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A mechanism for solvent extraction of first row transition metals from chloride media with the ionic liquid tetraoctylammonium oleate

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Aqueous waste streams of the metallurgical industry often contain considerable concentrations of metal salts. Previous research showed that the metal chloride salts of zinc(II), manganese(II) and iron(III) can be recovered by solvent extraction using a sustainable and renewable fatty acid based ionic liquid as the extractant. In this paper, the extraction mechanism of Zn(II), Co(II) and Ni(II) from chloride media has been studied systematically. The metal extraction performances of the precursors, sodium oleate and tetraoctylammonium chloride, were compared to the extraction performance of the ionic liquid tetraoctylammonium oleate. Slope analysis experiments were performed to determine the number of ionic liquid molecules involved in the extraction. The experimental data showed that Co(II) and Ni(II) were extracted in the pH range from 6 to 8 by the formation of negatively charged metal carboxylate complexes with tetraalkylammonium counter ions. In contrast, Zn(II) gets extracted as a mixed metal chloride carboxylate anionic complex with tetraalkylammonium counter ions. This extraction mechanism was supported by EXAFS measurements.

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Introduction

The chemical, metallurgical and mining industries produce large volumes of aqueous streams contaminated with valuable (heavy and light) metal salts. The existing conventional solvent extraction methods used to selectively recover these metal salts use volatile organic solvents and harmful chemicals, such as aliphatic hydrocarbons, sulphuric acid and organophosphorus extractants.^{1,2} Therefore, it is necessary to develop new methods that selectively extract metal salts and purify water in a more economical and environmentally friendly way. Research pointed out that ionic liquids (ILs) are interesting alternative solvents to overcome the above mentioned problems.^{3,4}

ILs have a large potential for a wide variety of applications in the chemical industry due to their interesting properties.^{5–12} ILs are organic salts with melting points typically below 100 °C. Other interesting IL properties for solvent extraction systems are their negligible vapor pressure, low flammability and broad liquid range. Moreover, they can be specifically designed for metal extraction by selecting a suitable cation and anion.^{13–20} Two main disadvantages which are often observed for hydrophobic ILs are their toxicity in direct contact and their poor biodegradability.^{21–23} Furthermore, losses of chemicals need to be minimized in industrial processes. Therefore, it is a challenge to develop environmentally friendly water immiscible ILs composed of non-toxic ions that have an extraction mechanism that is not based on ion-exchange. Recently, progress was made by developing ILs derived from natural fatty acids, namely tetraalkylammonium oleate and tetraalkylammonium linoleate.^{24,25}

Hitherto, some studies have already investigated the metal extraction mechanism of ILs in combination with an extractant.^{26–29} The extraction of metals can proceed in three different ways: (1) ion-pair extraction; which is the extraction of the metal cations with the corresponding anions from the aqueous phase towards the IL phase; (2) ion exchange; in which anions or cations from the IL or protons from the extractant are exchanged by metal ions from the aqueous phase; and (3) combinations of (1) and (2) depending on the conditions.³⁰

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Metal salt extraction by using specific extractants dissolved in the IL phase is sometimes accompanied by an increasing dissolution of components of the IL into the aqueous phase (mechanism 2), which cannot be regarded as environmentally friendly.³¹ Ion exchange can be suppressed or even avoided by selecting ILs with hydrophobic cations and/or hydrophobic anions. The mechanism of salt extraction for specific types of undiluted non-fluorinated hydrophobic ILs has already been investigated.³² For example, hydrophobic tetraalkylammonium or tetraalkylphosphonium chloride ILs are able to extract 3d transition metal ions as tetrachloro complexes.^{33,34} Undiluted bifunctional ionic liquids (*i.e.* ILs that are a combination of a deprotonated organic acid and an organic base) often extract metal salts by the formation of a negatively charged metal complex, having one or more IL counter cations to obtain charge neutrality.^{15,35–37}

In this paper, the metal extraction process for the transition metal ions zinc(II), cobalt(II) and nickel(II) by the bifunctional ionic liquid tetraoctylammonium oleate from chloride media is reported. This allows a better understanding of the mechanism for the removal of metal ions from the aqueous phase with this type of ILs. An insight into the mechanism is useful for the further development of more environmentally friendly ILs used for selective salt extraction, salt recovery and solvent reusability.

Experimental

Materials

Tetraoctylammonium oleate, [N₈₈₈₈][oleate], was synthesized as described in detail elsewhere (Fig. 1).²⁴ Boom B.V. (Meppel, The Netherlands) supplied manganese(II) chloride dihydrate (99%), nickel(II) chloride hexahydrate (99%) and perchloric acid (70%). Zinc(II) chloride anhydrous (99.999%) and cobalt(II) chloride hexahydrate (99%) were delivered by Sigma-Aldrich (Zwijndrecht, Belgium). Hydrochloric acid (37%) and sodium hydroxide (99%) were delivered by VWR® Chemicals (Amsterdam, The Netherlands). Milli-Q water ($\geq 18 \mu\Omega \text{ cm}$) was

obtained from a Millipore Milli-Q® Biocel, which used a Q-grade® column. All chemicals were used as received, without any further purification.

Experimental salt extraction procedure

A standard salt solution was prepared by dissolving 0.5 g of each salt (ZnCl₂ (3 mM), NiCl₂·6H₂O (2 mM) and CoCl₂·6H₂O (2 mM)) in 100 mL of Milli-Q water. Neither acid nor chloride salt was added to this solution. Then, 1 mL of this solution was added to 1 g of the organic phase and mixed in a Heidolph Multi Reax vortex mixer at 2500 rpm for 2 h at 293 K. Afterwards, the mixture was centrifuged on an Allegra X-12R Centrifuge of Beckman Coulter at 3000 rpm for 10 min to accelerate the phase disengagement. First, a preliminary experiment was performed giving an indication of the different metal extraction mechanisms that could occur with [N₈₈₈₈][oleate]. The metal extraction of the IL was compared to the precursors by extracting the metals towards: (1) 1 g of tetraoctylammonium oleate, (2) 1 g of oleic acid, (3) 1 g of tetraoctylammonium chloride and (4) 0.4 g of sodium oleate (0.6 M) dissolved in 0.6 g of oleic acid. Tests were performed on the standard salt containing 0.5 g of each salt (Co, Ni and Zn). None of the organic phases was presaturated with water. In all cases none of the organic solvents was diluted unless mentioned differently.

The distribution ratio (D) was calculated by dividing the metal concentration in the IL phase over the metal concentration in the aqueous phase:

$$D = \frac{[M^{2+}]_{\text{IL}}}{[M^{2+}]_{\text{aq}}} \quad (1)$$

where $[M^{2+}]_{\text{IL}}$ is determined by subtracting the total metal concentrations in the aqueous phase before extraction from the metal concentration of the aqueous phase after extraction.

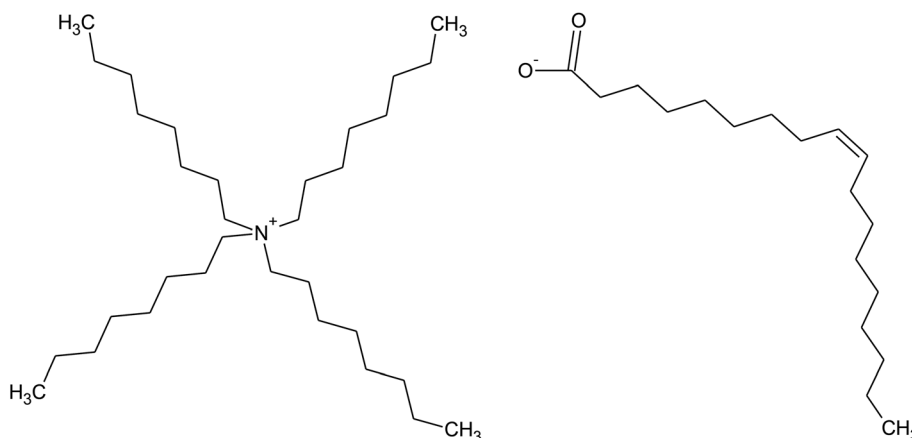


Fig. 1 Structure of [N₈₈₈₈][oleate].

Analysis of the metal anion and cation concentration in the water phase after metal extraction

After each extraction experiment, the aqueous phase was analysed with ion chromatography (IC) and inductively coupled plasma (ICP). Metrohm 761 Compact IC and 762 IC interfaces were used to analyse the anion concentration with a detection limit of 0.1 mg L^{-1} . A Metrohm column (Metrosep A Supp 5, 150/4.0 mm) was used with a mobile phase (3.2 mM Na_2CO_3 and 1 mM NaHCO_3 solution + 1% acetone + 5 μM KIO_3) and regenerated with suppressor liquids (100 mM sulphuric acid + 1% acetone and Milli-Q water + 1% acetone). Cations were measured with a Perkin Elmer ICP, which used an optical emission spectrometer (OES) Optima 5300 DV. Results were obtained *via* a Winlab 32 ICP continuous automated analysis. The ICP-OES has a detection limit of $50 \mu\text{g L}^{-1}$ for all elements, with an uncertainty of 2%. The pH of the water phase was measured after the metal extraction experiment with a Metrohm 827 pH lab.

Slope analysis

Slope analysis experiments with a changing IL concentration in toluene were performed with single element solutions of CoCl_2 , NiCl_2 and ZnCl_2 . Low chloride salt concentrations (500 ppm) were selected in order to maintain the pH in the same range. 3.5 g of IL was dissolved in 100 mL toluene ($4.7 \times 10^{-4} \text{ M}$) and 1 mL of the aqueous metal solution was mixed with different volumes (between 0.1 and 1 mL) of the IL/toluene solution and further diluted with toluene until a total volume of 1 mL was obtained for the organic phase.

Secondly, the extraction at a constant IL concentration (undiluted, water saturated) but with a changing pH was studied for CoCl_2 and for NiCl_2 . Therefore, 1 mL of water saturated IL was added to 0.5 mL of a 2000 ppm CoCl_2 or NiCl_2 solution. Then, different volumes of a 37 wt% HCl solution were added to the mixtures and further diluted with water, until the total volume of the aqueous phase was 1 mL. The pH of the aqueous phase was measured after the extraction and ranged between 6 and 8.

All the samples were shaken for 10 min at 313 K and 2000 rpm at room temperature on a thermo shaker TMS-200, centrifuged for 5 min at 3000 rpm on an Allegra X-12R Centrifuge of Beckman Coulter and analyzed with ICP.

EXAFS measurement

Extended X-ray Absorption Fine Structure (EXAFS) spectra of the Zn K-edge (9659 eV) were collected at the Dutch-Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in the fixed-exit mode using a Si(111) crystal pair. The measurements were done in the transmission mode using Ar/He gas filled ionization chambers at ambient pressure. A brass sample holder with Kapton[®] windows and a flexible polymeric spacer with a thickness of 1 mm were used as the sample holders for the liquid samples.

Standard procedures were used for pre-edge subtraction and data normalization in order to isolate the EXAFS function (χ). The isolated EXAFS oscillations, accomplished by a smoothing spline as realized in the program Viper,³⁸ were k^4 -weighted and Fourier transformed over the k -range from 3 to 14 \AA^{-1} using a non-window function. The data were fitted using the *ab initio* code FEFF 7.0,³⁹ which was used to calculate the theoretical phase and amplitude functions that subsequently were used in the non-linear least-squares refinement of the experimental data. Fitting of the model was performed in the k space with 4 different paths: the single scattering paths to the oxygen, chlorine and carbon atoms and the three leg multiple scattering path between zinc, oxygen and carbon. Estimated standard deviations are shown between parentheses and calculated by VIPER. The degeneracy of the paths was correlated, the total number of ligands was constrained to 4, E_0 was set flexible but equal for all paths and S_0 was set to 0.95.

Results and discussion

Metal chloride extraction: the IL in comparison with its precursors

First, the extraction of the metals Zn(II), Co(II) and Ni(II) with the precursor of the IL anion (sodium oleate) and the precursor of the IL cation (tetraoctylammonium chloride) was compared with the extraction of the IL (Table 1). It was observed that Co(II) and Ni(II) were extracted by sodium oleate and the IL. This indicates that these metals, at low chloride concentrations, can be extracted *via* the anion of the IL. This was expected, because commercially used carboxylic acids (*e.g.* Versatic acid) have similar extraction properties as the oleate anion.^{40–44} Literature data indicated that metal extraction with Versatic acid 10 and oleic acid occurs *via* the formation of a metal carboxylate complex and that the extraction is highly pH dependent.⁴⁵

Zn(II) is extracted with sodium oleate, tetraoctylammonium chloride and the IL (Table 1). This means that Zn(II) can be extracted *via* the oleate anion and *via* the tetraoctylammonium cation of the IL. Trihexyl(tetradecyl)phosphonium chloride (Cyphos[®] IL 101), an IL with a similar cation as the one used in this work, is a popular extraction agent for transition metals.^{26,33,46–49} The extraction of these metals by this agent always occurs in the form of metal chloro complexes and therefore, the extraction efficiency depends on the stability of the

Table 1 Distribution ratios of CoCl_2 , NiCl_2 and ZnCl_2 with $[\text{N}_{8888}][\text{oleate}]$, oleic acid, tetraoctylammonium chloride ($[\text{N}_{8888}]\text{Cl}$) and 0.6 M sodium oleate ($\text{Na}[\text{oleate}]$) in oleic acid

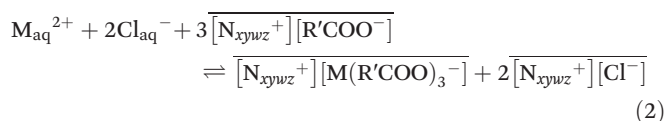
	$[\text{N}_{8888}][\text{oleate}]$	Oleic acid	$[\text{N}_{8888}]\text{Cl}$	$\text{Na}[\text{oleate}]$
Cl	>200	0.00	>200	0.00
Co(II)	20.4	0.05	0.06	>200
Ni(II)	13.5	0.05	0.03	>200
Zn(II)	>200	0.20	23.8	>200

chloro complexes. For most of the metals, high chloride concentrations (*e.g.* by using HCl or NaCl) are necessary in the aqueous phase to form chloro complexes. Metals like Zn(II) and Cu(II) easily form chloro complexes and are extracted by this group of ILs, even at relatively low chloride concentrations.^{15,50}

Chloride extraction does not take place using sodium oleate as an extractant, because the extraction is based on the exchange of sodium atoms for multivalent metal ions (Table 1). This is different from the extraction with the IL where chloride extraction also takes place, indicating that the mechanism is based on ion pair extraction. It was also observed that oleic acid is not able to extract metals in a sufficient way under the applied conditions (pH 6.33, low chloride concentration: 0.16 M).

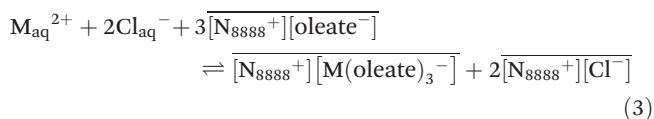
Determining the extraction mechanisms for Co(II) and Ni(II) via slope analysis

Sato *et al.* described the extraction mechanism for divalent transition metals by long-chain alkyl quaternary ammonium carboxylates via the formation of a metal carboxylate complex that goes to the organic/IL phase, together with the necessary counter-anions that keep the charge balance (eqn (2)):^{51–53}



where M = Co(II) and Ni(II), the bars indicate the species in the organic phase and x, y, w and z represent the different alkyl chains attached to the quaternary nitrogen atom.

A similar assumed equation can be written for $[N_{8888}][\text{oleate}]$:



The extraction constant (K_{ext}) for the extraction is:

$$K_{\text{ext}} = \frac{\overline{[N_{8888}^{+}][M(\text{oleate})_3^{-}]} \overline{([N_{8888}^{+}][Cl^{-}])^2}}{([N_{8888}^{+}][\text{oleate}^{-}])^3 [Cl^{-}]^2 [M^{2+}]} \quad (4)$$

This equation can be further simplified due to the ion-pair extraction mechanism and because no additional chloride salt or acid was added to the system.²⁴ Therefore, the remaining chloride concentration $[Cl^{-}]_{\text{aq}}$ in the aqueous phase equals two times the $[M^{2+}]_{\text{aq}}$ concentration in the aqueous phase ($2[M^{2+}]_{\text{aq}} = [Cl^{-}]_{\text{aq}}$) and the concentration of chloride extracted as $\overline{[N_{8888}][Cl]}$ equals two times the concentration of $\overline{[N_{8888}][M(\text{oleate})_3]}$. Eqn (4) then becomes:

$$K_{\text{ext}} = \frac{\overline{([N_{8888}^{+}][M(\text{oleate})_3^{-}])^3}}{(\overline{[N_{8888}^{+}][\text{oleate}^{-}])^3} (M^{2+})^3} \quad (5)$$

The insertion of D , defined in eqn (1), into eqn (5) on rewriting gives

$$\log D = \frac{1}{3} \log K + \log \overline{[N_{8888}^{+}][\text{oleate}^{-}]} \quad (6)$$

If three IL molecules are involved in the extraction, proposed by eqn (3), then one should obtain a slope of 1 if $\log D$ is plotted as a function of the IL concentration at a constant pH value. NiCl₂ was the first metal tested, because this metal does not form strong metal chloro complexes and can therefore only extract *via* the oleate anion of the IL (Fig. 2).³⁵ Afterwards, a slope analysis was performed for CoCl₂, which is also extracted *via* the oleate anion, because extraction *via* the cation is only possible at high chloride concentrations (Fig. 3). For both experiments, no acid or base was added to the aqueous

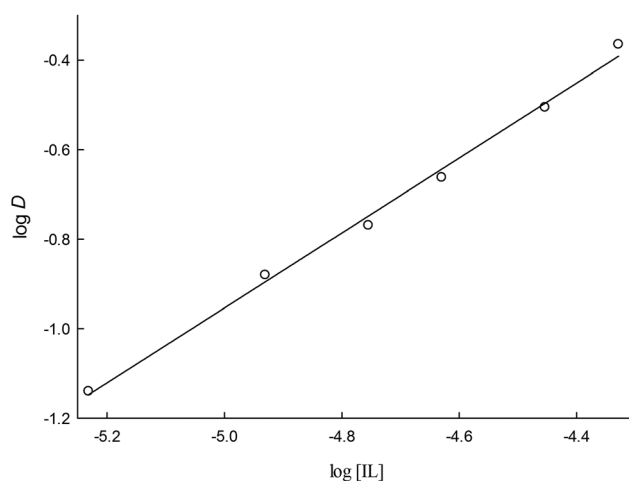


Fig. 2 Slope analysis for the extraction of NiCl₂ (2 mM) with $[N_{8888}][\text{oleate}]$ in toluene. The linear fit through the experimental data points is $y = 0.84x + 3.23$, the R^2 -value of the fit is 0.99.

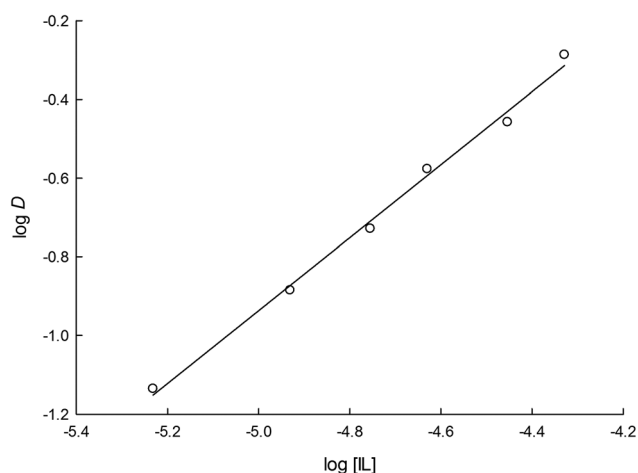
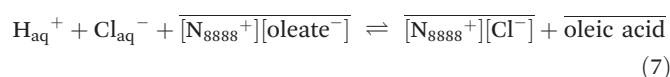


Fig. 3 Slope analysis for the extraction of CoCl₂ (2 mM) with $[N_{8888}][\text{oleate}]$ in toluene. The linear fit through the experimental data points is $y = 0.93x + 3.70$, the R^2 -value of the fit is 0.99.

phase and the equilibrium pH ranged from 7.50 to 7.95. The experiments were performed by dissolving the IL in toluene in order to accurately control the concentration of the IL and avoid volume changes resulting in inaccurate data. However, care should be taken with the interpretation of the obtained data as the extraction mechanism could be different in toluene in comparison with the pure IL. Therefore, additional data confirming the proposed extraction mechanism are required. Fig. 2 and 3 show that a linear fit through the data points gives a straight line with a slope close to 1, which is in agreement with eqn (3).

Adding an acid to the undiluted IL leads to the protonation of the anion (eqn (7) in the case of hydrochloric acid), forming oleic acid, which results in a decreased metal extraction (Table 1).



The lower the pH, the less is the metal extracted and for a $\text{pH} \leq 7$ no Co(II) and Ni(II) extraction is observed.⁵⁴ Plotting $\log D$ as a function of the pH for the pure IL shows straight lines with a slope of 3 (Fig. 4). This suggests again that three IL molecules are involved in the extraction of Co(II) and Ni(II) when using a pure IL, which is in agreement with the proposed extraction mechanism of these metals with the ionic liquid dissolved in toluene.

The pH of the slope analysis experiments was always measured directly after the extraction tests, because small fluctuations were observed over time. A possible explanation for this observation is the degradation of the anion of the IL, because it is known that unsaturated carboxylic acids can undergo catalyzed decomposition at higher temperatures.^{55,56} However, no changes in the NMR spectra of the IL after extraction were observed after one month of storage at room temperature, because it is assumed that the decompo-

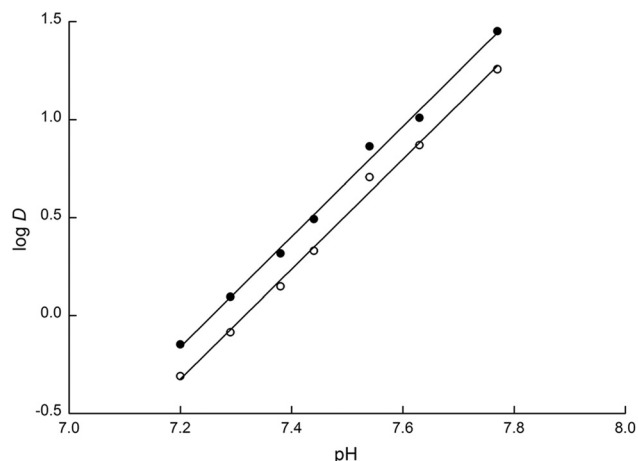
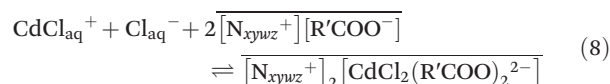


Fig. 4 Slope analysis for the extraction of CoCl_2 (●) and NiCl_2 (○) with $[\text{N}_{8888}][\text{oleate}]$ as a function of the pH. The linear fit through the experimental data points for Co(II) equals $y = 2.81x - 20.42$, the R^2 -value of the fit is 0.99 and for Ni(II) the linear fit through the data equals $y = 3.11x + 28.89$, the R^2 -value of the fit is 0.99.

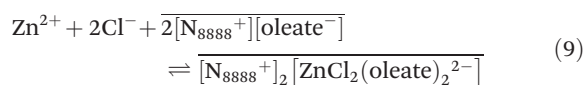
sition of the IL anion occurs in the concentration range of 10^{-6} to 10^{-7} M.

Determining the extraction mechanism for Zn(II) via slope analysis

According to Sato and Yamamoto, Zn(II) has a similar extraction mechanism compared to the metals Ni(II) and Co(II).⁵¹ Yet, from Table 1, it was observed that Zn(II) can be extracted both *via* the cation and *via* the anion of the IL, in contrast to Co(II) and Ni(II) that can only be extracted *via* the anion. Also, when a slope analysis experiment was performed for the extraction of ZnCl_2 , in which $\log D$ is plotted against the IL concentration, a slope of 0.5 was obtained. It is known that Zn(II) can form strong complexes with chloride anions (ZnCl^+ , ZnCl_2 , ZnCl_3^- and ZnCl_4^{2-}) depending on the pH and chloride concentration.^{57–60} Sato *et al.* observed a similar slope analysis for the extraction of Cd(II) with similar ILs, *i.e.* trioctylmethylammonium octanoate, trioctylmethylammonium decanoate and trioctylmethylammonium dodecanoate.⁵³ In this specific case, the extraction of Cd(II) was proposed to occur *via* a CdCl^+ complex in combination with two IL molecules (eqn (8)).



However, the authors were not able to mathematically derive the extraction mechanism from slope analysis experiments. A better equation for the extraction of Cd(II) and Zn(II) by mixed chloro-carboxylate complexes at low chloride concentrations in the aqueous phase is:



The extraction constant (K_{ext}) defined for an extraction described by eqn (9) is:

$$K_{\text{ext}} = \frac{\overline{[\text{N}_{8888}^{+}]_2 [\text{ZnCl}_2(\text{oleate})_2^{2-}]}}{([\text{N}_{8888}^{+}][\text{oleate}^{-}])^2 [\text{Zn}^{2+}][\text{Cl}^{-}]^2} \quad (10)$$

Without the addition of another chloride source (*e.g.* HCl or NaCl), the concentration of Cl^{-} is twice the concentration of Zn^{2+} ($2[\text{Zn}^{2+}] = [\text{Cl}^{-}]$). Substituting $[\text{Cl}^{-}]$ by $2[\text{Zn}^{2+}]$ and rewriting eqn (10) gives

$$\begin{aligned} \log D &= \log \frac{\overline{[\text{N}_{8888}^{+}]_2 [\text{ZnCl}_2(\text{oleate})_2^{2-}]}}{[\text{Zn}^{2+}]^3} \\ &= \log K'_{\text{ext}} + 2 \log \overline{[\text{N}_{8888}^{+}][\text{oleate}^{-}]} \end{aligned} \quad (11)$$

in which K'_{ext} stands for $(4 + K_{\text{ext}})$.

As proposed by eqn (11), if two IL molecules are involved in the extraction then one should obtain a slope of 2 if $\log \text{Zn}_{\text{org}}/\text{Zn}_{\text{aq}}$ is plotted as a function of the IL concentration at a constant pH value. From Fig. 5, it is concluded that eqn (9) is the correct extraction mechanism for Zn(II) at very low chloride concentrations as a slope of 1.7 is observed.

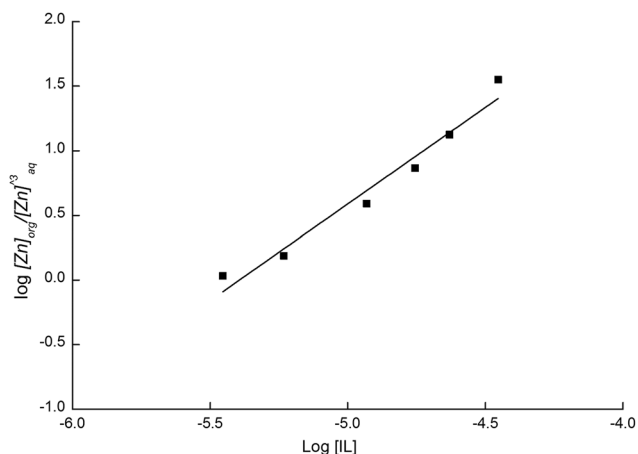


Fig. 5 Slope analysis with $\log[\text{Zn}_{\text{org}}]/[\text{Zn}_{\text{aq}}]^3$ as a function of $\log[\text{IL}]$ for the extraction of ZnCl_2 (3 mM) with $[\text{N}_{8888}][\text{oleate}]$ dissolved in toluene. The linear fit through the experimental data points is $y = 1.72x + 9.11$, the R^2 -value of the fit is 0.98.

No acid or base was added to the aqueous phase and the equilibrium pH ranged from 7.46 to 8.15. It has already been noticed in Table 1 that Zn has a much higher distribution ratio compared to Ni(II) and Co(II) (experiments performed at room temperature without an additional chloride salt or acid). This higher distribution ratio for Zn(II) is due to a difference in the extraction mechanism. However, we cannot conclude that this extraction mechanism is also valid at higher chloride concentrations. In this case, the formation of a tetrachloride complex in the organic phase is probably possible as well.

EXAFS measurements

Additional EXAFS measurements were performed to verify the formation of a metal complex consisting of zinc(II) surrounded by two chloride and two carboxylate ligands. The EXAFS function was fitted by including four different paths: three single scattering paths to the chlorides, oxides and the nearest carbon atoms and one three leg scattering path involving the carbon and oxygen atoms of the carboxylic acid group. No further multiple scattering paths were included, as the actual position and orientation of the carboxylate group towards the Zn atom are unknown. Therefore, the EXAFS function will not be fitted perfectly, whereas the Fourier transform will not be fitted correctly at a higher r value (between 3 and 4 Å) (Fig. 6 and 7). It turned out that the complex was tetrahedral which is mostly observed for zinc(II) complexes. Therefore, the total number of ligands was constrained to 4. The parameters obtained for the fit are shown in Table 2. The Zn–O and Zn–Cl distances were found to be 1.948(4) and 2.207(7) Å, which are remarkably low. D'Angelo *et al.* have shown for instance that the Zn–O and Zn–Cl distances in an aqueous solution are around 2.08 Å and 2.27 Å.⁶¹ The number of chloride and carboxylate groups coordinated to the Zn atom was found to be 2.1 and 1.9, which is in agreement with our data obtained

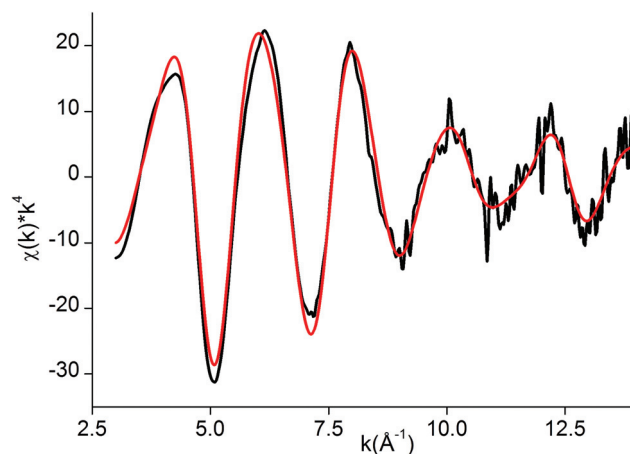


Fig. 6 EXAFS function (black) and model (red) of Zn being extracted by the IL fitted in the k space with four different paths.

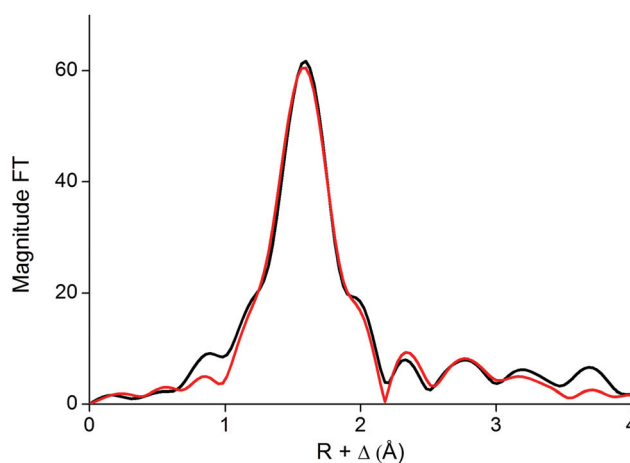


Fig. 7 Fourier transform (black) and model (red) of Zn being extracted by the IL fitted in the k space with four different paths.

Table 2 Distances, degeneracy and Debye Waller factors found for the nearest neighbors

	Zn–O	Zn–Cl	Zn–C
Distance (Å)	1.948(4)	2.207(7)	3.23(3)
Degeneracy	2.1	1.9	1.9
Debye Waller (Å ²)	0.0061(4)	0.0130(9)	0.008(3)

Fit in the k space between 3 and 14 Å⁻¹ with $S_0 = 0.95$.

by slope analysis (Fig. 5). The structure of the zinc(II) chloro oleate complex is given in Fig. 8.

Previously, it was mentioned that care should be taken with the interpretation of the obtained data from the slope analyses as the extraction mechanism could be different in toluene in comparison with the pure IL. However, results of the EXAFS measurements in the pure ionic liquid match the proposed

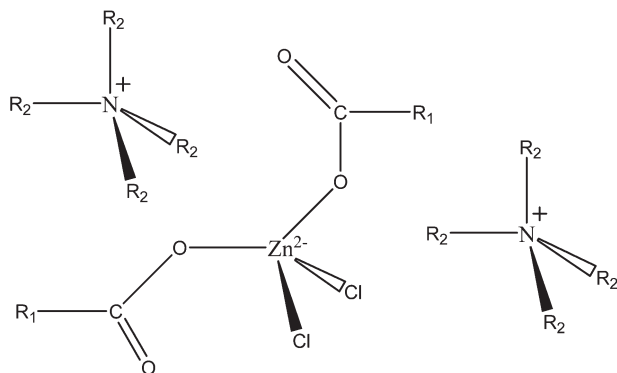


Fig. 8 Complex formed upon the extraction of Zn(II) towards the $[N_{8888}][\text{oleate}]$ IL phase.

metal extraction complex obtained by the slope analysis for Zn(II) in toluene.

Conclusions

The extraction mechanism of the transition metal ions Co(II), Ni(II) and Zn(II) with the ionic liquid $[N_{8888}][\text{oleate}]$ was investigated. For the metals Ni(II) and Co(II), the metal extraction mechanism was based on an IL metal complex, consisting of three IL molecules of which both the anion and cation are involved in the extraction of the metal ion, *i.e.* $[N_{8888}^+][M(\text{oleate})_3^-]$ with M being Co(II) or Ni(II). Zn(II) was extracted *via* a different extraction mechanism, in which the Zn(II) ion was extracted by two IL molecules as $[N_{8888}^+]_2[MCl_2(\text{oleate})_2]^{2-}$. The different extraction mechanisms for Zn(II) are responsible for the higher distribution ratio compared to Ni(II) and Co(II), and provide an insight into the separation of Zn(II) from both other metals. Applying the water saturated $[N_{8888}][\text{oleate}]$ ionic liquid, in conventional solvent extraction systems based on acidic extractants such as Versatic acid, avoids the use of volatile organic solvents as diluents and the related safety hazards.

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