Regeneration of the ionic liquid tetraoctylammonium oleate after metal extraction

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Abstract

Ionic liquids (ILs) have been presented as suitable candidates for metal extraction in the hydrometallurgy. It has already been proven that they have an adjustable selectivity towards metal ions. However, industrial applications of ILs are limited due to their high price. Therefore, regeneration of ILs is necessary. In this study the regeneration of the fatty acid based IL tetraoctylammonium oleate was investigated, because in a previous study we obtained excellent metal salt extraction efficiencies with this benign IL. Several methods for regeneration were investigated, i.e. electro-deposition and chemical regeneration. Electro-deposition turned out to be unfeasible for this IL. Chemical regeneration showed that the metal ions (Zn, Co and Mn) can be selectively back-extracted, so that metals can also be separated from each other in this step. The best stripping solution was aqueous sodium oxalate, which allowed the IL to be immediately reused.

Introduction

Ionic liquids (ILs) are a class of molten salts that are liquid below 100°C by definition, but mostly one refers to the room-temperature ionic liquids (RTILs), which are even liquid below room temperature. These liquids are composed of bulky organic cations in combination with organic or inorganic anions.[1] They recently gained a lot of interest, because they have several interesting properties, i.e. negligible vapor pressure, low flammability, high thermal stability, and a broad chemical window and liquid range.

Solvent extraction is one of the applications in which ILs are promising alternatives due to their negligible vapor pressure compared to volatile organic compounds (VOCs). ILs for selective metal extraction can be created by using organic ions that have metal binding functionalities. It has already been proven that some ILs present excellent metal extraction efficiencies.[2-6] Recently, non-fluorinated fatty acid based ILs were synthesized in the search for biocompatible, non-toxic metal selective ILs.[7] Oleic acid and linoleic acid were selected as anion due to their affinity towards metals combined with the voluminous and hydrophobic tetraalkylammonium cations to prevent the loss of the IL to the water phase. These hydrophobic ILs have been applied for the extraction of several transition metals and rare earth metals and showed excellent extraction efficiencies.[8]

Regeneration of ILs after extraction is much less investigated, but this step is very important, because one of the limiting factors for IL commercialization is their high price compared to VOCs. The pathways for IL regeneration after metal extraction depend on the properties of the IL and on the extraction mechanism.

The intrinsic IL properties are most important for non-chemical regeneration. For example, electro-deposition is only possible when the IL has a high conductivity, low viscosity and low water uptake.[9-11] However, in some cases a higher water content was beneficial due to the decrease in viscosity and corresponding increase in conductivity, even

though the electrochemical window also decreased.[12] Another option for recovery is fractional cementation, which is a type of precipitation that depends more on the selectivity of the IL towards one particular metal, which can then be co-precipitated together with a sacrificial metal with a more negative redox potential compared to the extracted metal.[13, 14]

On the contrary, chemical regeneration depends more on the extraction mechanism and not on the intrinsic properties of the IL. For metal salt extraction with ILs there are two main possible ways of extraction, i.e. the metal cation is extracted into the IL as a positive ion or as a negative complex. Extraction of the metal cation via a negative complex always proceeds via the cation of the IL by the uptake of a negatively charged metal complexes (e.g., $ZnCl_4^{2-}$, $PdCl_4^{2-}$, ReO_4^-).[15-19] This usally occurs at high acid conditions (low pH) and high chloride concentrations.[20] Regeneration of this type of ILs can be done by adding strong acids (e.g., H_2SO_4, HTf_2N) or strong bases (e.g., NH_4OH) that are able to break the negatively charged metal complexes. Recently, stripping of the metals out of this type of ILs has also been performed by applying the weak acid, oxalic acid. REF (T. Van der Hoogerstraete, Blanpain, Binnemans). In this case, the metals form a very strong water insoluble complex that also precipitates out of the IL.

Extraction of the positively charge metal ion (e.g., Zn^{2+}, Pd^{2+}, Co^{2+}) proceeds via functionalized ILs. These are ILs that contain a metal binding functionality most often in the anion[6, 21-24], but sometimes also in the cation[25-27] of the IL. Regeneration of these functionalized IL is mainly done by reducing the metal interaction of the functionality due to protonation or oxidation, which can also be achieved with weaker acids and/or bases.[22, 28-33] In most cases, these ILs cannot be directly reused for metal extraction.

In the present paper different options for the regeneration of the functionalized IL tetraoctylammonium oleate after metal extraction are to our knowledge investigated for the

first time. Preferably regeneration is done on a sustainable way, i.e. performed by minimal

consumption of electric energy and without the use of toxic chemicals.

Experimental

Materials

The IL tetraoctylammonium oleate ($[N_{8888}][C18:1]$) used throughout this research was synthesized conform literature.[7] Copper chloride anhydrous 98 wt% ($CuCl_2$) and manganese chloride dihydrate 99 wt% ($MnCl_2 \cdot 2H_2O$) were supplied by Boom BV. Zinc chloride 99 wt% ($ZnCl_2$), cobalt chloride hexahydrate 98 wt% ($CoCl_2 \cdot 6H_2O$) and sodium oxalate ≥ 99.5 wt% ($Na_2C_2O_4$) were obtained from Sigma-Aldrich. Sulfuric acid 95 wt% (H_2SO_4), acetic acid 99-100 wt% (CH_3COOH), hydrogen chloride 1 M (HCl), ammonium hydroxide 25 wt% (NH_4OH), sodium hydroxide pellets 99.2 wt% (NaOH), sodium sulphate anhydrous 99 wt% (Na_2SO_4), sodium acetate trihydrate 100 wt% ($NaCH_3CO_2 \cdot 3H_2O$), sodium bicarbonate 99 wt% ($NaHCO_3$) and sodium chloride 99 wt% (NaCl) were supplied by VWR chemicals. Milli-Q water (≥ 18 MΩ·cm) was obtained from a Millipore Milli-Q® Biocel, which used a Q-grade® column or a Synergy UV water purification system.

Electro-deposition experiments

First a test solution was made by dissolving 0.1g $CuCl_2$ in 5 mL of the pure IL $[N_{8888}][C18:1]$ (0.117 mol Cu/L or 7.45 g Cu/L). The IL had a water content of 7.2 wt%. This concentration was used for all test solutions throughout all electro-deposition experiments. Initially, 2 electrodes were applied based on titanium coated with platinum (1 cm by 3 cm). Afterwards, these electrodes were changed for 2 copper plates (1 cm by 3 cm). In this study, the cell was connected in series with a galvanostat (IviumStat, Ivium Technologies, The Netherlands) to maintain a constant potential. The conductivity of the IL was calculated via the measured resistance. Detailed information on how these calculations were done can be found in the supplementary info. Resistance of the IL was measured via a resistance meter (Agilent 4338B, Agilent Technologies), with a 0.4% basic accuracy, by placing 2 Pt80/Ir20 wires with a diameter of 0.25 mm on a distance of 1 cm from each other in the liquid.

Chemical regeneration experiments

A standard solution was prepared by dissolving 0.5 g of each salt ($ZnCl_2$, $MnCl_2$ and $CoCl_2$) in 100 mL Milli-Q water. Then, 1 mL of this salt solution was added to 1 g of the IL [N_{8888}][C18:1] as extractant and was mixed in a Heidolph Multi Reax vortex mixer at 2500 rpm for 2 h at room temperature. Later, the mixture was centrifuged on an Allegra X-12R Centrifuge of Beckman Coulter at 3000 rpm for 10 min to accelerate the separation of the water phase.

Regeneration experiments with the loaded extractant were executed similar to the extraction experiments except for the fact that a 1M solution of acid, base or salt was applied instead of the standard metal solution. After each extraction and regeneration experiment, the aqueous phases were analyzed with a Perkin Elmer, precisely Induced Coupled Plasma (ICP), which used an optical atomic emission spectrometer (AES) Optima 5300DV to detect if metal extraction/regeneration occurred. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-AES has a detection limit of 50 µg/L with an uncertainty of 2%.

Analysis of metal precipitates was done by a JEOL JSM-6480LV scanning electron microscope (SEM) for imaging and with energy dispersive X-ray analysis (EDXA) for element analysis. Precipitates were recovered by decantation of the samples.

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

$$\%E = \left(\frac{c_{aq,0} - c_{aq}}{c_{aq,0}} \right) \times 100\% \tag{1}$$

where C_{aq} is the metal concentrations in the aqueous phase after extraction, and $C_{aq,0}$ is the metal concentration of the initial aqueous phase.

After the metal extraction experiments, the regeneration of the IL was investigated. The percentage stripped from the organic phase was calculated by:

$$\%S = \left(\frac{C_{aq,s}}{C_{org,0}}\right) \times 100\% \tag{2}$$

where $C_{org,0}$ is the metal concentration in the IL before stripping ($C_{org,0} = C_{aq,0} - C_{aq}$) and $C_{aq,s}$ is the metal concentration in the aqueous phase after the stripping process.

IL recycling experiments

Cycle experiments were performed by repeating the extraction and regeneration procedures as explained in the chemical regeneration section in a subsequent order. In this case, 5 mL of IL and 5 mL of the start solution were applied. Extraction after regeneration was only once performed when testing acids as stripping solution, and three times when a salt solution or Milli-Q water were used as stripping agents. The sum of the stripping efficiency was reported when different stripping steps were directly performed after each other. A cycle experiment was also performed with a metal salt solution containing 1000 ppm NaCl and 1000 ppm $CoCl_2$ using two different stripping solutions, e.g. 0.05 M NaOH and 0.1 M $Na_2C_2O_4$. Extraction of the metals by the IL in every step of the cycle was calculated by equation 1. Stripping of the IL was calculated by taking into account the concentrations of metals that were remaining in the IL phase after previous metal extraction and stripping steps in the cycle experiment.

Results and discussion

Two different regeneration methods were tested for the reuse of the IL [N_{8888}][C18:1] after metal extraction. First, electro-deposition as a regeneration technique was investigated, because in theory this method should be the most sustainable, i.e. only electrical energy is consumed and there is no need of adding additional chemicals to the system. Unfortunately, this technique turned out to be not feasible. Therefore, the possibility of chemical regeneration was also investigated. The advantage of using fatty-acid-based ILs for metal extraction 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. This is a commonly observed problem for the regeneration of ILs with conjugated acids as anions, such as in phthalate[23] and β-diketonates,[6, 34] which are (partly) water miscible or volatile altering the reuse of these ILs.

Electro-deposition

When evaluating the capability of recovering metals by electro-deposition from the IL [N_{8888}][C18:1] after metal extraction, $CuCl_2$ was selected as model metal salt due to the specific standard potential for copper deposition. That is, electro-deposition in neutral and acidic solutions is a trivial process due to the reversible reduction potentials of hydrogen and copper. For many non-noble metals, the reduction potential of the metal is lower than the one of hydrogen, leading to the formation of hydrogen instead of the metal. With the presence of water in the present IL, we would like a model metal salt not to compete with hydrogen in the reduction process at the cathode and copper would have this property when not considering kinetic electrode effects. At a pH of 0 in aqueous solutions, the standard potential (referring to 1M Cu^{2+}(aq)) of forming copper metal would be 0.34 V higher than that of forming hydrogen.

When considering water, there are two phenomena that could favor the hydrogen reduction (formation) reaction in the present IL and both relates to the electrode surface concentration of copper. The first phenomenon to consider is of a reversible thermodynamic kind, the concentration of copper in the IL. When the concentration of copper is lowered, the electrode reduction potential lowers too. For every time the copper ion concentration is lowered by a factor of ten, the reversible reduction potential for copper is lowered by 30 mV (2.303*RT/2F). For the hydrogen reduction (formation) reaction the reversible potential is lowered by 60 mV (2.303 RT/F) for every time the concentration is lowered by a factor of ten (increase of one pH point). In all instances the pH of the solutions were indicated to be well above 7, which means that the copper will always be favored when evaluating the reversible potentials. The other phenomenon that would favor the hydrogen formation reaction is the transport of the copper ion species over the protons in the solution. Depending on how well copper is tied to the IL active sites and thereby protected from the electrode, copper will either not access the cathode or it could be impeded from diffusing to cathode surface to such an extent that the surface concentration becomes zero or so low (e.g. ten or more orders of magnitude below the standard) that the effective reversible potential becomes lower than the one of hydrogen. Since the former of the two phenomenon would never occur, the latter would demonstrate limitations currently effective for the IL $[N_{8888}][C18:1]$. Pinpointing challenges as such is important in developing adequate ILs and therefore an important aspect of this paper.

First, the resistance of the IL $[N_{8888}][C18:1]$ was measured in order to obtain an indication of the conductivity. A conductivity of 0.54 mS·cm^{-1} was obtained for the pure IL (7.2 wt% H_2O), which is rather low compared to other commercial ILs. For example, the ILs $[EMIM]^+[C(CN)_3]^-$, $[BMIM]^+[CF_3CO_2]^-$ and $[(n-C_8H_{17})(C_4H_9)_3N]^+[(CF_3SO_2)_2N]^-$ have a conductivity of 18 mS·cm^{-1}, 3.2 mS·cm^{-1} and 0.13 mS·cm^{-1}, respectively.[35-37] Adding Cu to the

IL resulted only in a small reduction of the resistance. The Cu IL test solution (7.2 wt% H_2O) gave a conductivity of 0.91 mS·cm^{-1} and adding more water to this mixture until the IL mixture is water-saturated (11 wt%) increased the conductivity to 5.4 mS·cm^{-1}. In order to minimize the electrochemical splitting of water it was decided to use the Cu IL test solution without the extra addition of water for further testing.

For the first trial, 2 electrodes of Ti coated with Pt were inserted into the IL [N_{8888}][C18:1] containing Cu. After applying a potential difference of 10 V for 20 h in atmospheric conditions over the electrodes, an IL color change from green to brown was clearly observed around the cathode. A brown layer was formed on the cathode (Figure 1). Placing the cathode in 10 mL of 0.01M HNO_3 dissolved the brown layer, but analysis of the nitric acid solution on ICP revealed that only 34.35 µg or 0.03% of the Cu was on the electrode. This indicated that this brown layer was not only due to Cu, but mainly due to a degradation product of the IL, in which some Cu molecules were enclosed.

Fig 1. A brown layer could clearly be observed on the cathode (left electrode)

By lowering the potential from 10 V to 3 V, we tried to prevent the degradation of the IL. Unfortunately, also then a brown layer of IL was observed around the cathode and no deposition of Cu was measured. Repeating the experiment with a potential of 10 V under a nitrogen atmosphere prevented the formation of a brown layer of IL around the cathode, but still no deposition of Cu was observed. Additionally, mixing and heating up the IL up to 70˚C to decrease its viscosity also did not result in a deposit. The fact that working under an inert atmosphere could prevent the IL from degradation indicates that oxygen is most likely reacting with the IL. We could not identify the degradation reaction that was occurring with

our IL, but from these results, the high viscosity and resistance of the IL and because of the many electro-active sites of our anion of the IL, i.e. the carboxyl group, the double bond and the allylic C-H bond.[38] It was decided that electro-deposition with our IL in not possible. Changing the titanium electrodes with copper electrodes only showed that our IL is able to polish their surface, even when no potential is applied, see Figure 2.
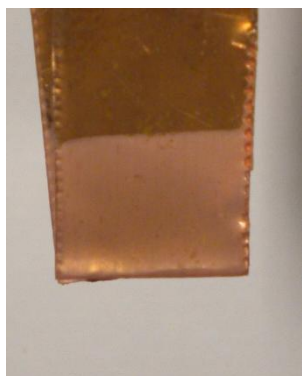

Fig. 2. Polished surface of the applied copper electrodes

Chemical regeneration

The metals Mn and Co were easily recovered from the IL by acidic stripping, because of the protonation of oleate anion (Table 1). Hereby, oleic acid is formed as well as a new IL, such as tetraoctylammonium Cl, SO_4 or CH_3CO_2, depending on the acid that was used. Unfortunately, due to the protonation of the anion direct reuse of the IL was impossible. With H_2SO_4 all metals could be recovered. Results with CH_3CO_2H were similar to H_2SO_4 except for the lower Zn recovery. HCl was only able to strip Co and Mn from the IL, however no Zn removal was observed. Reason is that Zn forms a $ZnCl_4^{2-}$ complex in the presence of high concentrations of HCl.[8]

Precipitates were always observed when using alkaline solutions as stripping agents. Therefore, because we analyze the aqueous phases after stripping, the recoveries of metals from ILs using alkaline solutions are much lower (Table 1). Zn showed the highest solubility

in the aqueous stripping phase due to the excess of base which promotes the formation of

soluble $Zn(OH)_4^{2-}$ or Zn ammonia $Zn(NH_3)_4^{2+}$ complexes.[39]

Table 1. Regeneration of the IL by the H_2SO_4, CH_3CO_2H, HCl, NH_4OH and NaOH.

%S	H_2SO_4	CH_3COOH	HCl	NH_4OH	NaOH
Co	100	91.7	90.9	19.7	0.9
Mn	100	96.2	100	1.5	1.4
Zn	77.5	52.0	0.5	78.4	62.8

Sodium salts of acids and bases were also tested to investigate if they can regenerate

the IL. Precipitates were observed for all the experiments with these salts as stripping agents,

which made it quantitatively impossible to investigate the stripping efficiency of these salts.

Most voluminous precipitate was observed for the regeneration with $NaHCO_3$. Figure 3

presents the analysis of this precipitate with SEM and showed sharp triangular crystals along

with smaller crystals. EDX analysis of this precipitate showed that the big triangular crystals

where $Zn(HCO_3)_2$ and the smaller crystals were $Co(HCO_3)_2$ and $Mn(HCO_3)_2$ (See

Supplementary Information). The formation of different crystals opens the possibility to
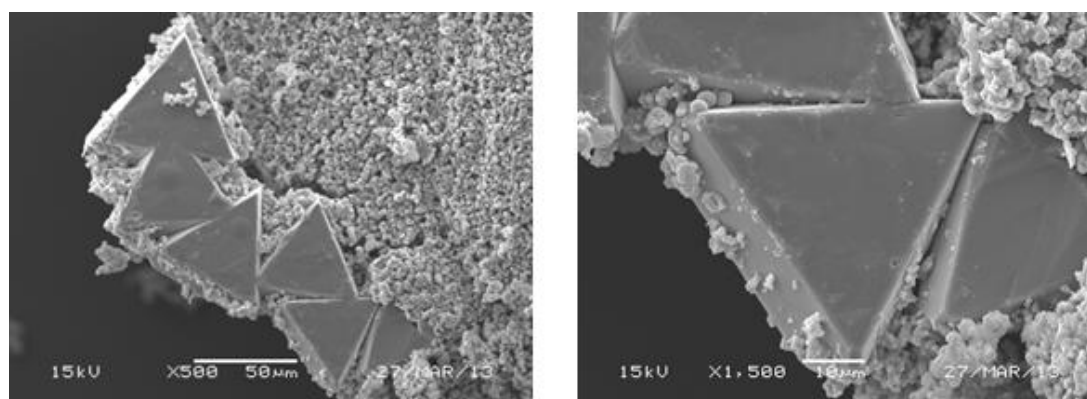
mechanically separate them from each other.

Fig 3. SEM analysis of the metal carbonate precipitate showed that the triangular crystals are

Zn carbonate, while granular precipitates are Mn and Co carbonate.

From the analysis of the aqueous stripping phase and the precipitate formation using

$NaHCO_3$, we could still get an indication of the interaction of the Na salts with the metals in

the IL (Table 2). Co and Mn could be recovered with all the salts used. However, Zn was only removed with $NaHCO_3$ as a $Zn(HCO_3)_2$ precipitate and with $Na_2C_2O_4$ as a ZnC_2O_4 precipitate. It was also possible to recover Co and Mn by washing with pure water, due to the weaker interaction of these metals with oleate compared to the interaction of the Zn tetrachloride complex with the IL cation tetraoctylammonium.

Table 2. Regeneration of the IL by Na_2SO_4, $NaCH_3CO_2$, $NaHCO_3$, NaC_2O_4 and Milli-Q water.

%S	Na_2SO_4	$NaCH_3COO$	$NaHCO_3$	$Na_2C_2O_4$	H_2O
Co	56.2	29.8	2.0	82.3	39.3
Mn	84.1	65.7	1.6	79.0	70.9
Zn	2.0	0.9	0.8	67.5	0.6

From these results, it can be concluded that regeneration with acids should be avoided because it leads to protonation of the anion, making direct reuse of the IL impossible. Regeneration with Na sulfate, $NaCH_3CO_2$ or Milli-Q water works only well for stripping the metals (Co, Mn) out of the IL that coordinate with the anion of the IL. Basic solutions or aqueous metal extractants, like $Na_2C_2O_4$, are good candidates for the regeneration of all metals from the $[N_{8888}][C18:1]$ IL.

It was expected that weak acids and bases can regenerate the metals that interact with the anion of the IL $[N_{8888}][C18:1]$, because this was previously observed in other functionalized ILs.[31] The observation that Zn, which is extracted as a negatively charged complex via the cation of the IL, can only be stripped with strong acids and bases is also consistent with previous observations in literature.[18] The most remarkable result is that $Na_2C_2O_4$ is able to extract all metals (that interact with either the cation or the anion of the IL).

Cycle experiment

Table 3 shows the extraction of the IL after regenerating it with the acids CH_3CO_2H and H_2SO_4. Before reuse the IL after applying these stripping phases, it is necessary to wash the

IL with an alkaline solution due to the protonation of the anion. NH_4OH was selected as base, because it is able to remove remaining Zn from the IL, which would be the main metal remaining in the IL after regeneration with both acids (See Table 1). No precipitate was observed after this alkaline washing step.

Regeneration of the IL with CH_3CO_2H and NH_4OH shows to be efficient to remove Co and Mn and for a moderate extend also for Zn, but reuse of this IL leads to a reduction in extraction efficiency for Co and Mn. Regeneration of the IL with H_2SO_4 and NH_4OH showed to be optimal to remove all the metal out of the IL. Unfortunately, reuse of the IL showed that all the anions of the IL are still fully protonated (leading to 0% extraction of Mn and Co in the second cycle). If oleate is protonated, then the cation of the IL has a SO_4^{2-} or OH^- as anion. These anions will interact differently with the metal ions in the aqueous phase and this is expected to be the explanation for the reduced Zn extraction. By increasing the NH_4OH concentration one could fine tune the deprotonation of the oleate anion.

Table 3. Cycle experiments for the acids CH_3CO_2H and H_2SO_4. From left to right: metal extraction with the IL, regeneration with the acid, washing with water, deprotonation of the IL with NH_4OH, washing with water, metal extraction with the IL in a second round.

	%E	%S 1 M CH_3CO_2H	%S H_2O	%S 1 M NH_4OH	%S H_2O	%E
Co	70.3%	91.5%	96.1%	96.3%	96.5%	58.6%
Mn	66.6%	90.6%	95.8%	96.2%	96.5%	50.3%
Zn	99.4%	25.7%	60.2%	64.4%	65.0%	99.3%
	%E	%S 1 M H_2SO_4	%S H_2O	%S 1 M NH_4OH	%S H_2O	%E
Co	69.2%	93.4%	96.5%	96.7%	96.8%	0.0%
Mn	65.6%	93.8%	97.0%	97.3%	97.6%	0.0%
Zn	99.4%	91.2%	98.3%	99.4%	100.0%	26.6%

Reuse of the IL after regeneration with Na sulfate and Milli-Q water was also tested (Table 4), because these chemicals are safer and easier to use compared to strong acids and bases. From Table 2 it was expected that both regeneration methods would only remove the metals Co and Mn, and that Na sulfate would be a slightly better stripping solution. Therefore,

is was surprising to see that both regeneration methods show similar stripping efficiencies. Reduced extraction of all metals for the reused IL could be explained by the remaining metal concentration in the IL.

Table 4. Cycle experiments for Na_2SO_4 and Milli-Q water. From left to right: metal extraction with the IL, regeneration with the salt/water, washing with water, regeneration with the salt/water, metal extraction with the IL.

	%E	%S 1M Na_2SO_4	%S H_2O	%E	%S 1M Na_2SO_4	%E
Co	69%	27%	50%	58%	24%	49%
Mn	65%	27%	50%	52%	22%	40%
Zn	99%	1%	2%	99%	1%	99%
	%E	%S H_2O	%S H_2O	%E	%S H_2O	%E
Co	71%	26%	48%	61%	24%	53%
Mn	69%	27%	47%	55%	25%	47%
Zn	99%	1%	1%	99%	0%	99%

In the previous section a basic solution or an aqueous metal extractant, like $Na_2C_2O_4$, were selected as the best candidates for the regeneration of all metals from the IL [N_{8888}][C18:1]. Unfortunately, in previous experiments precipitates were observed, which did not allow us to obtain a quantitative observation of the stripping efficiency. To minimize the occurrence of the precipitate formation, we performed cycle experiments with NaOH and $Na_2C_2O_4$ as stripping solutions for a single metal (Co) solution (See Tables 5 and 6, respectively).

Table 5. Cycle experiment with 0.05 M NaOH as stripping solution.

	%E	%S	%E	%S	%E	%S
Co	99.7	0.5	99.7	0.3	99.7	0.3
pH	8.87	11.26	9.53	12.32	9.03	10.62

Table 6. Cycle experiment with 0.1 M $Na_2C_2O_4$ as stripping solution.

	%E	%S	%E	%S	%E	%S	%E	%S	%E	%S
Co	99.5	24.3	93.4	22.7	88.1	22.0	88.5	18.9	92.1	16.5
pH	9.29	9.52	8.63	9.34	8.26	9.14	8.12	9.21	8.49	9.16

With NaOH (Table 5) only small stripping percentages were observed, which could be explained by the fact that a precipitate was still observed after stripping. Only 3 cycles were recorded, because after the third cycle a stable emulsion was observed that prevented further metal extraction. It is assumed that regenerating with NaOH results on a longer term into the formation of an excess of Na oleate, which is an emulsifier. Therefore, it is concluded that basic solutions are not suited as stripping solutions. Additional washing steps after stripping could suppress the formation of this emulsion.

From Table 6 it can be concluded that $Na_2C_2O_4$ is the most promising candidate as stripping solution for a continuous metal extraction process with the IL $[N_{8888}][C18:1]$. Table 6 shows a stabilization of the metal extraction performance of the IL after regeneration by stripping ($\pm 90\%$), while the stripping efficiencies remains around 20%.

Contrary to previous research, it was noticed that strong and weak acids are not suitable for the regeneration of the IL $[N_{8888}][C18:1]$. Instead, the cheap aquatic metal extractant, $Na_2C_2O_4$, was selected as the best stripping solution.

Conclusions

Regeneration by electro-deposition of the IL [N_{8888}][C18:1] after metal extraction was not possible due to the high resistance and viscosity of the IL. Furthermore, degradation of the IL occurred. By using chemical regeneration it was possible to selectively strip different metals from the IL as a result of the different mechanism by which these metals were in first instance extracted into the liquid. Strong acids and bases were able to remove all the metals from the IL, while weak acids and bases were only able to remove the metals Co and Mn, which are extracted into the IL via the anion. However, direct reuse of the IL in a continuous mode after applying these stripping solution is not possible due to the protonation of the anion of the IL (in case acids are used) or due to the formation of the emulsifying agent Na oleate (in case bases are used). It was concluded that $Na_2C_2O_4$ is the most promising stripping solution for the regeneration of the IL [N_{8888}][C18:1] after metal extraction, because the IL does not lose its high extraction efficiency for Co, Mn and Zn after multiple regeneration cycles.

Acknowledgements

Supporting info available

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