosphonium oleate $[P_{888}][oleate]$ was used in its undiluted form as both the organic phase and the extraction agent for the recovery of metals from aqueous chloride media. It is shown that this IL has a very low viscosity due to the solubility and uptake of water, which is mainly related to the anion of the IL. The HCl concentration (and thus the chloride concentration and pH) was found to have a large influence on the extraction efficiency of the different metal salts. $[P_{888}][oleate]$ showed excellent extraction efficiencies for most of the metals used (Li, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, In, La, Nd, Sm, Dy, Er, Yb) at their optimal pH. Full extraction of Na and K is not possible, due to the formation of the emulsion agent, i.e., Na or K oleate at higher pH values. The transition metals Mn, Co, and Ni are extracted via the anion of the IL from a pH = 6–7, while all rare earths are extracted from a solution with pH = 5–6, meaning that there is a pH difference of one unit between these metals, which shows that $[P_{888}][oleate]$ is a potential extractant for the separation of transition metals from rare earths. Zn, Cu, Fe, and In can be separated from the rare earths at pH < 5, because these metal salts are extracted as anionic chloro complex via the cation of the IL at low pH. The naturally occurring anion, the cheap starting products, low water solubility, and a low viscosity make this IL interesting as a greener alternative for organic solvents in industrial solvent extraction processes.

ASSOCIATED CONTENT

Supporting Information

DSC and TGA scans of the dried and water saturated IL, table with the separation factors of Nd, Dy, Sm, Er, and Yb to La, picture of the oxalate precipitate obtained upon stripping of Nd from the IL, and distribution ratio in function of the pH for all metal extractions. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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